AquaConSoil

11 - 15 september 2023 | Prague

Topic 3 – abstracts

This document contains the abstracts for topic 3. Topic 3 contains the sessions listed below. The abstracts are ordered by session.

The complete programme and session overview can be found on our website at: https://aquaconsoil.com/aquaconsoil-2023/scientific-programme/

Session	**TOPIC 3: Sustainable remediation, emerging contaminants and prevention towards zero pollution**
3a1	*Remediation of historical large-scale pollutions (e.g. landfills, mine wastes) using sustainable resources and energy - session 1*
3a2	*Remediation of historical large-scale pollutions (e.g. landfills, mine wastes) using sustainable resources and energy - session 2*
3b1	*Integrated Remediation Processes*
3b2	*Biodegradation of chlorinated solvents - session 1*
3b3	*Biodegradation of chlorinated solvents - session 2*
3b4	*Electrochemical treatment technologies*
3b5	*PFAS electrochemical treatment technologies*
3b6	*Soil washing and flushing*
3b7	*Thermal remediation methods*
3b8	*Application of Zero-Valent Iron nanoparticles for Soil and Groundwater*
3b9	*New Approaches to Subsurface Injection of in-situ remedial reagents*
3b10	*Sustainable Technology Combinations*

3b11	Thermal Remediation
3b12	PFAS management - session 1
3b13	PFAS management - session 2
3b14	Monitoring & investigation
3b15	Remediation technologies
3b16	Management strategies
3b17	Isotopic and chemical fingerprinting methods
3c1	Persistent organic pollutants (POPs)
3c2	PFAS Fate and transport
3c3	PFAS Immobilisation and Separation
3c4	PFAS Oxidation and Reduction
3c5	Special contaminants
3c6	Innovative Site Investigation Approaches
3c7	Management and remediation of micropollutants
3c8	Antibiotic contamination and systemic remediation
3sps1	Integrating Green Remediation Practices in Superfund Cleanups: A United States Environmental Protection Agency Perspective
3Sps2	Towards optimised risk-based aftercare at tar sites
3sps3	Best Practices for Applying In Situ Chemical Oxidation (ISCO) in 2023
3sps4	Decision support framework for risk management of persistent, mobile and toxic chemicals in a circular economy.

Session 3a1

Thursday 09:00-11:30

Room Z-II / 111

ID	Name	Organization	Title
65	Xavier Lepere	DEME Environmental	Remediation of the Slettebakken landfill in Bergen, Norway
145	Jonathan Smith	Shell	Remediation of 1000 ha of Hydrocarbon Impacted Mangrove Sediments in Bodo, Nigeria
221	Paul Verhaagen	HMVT	Optimizing Remediation Strategy at a Former Large Industrial Site Using a Multiple Lines of Evidence Analytical Approach
293	Dr. Annika Beckmann	HPC AG	Experience in Operation and Tunning of Wetland+® Technology for Treatment of HCH-Contaminated Water
190	Jan Němeček	Technical University in Liberec	Results of a pilot for the treatment of landfill leachate using an innovative biological test facility. A significant step towards more sustainable, low carbon and biodiverse water treatments
37 – Backup	Ulf Jenk	Wismut GmbH	Breakthrough in the implementation of the complete flooding of the Königstein uranium mine (Germany) after more than 10 years

Session 3a2

Wednesday 09:00-10:30

Room D217

ID	Name	Organization	Title
121	Rajandrea Sethi	Politecnico di Torino	The first Italian permeable reactive barrier: performance assessment during 20 years of operation
288	Edoardo Masut	ERM Environmental Resources Management	Quantifying Carbon and Water Footprint reduction for in-situ Site Remediation vs conventional Plume Management approaches
306	Raphi Mandelbaum	LDD Advanced Technologies (2005) LTD	Remediaiton Plan for contaminated soils in a 43 hectares former PVC plant in Israel
326	Rogier de Waele	Greensoil group	Chromium (VI) and vanadium (V) in groundwater: investigating bioremediation solutions
354	Martin Slooijer	GreenSoil Group	SUSTAINABLE CYCLIC REMEDIATION OF A HEAVILY IMPACTED SITE WITH XYLENE – 100% BIOLOGICAL TREATMENT OF SOIL, GROUNDWATER AND SOIL VAPOR
255 – Backup	Laura Quintarelli	Ramboll Italy S.r.l.	Green review of a soil remediation Project and cost estimate update for a Former industrial site redevelopment
291 - Backup	Yongming Luo	Institute of Soil Science, Chinese Academy of Sciences	Facile removal of Cd and Cu from farmland soils and waste eluent by waste biomass extracts and its residues

[3b - backups]

ID	Name	Organization	Title
28 – Backup	Radek Červinka	Dekonta	The full-scale remediation of an impregnation facility polluted with creosote oil using on-site co-composting
32 – Backup	ALBERTO LEOMBRUNI	Evonik Operations GmbH - Filiale Italiana | Divisione "Smart Materials"	Application of an All-In-One ISCO Technology for the treatment of Hydrocarbons, BTEX and MTBE at a Former Retail Petrol Station in Italy
35 – Backup	Mujahid Farid	University of Gujrat, Gujrat, Pakistan	Accumulation and tolerance appraisal of Phragmites australis L. for the treatment of textile processing effluents in a constructed wetland blended with oxalic acid
47 – Backup	Marcello Carboni	REGENESIS	Rapid remediation of a chlorinated solvent plume using an injectable barrier combining in situ sorption, biological degradation and chemical reduction
115 – Backup	Diana Puigserver	University of Barcelona	Pilot test of PCE sources mobilization in the transition zone to aquitards by combining ISCO and biostimulation techniques
136 – Backup	Joseph Rossabi	Redox Tech, LLC	The conceptual model of a persistent chlorinated solvent plume must include the consideration of micro DNAPL far from the source release area
212 – Backup	Petrangeli Papini	Universidad Complutense de Madrid	Adsorption and biodegradation modelling of TCE on biochar, enhanced by PHA addition
400 – Backup	Nanna Isbak Thomsen	Ramboll	Understanding nanoparticle transport and retention from the pore scale up with X-ray μ-CT
403 – Backup	George Ivey	Ivey International Inc.	PFAS – Danish Guidelines for investigation and Remediation
418 – Backup	Sylvie Braekevelt	Ramboll	Enhanced PFAS Removal From Soil and Groundwater Via Surfactant Flushing
423 – Backup	ALBERTO LEOMBRUNI	Evonik Operations GmbH - Filiale Italiana | Divisione "Smart Materials"	Removal of long- and short-chain PFAS, hydrocarbons and heavy metal compounds from contaminated groundwater by advanced groundwater treatment technologies

Session 3b1

Tuesday 11:00-12:30

Room Z-I / 111

ID	Name	Organization	Title
110	Dilan Aydin	Wageningen University & Research	Biodegradation of B, T and BTEXIelaN under NO3- and SO4- reducing conditions in column studies
207	Maria de Lourdes Tovilla Coutino	Ecole Centrale de Lyon	Four innovative technologies for in situ bioremediation developed for a range of environmental pollutants (EiCLaR EU-China project)
304	John Dijk	Greensoil Group	Biological degradation of high concentrations of 2,4- and 2,6-DNT on laboratory and field scale
397	Phil Dennis	SiREM	In Situ Bioaugmentation for Anaerobic Benzene, Toluene and Xylene Remediation
425	Mentore Vaccari	University of Brescia	Bio-electrochemical treatment of soil contaminated by petroleum hydrocarbons with biosurfactant obtained from agricultural waste

Session 3b2

Thursday 14:00-15:30

Room Z-II / 113

ID	Name	Organization	Title
132	Jesica M. Soder-Walz	Autonomous University of Barcelona	Lab studies with field-derived microcosms and stable isotope analysis to evaluate the intrinsic biodegradation potential of lower-chlorinated benzenes in a coastal aquifer
164	Steffen Hertle	TZW:DVGW - Technologiezentrum Wasser	Stimulation of metabolic aerobic TCE degradation by bioaugmentation and in bio-electro-systems
206	Daniel Leigh	Evonik Corporation	Biogeochemically Enhanced In Situ Treatment of Chlorinated Organics and Metals
217	Marçal Bosch	LITOCLEAN, SL	Outlining the best remediation strategy at a multi-focus site where both shallow and deep aquifers are contaminated by chlorinated ethenes: hydrogeological characterization, treatability studies and in situ pilot tests.
224	Nina Tuxen	Capital Region of Denmark	Remediation of Chlorinated Ethenes Plume in Denmark by Retardation and Enhanced Biodegradation – Lessons Learned

Session 3b3

Wednesday 11:00-12:30

Room Z-I / 111

ID	Name	Organization	Title
225	Scott Wilson	REGENESIS	Solid Phase Colloidal Organic Amendments Promote Sustained In-Situ Biodegradation of Groundwater Contaminants Within Permeable Barriers
234	Alastair Dunster	Arcadis	Remediation of Chlorinated Solvents in a Chalk Aquifer used for Public Water Supply
249	Lukas Scholz	NTP Umwelt	Use of a bioreactor for the continuous cultivation of DHC bacteria for the complete dechlorination of a CHC-contaminated site
356	Rogier de Waele	GreenSoil Group	NATURE BASED REMEDIATION APPROACH FOR THE CVOC CONTAMINATION UNDERNEATH AN ELECTRONIC MANUFACTURER SITE
393	Diderik Göschel	Ramboll Iberia	Remediation of residual PCE Impact in Groundwater: Enhanced bioremediation approach to facilitate remediation in a complex hydrogeological setting

Session 3b4

Tuesday 16:00-17:30

Room D218

ID	Name	Organization	Title
174	Paqui Blánquez	Universitat Autònoma de Barcelona	Sequential dechlorination of chloroform to dichloromethane and acetate bioelectrochemically assisted
177	Miguel Herraiz-Carboné	Complutense University of Madrid	Treatment of groundwater polluted with DNAPL by electrochemical oxidation
279	Torben Højbjerg Jørgensen	COWI A/S	Bench Test Evaluation of Arsenic Immobilization in Shallow Soils at Collstrop-Grunden, Hillerød, Denmark
281	Alberto Soto	ICCRAM	Pragmatic approach to upscale a macrophyte based metal(loid)s phytoremediation to treat polluted ground water
362	Kathrin Leicht	Institute for Modelling Hydraulic and Environmental Systems	Testing Electro-Nano-Bioremediation of chlorinated hydrocarbons at medium and large scale under ideally controlled boundary conditions

Session 3b5

Wednesday 11:00-12:30

Room Z-II / 113

ID	Name	Organization	Title
96	Carme Bosch	Eurecat	Advanced industrially influenced wastewater treatment scheme for agricultural water reuse
241	Yue Wang	Sun Yat-sen University	Electroreductive defluorination of unsaturated PFAS by a quaternary ammonium surfactant-modified cathode via direct cathodic reduction
318	Emily Brown	Photon Energy Group (Photon Water)	Global first trial and assessment of In-situ electrochemically enhanced nanoremediation for PFAS removal
347	Anett Georgi	Helmholtz Center for Environmental Research - UFZ	Electrosorption for enhancing adsorption of short-chain perfluoroalkyl acids on activated carbon and on-site regeneration of the adsorbent
133 - WITHDRAWN			

Session 3b6

Thursday 09:00-10:30

Room Z-I / 111

ID	Name	Organization	Title
63	Stany Pensaert	DEME Environmental	The hybrid soil washing system for the treatment of PFAS contaminated soils
123	Amir Alamooti	BRGM (French Geological Survey)	In situ flushing of multilayer DNAPL contaminated soils using a polymer/alcohol/surfactant mixture
137	Ali BATIKH	BRGM	Mobilization of PFAS from heterogeneous soils: Desorption by ethanol/xanthan gum mixture
147	Adil Baigadilov	BRGM (French geological survey)	Evaluation of stability and performance of foam composed of complex mixtures of surfactants, nanoparticles and polymer for in-situ remediation of LNAPL
200	Benjamin Faigle	Züblin Umwelttechnik GmbH	Successful treatment of PFAS-contaminated soils on large scale: practical experience with soil washing

Session 3b7

Tuesday 11:00-12:30

Room D218

ID	Name	Organization	Title
51	Jan Haemers	Haemers Technologies	State of the art for PFAS-impacted soils. What are the available remediation technologies?
191	Gorm Heron	TRS Group	Thermal Treatment of PFAS Impacted Soil – Field Demonstration and Scale-Up Considerations
226	Rodolfo Costa	Arcadis Italia	Thermal Conductive Heating (TCH)
276	Søren Eriksen	Krüger A/S	CAN LOW TEMPERATURE THERMAL DESORPTION BE CONVERTED TO DESTRUCTION AND BE MORE SUSTAINABLE THAN TRADITIONAL INCINERATION
333	Pierre-Louis Guillerm	Ramboll	Validation of the applicability of In Situ Thermal Desorption (ISTD) for the remediation of a site contaminated with mercury beads

Session 3b8

Tuesday 14:00-15.30

Room Z-II / 113

ID	Name	Organization	Title
129	Clarissa Settimi	University of Rome Tor Vergata	INVESTIGATING THE USE OF ZERO-VALENT BIMETALS FOR THE DEGRADATION OF CHLORINATED SOLVENTS VAPORS IN THE SUBSOIL
152	Ida Dyrlund Damgaard	Central Jutland Region	Evaluation of chlorinated ethene degradation by an integrated approach in the risk assessment of a contaminant plume influenced by source and barrier remediation
170	Dani Salom	Universitat Autònoma de Barcelona (UAB)	Effect of zero-valent iron on anaerobic dechlorinating bacteria for remediation of chlorinated methanes and 1,2-dichloroethane
384	Lorenzo Sacchetti	Carus LLC	Technologies options for Rebound control and rapid site closure for ISCO/ISCR treatments
413	Daniel Leigh	Evonik Corporation	Biochemical Destruction of Chlorinated Pesticides and Organic Explosive Compounds with Sustainable Organic Carbon/ZVI Reagents

Session 3b9

Tuesday 16:00-17:30

Room Z-I / 111

ID	Name	Organization	Title
50	Léa Lévy	Lund University	CROSS-BOREHOLE ELECTRICAL MONITORING IN GROUNDWATER REMEDIATION PROJECTS: UNDERSTANDING THE FLOW PATH OF REMEDIATION AGENTS
93	Jeroen Vandenbruwane	Injectis	Injection of colloidal reagents for in situ soil remediation: lessons learned on more than 100 projects over Europe
166	Uwe Dannwolf	Riskcom GmbH	LNAPL Recovery from low permeability strata by means of sand layer injection using i-SAV© technology and non-ionic surfactant application
412	Stijn Decru	ABO nv	LIFE Frac In: Enabling in situ soil remediation on low-permeability sites through hydraulic and pneumatic fracturing
125	Ondřej Lhotský	DEKONTA, a. s.	In-situ soil remediation at low-permeability sites using the hydraulic/pneumatic fracturing (FRAC-IN) approach

Session 3b10

Wednesday 09:00-10:30

Room Z-II / 113

ID	Name	Organization	Title
21	Mark Mejac	Ramboll	Large-Scale In-Situ Biotic and Abiotic Dechlorination of Groundwater Impacted with Co-Mingled Chlorinated Ethenes and Chlorinated Methanes
58	Kirsten Rügge	COWI Denmark	Innovative ZVI application for sustainable remediation of chlorinated solvent plumes
91	Helena Nord	Sheeba Environmental Engineering AB	The winner takes it all – trialling three parallel remediation options at the same site in order to select one remediation strategy for the entire site
107	Marco Papini	University of Rome La Sapienza	A Sustainable Approach For TCE Contaminated Groundwater Remediation: Raw Polyhydroxyalkanoates (PHA) As Electron Donor for BRD Coupled With Adsorption On Biochar
195	Dominique J. Tobler	University of Copenhagen	GreenCat - Green catalysis for groundwater remediation - from waste material to universal catalyst for chlorinated solvent degradation

Session 3b11

Thursday 11:00-12:30, Room D217

ID	Name	Organization	Title
43	Per Johansson	WSP Sweden	Remediation of vinyl chloride in organic sediments using Hot Air Sparging
52	Aline Jordens	Haemers Technologies	Thermoreact® - An innovative remediation product for In Situ neutralization of halogens and sulphur during Thermal Desorption
68	Jonah Munholland	Arcadis	Ecosystem Restoration by Thermal In-Situ Sustainable Remediation (TISR)
81	Carlo Bianco	University of Catania	The use of Liquid Activated Carbon (LAC) in enhanced-microwave remediation of soils impacted by Polycyclic Aromatic Hydrocarbons (PAHs)
235	James Baldock	ERM	Steam Injection in Low Permeability Environments to Improve Thermal Sustainability

Session 3b12

Tuesday 14:00-15:30

Room Z-I / 111

ID	Name	Organization	Title
196	Jussi Reinikainen	Finnish Environment Institute (SYKE)	How does EU's policy framework tackle prevention and management of PFAS pollution?
261	James Rayner	Geosyntec Consultants	Predicting PFAS soil porewater concentrations – implications for hydrogeological risk assessment & sustainable soil remediation
286	Griet Van Gestel	OVAM - Public Waste Agency of Flanders	New insights in human health risk assessment of PFAS contaminated sites, and the setting of soil remediation values
319	Rachael Casson	AECOM	PFAS Mass Flux – A Platform for Developing Realistic Remedial Goals and Sustainable Action (An Australian Perspective)
404	Tomáš Cajthaml	Charles University	Per- and polyfluoroalkyl substances (PFAS) in the aquatic environments in the Czech Republic
172 – Backup	Martin Cornelsen	Cornelsen Umwelttechnologie	Sustainable Treatment Approach for Liquids with high PFAS Values
387 – Backup	Robin Axelson	Envytech Solutions AB	Stabilization of PFAS contaminated soil to minimize cost for construction works and carbon footprint for widely contaminate and active areas

Session 3b13

Wednesday 09:00-10:30

Room Z-I / 111

ID	Name	Organization	Title
114	Dorien Gorteman	Witteveen+Bos	Background values of PFAS in soil and groundwater
229	Jake Hurst	Arcadis UK Ltd	PFAS Catchment Management - UK and Jersey
239	Johan Ceenaeme	OVAM	PFAS and excavated soils: how do we prevent the spreading of PFAS-contamination in Flanders?
263	Tessa Pancras	Arcadis Nederland B.V.	PFAS in crops near a fluorochemical plant. Links between distance, soil concentrations and uptake.
283	Michiel Maertens	VITO	Leaching-behavior and transport of PFAS: review and update of the Flemish methodology for dispersion risk assessment
109 – Backup	Glein Roggeman	Arcadis Belgium	Flame retardants related to risk activities - Brussels guidelines
240 – Backup	Johan Ceenaeme	OVAM	Mapping and investigation of PFAS suspected sites in Flanders

Session 3b14

Wednesday 14:00-15:30

Room Z-II / 113

ID	Name	Organization	Title
70	Emma Evans	Arcadis	A New UK Approach: Development of Vertical Screening Distances to support more Sustainable Assessment of the Petroleum Vapour Intrusion Pathway
74	Thorsten Hueffer	University of Vienna	Tire-derived compounds from biosolids contaminate soil and might be taken up by edible plants
75	Thorsten Hueffer	University of Vienna	Micro-or nanoplastics do not enhance the relocation of contaminants in agricultural soil
284	Griet Van Gestel	OVAM - Public Waste Agency of Flanders	An approach for diffuse soil contamination in Flanders – development of policy & tools
344	Eugen Martac	Fugro Germany Land GmbH	High resolution characterization technology with continuous monitoring of contaminants composition and intensity

325 – Backup	Niluka Wickramasinghe	Czech University of Life Sciences	The fate and uptake of sewage sludge-derived emerging organic contaminants in winter wheat
407 – Backup	Harry O'Neill	Beacon Environmental	Sustainable Remediation Starts with an Effective Sustainable, High-Resolution Site Characterization Program

Session 3b15

Tuesday 16:00-17:30

Room Z-II / 113

ID	Name	Organization	Title
237	Steve Thornton	University of Sheffield	Aerobic biodegradation potential of ETBE in groundwater: Observations and management perspectives
243	Stefan Niewerth	HUESKER Synthetic GmbH	Permeable contaminant barriers: A new technology for interrupting exposure pathways while avoiding surface sealing
295	Dirk Paulus	TAUW Belgium	In Situ Metal Precipitation (ISMP) of heavy metals
360	Massimo Marchesi	Environmental research scientist	The use of compound-specific isotope analysis (csia) to allocate the potential sources of dissolved chlorinated solvents contaminant in large urban areas: lessons learned from few case studies
394	Jaroslav Semerád	Institute of Microbiology of the CAS, v. v. i.	Detection of new organic micropollutants in drinking water supply system using high resolution mass spectrometry
332 – Backup	Oliver Trötschler	VEGAS, University of Stuttgart	What about the CO2 Fingerprint of a Successfully Finished In Situ Thermal Remediation (ISTR) of a CHC Source Area after 16 Years of Groundwater Remediation (P&T)

Session 3b16

Wednesday 14:00-15:30

Room D218

ID	Name	Organization	Title
87	Marco Falconi	IMPEL	The IMPEL project "Water and Land Remediation"
219	Rob Sweeney	CL:AIRE	Case Studies and Analysis of Sustainable Remediation Techniques and Technologies
236	Halfdan Sckerl	Central Denmark Region	PFAS in coastal areas – implications of diffuse impact from dispersion via aerosols and sea foam
292	Petra Krystek	Deltares	Plastics are everywhere, including in the soil. But what are the risks for us?
294	Tetsuo Yasutaka	National Institute of Advanced Industrial Science and Technology (AIST)	Current Status and Challenges of, and Preparedness for Sustainable Remediation from Nuclear Disaster
40 – Backup	Chihhao Fan	National Taiwan University	Non-point source pollution control for farmland by biochar application in agricultural practice
428 – Backup	Tom Bosma	WUR	How to deal with very Persistent and Mobile Toxins – best strategy to go forward

Session 3b17

Wednesday 14:00-15:30

Room Z-I / 111

ID	Name	Organization	Title
141	Vladislav Knytl	Dekonta, a.s	Compound-specific stable isotope analysis to determine sources and sinks of PFAS
134	Kevin Kuntze	Isodetect GmbH	The Use of the Combined OIHPT Probe to evaluate the Distribution and Efficiency of a Remediation Agent supplemented with a Fluoresceine Tracer
250	Anne togola	BRGM	Improvement of the global quantification of PFAS through TF, AOF and EOF measurements: Application to complex environmental matrices (sludge and compost) from wastewater treatment plants
361	Kim Pingree	Albemarle Corporation	A sustainable approach of mercury sequestration in sediments resulting in the reduction in concentration of methylmercury and suppression of mercury bioaccumulation
390	Axelle Mineur	ABO nv	Development of a robust analytical protocol for PFAS contamination in soil and groundwater by the LIFE Capture project

Session 3c1

Thursday 11:00-12:30

Room D222

ID	Name	Organization	Title
213	Anton Grønne Kühl	GEO	GreenCat - Green Catalysis for Groundwater Remediation: A Sandbox Experiment for Evaluating the Degradation of Chlorinated Solvents with a Catalyst Made from Waste Materials in an artificial confined aquifer.
289	Winnie Hyldegaard	Central Region Denmark	Measurements for chlorinated solvents in sewer gas is not that simple, do we use the best sampling methods?
296	Sebastian Gustafson	Ultraaqua A/S	Removal of chlorinated solvents in air by Vacuum UV
315	Ilaria Chicca	NOVOBIOM	A fungal biostimulation and biaugmentation orientation study for the bioremediation of a PCE and TCE contaminated loamy sand soil
373	Simon M. Kleinknecht	Research Facility for Subsurface Remediation (VEGAS)	Experimental upscaling to develop a remediation design for surfactant-enhanced in-situ chemical oxidation (S-ISCO)

Session 3c2

Thursday 11:00-12:30

Room Z-I / 111

ID	Name	Organization	Title
45	Jim Fenstermacher	Ramboll	How the Site Remedial Setting Drives the PFAS Remedial Response
165	Xin Song	Institue of Soil Science, Chinese Academy of Sciences	Effects of per- and polyfluoroalkyl substances (PFASs) and chlorinated aliphatic hydrocarbons (CAHs) co-contamination on the native microbial community in the field and associated biodegradation potential for PFASs
173	Johan van Leeuwen	KWR	PFAS behavior in the unsaturated subsurface
350	Jeremy Birnstingl	Regenesis	Long Term Performance of a Carbon Barrier Evaluated Through Integrated Use of Aspect Ratio, Passive Flux and Modelling Analytical Tools

Session 3c3

Thursday 11:00-12:30

Room Z-II / 113

ID	Name	Organization	Title
13	Rick McGregor	InSitu Remediation Services Ltd	The In Situ Treatment of PFAS at the Air-Water Interface in a Source Zone Using Colloidal Activated Carbon
46	Jack Shore	REGENESIS	Flexible and sustainable in situ solutions for PFAS source-plume systems using a variety of colloidal activated carbon application methods
82	Niels Døssing Overheu	Capital Region of Denmark	Experience with PFAS as secondary component in pump-and-treat plants
105	Laura del Val Alonso	Eurecat	TESTING INNOVATIVE TECHNOLOGIES TO ENHANCE PFAS POLLUTED GROUNDWATER TREATMENT – LIFE SOURCE PROJECT
88	Jurgen Buhl	Cornelsen Umwelttechnologie GmbH	Immobilisation of PFAS - What happens under stress?

Session 3c4

Tuesday 11:00-12:30

Room Z-II / 113

ID	Name	Organization	Title
80	Sarah Sühnholz	Intrapore GmbH	Iron minerals as catalytic activators for persulfate for in-situ oxidation of PFAS in aquifers - From laboratory to field application.
193	Leonidas Perez-Estrada	EURECAT	Applicability of different iron and persulfate-based oxidation processes for the elimination of PFAS compounds in groundwater
214	Christos Tsakiroglou	Foundation for Research and Technology Hellas - Institute of Chemical Engineering Sciences	Remediation of water from per- and poly-fluoroalkyl substances (PFAS) with advanced oxidation processes: a comparative study of ozonation and photocatalysis
230	Baxter Miatke	Arcadis US Ltd	Foam Fractionation of PFAS with Combined Air / Ozone

Session 3c5

Wednesday 11:00-12:30

Room D217

ID	Name	Organization	Title
27	Anjali Jayakumar	Newcastle University	Nature-based solution for water treatment using Biologically Enhanced Biochar
211	David Lorenzo	Universidad Complutense de Madrid	RECOVERY OF SURFACTANS AND ADSORBENTS IN SELECTIVE POLLUTANTS ABATEMENT IN POLLUTED SOIL FLUSHING EMULSIONS
265	John Dijk	Greensoil Group	Biological degradation of high concentrations of 1,4-dioxane: from laboratory to field and back
273	Aurora Santos	Universidad Complutense de Madrid	DNAPL Extraction and Oxidation enhanced by Surfactant addition: LIFE SURFING PROJECT
408	Ivan Titov	Charles University, Faculty of Science, Institute for	Study of sorption of micropollutants to microplastics under field conditions

		Environmental Studies	
274 – Backup	Giovanni Scaggiante	University of Rome "Tor Vergata"	Removal of halogenated compounds in water by persulfate and peroxymonosulfate activated by iron-copper bimetals and zero-valent iron

Session 3c6

Thursday 14:00-15:30

Room Z-I / 111

ID	Name	Organization	Title
29	Ondřej Lhotský	DEKONTA, a. s.	The Utilisation of Innovative Site Survey and Remediation Methods at the Duchcov Site with Complex Conditions and Geology
101	Patrik Nilsson	Rosmarus Enviro	Innovative reactive liner technology for delineating chlorinated solvents in fractured bedrock and determining sustainable remediation methods
151	Alessandra Cecconi	University of Rome "Tor Vergata"	Evaluation of the applicability of the radon deficit technique in soil gas for quantifying residual LNAPL contamination
154	Isak Hjort Dahm	WSP Denmark	Comparison of different methods for investigating indoor air quality and vapor intrusion at a chlorinated solvent site. Dynamics between groundwater, drainage system and indoor air.
189	Majken Frederiksen	Ramboll/Technical University of Denmark	Mechanisms of long-term leaching of persistent and mobile chemicals (PMOCs) from clayey till to groundwater aquifers

Session 3c7

Wednesday 09:00-10:30

Room D218

ID	Name	Organization	Title
268 - withdrawn			
365	Glenn Heernaert	TerraCorrect bv	In-situ Soil Washing as Lead-out for more effective ISCO and ISCR. Full-scale Implementation For Chlorinated Solvents
383	Enrique Eymar	University Autonoma of Madrid	Development of biogeofilters to remediate intensive horticultural ecosystems polluted with antibiotics
385	Felipe Solano	Geosyntec Consultants	Sequenced S-ISCO® , ISCO and Bioremediation for Treatment of a Pharmaceutical Waste Mixture – Full Scale Application

Session 3c8

Tuesday 14:00-15:30

Room D217

ID	Name	Organization	Title
161	Andreas Tiehm	TZW: DVGW - Technologiezentrum Wasser	International comparison of antibiotic resistance surveillance and reduction by wastewater treatment
242	Poul Bjerg	Technical University of Denmark	Natural attenuation of sulfonamides in contaminated groundwater – Assessment of monitoring techniques
168	Josefine Gram Hansen	Technical University of Denmark	FDOM as a field screening technique for fluorescent pharmaceuticals in a contaminant plume
203	Cecilie Ottosen	Technical University of Denmark	Fate of sulfonamides in a complex plume discharging to a stream – a multiple line of evidence approach in the hyporheic zone
391	Marc Viñas	Institute of Agrifood Research and Technology (IRTA)	Use of outdoor pilot-scale photobioreactor and cork-wood pellet-based biofilter for simultaneous nitrate and micropollutant removal in polluted groundwater

Session 3sps1

Thursday 14:00-15:30

Room D222

ID	Name	Organization	Title
307	Lucila Dunnington	United States Environmental Protection Agency	Integrating Green Remediation Practices in Superfund Cleanups: A United States Environmental Protection Agency Perspective

Session 3sps2

Wednesday 14:00-15:30

Room D226

ID	Name	Organization	Title
257	Frank Volkering	TAUW bv	Towards optimized risk-based aftercare at tar sites

Session 3sps3

Thursday 09:00-10:30

Room D222

ID	Name	Organization	Title
381	Brant Smith	Evonik	Best Practices for Applying In Situ Chemical Oxidation (ISCO) in 2023

Session 3sps4

Wednesday 11:00-12:30

Room D222

ID	Name	Organization	Title
297	Julia Hartmann	RIVM (Dutch National Institute for Public Health and the Environment)	Decision support framework for risk management of persistent, mobile and toxic chemicals in a circular economy

Session 3a1 orals

Session 3a1 / Abstract title: Remediation of 1000 ha of Hydrocarbon Impacted Mangrove Sediments in Bodo, Nigeria

ID: 145

Key words: Remediation, Sediment, Mangrove, Revegetation

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Organization: Shell

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Session: 3a1

Abstract

Purpose of study
The Bodo Remediation and Revegetation Project, covering ~1000 ha of intertidal mangrove habitat, mud flats, shorelines and numerous channels and creeklets, is the largest remediation and reforestation action ever undertaken globally as a result of hydrocarbon contamination in a mangrove habitat. Chemical analyses of over 600 sediment samples found surface (0-5 cm depth) and subsurface (15-25 cm depth) total petroleum hydrocarbon (TPH) concentrations of 59,652 ± 78,122 mg/kg (mean ± standard deviation) and 21,752 ± 33,358 mg/kg respectively. The aim of the remediation effort is to reduce the hydrocarbon concentration to a level able to support revegetation with mangrove seedlings and minimal disruption to the sediment structure while meeting government approved chemical Site-Specific Target Levels (SSTLs).
Methodology
Tier 2 risk assessment was employed to determine Site Specific Target Levels (SSTLs) based on the ASTM Risk Based Corrective Action (RBCA) framework combined with a Net Environmental Benefit Analysis (NEBA). The primary remediation technique for oil extraction within sediments is low-pressure, high-volume flushing using either single personnel carried pumps or barge mounted systems having multiple hoses. Oil released from sediments are (a) contained using a 3-tier booming system comprised of combinations of fence, river and

sorbent booms, (b) recovered manually and siphoned into plastic containers, and (c) transported by boat to a central waste storage facility for subsequent transport and thermal treatment at a government approved facility. Other remedial activities include raking and agitation of surface sediments to remove thick algal mats and promote aeration of underlying sediments, physical removal of tar/carbonised crusted hydrocarbons found in illegal refining locations and removal of oiled debris and garbage. Compliance with project criteria is confirmed by a combination of Shoreline Cleanup Assessment Technique (SCAT) surveys followed by sediment sampling for petroleum hydrocarbon analysis to verify alignment with SSTLs prior to revegetation.

Summary of findings/results

Contamination is primarily limited to 0.5 m due to the retention of tidal water at 15-25 cm depths even as the tide drops and increasing compaction with depth. Over 3 million litres of oily sludge have been flushed out, contained with booms, and recovered manually. Flushing to meet SCAT observational levels has translated to compliance with the regulatory approved SSTLs for the project. As of January 2023, 87% of the area had been confirmed completed by remediation contractors through SCAT surveys with 84% verified by Project chemical sampling and >300,000 planted mangrove seedlings (out of ~2 million to be planted) passing 1-month monitoring criteria.

Conclusion

High-volume low-pressure flushing, using creek waters pumped through hoses and nozzles inserted into the sediments to release underlying oils has proven the most effective method for the mangrove platforms and intertidal sediments. These methods did not cause undue disruption to the sediment structure as remediated areas fully supported survival and growth of planted mangrove seedlings and return of associated biota.

Significance / contributions of study

The mangrove ecosystem is a critical habitat that is rich in biodiversity, provides shoreline protection against erosion and flooding and is relevant in addressing climate change and sea-level rise. Mangroves have the unique ability to act as a carbon sink sequestering large amounts of carbon, and to protect coastal communities. Application of the RBCA-NEBA approach serves as guidance to set close-out levels following the remediation of similarly oil-damaged mangrove and swamp habitats in the Niger Delta. A government program using similar remediation methods is now in place for other areas of the Niger Delta needing remediation and mangrove reforestation.

<u>Session 3a1 / Abstract title</u>: Results of a pilot for the treatment of landfill leachate using an innovative biological test facility. A significant step towards more sustainable, low carbon and biodiverse water treatments

ID: 190

Key words: Sustainable water treatment, Constructed Wetland. Pilot. Landfill leachate

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Organization: HMVT

Co-authors: HMVT

Session: 3a1

Abstract

Introduction Most contaminated waterflows are treated with energy intensive technologies, producing large quantities of CO2, occupying space that cannot be used otherwise. These solutions may be acceptable for short term projects. However, in case of long-term projects, or projects where waterflows require indefinite treatment, these technologies have a significant negative environmental impact. An example of projects where indefinite treatment is required are landfills. In most landfills, leachate is continuously produced by infiltration of rainwater, potentially forming a risk for decades to the environment. Treatment of leachate can be very costly and energy consuming.

Innovative test facility After more than 20 years in operation the current conventional treatment system needs to be replaced. To test a treatment method that fulfills sustainability requirements, a constructed wetland pilot was conducted between July 2021 and august 2022, at the Nedereindse Plas landfills (Utrecht) in the Netherlands. The purpose of the pilot was to assess if the replacement of the current conventional treatment installation by a full-scale biological treatment system is feasible. The final goal is the realization of a constructed wetland as a treatment method, which should also provide settlement space for wetland flora and fauna and improve biodiversity in the area.
The leachate constitutes a waterflow of 2 m3/hr. Leachate is supplied by two landfills. The composition of the leachate is quite complex: it contains contaminants such as mineral oil and PAH. Apart from the contaminants, the leachate contains very high levels of calcium, ammonium, bicarbonate and sulfur. The conductivity (Ec) of the leachate is very high, providing a challenge for plant growth.
Design of a biological water treatment system always requires a tailor-made approach. Apart from the contaminants, parameters such as pH, conductivity, redox potential, macro-chemicals, seasons etc. all have an impact on the biological processes.

To overcome the site-specific issues for testing, a state of the art open top container with several wetland modules was designed and installed on the site, treating a split-off stream of 20 l/hr. With the test facility it was possible to apply various biological conditions and alternations of the biological conditions. The pilot thus mimics the natural conditions in order to represent a full-scale wetland. Ambient temperature, nighttime – daylight alteration, sunlight and moisture are all kept identical to those on the site. The monitoring program included pH, Ec, Redox, macro-chemicals, temperature, and the analyses of contaminants.

Results The results of the pilot clearly demonstrated the potential of the Constructed Wetland for the treatment of the leachate. For mineral oil, naphthalene and BTEX, removal efficiencies of >80% were reached, independent of the season. Macro chemicals such as Calcium were reduced by 80%.
Based on the results of the pilot an initial design has been made for a full scale Constructed Wetland system at the site. If applied on the site, energy consumption can be reduced by 40%. At the same time, the Constructed Wetland will capture a significant amount of CO2 (instead of emitting CO2 with the current treatment system). The plants that are part of the wetland will contribute to the biodiversity in the area.
The future outlook for this type of biological treatment systems for permanent contamination long duration waterflows is very good. A thorough understanding of site specifics issues (contaminants, waterflows) and biological processes is required in the design phase. All this information can be collected using the test facility.

We will present results of the pilot and its implications for the treatment of landfill leachate. We will explain the set up of the pilot in detail and present in detail the results and the possibilities of a full-scale biological treatment system for the site.

<u>Session 3a1 / Abstract title</u>: Optimizing Remediation Strategy at a Former Large Industrial Site Using a Multiple Lines of Evidence Analytical Approach

ID: 221

Key words: MLEA, NA/ENA, CSIA, remediation measures

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Organization: HPC AG

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Session: 3a1

Abstract

Purpose of study
For the remediation of contaminated sites, the aim is always to find the most ecologically, sound, economically feasible and technically optimal strategy. Such remediation strategies may include the use of natural or stimulated degradation processes, but the integration of these processes in the remediation concept must be carefully examined. If relevant biological removal of pollutants can be demonstrated, cost-effective and environmentally friendly remediation options are possible. The characterization of biodegradation processes is therefore an important part of remedial investigations.

Methodology
A multiple lines of evidence approach (MLEA) provides synergistic effects of the individual monitoring methods that enables mutual validation and a high level of confidence in the results. Compound-specific stable isotope analysis (CSIA) is an advanced monitoring tool for evaluating remediation of organic pollutants at contaminated field sites. CSIA is a robust and proven method to provide source identification, via the source's isotopic fingerprint, as well as for evaluation of contaminant degradation, as changes in isotope ratios are directly linked to this process. The composition of the microbial populations as well as the abundance of functional genes, encoding specific enzymes for pollutant degradation can be quantified by qPCR analysis (Gene-Trac), that highlight zones with significant potential for in situ pollutant biodegradation. Treatability tests allow the ascertainment of the stimulation potential for pollutant degradation by remediation measures in the laboratory under site specific conditions.

For a former large-scale industrial site contaminated with organic pollutants (mainly

chlorinated ethenes, and some BTEX, PAH's), we developed and applied a conclusive MLEA based on the combination of advanced monitoring tools to determine robust parameters for evaluating pollutant degradation processes, e.g. estimated in situ biodegradation and mineralization rates under natural as well as stimulated conditions.

Summary of findings/results

At the field site, three distinctive sources of contamination were identified and sustainable natural pollutant degradation was demonstrated in both the source areas, and in the downgradient plume. Obtained biodegradation rate constants were implemented in a numerical site model to forecast future development of the extent and concentrations in the contaminant plume at the site. To assess the effectiveness of a possible aerobic in situ biostimulation remedy, a laboratory study was conducted using 13C-labeled target pollutants under in situ-like conditions. In this way complete degradation can be sensitively proven and quantified for a great variety of environmental conditions and pollutants observing the 13C-accumulation in the mineralization or end products (e.g., CO2, CH4, ethene).

Conclusions

With the help of model calculations site-specific remediation scenarios were derived and the future evolution of the contaminant plume for two preferred scenarios Monitored Natural Attenuation, and Enhanced Natural Attenuation with stimulation of aerobic pollutant degradation) could be demonstrated. This coordinated MLEA made it possible to use synergistic effects of the methods to enable mutual validation. As a result, natural biodegradation was determined to be a feasible and effective remediation strategy at this industrial site.

<u>Session 3a1 / Abstract title</u>: Experience in Operation and Tunning of Wetland+® Technology for Treatment of HCH-Contaminated Water

ID: 293

Key words: hexachlorocyclohexane, lindane, treatment, wetland, ZVI

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Session: 3a1

Abstract

At the Hájek site dump (the Czech Republic), approximately 5,000 tons of HCH residue were disposed of in the 1970s. The drainage systems of the Hájek dump discharged approximately 1 - 3 l/s of leachate with an average content of 100 µg/l of HCH and 600 µg/l of chlorobenzenes (ClB), which are intermediates of HCH transformation. These pollutants flowed through a channel into Ostrovsky Creek and contaminated the surrounding ecosystem. Within the LIFEPOPWAT project, the Wetland+® full-scale demonstration prototype for treating the dump leachate containing these contaminants has been installed, and its efficiency tested.

The Wetland+® cascade contains four sequential stages: (A) aeration and sedimentation module for removal of dissolved iron in the outflow, (B) permeable reactive modules with zerovalent iron fill to reduce HCH to chlorobenzenes, (C) biosorption module for bioreduction of contaminants, and (D) aerobic wetland module for the final cleaning.

During the testing period of 14 months (the test is ongoing), the total concentrations of HCH isomers at the inlet to the Wetland+® varied from 52 to 265 µg/l, and total concentrations of chlorobenzenes (ClB) from 103 to 1330 µg/l. After the system commissioning, the HCH removal efficiency reached 97%, but during the following first five months of operation, the removal efficiency descended to 54%. The analysis of chemical data and geochemical modelling revealed that the descending efficiency resulted from prevailing aerobic conditions in the B modules that led to the clogging of the reactive fill by ferric hydroxide and oxyhydroxide precipitates. These precipitates were also present in the form of colloids in the water feeding the B modules, as the sedimentation of iron-oxides in the A module was not satisfactory. In addition, the original design of the B modules led to an improper flow pathway of contaminated water through these modules.

In the following period, corrective measures have been comparatively tested to maintain the

B modules in the reducing state and to minimize the formation of iron precipitates. Within these measures, B modules were directly fed by the dump leachate (aeration module A was bypassed) to keep water in an anoxic state. Furthermore, B modules were equipped with floating foil and partitions to limit the diffusion of atmospheric oxygen into water and increase the contact of contaminated water with the reactive fill (iron chips).

Bypassing the A module and modification of B modules suppressed the unwanted geochemical processes and increased the overall HCH removal efficiency of Wetland+® to over 95%. The removal efficiency was not uniform for individual HCH isomers but exhibited the trend: $\alpha = \gamma = \delta > \beta = \varepsilon$. Consequently, while δ-HCH isomer dominates in the inflow, ε-HCH prevails in the outflow from Wetland+®. The operation of the Wetland+® led to a significant decrease in HCH mass discharge to the Ostrovský Creek from initial 24 g/day to 0.8 – 0.9 g/day (approximately 97% decrease).

In sum, testing of the tunned Wetland+® full-scale demonstration prototype indicates that the technology is a promising remedial approach for the treatment of leachates from uncontrolled HCH dumps or other HCH-contaminated sites.

<u>Session 3a1 / Abstract title</u>: Breakthrough in the implementation of the complete flooding of the Königstein uranium mine (Germany) after more than 10 years

ID: 37

Key words: uranium mining, mine flooding, ground water remediation, in situ water treatment

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Session: 3a1 backup

Abstract

Between 1967 and 1990, the SDAG Wismut mined about 18,000 t uranium at the Königstein mining site in Saxony, Germany. The deposit, located in direct vicinity of a national park, is hosted in a cretaceous sandstone formation at depths from 200 to 300 m below surface. In addition to conventional mining, uranium was extracted also by underground chemical leaching. Therefore, remediation of the Königstein uranium mine is a complex project, where conventional remedial measures alone are not sufficient.
In the applied leaching process enormous amounts of sulfuric acid were introduced into the sandstone layers of the deposit.Uranium and many other metals were dissolved and removed. When mining stopped around 2 million m³ of sulfuric acid and polluted pore water remained in the porous rock within the mine.
After more than 10 years of research and preparatory work, in January 2001 the flooding of the first section up to a maximum of 140 m above sea level began. The controlled flooding took place in parallel with the withdrawal from the mine and the approved impounding level was reached in 2013. This means that about 2/3 of the mine is flooded.
As early as 2011, Wismut applied for approval of the flooding of sub-area II under mining law. By this flooding the natural impoundment level of approx. 200 m above sea level should be reached. This application was rejected by the authorities because of major concerns that there would be uncontrollable transfer of contaminated water from the mine into the overlying aquifer. Wismut filed an objection to the rejection, and the approval process was ultimately suspended.
Since 2015, there have been intensive discussions with authorities and scientists at a technical level in order to find a way to allow an environmentally friendly approach to the mine flooding and thus avoid permanent water pumping and treatment.
As a result of these discussions, the first hydraulic test (2017/18) was carried out, where the

water level in the mine was temporarily raised by 10 m to 150 m above sea level. Subsequently, a hydrochemical test was carried out in a small part of the flooded mine. The aim was to improve the water quality using a reactive solution. At the same time, the responsible authorities accepted Wismut's strategy for the gradual flooding of sub-area II. This envisages raising the water level in steps of 10 m each time with an intensive monitoring of the hydraulic and chemical impacts during an at least two-year holding phase before the next flooding step is realised. This gradual flooding is accompanied by the injection of a reactive solution into the partially flooded mine.

The next flooding step with the injection of caustic soda or potash lye and butanol into the southern central part of the former mine as supporting measure is considered as start of the final flooding of the mine. Designated as hydraulic test 2 it will be intensely monitored to gather additional data for process understanding and identification of relevant parameters and their parametrisation. By that predictions of possible impacts will be improved to better manage the flooding of the mine in the future.

The test was applied for in March 2022, and all the necessary approvals were in place by the end of November last year. This means that the legal approval requirements for starting the complete flooding of the mine and thus also for the final clean-up of the site are now in place.

<u>Session 3a1 / Abstract title</u>: Remediation of the Slettebakken landfill in Bergen, Norway

ID: 65

Key words: landfill mining separation process recycling

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Organization: DEME Environmental

Co-authors: nan

Session: 3a1

Abstract

The Slettebakken district is a residential area in the suburbs of the city of Bergen in Norway. Between 1941 and 1960 a small valley in this district was used as municipal landfill. After this period the landfill area, covering around 5 hectare, was levelled and covered with half a meter of gravel and sand, and then hosted several sport pitches and a parking spaces that were used until a few years ago.
At the time no liner was installed to protect the subsoil from pollution and the percolate water drained in an uncontrolled way to the nearby lake Tveitevannet. Various site investigations showed that the digested waste material contains heavy metals, PCBs, and PAHs, and the draining water shows elevated concentrations of zinc and some PAHs. The waste matrix itself is a complex mixture of soil, coal slag, glass, ceramics, textile, bones, plastic, leather, and scrap metal.
The city of Bergen decided to remediate the landfill and preferred a sustainable method with maximal reuse of materials.
In 2020 a joint venture of the Norwegian civil contractor Veidekke and the Belgian remediation specialist DEME Environmental was appointed partner in the partnering contract to further develop the remedial solution. The contract entails two stages: a first detailed design and permitting stage in collaboration with the client and the consultant COWI and a subsequent execution phase.. Based on previous site investigation studies an additional sampling campaign was set up in the summer of 2021 in order to gain better insight on the quality and variations of the landfill material and the groundwater and to collect large volume samples for lab scale and pilot testing.
Samples were sent to the research lab of DEME in Belgium where the physical and chemical composition of the samples was analysed and the separation process was designed. In addition to dry separation techniques such as screening, wind shifting and handpicking, a washing process was elaborated based on a mobile soil washing plant in order to clean and recover a gravelly and sandy fraction consisting of natural and man-made minerals, glass and ceramics. As a result about 60 % of the landfill volume can be processed into a

recoverable mineral fraction, 5% recyclable ferrous and non-ferrous metals, and 35% into high and low calorific waste for external treatment or disposal. For the groundwater the necessary treatment steps and the dimensions of the water treatment plant were defined based on lab scale tests.
The last quarter 2022, once the permits were obtained, both the landfill waste processing plant and the groundwater treatment plant were mobilized to the site. Excavation works began in December 2022 and water treatment and waste processing started in January 2023.
Every day about 500 tons of the excavated landfill waste is processed resulting in a about 300 tons of reusable gravel plus sand mixture. After verification of the chemical quality the material is backfilled at the site and compacted to meet the appropriate bearing capacity requirements. When the project will be finalized (spring 2024) about 144000 tons of waste will have been processed and 80000 tons mineral fraction will have been recycled on site as engineered backfill.

The groundwater and site water is collected in a large buffer lagoon. Then it is treated first in a coagulation-flocculation-sand filtration step for removal of the dissolved metals, and secondly granular activated carbon removes any dissolved hydrocarbons. The clean effluent is discharged in the Tveitevannet lake.

Session 3a2 orals

Session 3a2 / Abstract title: The first Italian permeable reactive barrier: performance assessment during 20 years of operation

ID: 121

Key words: Permeable Reactive Barrier; Zerovalent Iron; Chlorinated hydrocarbons; High Resolution Site Characterization

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Session: 3a2

Abstract

The aim of the study is to present the long-term performance monitoring of the first zerovalent iron permeable reactive barrier (ZVI PRB) installed in Italy. The PRB was emplaced in 2004 to remediate a chlorinated plume at an old industrial landfill site, in Avigliana, near the city of Torino, in Piedmont. The construction of the 120 m long, 13 m deep, and 0.6 m thick barrier was conducted by means of a crawler crane equipped with a hydraulic grab. The excavation was supported by a viscous guar-gum slurry, and it was then backfilled using 1700 t of granular zerovalent iron.
The monitoring campaigns started in 2005 with the aim of verifying the performance of the barrier and its capacity to decrease the chlorinated hydrocarbons below the cleanup goals. Monitoring was not only focused on contaminant abatement, but also on the capacity of the PRB to capture the whole plume. Therefore, particular attention was devoted to assessing the role of biogeochemical processes (e.g., mineral precipitation, microbially mediated redox transformation, gas accumulation) on the hydraulics of the systems, and more specifically on the evolution of the conductivity (and porosity) of the reactive material. Moreover, some mineralogical analysis to characterize the precipitates were conducted by X-ray diffraction and scanning electron microscopy. A porosity loss of 4.9% was calculated for the first years of operation which decreased to lower values due to passivation and slowdown of precipitation rate with time.
After almost 20 years of operation the PRB has treated more than 1.6 Mm3 at an average cost of 0.9 €/m3. The removal efficiency of total carcinogenic chlorinated hydrocarbons decreased from an average value of 98.3% in the first 5 years of operation, to the current

84.1%.If the central part of the PRB is still able to abate the carcinogenic chlorinated hydrocarbons below the target values, an high resolution investigation conducted by means of passive flux meters and by MiHPT-EC probe (Membrane Interface Prove – Hydraulic Profiling Tool Electric Conductivity) reveals a limited lateral bypass, associated with a decrease of the performances, at the far ends of the PRB. To enhance the reactivity in these areas, two pilot scale injections of microscale zerovalent iron (DeltaNova IronGEL-S, 40 m3 at a concentration of 62.5 g/l of bare and sulfidated ZVI particles in the range 1-100 µm) were recently successfully conducted.

<u>Session 3a2 / Abstract title</u>: Green review of a soil remediation Project and cost estimate update for a Former industrial site redevelopment

ID: 255

Key words: Sustainable remediation, Green Infrastructures, Urban redevelopment

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Co-authors: Roberta Sauro Graziano, Mauro Fortugno, Andrea Campioni - Ramboll Italy S.r.l., enviromental consultants

Session: 3a2 backup

Abstract

Ramboll has been asked to review a soil remediation project for a former graphite manufacturing factory to help a client to evaluate an alternative, more sustainable, remediation approach. The site area is about 25 ha and it has been disused for the last 20 years, buildings have been abandoned and Polycyclic Aromatic Hydrocarbons (PAHs) contaminated soil was detected in about 15 ha, but no remedial action has been done. In 2010 the Site was purchased by the Client (a private) with the goal of redevelop it into a mixed-use area: residential, commercial, cultural, institutional, entertainment. The soil remediation project, prepared by the Client's former Advisor, involved contaminated soil excavation and on-site treatment with an estimated clean-up cost of about 25 M€. At this stage, that remediation cost is no more sustainable.
Ramboll approach encompasses a risk-based remediation approach and a deep assessment of mobility and toxicity of contaminants alongside a detailed analysis of the contaminant exposure pathways. Moreover, Ramboll proposed a sustainable remediation approach, alternative to the traditional and expensive "excavation and treatment", compatible with the residential and mixed-use redevelopment of the area. Contaminated soil can be left in place and contained by means of engineered capping systems to interrupt the contaminants exposure pathways (permanent safety measures allowed by Italian law) as an alternative of excavation and on-site treatment, that are costly. Soil containment can be operated by a "green capping" (multi-layer capping, top layer made of soil and grasses or trees) which enables the restoration of nature and ecosystems.
The most valuable buildings shall be recovered and reused, and part of the site shall be transferred to the Local Municipality, thus increasing the added value of the intervention for the local community and reducing the impacts of demolition, in compliance with the principles of environmental sustainability.
The sustainable remediation and urban redevelopment of the Site proposed by Ramboll

allow to revitalize an abandoned, contaminated and underutilized area of about 25 ha in the middle of the city by green infrastructures and nature-based solutions, that bring value to urban areas, allow the restoration of nature and ecosystems and give value to one of the city's most underutilized resources.
The proposed "green" site redevelopment represents an alternative and sustainable approach for this site remediation with a relevant cost saving (5M€ Vs 25 M€ of the previous project) and with considerable ecological, economic and social benefits, in line with the strategy of European Union of the "green infrastructure network" aimed to create urban parks and forests, according to the concepts of urban landscape and urban forestry introduced by the European Commission in 2019. The creation of urban parks and forests can improve the air quality (blocking of dust, storage of CO2), mitigate climate changes, reduce the "urban heat island" effect, protect biodiversity and prevent the soil erosion.
Ramboll supports Clients in brownfield holistic and sustainable redevelopment and provides a variety of services, like nature-based solutions, site dismantling, decommissioning and demolition management, permitting, landscaping and more. Ramboll Landscape Architecture Division (Henning Larsen) can design new development solutions for brownfields, that balance city and nature, combining sustainable architecture and environmental issues.
The proposed solutions contribute also to the achievement of some of the Sustainable Development Goals (SDG) define by the 2030 Agenda as good health and well-being, Sustainable cities and communities, Life on Earth.

<u>Session 3a2 / Abstract title</u>: Quantifying Carbon and Water Footprint reduction for in-situ Site Remediation vs conventional Plume Management approaches

ID: 288

Key words: Carbon footprint; Water footprint; Sustainable Remediation

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Session: 3a2

Abstract

Purpose of study:
Sustainability evaluations are becoming an increasingly relevant driver for Site owners in the site remediation sector, alongside economical evaluation of remediation alternatives.
The aim of this study is to quantify the potential savings in terms of carbon and water footprint, of adopting an in-situ remediation approach for managing groundwater impact at contaminated sites, compared to a traditional plume management via Pump (P).

Methodology:
A comparative Carbon Footprint (CF) was carried out considering Scope 1, 2 and 3 carbon emissions for two real-case contaminated sites in northern Italy, where an in-situ bioremediation approach was implemented for managing groundwater contamination, at two different stages of the remediation process, in lieu of a conventional P system:
- In Site A, in-situ bioremediation with Oxygen Microdiffusion was selected during remedial option appraisal, avoiding the need for installation of a large hydraulic barrier;
- In Site B, an existing P system was replaced by an in-situ bioremediation with Emulsified Vegetable Oils (EVO) injections for supporting the biological degradation of the Site contaminants.
The CF evaluation was implemented, as part of a sustainability evaluation of alternatives, through a “Carbon Footprint Calculator” spreadsheet proprietary of ERM. Each Carbon emission calculation is obtained by multiplying a unit quantity of material or activity for a defined Emission Factor (EF), mostly derived from international literature. Results are given in terms of weight of CO2 equivalents generated (kgCO2e) both during the installation phase, and for the O activities as an annual basis.
Additionally, a Water Footprint (WF) evaluation have been conducted quantifying the water consumption directly associated to each remedial technology considered. The WF

associated to the product chain of the products used for the remediation activities, defined as indirect WF, has not been considered for this study.

Summary of results:
In Site A, the implemented in-situ Oxygen Microdiffusion is associated to a total CF almost 1/1000 times that of a theoretical P over the same assumed remediation timeframe (20 years).
In Site B, the installation activities for P and EVO injection have a roughly similar CF. However, the average yearly CF of the P management is more than one order of magnitude higher than with the current in situ bioremediation approach, even if an additional EVO injection is considered every 4 years. Moreover, the in-situ bioremediation with EVO injection is offering a further advantage since it has been applied also at the contamination source, thus helping to lower the total lifespan of remediation and plume management actions.
For both Site A and B, the remedial approaches alternative to the P correspond to relevant water savings, confirming that they are largely preferable also from a water sustainability standpoint.

Conclusions:
Adopting in situ bioremediation approaches may have a positive impact on the overall remedial process sustainability quantified via CF and WF assessment, compared to conventional P approaches, both when in situ bioremediation is selected during remedial option appraisal, and when it is used to replace an existing P system during remedial operations.

Significance/contributions of study:
CF and WF assessments are applicable to site remediation processes and technologies through the use of user-friendly tools and calculations. CF and WF may help Site owners to measure the consistency between corporate sustainability goals (concerning GHG emission targets), Carbon Footprint and water stewardship indicators specific for remediation activities.

<u>Session 3a2 / Abstract title</u>: Facile removal of Cd and Cu from farmland soils and waste eluent by waste biomass extracts and its residues

ID: 291

Key words: Soil remediation, Farmland soil, Cd and Cu, Waste biomass extracts, Waste eluent treatment

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Session: 3a2 backup

Abstract

Purpose: Heavy metal pollution in farmland soil threatens sustainable utilization of land resources and safe production of food crops. At present, washing with chelating agents (e.g., organic acids, synthetic chemical compounds) is a promising technique to permanently remove heavy metals from farmland soils. However, there is still a lack of inexpensive, high-efficiency and environmentally sustainable chelators and the safe treatment of waste eluent. This study aims to develop a facile two-stage sequential washing method using waste biomass extracts for rapid removal of cadmium (Cd) and Copper (Cu) in farmland soil.
Methods: In this study, the optimal washing extracts from agro-forestry wastes (pineapple peel, PP; lemon peel, LP; grapefruit peel, GP; gardening crabapple fruit, GC) were determined and a facile two-stage sequential washing method (extracts and/or citric acid (CA) and coupled with extracts) was developed through batch and soil column experiments. The mobility and availability of Cd and Cu in soils were assessed by BCR sequential extraction method. The Cd and Cu in the collected waste eluent from the experiment were removed by PP waste biomass extract residues.
Results: The results showed that the washing efficiencies of Cd and Cu were significantly increased by PP using the two-stage sequential washing with the sequence of PP+CA-PP > CA-PP>PP-PP. The potential pollution risks of Cd in soils decreased by 28.6%-36.7% from moderate to low risk due to the significant decrease of exchangeable and reducible Cd fractions. Majority of Cd (80.9%) and Cu (81.3%) in the waste eluent could be removed by PP extract residues. The removal mechanisms of metals in soils and eluent by PP washing agents and residues can be attributed to acid activation, cation exchange and complexation between metal ions and carboxyl groups.
Conclusion and Significance: A rapid removal of Cd and Cu in contaminated farmland soil

and waste eluent using two-stage PP extracts washing and its residues treatment might be feasible. But scale-up and practical investigations are needed for further examination of this method under field conditions in particular. This study will help scientific and industrial community to develop more environmentally friendly, efficient and economical agricultural soil remediation products and green sustainable soil remediation technologies.

<u>Session 3a2 / Abstract title</u>: Remediaiton Plan for contaminated soils in a 43 hectares former PVC plant in Israel

ID: 306

Key words: Mercury, chlorinated solvents, chloroalkali, biological treatment, thermal treatment, soil washing

Submitter: Raphi Mandelbaum

Organization: LDD Advanced Technologies (2005) LTD

Co-authors: Hanan Meron Msc., LDD Advanced Technologies (2005) LTD, Hydrogeologist

Session: 3a2

Abstract

The purpose of this work is to develop a sustainable soil and groundwater remediation plan, protective for humans and the environment, while allowing the redevelopment of the site for commercial and residential use.
The site that was operational for about 40 years till 2004 is located on the beach of the Mediterranean south of the city of Akko. The site soil and groundwater are largely polluted with a combination of chlorinated solvents and mercury and was investigated since 2010 to delineate the impacts within the source areas. A passive soil gas campaign with over 1000 samplers helped delineate the two dimensional spread of contaminants and focus further intrusive investigations. More than 1100 boreholes were drilled to the soil and shallow groundwater (gw) to elucidate the 3- dimensional spread of the contaminants. Beach sediments were also investigated.
Mercury in significant concentrations was found in the Electrolysis plant, the drains around it, and its vicinity, but also the practice of land disposal of Mercuric chloride on premise impacted larger area of the site. Methyl mercury was found in very small amounts in soils which reduces the potential need for remedial action to mitigate methyl mercury risk.
The soil remediation plan was aimed to minimize off-site disposal and to prefer the treatment of contaminated soils and demolition debris over landfill.
The buildings on site were found to be in a very poor structural condition, which prohibited their safe sampling. Therefore, they were demolished based on 3 predetermined categories based on their historical use: Clean buildings (offices, storage of final products); Suspected to be contaminated (laboratories, storage of wet products) and certainly contaminated (Tank farms, electrolysis plant, mercury recycling facility). The clean debris were crushed and recycled for development on site; The suspected buildings were sampled after demolition and categorized to either clean or contaminated debris. The contaminated debris were crushed under emission controlled conditions all together with the debris from the contaminated buildings. Contaminated gravel arising from the crushing of contaminated

gravel were treated on site and recycled as a base material for a sound barrier separating the developed site from their neighboring proving ground south of the site.

After an exhaustive review of the applicable methods for soil treatment, four methods of choice were selected for lab and field pilots.

1. Soil Washing of up to 220,000 metric tons of soil contaminated with mercury and/or chlorinated solvents with moderate concentrations.
2. Thermal treatment of up to 30,000 metric tons of soil contaminated with mercury and/or chlorinated solvents with moderate to high concentrations.
3. Bioremediation of up to 100,000 tons of soils contaminated with low to moderate level of chlorinated organic solvents.
4. Landfill in a Hazardous Waste landfill of a relatively small amount of soils contaminated with high levels of mercury

Over the 20 years between the cessation of production and the remediation, a population of the invasive plant species Acacia Saligna has overgrown the site. The plants were tested for mercury content and disposed based on their mercury level.

The full scale remediation is underway. The talk will discuss the process of remedial methods selection and a discussion of the results.

<u>Session 3a2 / Abstract title</u>: Chromium (VI) and vanadium (V) in groundwater: investigating bioremediation solutions

ID: 326

Key words: Bioremediation, heavy metals, biological reduction, chromium, vanadium

Submitter: Rogier de Waele

Organization: Greensoil group

Co-authors: Michaela Bhend (Greensoil group, Environmental Engineer R), Dr. John Dijk (Greensoil group, Microbiologist and R Manager), Martin Slooijer (Greensoil group, Managing Director)

Session: 3a2

Abstract

Purpose of study
Chromium (VI) and vanadium (V) are emerging toxic and mobile contaminants in groundwater. The potential risks can be decreased by reduction to its less toxic counterparts; i.e. Cr (III) and V (IV/III). Those reduced forms typically precipitate and are therefore less mobile as well. The reduction can be facilitated by microorganisms via microbial reduction or indirectly via biologically produced reductants like iron sulfide. This mechanism was applied in a full-scale bioremediation project for a site contaminated with chlorinated solvents (>100 mg/L TCE) and Cr (VI) (>1000 mg/L). For a site contaminated with V (V) (>150 mg/L), a similar approach was tested at lab-scale with the aim to investigate it as a feasible remediation technique and to gain more insights into the reduction processes.

Methodology
Biologically mediated reduction was applied to remediate the groundwater plume of chlorinated solvents and Cr (VI). To create anaerobic conditions, injections were carried out with an electron donor. The aim was to achieve (indirect) reduction of Cr (VI) to Cr (III) via biological processes. A laboratory study with sulphate-rich groundwater from a vanadium contaminated site was carried out to test if reduction of V (V) can be achieved. Sulphate reduction was monitored by measuring sulphate concentrations and the microbial community was assessed with NGS (Next Generation Sequencing) analyses. Electron donor was added to stimulate sulphate and vanadium reduction.

Summary of results
In a full-scale remediation project the required geochemical environment for Cr (VI) reduction was created and the biologically mediated process stimulated. The results showed a successful reduction of the toxic Cr (VI) contamination to Cr (III). The reduction of the mobile

Cr (VI) fraction was > 99% within a year.
For vanadium, the results of an anaerobic lab test show that 64 – 84% of aqueous V (V) was reduced in the presence of an electron donor. To investigate the fate of the V removed from the dissolved phase, ICP-OES, XRD and SEM-EDX analyses were performed on the precipitate. The precipitate appeared to be reduced V in the form of different oxides with calcium, iron and aluminium. The V speciation analyses showed that most reduction of V (V) to V (IV) occurred during the first three weeks of the test when conditions were not fully anaerobic yet. According to the NGS, the aerobic bacterium Pseudomonas putida was the most abundant (8%) and likely candidate for vanadium reduction based on literature. Therefore, a second test was conducted under both aerobic and anaerobic conditions. In the aerobic conditions after 4 months, ± 5 % of the total V was present as V (IV) and 10 – 35 % remained present as V (V). 60 – 80% of total V likely precipitated or further reduced to V (III) or V (II). The aerobic samples all developed a bright yellow colouration which indicated the presence of predominantly V(V). In one anaerobic condition, more than 98% of V (V) was reduced and precipitated or further reduced to V (III) or V (II) in the water, since dissolved V (IV) could only account for 0.4 %. The colour change to petrol blue also indicated that dissolved V (III) was present.

Conclusions
Cr (VI) was successfully reduced to Cr (III) in a full-scale project within less than a year. V (V) was reduced to V (IV) under anaerobic and aerobic batch conditions in the lab. To better understand the reduction process, NGS were performed and the composition of the precipitate in the samples will be analysed with specialized geochemical analyses. Also long-term stabilization of the formed reduced vanadium will be investigated.

Significance of study
Sustainable biological treatment approaches of Chromium (VI) in full-scale and of vanadium (V) at laboratory scale showed promising results. Advanced geochemical and microbial analyses play a crucial role in understanding heavy metal reduction and determining a reliable full-scale approach.

<u>Session 3a2 / Abstract title</u>: SUSTAINABLE CYCLIC REMEDIATION OF A HEAVILY IMPACTED SITE WITH XYLENE – 100% BIOLOGICAL TREATMENT OF SOIL, GROUNDWATER AND SOIL VAPOR

ID: 354

Key words: sustainable remediation, bioremediation

Submitter: Martin Slooijer

Organization: GreenSoil Group

Co-authors: R. de Waele, GreenSoil, Sales and Accountmanager

Session: 3a2

Abstract

Purpose of Study
A former triacetate production site caused a heavy xylene contamination up to 27,850 mg/kg in soil and 89,000 µg/l in groundwater, to a depth of 10 m-bgl resulting in a total contaminant mass of 100 ton of Xylene. 100% on-site and in-situ biological remedial approach were proposed to remediate soil and groundwater heavily impacted with BTEX, mainly Xylene, being both more sustainable and economic compared to conventional (off-site) techniques. The project was conducted in a lump sum contract with guaranteed outcome.
The present high mass of volatile contaminants, presented a high financial risk in this project mainly related to treatment of highly contaminated air from the biopiles and water treatment system. With his project different biological airtreatment systems were developed to mitigate this financial risk and present a most sustainable remediation technique compared to active carbon.
Methodology
The remediation consisted of 100% on-site and in situ biological techniques including on site biopiling and in-situ biosparging for groundwater. The excavated soil was placed in biopiles within the excavation pit, where dosing of nutrients and bioventing stimulated biodegradation of the contaminants. In this way, transport of contaminated soil to a different location was avoided, thus no trucks were needed, and nuisance to the neighborhoods was limited.
Contaminated air was extracted from the biopiles and treated by means of activated carbons (GAC). However, working under a lump sum contract and being GAC not environmental-friendly, an innovative biological air treatment (BAT) technique was developed during the project to reduce cost and use of GAC. The BAT consisted of redesigning the biopiles, after the soil treatment was completed, to treat soil vapors (500-2,000 ppm) originating from new biopiles, as they still contain nutrients and active bacteria.
After soil treatment, the site was levelled and an enhanced in-situ biosparging system was

installed to treat residual soil and groundwater contamination.

Summary of findings/results

All 25,000 m3 of heavily impacted soil have been cleaned far below the remedial target values in 1.5 year. Starting from concentration levels up to 10,000 mg/kg, biopiles concentrations were reduced within 60-80 days to concentrations levels below 50 mg/kg.

The BAT process worked with an average and constant efficiency of 80% which resulted in a strong reduction of the GAC consumption.

The impacted groundwater (up to 89,000 µg/l of xylene) was treated by in-situ biosparging resulting in a structural 70-99% decrease of concentration levels within one year.

The biological water treatment system, used to treat contaminated groundwater extracted to lower the groundwater table, worked with high efficiencies, especially given the high influent concentrations (efficiency rate up to 99-99,9%) and removed the bulk of the incoming groundwater mass, leading to a noticeable reduction of activated carbon as well.

Conclusion

The project showed the power of circular bioremediation and has evidenced that innovation, sustainability, and cost can go hand in hand. 99% of the contamination was degraded biologically either in soil, groundwater, or air. In addition, 0 m3 of soil left the site seriously reducing transport movements around the site. Cleaned-soil was used as air-treatment. Another remarkable outcome is that the active carbon consumption was reduced with 98% reducing waste and costs.

Significance / contributions of study

The project shows how lump sum contracting drives innovation and cost efficiency with the development of innovative biological air treatment techniques. Circularity in essence : contaminated soil is treated biological on-site to harmless end products and subsequently used as biological filter to treat contaminated air, and finally used as backfill material at the site.

Session 3b10 orals

Session 3b10 / Abstract title: A Sustainable Approach For TCE Contaminated Groundwater Remediation: Raw Polyhydroxyalkanoates (PHA) As Electron Donor for BRD Coupled With Adsorption On Biochar

ID: 107

Key words: Chlorinated compounds; biological reductive dechlorination; polyhydroxyalkanoates; adsorption; biochar.

Submitter: Marco Papini

Organization: University of Rome La Sapienza

Co-authors: Lorenzo Gianni, University of Rome La Sapienza Rome, Environmental scientist and chemist Dr. Bruna Matturro, Water Research Institute Rome, Environmental Biotechnologist Dr. Simona Rossetti, Water Research Institute Rome, Research Director Prof. Marco Petrangeli Papini, University of Rome La Sapienza, Full Professor

Session: 3b10

Abstract

Purpose of study. Previous studies showed the potentialities of bio-based materials for bioremediation purposes, including polyhydroxybutyrate (PHB), a biodegradable microbial polyester tested as a fermentable source of slow-release electron donor for sustaining the biological reductive dichlorination (BRD). On the other hand, a low-cost biobased material, biochar (BC), also used as sorbent, has recently been proposed to accelerate the BRD reactions. Here we proposed a Coupled Adsorption and Biodegradation (CAB) process for trichloroethylene (TCE) removal in a mini-pilot-scale reactor filled with a raw PHA produced from mixed microbial cultures (MMC) and fermented organic waste (as feedstock) and pinewood BC. This work aimed to evaluate the performance of the CAB process with particular regard to the effectiveness of the BC in sustaining the dechlorinating biofilm (mostly enriched by Dehalococcoides mccartyi (Dhc)) growth, and the effects of a raw PHA as source of electron donor.

Methodology. The Reactor was carried out in a column of 150x10 cm, in which the dechlorinating biofilm was supported by pinewood biochar (4% wt) mixed with sand for the entire length of the reactor. Moreover, in the first half of the column, from the bottom, called the "fermentation zone", a dry raw PHA-rich biomass (35 %wt of PHA) in powder form was

added. The reactor was equipped with 13 gates for lateral sampling. The start-up was carried out with an active TCE-to-Ethylene consortium. After the tracer test, the flow rate was maintained at 2.9 ± 0.6 L/d on average, with 35 hours as Hydraulic Retention Time (HRT). The feed solution consisted of contaminated tap water, resulting in a final TCE concentration of 100 µM. The monitoring of volatile fatty acids (VFA) and Chlorinated compounds was carried out through regular sampling of the side doors of the column. Samples were stored for microbiological analysis.

Results. During the first two months of operation, the reactor has treated 180 Liter of contaminated water (10.5 ± 1.7 mg L-1 was the average of TCE IN) removing 2.6 g of TCE. The PHA compartment yielded a very high concentration of total VFA at the beginning of the experiment (1.3 g/L of VFA during the first week, at the outlet), decreasing progressively until a constant concentration of 6 mg/L from day 118 to 214. After 214 days of operation, a complete conversion of TCE to cis-dichloroethylene and the following daughter product vinyl chloride was observed in the fermentative zone, while the final product, ethylene, was detected only in outlet. A slow and constant release of Acetate from the PHA compartment and the high flow rate used are interesting conditions for field applications. This configuration also allowed the treatment of high contaminant load at high solution feed rate (30.6 mg TCE day-1; 1.5 m day-1).

Conclusion. The promising results open doors to the circular economy concept where a by-product of biomass thermal treatment and a biopolymer obtained from organic waste could support specific dechlorinating biofilm for bioremediation application.

Significance. Recent field application studies in Italy have shown the effectiveness of combining the immobilization of chlorinated solvents and the biostimulation, allowing the quick reduction of dissolved contaminant levels and promoting the BRD kinetics. In compliance with sustainability and circular economy principles, the current research interest is focused on alternative materials such as long-lasting electron donors and possible growth support for biofilm as adsorbents. This study is particularly relevant for possible field application, indeed the tubular reactor configuration could be applied on a larger scale for an ex situ treatment of a contaminated groundwater. On the other hand, the same technology could be involved in a PRB configuration.

<u>Session 3b10 / Abstract title</u>: GreenCat - Green catalysis for groundwater remediation - from waste material to universal catalyst for chlorinated solvent degradation

ID: 195

Key words: iron-biochar reductant, chlorinated solvents, reductive dechlorination

Submitter: Dominique J. Tobler

Organization: University of Copenhagen

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Session: 3b10

Abstract

GreenCat, a 4-year Danish Innovation Fund project, aims to refine a new sustainable iron-biochar composite (IBC) technology for in-situ remediation of sites contaminated with chlorinated solvents (CS). The IBC product is a pH neutral suspension composed mainly of a synthetic layered iron(II)/iron(III) hydroxide (green rust) and biochar produced by pyrolysis of organic waste materials such as wheat straw, bonemeal and wastewater sludge. Together, they create a powerful composite for full and rapid CS dechlorination while the IBC itself integrates into the contaminated sediment. The biochar functions as a catalyst by easing electron transfer between the green rust and the CS. The biochar component is critical for reaction rates and end product, and nitrogen-rich biochars produced by pyrolysis at temperatures of 800 - 900 °C are found particularly efficient. Typically, full conversion to acetylene is obtained when IBC is used to treat tetrachloroethylene, trichloroethylene, and dichloroethylene, while vinyl chloride is reduced to ethylene. Typical half-lives of CS in aqueous solution are within hours to a few days, and comparable to rates that can be obtained using zero-valent iron (ZVI) for CS reduction.
In the first 3 years of the project, the IBC technology has been vigorously tested at laboratory scale in terms of reactivity, stability, and longevity in groundwater and sediments, and its formulation further developed. Furthermore, the IBC injectability and radius of influence have been assessed and modelled to help planning and dimensioning aquifer remediation. Large

scale batch production of the IBC product and a first demonstration at the tank (3 m3) scale are underway.

Here, we will showcase the development of the IBC technology from laboratory to industrial scale, its performance under varied groundwater/sediment conditions, also relative to other existing in-situ injection reactants (e.g., ZVI), and provide an outlook for its main application field and potential market share.

<u>Session 3b10 / Abstract title</u>: Large-Scale In-Situ Biotic and Abiotic Dechlorination of Groundwater Impacted with Co-Mingled Chlorinated Ethenes and Chlorinated Methanes

ID: 21

Key words: Groundwater, Remediation, In-Situ, Dechlorination, Reductive

Submitter: Mark Mejac

Organization: Ramboll

Co-authors: Uma Patel, Ramboll, Environmental Consultant; Nick Walchuk, Ramboll, Environmental Consultant; Farshad Razmdjoo, Ramboll, Environmental Consultant.

Session: 3b10

Abstract

Purpose: The site covers approximately 5 hectares and has been used for industrial purposes since the 1940s. A 2018 site investigation conducted as part of facility closure identified the presence of chlorinated volatile organic compounds (cVOCs) in groundwater including trichloroethene (TCE) concentrations as high as 3,400 micrograms per liter (µg/L), carbon tetrachloride (CT) concentrations as high as 2,400 µg/L and chloroform (CF) concentrations as high as 1,060 µg/L. This cVOC impacted groundwater covered an area of approximately 7,000 square meters to a depth of approximately 6 meters below ground surface and is present within interbedded silty clay and silty sand soils. Remedial objectives include minimizing human health risks to future receptors due to ingestion and direct contact to groundwater and also due to inhalation of soil vapor. Substantial heterogeneities within the treatment zone, and the presence of a shallow water table and adjacent surface water receptor posed significant challenges to effective distribution of injected amendments. Methodology: Groundwater remediation using in-situ chemical reduction (ISCR) paired with enhanced in-situ anaerobic bioremediation (ISB) was implemented in late 2021 to address the cVOC-impacted groundwater. Pre-design testing of pressurized direct push injection (DPI) and pneumatic enhanced injection of zero-valent iron (ZVI), organic carbon substrate and bioaugmentation consortium was conducted to refine injection parameters and identify a preferred injection technology for full-scale remediation. Based on the occurrence of amendment daylighting during late 2021 pre-design testing, the pneumatic enhanced injection alternative was removed from consideration and the efficacy of pressurized DPI was solely evaluated based on several lines of evidence, including magnetic susceptibility (MS) measurements. A full-scale injection design was subsequently formulated based on the results of the pre-design testing. A total of 62,000 kilograms (kg) of ZVI, 148,000 kg of organic carbon substrate and 208 liters of dechlorinating culture was then injected through 264 DPI points in late 2021.

Summary of Findings: The results of post-injection groundwater monitoring revealed effective electron donor distribution based on total organic carbon concentrations, establishment of reducing conditions based on nitrate, ferrous iron, sulfate, and methane data, and substantial reductive dechlorination based on evaluation of cVOC molar concentrations and molar fractions. The following reductions in cVOC concentrations have been observed (without rebound) in the most heavily impacted monitoring wells, two to 10 months post-injection:

- TCE decreased from 1,400 µg/L to 2.5 µg/L;
- CT decreased from 1,200 µg/L to 0.050 µg/L; and
- CF decreased from 660 µg/L to 28 µg/L.

Conclusions/Significance: Based on the most recent (late 2022) groundwater sample results, treatment zone groundwater no longer contained detectable TCE or CT, or their respective degradation products cis-1,2-dichloroethene or methylene chloride. Only one late 2022 sample contained vinyl chloride at a concentration above the Safe Drinking Water Act Maximum Contaminant Level (MCL) of 2 µg/L. Post-injection groundwater data interpretation will be presented, along with discussions of rationales regarding injection approaches and next steps.

<u>Session 3b10 / Abstract title</u>: Innovative ZVI application for sustainable remediation of chlorinated solvent plumes

ID: 58

Key words: chlorinated solvents, sustainable remediation, PRB, ZVI

Submitter: Kirsten Rügge

Organization: COWI Denmark

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Session: 3b10

Abstract

Purpose of study. There is a large demand for sustainable remediation techniques to ensure clean water as also indicated by UN's goal no. 6. The objective of this project is to thoroughly test and document a new method that can be used for remediation of chlorinated solvents (cVOC's) in groundwater all over the world.
Methodology. Pre-design microcosm and column test reactors with five different ZVI-products were prepared using groundwater and aquifer materials from a cVOC contaminated site to identify an optimal ZVI-product for remediation. Provect-IR® with bio¬augmen¬tation with KB-1® culture achieved the most complete treatment and was selected for a pilot test at the site. Provect-IR® contains a natural anti-methanogen compound to inhibit methane production, which can be problematic in urban areas.

Subsequently, a pilot scale "Permeable Reactive Barrier" (PRB) was installed at the site. Using a PRB for remediation is an in-situ method and after installed it will work passively. Thereby the method is much more sustainable that active pump treat methods. The Provect-IR® design dose was 1% by weight of soil and KB-1® dechlorinating culture (4 L per injection point) was added. Installation of the PRB was followed by a detailed documentation of the distribution of ZVI by means of soil core sampling and analyses (magnetic susceptibility, visible iron, and laboratory iron analysis) and comprehensive depth specific water sampling. In addition, the distribution was monitored by use of a cross-borehole geophysical method "Direct Current, Induced Polarisation" (DCIP) that allows for detailed spatial information. Furthermore, the IP properties was used to infer spatial information on hydraulic conductivity, which was used in assessment of contaminant mass discharge (CMD) before and during remediation.

To allow PRB performance monitoring, three transects of monitoring wells were installed. Baseline monitoring confirmed expected iron reducing conditions, significant concentra¬tions of TCE and cDCE. Low concentration of VC and only trace concentrations of ethene and ethane revealed incomplete reductive dechlorination. The performance monitoring program included chemical as well as microbial analysis and Compound Specific Isotope Analysis (CSIA) to document and quantify biotic and abiotic degradation. Quarterly groundwater sampling enabled the establishment of cVOC degradation trends and the calculation of cVOC mass/flux removal in the plume. The final monitoring was performed in October 2022 and the final interpretation will be completed February 2023.
Summary of findings/conclusions. Complete degradation of cVOCs to ethene/ethane was observed in areas with sufficient distribution of Provect-IR® and KB-1® culture. The degradation was predominantly caused by the injected Provect-IR® and KB-1® culture, since only 8% decrease was observed to occur naturally. In areas where the distribution was less successful, also less degradation was observed.

Dual isotope plots indicated that degradation pathways changed from solely biotic to a combina-tion of biotic and abiotic degradation after creation of the PRB. Only minor methane production was observed in the groundwater, and it seems that the methane inhibitor in the product was sufficient to avoid critical methane spreading in the area .
Significance. The remediation is done in a sustainable way, and where sufficient distribution of Provect-IR® and KB-1® culture is obtained, the remediation is very promising. Furthermore, the method will be applicable to contaminated sites all over the world. Thereby the method can help in fulfilling the goal indicated by UN´s goal no 6.

<u>Session 3b10 / Abstract title</u>: The winner takes it all – trialling three parallel remediation options at the same site in order to select one remediation strategy for the entire site

ID: 91

Key words: Pilot, chlorinated solvents, remediation design, direct push injection,

Submitter: Helena Nord

Organization: Sheeba Environmental Engineering AB

Co-authors: Jonny Bergman, Sheeba Environmental Engineering, Remediation expert; Malin Johnsson, City of Varberg, Project manager; Johannes Hedtjärn, Sortera Materials Nordic AB, Project manager; Jack Shore, Regenesis, Senior District Manager UK and Scandinavia; Josephine Molin, Evonik, Technology Applications Manager ISCO

Session: 3b10

Abstract

Purpose of study: In the city of Varberg, South West Sweden, a mechanical industry has caused extensive chlorinated solvent contamination , impacting superficial deposits and superficial groundwater, bedrock and bedrock groundwater. The contamination has migrated in under the Kattegatt sea, and is currently impacting the construction of a train tunnel built beneath the city. The remediation of the site is being performed in three phases. The first phase was to excavate the contaminated soil from the industrial area. Once completed, thermal treatment commenced, targeting the source area in bedrock to 50 m bgl. This presentation covers the third and last remediation phase, to remediate the soil groundwater to a level of 0.1 mg/l CVOC (TCE, TCA, DCE, DCA, VC).

Methodology: As the remediation area consists of 12,000 m2, it was decided to start by trialling possible technologies in an area with relatively high contaminant concentrations. The contaminant levels in the trial area were up to 6,300 µg/l for TCE, 6,800 µg/l for DCE and 1,800 µg/l for VC. Ethene and ethane were also present, indicating that reductive dechlorination is ongoing. The superficial geology is heterogeneous, comprising a mixture of sands, silts, gravels and clays in alternating layers down to 6 m bgl. This overlies the fractured granite bedrock, with the superficial groundwater level at 2 m bgl.

The trial area is approximately 300 m2 and was divided into three 100 m2 subareas. Each subarea was utilised for a unique pilot test, where two competing remediation product suppliers were tested against each other.

All testing was performed using direct push injection, and the results were monitored for

approximately 29 weeks. Trial 1 was performed using PlumeStop (colloidal activated carbon), S-MicroZVI (colloidal zero-valent iron),HRC Primer (carbon source) and HRC (carbon source) from REGENESIS. Trial 2 was performed with the same products but with a higher dose of colloidal active carbon and no colloidal zero-valent iron. Trial 3 was performed using EHC+ (all in one combination of activated carbon, zero-valent iron and carbon source) from Evonik.

Summary of findings/results: After 29 weeks, sampling in the two monitoring wells per pilot area showed that the contaminant levels of TCE and DCE had decreased by 83-100 % in all areas (except for one monitoring well in Trial 2 pilot area where the decrease of DCE was 21 %). Carbon adsorption was evident from the start, with a faster contaminant reduction where zero-valent iron had been used, and biological degradation has increased over time.

Conclusion: The pilot trials have provided the project with important information about the different remediation options available for the site. While the remediation results are important, other factors play a crucial role in deciding remediation methodology, including injectability, handling and storage on site, H, effectivity, cost, and estimated time to reach the targets. Also, the experiences of the site crew are very important in designing the best remediation option that will provide effective site work.

Significance/contributions of study: This study proves the benefits of trialling different remediation methods on a site to obtain valuable data to aid selection of the preferred strategy. The presentation will also include practical lessons learned from the site works. By the time of the presentation, the methodology chosen for the remediation of the whole site hopefully will be selected and shared.

Session 3b11 orals

Session 3b11 / Abstract title: Steam Injection in Low Permeability Environments to Improve Thermal Sustainability

ID: 235

Key words: Steam, Low Permeability, Thermal, Sustainability

Submitter: James Baldock

Organization: ERM

Co-authors: Joanne Dinham, ERM

Session: 3b11

Abstract

This paper outlines ERM's recent successful experience in application of Steam Enhanced Extraction (SEE) in unconventional settings. Two case studies will be presented, both of which are operational manufacturing facilities located in Europe, impacted by solvents (Site 1) and petroleum hydrocarbons (Site 2). Site 1 is underlain predominantly by clays and silts, whilst Site 2 is situated upon fractured Chalk bedrock.

At Site 1, field data suggested the lithology to comprise predominantly low permeability silty clays; therefore, Electrical Resistance Heating (ERH) was initially expected to be the selected heating method; however, following detailed high resolution investigation the material was shown to be more silt rich. Given this, the possibility to use SEE was further evaluated by steam injection into a single well, which confirmed relatively high flow rates of steam could be injected to achieve the required treatment temperature.

It was also expected that heating at Site 2 would be undertaken using ERH. However, this would have meant electrode installation at a spacing of 4.5m, which was not acceptable to site management from an operational perspective. Therefore, a field scale steam trial, similar to that undertaken at Site 1, was carried out to evaluate SEE using more widely spaced heating locations. As expected, fractures influenced the steam flow, but the area containing the greatest contaminant mass was heated in a controlled way.

At both sites, the change in heating methodology resulted in significant cost savings and at Site 2 allowed the thermal remediation approach to be accepted by site management. Multiple lines of evidence were evaluated at both sites to support possible use of SEE, and

subsequent field scale steam injection trials confirmed successful application within geology where use of this heating methodology would not have traditionally been considered.
The advantages of increasing the SEE operational window are reduction in drilling and equipment costs compared to using ERH, where heating locations need to be significantly more closely spaced and where more power intensive equipment would otherwise be required. This is particularly relevant given pilot scale steam generators are now more routinely in use and steam is often available at a broad range of industrial sites, enabling further cost savings and reduced energy consumption.

<u>Session 3b11 / Abstract title</u>: Remediation of vinyl chloride in organic sediments using Hot Air Sparging

ID: 43

Key words: Chlorinated solvents, urban environment

Submitter: Per Johansson

Organization: WSP Sweden

Co-authors: nan

Session: 3b11

Abstract

The City Board in Eskilstuna, Sweden, had decided that a boardwalk should be constructed along the river in the city. The shore of the river consisted of flood deposits with high organic content, this material was to be excavated for geotechnical reasons. Since the area had former been used for different industrial purposes, high rates of contaminants could be expected and investigations in soil and groundwater were performed by WSP along the shore.

The investigations revealed that soil and groundwater had high rates of several contaminations, among them TCE, cDCE and very high rates of VC, up to 50 mg/l in the ground water.

Since all the material in the contaminated area was to be removed, this was not considered a large problem. But given the high rates and the volatility of VC, WSP pointed out that vapors could be a health risk during the excavation works. WSP was given the assignment to calculate the rate of VC that could be expected in the air at the site during the excavation works and if this could be a risk. The calculations showed that VC was a tangible risk and WSP recommended that the site should have extended cordons and that all personnel on the site should use protective equipment such as gas-masks.

Since the site was located in the central parts of the city, the Board was reluctant to these actions and asked WSP for another solution.

Provided that the VC could be removed to an extent where the excavation works could be done without risk, the problem should be solved. WSP calculated that a rate of 1 mg/l would be safe.

Since the excavation works would had to start within three months, any biological method

was considered too slow. Permeability tests showed that pump and treat or traditional vacuum extraction/air sparging should be unsuitable. The soil consisted more or less of organic material, so ISCO was not an option. Finally, the choice of method was Hot Air Sparging (HAC).

HAC means that electrical heating is installed in sparging wells. The hot air that is injected has two effects: Beside the usual sparging effect it also rises the temperature which increases the vaporization. The vapors are then collected in horizontal perforated tubes under a tarpaulin.

The technology was not available in Sweden, but equipment was brought in by a German subcontractor. WSP took the role to monitor the equipment and the levels of VC. First, the temperature was set to 100 C. After one week, the rates of VC had doubled. That was not the desired result. Most likely the raised temperature had increased the ongoing biological breakdown of TCE and cDCE. To increase the vaporization and hopefully dampen the biological activity, the temperature was risen to 350 C . After that, the rates of VC started to go down steadily.

After three months, the time WSP were given, the rates of VC were well below 1 mg/l and the excavation works could be performed as planned.

<u>Session 3b11 / Abstract title</u>: Thermoreact® - An innovative remediation product for In Situ neutralization of halogens and sulphur during Thermal Desorption

ID: 52

Key words: Sulfur, chlorinated solvents, thermal desorption, ISTD

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Session: 3b11

Abstract

During In Situ Thermal Desorption, polluted soil (generally with TPH, PAH, Mercury, chlorinated solvents, etc.) is heated until the vaporization of the pollutants, which are then drawn through perforated steel tubes, called vapor tubes, surrounded by gravel acting as a draining medium preventing the clogging of the tube perforations (by fine particles, sludge, etc.). These recovered vapors are then either treated in a vapor treatment unit or re-injected into the flame (in case of hydrocarbon pollution and heating with Smart Burners).
In many cases, the pollutants to be treated in the soil are accompanied by other process-disturbing elements (such as phosphorus, sulfur or halogenated compounds like chlorine). The heat causes the vaporization of many chemical compounds, including those corrosion agents that are conducted through the porous medium to the extraction wells. The problem with these agents is that, in some cases, they become very corrosive and therefore tend to destroy equipment and make remediation technology less effective. Additionally, if not treated, they can cause non-compliant air emissions as well.
Thermoreact® is an innovative and patented (Haemers, 2022) product that replaces the conventional gravel around vapor tubes. The product allows for in-situ neutralization of the vapors before exiting the soil pack, reducing the treatment requirements, and saving substantial treatment costs overall. Its composition varies, depending on the nature and concentration of the pollutants present in the soil in order to always obtain the best neutralization reaction while keeping permeability at the required level for proper vapor extraction. The products of said neutralization are inert minerals that can be left in the soil, making In Situ Thermal Desorption a truly zero-waste treatment for many other contaminants than is currently the case.
This paper presents the performance results of the in-situ thermal desorption treatment

using Thermoreact® as a sulfur neutralization filter media around the vapor tubes.
This study shows that:

- Haemers Technologies' patented Thermoreact® technology is effective in neutralizing sulfurcontaining vapors.
- The effectiveness of Thermoreact® in neutralizing sulfur is not affected by the presence of other pollutants.
- There is no change in the appearance of the soil or Thermoreact® after treatment. Leaving the neutralization products in the soil, inert after reaction, is therefore possible without impacting the visual aspect of the site.
- The composition of Thermoreact® can be tailored to specific site parameters such as moisture, sulfur, hydrocarbon and halogen concentrations, and other soil chemicals

<u>Session 3b11 / Abstract title</u>: Ecosystem Restoration by Thermal In-Situ Sustainable Remediation (TISR)

ID: 68

Key words: Sustainable remediation, low-temperature, bioremediation, thermal

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Session: 3b11

Abstract

Background/Objectives.
As of 2017, US EPA and its partners reported overseeing up to approximately 1,319,100 facilities with varying degrees of contaminant clean-up and monitoring. Traditional environmental restoration is inherently energy intensive. Driven by a sustainable energy source (solar collection or waste heat capture), TISR (US Pat. Nos. 10,384,246, 10,688,545) is an innovative technology that utilizes renewable energy, and low-maintenance borehole heat exchangers (BHEs) for low temperature heating of the subsurface to treat environmental contaminants in soil and groundwater. The closed-loop heating system relies on thermal conduction and advection to increase the target treatment zone approximately 10 to 20°C above ambient temperature. This elevated temperature results in the enhancement of biological, chemical, and physical processes that attenuate, degrade, and remove contaminants. TISR is an alternative to the physical contaminant mass recovery such as excavation, or unsustainable energy-consuming treatment systems prevalent among practitioners. TISR can be complimentary to many other remedial technologies – air sparge, biosparging, chemical oxidation, or reductive dichlorination, for example. Operational ease to incorporate TISR into existing infrastructure reduces environmental restoration time, project life-cycle cost, and overall carbon footprint. Ecosystem restoration using sustainable technologies, such as TISR, offer an innovative tool for environmental practitioners, facility owners, and our society.

Approach/Activities.
Following the introduction of TISR in 2015, several studies and applications have been completed and have validated TISR as a successful remedial technology proving that a sustainable approach does not limit the effectiveness of the remediation technology. Utilizing solar collectors, TISR has now been implemented at 21 sites worldwide including in the United States, Canada, Mexico, Brazil, and the Netherlands. The scale and magnitude of these systems has expanded, while best practices and guidance continue to be refined for

greater efficiencies and optimization of heat transfer and energy use. Additionally, waste heat capture from traditional remedial technologies has been utilized to reduce operating timeframes and the overall environmental impact. Installation of a TISR system utilizing an active manufacturing facility waste steam is currently underway to integrate production and remediation in a symbiotic manner.

Results/Lessons Learned.

Solar collection, or waste heat capture to operate TISR systems has been successful beyond initial testing and optimization. It continues to evolve by integrating alternative sustainable heat sources as well as synergistic enhancements with existing infrastructure to enhance ecosystem restoration and reduce operational carbon footprint. An overview of TISR projects from 2015 to present, operational data, lessons learned, design criteria, and a focused alternatives comparison through the carbon footprint lens will be presented.

<u>Session 3b11 / Abstract title</u>: The use of Liquid Activated Carbon (LAC) in enhanced-microwave remediation of soils impacted by Polycyclic Aromatic Hydrocarbons (PAHs)

ID: 81

Key words: in situ soil remediation, thermal desorption, microwave enhancers, colloidal activated carbon, Polycyclic Aromatic Hydrocarbons.

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Session: 3b11

Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) – contaminated soils are a very important concern worldwide due to their persistence and carcinogenic nature. Several chemico-physical and biological treatments have been considered for their remediation, however their poor biodegradability and low water solubility make most of these remediation alternatives inappropriate or ineffective. Rapid and effective alternatives such as enhanced-thermal techniques are consequently strictly needed.
Microwave (MW) heating has recently been shown as a potent technology in several environmental applications, among which hydrocarbon – contaminated soil remediation. However, recent studies showed a limited ability of MW heating in removing selected PAHs from soils, mainly due to the dielectric properties of the irradiated matrix.
Several solid MW-enhancers have been largely investigated in lab-scale applications in order to increase the dielectric features of the contaminated soil before irradiation. Activated carbons (ACs) are the most used; however, their granular or powder nature requires soil excavation, limiting the remediation treatment to ex-situ applications. On the other hand, world environmental policies encourage the application of in situ technologies, making the

investigation of liquid MW-enhancer a very active research topic.
In the continuous search for liquid enhancers, Liquid Activated Carbon (LAC) is an innovative and non-hazardous material that could represent a very favorable alternative. LAC is a highly concentrated water-based suspension consisting of nano-to-micron-scale AC, typically applied in groundwater to form adsorptive/reactive zones for contaminant removal from the aqueous phase. It is generally injected through wells or direct push injection, with the dual function of adsorbing contaminants onto AC particles and stimulating organic biodegradation. The use of LAC in enhanced-MW treatments, still unexplored, would allow to increase the dielectric properties of the soil by means of its direct injection in combined in situ applications. Literature reports a high LAC mobility in the porous medium, on average higher than other nano- or micro-materials typically applied for in-situ remediation. If an extremely high mobility can be potentially an issue when these materials are applied in groundwater, this characteristic represents a positive factor in view of their possible application in unsaturated soils. This opens perspective for LAC delivery in top soils or at the bottom of excavated areas directly by ground flooding and percolation via gravity, similarly to liquid reactants used for other in situ soil treatments.
In this study, a new LAC-enhanced MW heating treatment was studied in simulated lab-scale remediation of PAH-contaminated soil, investigating different doses of LAC, MW energy and irradiation times. Laboratory transport tests were also designed to assess the potential mobility of LAC suspensions in unsaturated porous media under the effect of gravity.
The main results revealed that the LAC can significantly increase the MW electric field absorbing performance of the irradiated medium, leading to very high soils temperatures up to □1100 °C within 3-min irradiation time (LAC 10%). This resulted in largely shortened PAH removal kinetics. Transport tests in unsaturated sand-packed columns evidenced a good mobility of LAC when dispersed both in deionized water and tap water and applied by gravity-driven percolation, without active injection. In 18 cm long columns, 30% of LAC was retained when transport test was performed in tap water, and 37% when deionized water is used, with a fairy homogeneous distribution along the bed length.
Experimental and modelling results demonstrated the importance of liquid enhancer for in situ MW-heating treatments. A comparison with existing literature reveals that available clean-up alternatives for PAH-contaminated soils cannot lead to a similar rapid and effective achievements.

Session 3b12 orals

Session 3b12 / Abstract title: Sustainable Treatment Approach for Liquids with high PFAS Values

ID: 172

Key words: high PFAS, low residues, PFAS sludge, sustainable treatment

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Session: 3b12 backup

Abstract

Purpose of Study
In some sectors, challenging levels of PFAS in water occur. Sources of such water are fire-fighting operations or the cleaning of fire-fighting systems in vehicles or buildings, when subsequently fluorine-free foams are to be filled into the system. The high concentrations of PFAS, sometimes in combination with particles and/or increased dissolved organic carbon (DOC) content, make treatment very difficult for classic techniques such as granulated activated carbon (GAC) or ion exchangers (IX). Sometimes components of the extinguishing agents that are not analysed by the laboratory (e.g. precursors, surfactants) also play a role in the treatment. An alternative approach was therefore tested together with GAC and IX for the treatment of such waste waters.

Method
First, the premix of an extinguishing agent commonly used in Germany was analysed for its composition. In addition to PFAS, the concentration of other fluoro-organic compounds as well as cationic and anionic surfactants were determined in the laboratory. An alternative chemical for the treatment of such a liquid was tested on this premix in the technical laboratory. This product generates a connection with the PFAS in the water and thereby produces a floc which can be removed by filtration (sand filter).
Following its success, a comparative study was carried out for a fire-fighting water with elevated levels of PFASs. Two approaches were compared for the purification of the water using GAC and IX. With and without pre-treatment of the water using the alternative technique. For this purpose, small columns (about one metre high and 5 cm in diameter) were filled with GAC as well as IX and then exposed to the water to be purified in a steady

flow. Samples were taken from the outlet of the columns and analysed by an external laboratory for PFAS level.

Result

The first test batch with the premix showed that about 99% of the PFAS could be removed with the alternative cleaning batch. It was also evident that the contents of fluoro-organic compounds were much higher than those of PFAS. But of these compounds and the anionic surfactants, very high proportions could be eliminated.

The comparative observation in the purification of the extinguishing water made it clear that with the approach without further pre-treatment, good purification efficiencies are initially achieved for GAC and IX. But then the effluent values increase rapidly and strive towards the level of PFAS concentrations in the influent.

In a supplementary approach, the water was first pretreated with the alternative technique before the columns (GAC, IX) were again exposed to this pre-treated water. In the effluent, the analyses showed consistently low concentrations of PFAS.

Conclusions

The tests showed that a two-stage purification process in the form of pre-treatment and subsequent application of GAC/IX enables reliable treatment of fire-fighting water or similar problematic water. In addition, parameters can be removed that may be components of AFFF but are not part of the normal PFAS analysis.

Since the pre-purification removes most of the PFAS, the need for GAC/IX is significantly reduced. Pre-purification instead produces a low volume of sludge with increased levels of PFAS.

Session 3b12 / Abstract title: How does EU's policy framework tackle prevention and management of PFAS pollution?

ID: 196

Key words: Policy, management, risk, pollution, PFAS

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Session: 3b12

Abstract

Introduction
The EU's zero pollution ambition and its associated chemical strategy strive for preventing and reducing pollution and establish a vision for a toxic-free environment. Specific actions in this policy framework include phasing out per- and polyfluoroalkyl substances (PFAS) from the European market and harmonising the principles of the EU's chemical risk assessment by the 'one-substance once-assessment' (OS-OA) approach. Many recent EU regulations have also been amended by setting new quality standards for PFAS in different environmental matrices. In our study, we critically review and analyse the recent development on regulating the environmental and health risks of PFAS within the context of the EU policy. The study is part of the European Partnership for the Assessment of Risks from Chemicals (PARC), co-funded by the Horizon Europe research and innovation framework programme.

Methodology
Using PFAS as a relevant case example, the study addresses the interlinkages and incompatibilities between the policies and approaches on pollution prevention and management of existing pollution and conducts a comparative analysis of the EU regulatory thresholds recently set for PFAS in different media, by examining their foundation, derivation, and application. The analysis covers the quality standards of the Drinking Water Directive (EU) 2020/2184, maximum levels in food according to the Commission Regulation (EU) 2022/2388, the proposed environmental quality standards of the pending Priority Substances Directive 2008/105/EC, and the new tolerable daily intake value by the European Food Safety Authority (EFSA).

Summary of results
Our study demonstrates that the fundaments of the quality standards for PFAS vary

substantially in different regulations, and they are not always transparent. The level of safeguarding, for example, may differ by several orders of magnitude, even in similar regulatory contexts and for the same protection target (e.g., allowable human exposure from eating fish). This indicates that the chemical risk assessment procedures, such as the OS-OA approach, as well regulatory decisions in the context of environmental and health protection may not be consistent. Moreover, such irregularities confuse the scientific basis and understanding of the toxicity and risks of PFAS and may compromise the achievement of the policy objectives regarding their management.

We also demonstrate that risk assessment approaches and chemical thresholds designed primarily for the prevention of pollution within the chemical registration frameworks, such as REACH, are often impractical for the management of existing environmental contamination, especially for persistent and ubiquitous chemicals, such as PFAS. Consequently, the risks to human health and the environment due to actual PFAS exposure may remain low and acceptable despite the exceedance of the most stringent regulatory thresholds.

Conclusion

Current regulatory approaches and thresholds for PFAS are partly inconsistent and impractical. This calls for open dialogue and expedient policy decisions regarding the management of environmental pollution and risks arising from PFAS. Moreover, understanding the fundaments and the regulatory objectives of any risk-based decision benchmarks, such as environmental quality standards, is a prerequisite for sustainable risk management practice.

Significance of study

The study gives an in-depth outlook on the recent regulatory development in the management of environmental pollution and risks of PFAS, addressing constructively its complications and inconsistencies. The findings facilitate necessary dialogue in the field of EU’s environmental and chemical policy and support justified regulatory decisions.

<u>Session 3b12 / Abstract title</u>: Predicting PFAS soil porewater concentrations – implications for hydrogeological risk assessment sustainable soil remediation

ID: 261

Key words: PFOS; PFOA; leaching; adsorption; air-water interface

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Session: 3b12

Abstract

The vadose zone has increasingly been identified as a significant reservoir for per- and polyfluoroalkyl substances [PFAS] at sites impacted by different sources, including fire-fighting foam applications, manufacturing processes and land applications of biosolids. PFAS concentrations in unsaturated soils are often orders of magnitude higher than the underlying groundwater at these sites, where the potential impacts of long-term leaching on groundwater quality, and dependent receptors, is a primary concern.

Evaluating the risks posed by PFAS leaching to groundwater requires quantitative understanding of soil porewater concentrations and infiltrating water discharge. Direct measurements of PFAS discharge due to leaching may be impractical at environmentally relevant scales and applying comprehensive vadose zone models for PFAS transport requires considerable information for parameterisation. Partitioning-based estimates for soil porewater concentrations and leaching discharge, of the type frequently used in screening-level transport models, may provide a viable alternative. However, the relationship between soil and soil porewater concentrations is more complex for PFAS than for non surfactant solutes, due to the adsorption of PFAS at phase interfaces, which are dependent on fluid contents and soil properties.

A PFAS partitioning model from the literature has been applied within the UK's hydrogeological risk assessment methodology to predict soil porewater concentrations, risk characterisation and risk-based targets for vadose zone soil remediation. Estimates of soil porewater concentrations of perfluorooctanesulfonic acid [PFOS] and perfluorooctanoic acid [PFOA] were calculated from total soil concentrations using the PFAS partitioning model, including phase and interface adsorption terms, and a conventional non-surfactant partitioning model. These calculations were based on PFOS and PFOA sorption properties and physical characteristics for ten different soils of varying particle sizes and organic contents.

The soil porewater concentrations predicted for representative water contents using the

PFAS partitioning model were up to two orders of magnitude lower than those predicted using the conventional partitioning model, demonstrating the significance of PFOS and PFOA retention on air- water interfaces in unsaturated soils. Soil porewater concentrations decreased by between 2- and 5- times for an order of magnitude increase in soil water content. These differences are proportional to the predicted discharge via leaching to groundwater and highlight the likely sensitivity of PFAS risk assessment modelling to temporal variability in source zone water contents. Furthermore, soil porewater concentrations are inversely proportional to calculated risk-based soil remediation target concentrations. Remediation targets that do not consider PFAS-specific adsorption processes may be biased low, unrepresentative and unachievable with current treatment technologies, potentially pushing stakeholders towards less sustainable risk-management strategies for PFAS impacted sites.

The role of PFAS partitioning modelling within an integrated strategy to assess risks to groundwater from leaching and discharge through the vadose zone will be presented, including concepts to parameterise such models, which should better inform soil remediation objectives and soil treatment selection, reducing remediation volumes and project costs.

<u>Session 3b12 / Abstract title</u>: New insights in human health risk assessment of PFAS contaminated sites, and the setting of soil remediation values

ID: 286

Key words: PFAS, human health risk assessment, soil remediation values, soil policy, emerging contaminants

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Session: 3b12

Abstract

The PFAS crisis in Flanders resulted in an accelerated approach of PFAS contaminated soil and groundwater. Possible contaminated sites have been inventoried, and investigations have started. At the same time many research projects and measuring campaigns have been set up.

The results of these studies are now used to improve methodologies for human health risk assessment of PFAS contaminated sites, as well as calculation models for deriving soil remediation standards for PFAS.
Following studies will be discussed concisely, each time with focus on what the results mean for risk assessment methodologies:
- PFAS@home: a study aiming to gain more insight in the major routes of exposure through which PFAS can enter the human body. PFAS was measured in blood serum and in different compartments of the living environment of the participants (house dust, soil from vegetable garden, vegetables, home-produced chicken eggs, drinking water, …);
- A case study where PFAS was measured in house dust, air and soil in the surroundings of a PFAS contaminated site (former paper plant). Target and non-target analyses were performed;
- PFAS measurements in soils, vegetables, chicken eggs, … in the surroundings of a PFAS production site;
- Others relevant studies.

At the hand of these results, different issues will be discussed. What are the major routes of exposure? How to deal with background concentrations in food, in other media, …? Which individual PFAS's need to be considered? How to perform risk assessment for a group of PFAS's? …

In the presentation will also be explained how these new findings are affecting the derivation of soil remediation standards in Flanders.

<u>Session 3b12 / Abstract title</u>: PFAS Mass Flux – A Platform for Developing Realistic Remedial Goals and Sustainable Action (An Australian Perspective)

ID: 319

Key words: PFAS Mass Flux, Sustainable and Practical Remediation Goals and Actions

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Organization: AECOM

Co-authors: nan

Session: 3b12

Abstract

Background: When considering remedial and / or management action, what is practically achievable, is it reasonable to expect complete removal or all residual PFAS mass from the environment?
Traditional approaches for establishing site specific risk based remedial criteria for conventional contaminants require an understanding of contaminant partitioning from soil to surface and groundwater. The leachate tests currently adopted by Australian commercial laboratories likely overestimate the desorption of per- and polyfluoroalkyl substances (PFAS) from soil to pore water, surface water and groundwater due to the enhanced surface area and the aggressive end-over-end analytical preparation methods employed by the laboratories. A review of Australian groundwater concentrations in regions where soils have undergone traditional leach testing suggest that leach testing is neither reliable nor representative of in-situ pore water/surface water/groundwater concentrations within source areas and/or the surrounding environment.
Developing site specific remedial criteria using such an approach results in unusable soil values that are often less than the level of reporting. Resulting in remedial estimates of volume which are not pragmatic or achievable for large areas, which are often the scenario for former aqueous film forming foam (AFFF) training areas. A review of the potential for site specific risk based soil criteria based on traditional leachate testing was compared to site specific risk based estimates adopting lysimeter data collected in-situ and hose down testing.
Direct measurement of the concentration of PFAS in pore water, surface water (via telemetry based autosamplers or during hose-down tests) across the soil profile will result in a more representative quantification of the flux of PFAS from surface soils and the vadose zone and allow for the development of more robust and representative soil remedial criteria.
Approach: Reducing mass flux by an order of magnitude or so far as reasonably practicable in different media compartments (soil, surface water and groundwater) is an approach that

has been adopted at a number of PFAS impacted sites across Australia.
Mass balance compartment models are developed pre-and post-remediation by measuring:

- Residual soil mass (collection of high-resolution data in the source zone married with EVS and / or surfer modelling for extrapolation or percentage mass laterally and vertically)
- Flux to surface water via:
  - Rainfall event sampling (Telemetry flow meter, auto-samplers v rising stage samplers)
  - Rainfall simulation (hose down tests)
  - ASLP / Modified ASLP
  - Multiple Extraction Procedure (MEP)
- Flux to groundwater via:
  - Lysimeter / tensiometer (porewater)
  - Well transects / polygons
  - Aquifer conditions (PSD, slug testing and concentration)

Lessons Learnt: The high propensity for PFAS to leach under traditional laboratory testing in conjunction with the very low groundwater protection values currently being applied by regulators, results in overly conservative approaches to PFAS impacted soil remediation. Site specific development of a wholistic mass flux compartment models is critical for determining appropriate and pragmatic remedial strategies for the protection of groundwater and surface water receptors (refer to Figure 4). Validation of remediation performance should use multiple lines of evidence (rainfall event downgradient mass flux, rainfall simulation at source zone, ASLP Linear regression modelling, groundwater mass flux etc). As it results in a more informed site conceptual model that leads to a precise and sustainable remedial response commensurate to the environmental risk the site(s) present. Lastly, utilizing autosamplers and lysimeters can be challenging but the data is worth the patience.
The presentation will share mass flux data pre- and post-remediation for different sites with varying soil types and different climatic conditions.

<u>Session 3b12 / Abstract title</u>: Stabilization of PFAS contaminated soil to minimize cost for construction works and carbon footprint for widely contaminate and active areas

ID: 387

Key words: Remediation, PFAS, Sustainable, Emerging contaminants, Stabilization

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Session: 3b12 backup

Abstract

Introduction and study objectives
The management of soil contaminated with per- and poly-fluorinated alkyl substances (PFAS) is a major challenge worldwide. Traditional remediation processes are not applicable due to the inherent chemical stability of the PFAS substances. Landfill disposal, a common practice in Europe for other soil contaminants, has its own challenges for PFAS contaminants because disposal of PFAS soil in a landfill creates a concentrated point source of these toxic and water-soluble substances, which creates a risk to human health and the environment through transfer via the landfill leachate.

For construction works within large areas with PFAS concentrations, as well as active sites, these soils become an expensive part of construction works. Excavated soil needs to be transported to landfills or incinerated, creating both a large cost as well as a large carbon footprint. As additional cost and environmental liability new “clean” soil needs to purchased and transported, and deposited in contaminated areas, becoming contaminated as soon as they reach the ground, without remediating the area in any detectable way.

As both an economical and more environmentally friendly solution, Envytech has, in cooperation with the Swedish Defence Estate Agency (SDEA), carried out stabilization of PFAS contaminated soil arising from construction works within a large contaminated active firefighting training area using Rembind by Rembind PTY Ltd. As the works begun, permission to stabilize and reuse of soil was not yet granted, and approx. 1000 tonnes of PFAS contaminated soil were transported to a landfill where stabilization was carried out.

For the second stage of the works, EPA had granted the SDEA permission to reuse stabilized soil if minimization of PFAS leachability could be achieved and documented.

By presenting the results from these two stabilizations of PFAS contaminated soils we will verify that 1) stabilization could minimize PFAS leachability of excavated soils enough for the EPA to grant permission for reuse of treated soils on site, 2) Stabilization can vastly reduce the costs by minimizing the costs of transporting contaminated material to landfill, where a point source can be created, and by minimizing the need to purchase and transport new fill material, and 3) minimize the carbon footprint.

Methodology

As a first step for proving the efficiency of the product to stabilize the different soils and concentrations, soil samples were taken out and analyzed for the Swedish SLV SUM PFAS11 concentrations. A two step leachability test, L/S2 and L/S8 was conducted on all samples, to measure the amount of PFAS the untreated soil leach over time.
To evaluate the effect and cost for stabilization of the different soil samples, separate samples were taken out, and depending on contamination level, stabilized with two different percentages of Rembind, one higher and one lower. This to evaluate what different percent stabilization product would be needed to minimize leaching of PFAS for each sample.
From the results achieved, the soils were stabilized, first batch at a landfill, and the second on-site as permission had been granted from the EPA to use stabilized soils for backfill material, if proven that minimization of PFAS could be achieved.

Results and conclusions

Approx. 1000 tonnes of PFAS contaminated soil were transported to a landfill where stabilization was carried out, and where permission for depositing had been granted for treated soil where leachability could be decreased >80%. Envytech carried out the stabilization works and the soil was deposited as leachate was decreased up to 99%.

For the second stage of the works, the soil was stabilized on site, and results proves that minimizatio of leachability was achivied with > 97%. The stabilized soil was approved to be reused on site and was used as back fill.

<u>Session 3b12 / Abstract title</u>: Per- and polyfluoroalkyl substances (PFAS) in the aquatic environments in the Czech Republic.

ID: 404

Key words: Per- and polyfluoroalkyl substances; PFAS; wastewater treatment plant; drinking water; fish

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Session: 3b12

Abstract

The group of pollutants called per- and polyfluoroalkyl substances (PFAS) currently represent more than 10.000 identified substances. The structure of these substances is made up of a per- of polyfluorinated hydrocarbon forming a hydrophobic part of the molecules and a functional group which, on the other hand, forms a hydrophilic part. According to the type of functional group, PFAS can be divided into sulfonates, carboxylates, sulfonamides, phosphonates, acrylates, acetates and other minor groups. In general, these substances are considered highly persistent in nature. In fact, all the structures, that have been studied regarding their toxicity, revealed some of adverse effects towards organisms including human beings as: liver enlargement, steatosis, hepatocellular hyperplasia, oxidative stress, neurotoxicity, endocrine disruption, and teratogenicity. Despite these facts, there is still a lack in understanding of inputs of the compounds into the environment and further their transport and fate.

This study documents the situation of PFAS contamination in Czechia that is represented by three rather huge monitoring campaigns including wastewater treatment plant sludge, drinking water and fish across the whole country. The data presented in the sewage sludge study showed a serious contamination by the screening of 43 wastewater treatment plant of various sizes. Considering that 30% of the sewage sludge is used as fertilizes without any analysis regarding these substances suggests, that there is a high possible risk of contamination of agriculture soil and the cultivated plants. In fact, our calculations based on available bioaccumulation factors revealed, that theoretically only one kilogram of lettuce cultivated on such a fertilized soil could reach the tolerable weekly intake by the European

Food Safety Authority (EFSA). As well as the data regarding the fish contamination, assessed by analysis of fish meat, showed similar results. Nevertheless, only about 30 grams of fish meat contain the tolerable weekly intake limit by EFSA. The data also document that contamination of freshwater fish is increasing through the continuum of the Elbe River and its largest tributary, the Vltava River, considering also, that Czechia is the beginning of the respective catchment. The data regarding the contamination of drinking water around the whole country showed, that drinking water can also contribute significantly to the total intake of PFAS. The quality of the drinking water varied, nevertheless, in some towns the content of PFAS represents 50-100% of the EFSA limit.
The results of all these three studies emphasize the importance of a rapid action toward drastic restriction of the PFAS use, monitoring of the environment, and development of decontamination methods for their removal from the environment.

Session 3b13 orals

Session 3b13 / Abstract title: Flame retardants related to risk activities - Brussels guidelines

ID: 109

Key words: Emerging contaminants, policy, brominated flame retardants

Submitter: Glein Roggeman

Organization: Arcadis Belgium

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Session: 3b13 backup

Abstract

Purpose of study
Emerging contaminants are receiving increasing attention in soil and groundwater research. Emerging contaminants often belong to very broad substance groups, with thousands of individual substances, such as pharmaceuticals, pesticides, dioxins, flame retardants, plastics, plasticizers, endocrine disruptors, etc.
Usually, there is not yet sufficient data to establish standards and regulation for soil and groundwater, or no suitable, standardized analytical method is available. It is therefore not easy to determine whether and which emerging substances should be analyzed in a soil study.
This study initially seeks to identify which emerging substances are most relevant for soil testing in the Brussels Capital Region and to determine in which cases these substances should be included in a soil study.
Methodology
To determine which emerging contaminants are most relevant in Brussels, 3 approaches were considered:

1. The main emerging substances according to the literature (international)
2. The main risk activities in Brussels
3. Available monitoring results of soil and groundwater in Brussels

The results of these 3 approaches were combined to determine the most relevant emerging contaminants in Brussels.

Results

Brominated flame retardants were identified as most relevant emerging contaminants for soil and groundwater linked to specific activities in Brussels. A literature review identified the history, behavior, and release in the environment. A summary of the applications and possible sources of brominated flame retardants was provided, dividing the activities in 4 categories: productions of BFR, Processing of BFR, use of consumer products with BFR and waste treatment. The activities were linked to the activity categories as used in the Brussels environmental permits, to determine on which sites these substances should be included in a soil investigation.

Conclusion - Significance/contribution of study

The study provides soil remediation experts with a tool and background information to check whether they should include brominated flame retardants when performing a soil study. Good historical research remains crucial for determining the correct substances of interest when investigating a site. The literature review and summary table in the study provides the expert with the necessary information to take flame retardants in consideration when doing the historical research of activities on a site and thus to determine whether analysis of brominated flame retardant in soil or groundwater is appropriate.

<u>Session 3b13 / Abstract title</u>: Background values of PFAS in soil and groundwater

ID: 114

Key words: Emerging contaminants, PFAS, policy, management

Submitter: Dorien Gorteman

Organization: Witteveen+Bos

Co-authors: Sigrid Willems, Witteveen+Bos, consultant Dorien Gorteman, Arcadis Belgium, consultant Karen Van Geert, Arcadis Belgium, senior consultant Jonas Mareen, Witteveen+Bos, consultant Griet van Gestel, OVAM Bruno Billiaert, OVA

Session: 3b13

Abstract

Purpose of study
The purpose of the study is to determine background values of PFAS in phreatic groundwater in Flanders. PFAS contamination plumes can be very extensive, moreover, it is suspected that the groundwater in Flanders is diffusely enriched with PFAS, so delineating a contamination plume is not straightforward. Determining the background values can help to distinguish groundwater plumes originating from a PFAS source from regional elevations. The derivation of background values will support the PFAS policy in Flanders in soil investigation and in remediation strategies.
Methodology
PFAS concentrations are analyzed in 150 groundwater samples, originating form areas without activities that use/used PFAS and without known PFAS- contamination.
To select the 'greenfield zones' as background sampling locations, existing maps with following information in Flanders were used:

- locations with known PFAS contaminations
- information on type of PFAS activities that is present or was present in the past, per parcel (Land Information Register in Flanders)
- firefighting sites
- sites where heavy fires occurred in the past
- Sites that are known to discharge wastewater containing PFAS
- known landfills
- Sites with other contamination
- wastewater treatment plants

The chosen 'background' locations were evenly distributed across Flanders.
Existing PFAS results of the groundwater collected by different government departments will evaluated and, if useful, used as a second database to determine the background values.

75 soil samples will also be analyzed to fine-tune the existing background values for soil.
10 soil- and groundwater samples are selected for a non-target TOP analysis. The results of the TOP analyses give us more insight into the PFAS components that are currently not included in the standard PFAS analysis package and can therefore influence the interpretation/determination of the target values.

Results

Background values will be determined for PFAS compounds above detection limit and if possible, for the EFSA-4 and EU 20 PFAS. The data will also be examined to determine regional differences or differences depending on land use, effects of groundwater level and soil type. Relations between certain compounds will be examined.
The existing background values for soil, will be verified and fine-tuned. The correlation between soil and groundwater results will be examined.

Conclusion

The results of the study will be presented at the conference.

Significance/contribution of study

The results of this study will contribute to a regulatory framework clarifying how to deal with the delineation of PFAS contaminations in soil studies and how to deal with regionally elevated PFAS concentrations and risk assessment.

<u>Session 3b13 / Abstract title</u>: PFAS Catchment Management - UK and Jersey

ID: 229

Key words: PFAS Drinking Water Catchment Management

Submitter: Jake Hurst

Organization: Arcadis UK Ltd

Co-authors: James Lemon, Arcadis UK, Associate Technical Director

Session: 3b13

Abstract

Purpose of study

The combination of persistence, mobility and toxicity of many Per- and Polyfluoroalkyl Substances (PFAS) has resulted in widespread ambient (background) concentrations with the environment as well as potential for contamination of drinking water supplies from PFAS source sites.

There are multiple pressures currently converging on drinking water supplies including from emerging contaminants such as PFAS, where a greater number of PFAS are being regulated to increasingly lower threshold limits, alongside climate change related drought and increased seasonal variability and population related water demand.

Therefore, there is a need to robustly but pragmatically assess and manage potential PFAS sources within drinking water catchments in order to ensure safe and secure drinking water supplies. This presentation presents the approaches and lessons learnt from several recent PFAS related projects employing digital tools, risk prioritisation and holistic catchment management including for the Government of Jersey and UK water companies.

Methodology

The presentation will first summarise the how emerging contaminants, climate change and population growth combine to create significant challenges to the drinking water industry e.g. by increased abstraction from contaminated aquifers, water reuse constraints and compliance with increasingly stringent PFAS regulations.

A novel, GIS based PFAS source site assessment model will then be described which was developed by Arcadis to support a UK water company complete a robust, catchment wide

risk assessment in accordance with new statutory PFAS guidelines. Site profiles were developed to summarise types of PFAS used at different sites, novel replacements, release routes and appropriate analysis.

The final part of the project will give an overview of the PFAS hydrogeological and risk assessment work undertaken on behalf of the Government of Jersey across two drinking water catchments around Jersey Airport which is a high-profile project involving multiple stakeholders and significant media attention.

Summary of findings/results

The introduction will demonstrate the need for a holistic, catchment wide approach to target assessment and industry investment and to identify cost effective solutions which balance source site remediation, pathway interception and drinking water treatment.

The GIS tool included public and private datasets combining environmental sensitivity with potential PFAS source sites including biosolids application areas. PFAS source sites were risk ranked and scored based on a source, pathway, receptor-based approach to target catchment wide monitoring. This approach broadly follows the national UK Environmental Agency (EA) PFAS Risk Screening Project but allows more detail at a catchment scale.

The first phase of works in Jersey involving the review and digitisation of historical data to develop a catchment wide PFAS Conceptual Site Model (CSM) within a GIS model to visualise complex pathways involving drainage outfalls, groundwater / surface water interactions as well as data gaps for further assessment. The works support hydrogeological modelling and risk assessment based on agreed future scenarios (including modelled trends, assumed regulatory trajectories, remediation works, increased abstractions) to inform a remediation options appraisal identifying effective, cost-efficient solutions to protect future drinking water supplies.

Conclusion

To address growing pressures on our drinking water supplies there is a need to robustly identify and prioritise potential PFAS sources across catchments to target assessment and investment where it is most needed.
Significance / contributions of study
The presentation showcases cutting edge PFAS assessment approaches and use of digital tools to conceptualise catchment wide PFAS migration at high profile sites to protect drinking water into the future. The approaches are in line with recent UK regulatory di

<u>Session 3b13 / Abstract title</u>: PFAS and excavated soils: how do we prevent the spreading of PFAS-contamination in Flanders?

ID: 239

Key words: Excavated soil materials - PFAS - screening values - circular use of soil materials - prevention of spreading soil contamination

Submitter: Johan Ceenaeme

Organization: OVAM

Co-authors: Dirk Dedecker, OVAM, policy coordinator excavated soil materials

Session: 3b13

Abstract

PFAS and excavated soils: how do we prevent the spreading of PFAS-contamination in Flanders?

The rules concerning the transport and use of excavated soil (earth-moving) are also aimed at prevention. Since 2001, Flanders has a regulation for the use of excavated soil. This regulation stipulates the conditions for the application of ‘excavated soil materials’, oriented at the highest quality reuse option, with initiatives for ‘regenerative approaches’ on their way. Two certified, independent soil management organisations – Grondbank and Grondwijzer – have been established to help project developers and owners to deal with excavated soil and sediments.

In Flanders, standards were published in the spring of 2021 for PFAS for soil and groundwater. During the same period, measurements in a residential area near a 3M site in Antwerp (Zwijndrecht) found elevated PFAS levels in the soil. This was the beginning of a PFAS crisis, which meant that these forever chemicals dominated the news and the political world in Flanders for several months. The experiences and the knowledge gained on the field of the reuse of excavated soil materials are explained in the presentation.

If for destination types nature and agriculture the derivation of the screening values for excavated soil materials would only take place based on the human risk, screening values are calculated to be 0,2 µg/kg PFOS and 0,6 µg/kg PFOA. Those values are lower than the average concentration in unpolluted soil (the target value) and are at or just above the determination limit.

Therefore they are not enforceable and a switch is made to the specific calculation rules that are used in Flanders to determine screening values. In that sense, setting standards means

that we accept a certain risk. An expert panel unanimously agreed with this approach, but would like to clarify the risk. The scientific report estimates these risks based on worst case assumptions.

The value calculated in this way confirms the valid value free use for PFOS of 3 µg/kg dw. For PFOA the applicable value of 3 µg/kg dw is adjusted to 2 µg/kg dw. This to maintain full consistency with PFOS and other parameters. Next the specific free use value for PFAS and PFOA also applies to a sum parameter of 8 µg/kg dw for sum of all quantitatively measurable PFAS.

In Flanders, a great deal of attention and effort went into measuring and mapping PFAS contamination in the past year. This went hand in hand with the gathering of new knowledge about the risks and spread of PFAS. The presenter brings the insights concerning the screening values for excavated soil materials that these experiences have yielded.

<u>Session 3b13 / Abstract title</u>: Mapping and investigation of PFAS suspected sites in Flanders

ID: 240

Key words: PFAS suspected sites, PFAS, investigation, mapping sites, training locations for fire fighting

Submitter: Johan Ceenaeme

Organization: OVAM

Co-authors: Griet Van Gestel, OVAM, policy coordinator

Session: 3b13 backup

Abstract

Mapping and investigation of PFAS suspected sites in Flanders

In Flanders, standards were published in the spring of 2021 for PFAS for soil and groundwater. During the same period, measurements in a residential area near a 3M site in Antwerp (Zwijndrecht) found elevated PFAS levels in the soil. This was the beginning of a PFAS crisis, which meant that these forever chemicals dominated the news and the political world in Flanders for several months. The experiences and the knowledge gained are explained in the presentation.

A large number of locations in Flanders were flagged for further investigation on PFAS. Typically, the most worrying of these are industrial sites where PFAS is/was produced and used, as well as the training grounds of fire departments and sites of historical fire incidents where extinguishing foams containing PFAS have been used.

The OVAM started a campaign to map and investigate the locations with suspected PFAS contamination. The inventory of risk sites in Flanders shows that more than 3/4 of the training locations for firefighters have PFAS contamination of the groundwater and often also of the soil. It concerns hundreds of contaminated sites spread across Flanders. The inventory of industrial sites is still ongoing, but based on examples in different sites, we can expect that several additional contaminated sites will be identified.

The evaluation of the necessity and the method for remediation for these locations must be made on the basis of further (descriptive) soil research. Remediation must ensure the demarcation of the contamination and the prevention of further spread or exposure. In hot spots, different sources or routes of exposure come together, vulnerable groups are present and there is possible prolonged exposure. A coordinated and integrated approach to reduce

that exposure is required. In addition to the remediation, discussions are conducted with local actors to establish which additional measures can be taken to limit exposure and risk. In a non-hotspot, the approach is aimed at integrated remediation: limiting human exposure, impact on fauna and flora and spread.

Instruments to arrive at a substantiated remediation approach are: the assessment values soil remediation standard, the methodology for 'clear indication of serious soil contamination (DAEB in Dutch), the codes of good practice and the S-risk model. The responsibility for the elaboration of the remediation approach lies with the certified soil remediation experts. The development of soil remediation techniques poses another important challenge.

From the many studies on PFAS and the ongoing social debate, it became clear that the existing Flemish standards frameworks must be tightened. Several gaps in knowledge remain in order to arrive at a conclusively human risk assessment framework: transfer from soil to crops/eggs, contribution of inhalation, uncertainty on measured values at very low concentrations, mixture toxicity. The background exposure through food already leads to the threshold value being exceeded. The experiences lead to a tightening of the action framework for soil and groundwater.

In Flanders, a great deal of attention and effort went into measuring and mapping PFAS contamination in the past year. This went hand in hand with the gathering of new knowledge about the risks and spread of PFAS. The presenter brings the insights that these experiences have yielded concerning the mapping and investigation of PFAS suspected sites.

<u>Session 3b13 / Abstract title</u>: PFAS in crops near a fluorochemical plant. Links between distance, soil concentrations and uptake.

ID: 263

Key words: PFAS, crops, fluorochemical plant, soil, water

Submitter: Tessa Pancras

Organization: Arcadis Nederland B.V.

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Session: 3b13

Abstract

In Dordrecht, the Netherlands, a fluorochemical production plant has been emitting PFAS (mainly PFOA) into the air and surface waters for decades. The risks for vegetable gardens users downwind of the factory were determined 5 years ago, but had to be reassessed based on the new EFSA TDI for PFAS.

A new investigation was carried out in 17 vegetable gardens up to 20 km downwind from the factory. The concentrations in crops were determined using the most recent analytical technology to determine PFAS at a very low detection level (picogram/gram).
At the same time, concentrations in soil, groundwater, surface water and irrigation water were assessed. Gardens were clustered based on their distance from the plant and the prevailing wind direction. Two additional gardens with less influence of the factory (outside prevailing wind direction) were used as reference.

The results were used by the Dutch National Institute for Public Health and the Environment (RIVM) to determine whether the intake of PFAS through local crops posed a risk to human health and whether it is safe to eat crops from the gardens. In addition, the results were used to study how PFAS are distributed in soil, water and crops in the region. This information resulted in practical guidelines for the users of the vegetable gardens.

Furthermore, the relationships between crop PFAS concentrations and PFAS concentrations in the environment were evaluated in multiple ways (type of PFAS, type of environmental media, with and without mixture toxicity). This resulted in interesting conclusions concerning bioconcentration of PFAS and how to address mixture toxicity at this site.

In our presentation, we intend to show graphs that illustrate the links between concentrations in the soil, vegetables and distances to the plant, and between the concentrations in soil,

water and the uptake in vegetables.

<u>Session 3b13 / Abstract title</u>: Leaching-behavior and transport of PFAS: review and update of the Flemish methodology for dispersion risk assessment

ID: 283

Key words: PFAS, leaching behavior, Hydrus, column tests, Kd-values

Submitter: Michiel Maertens

Organization: VITO

Co-authors: Dr. Michiel Maertens, VITO, Hydrologist; Dr. Ilse Van Keer, VITO, Project Manager Soil Pollution; Dr. Ingeborg Joris, VITO, Project Manager Environmental Modelling; Ir. Johan Vos, VITO, Researcher, Ir. Griet Jacobs, VITO, Researcher; Dr. Griet Van Gestel, OVAM, Policy Coordinator

Session: 3b13

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been widely used in industrial and consumer products. Due to their persistence in nature and their potential health risks, the leaching of PFAS into the environment has become a major concern. In Flanders, severe PFAS contamination has been detected in soils and groundwater at several sites, mainly due to industrial activities and the use of PFAS-containing aqueous film-forming foams. Although many questions remain about the leaching behavior of PFAS, an assessment of dispersion risks is already required as part of descriptive soil investigation and the evaluation of soil displacement.

In Flanders, a step-by-step methodology to assess the leaching risk for the so-called classic pollution parameters (heavy metals, PAKs, mineral oil, volatile organic carbons, etc.) has been developed. This methodology includes the evaluation of the leaching risk of pollutants from the unsaturated zone and the assessment of soil quality over time using a model approach. In this study, the applicability of this methodology to evaluate the leaching behavior of PFAS was investigated.

To this end, (i) a literature review was conducted to gain insight into the adsorption behavior of PFAS in the unsaturated zone, (ii) soil and groundwater samples were collected from two PFAS-contaminated sites in Flanders (i.e. a fire-fighting training site and a former paper plant), on which single-stage shaking tests and column tests were performed, and (iii) the leaching behavior of PFAS was simulated using models with different levels of detail in process description.

The targeted chemical analyses of soil, groundwater, and eluate included approximately 40 individual PFAS. With respect to the shaking and column test, potential cross-contamination, or adsorption of PFAS associated with the recipients applied was evaluated, as well as the effect of filtration versus centrifugation. Calculations of evolution of PFAS concentrations were done with both the F-Leach model, a process-based analytical transport model that takes into account transport by infiltrating rainwater and sorption and with the Hydrus-1D model, a numerical model with a detailed description of PFAS sorption in unsaturated conditions. The recently developed PFAS module in Hydrus allows adsorption of PFAS at the air-water interface, which has been shown to be an important PFAS retention mechanism. To evaluate the importance of adsorption at the air-water interface in the selected cases simulation results were compared with experimental data and F-Leach output.

The main results of this study show that the leaching risk varies between different PFAS depending on the type of functional group (PFAS family) and the length of the carbon chain. For the selected sites, the simulations with Hydrus and F-Leach show that the effect of adsorption at the air-water interface is rather small compared to adsorption at the solid phase. However, sensitivity experiments showed that the effect of adsorption at the air-water interface strongly depends on the hydraulic properties of the soil. The results of this study led to the adaptation of existing protocols for conducting laboratory tests to assess the risk of PFAS leaching, and an updated methodology for evaluating the effects of PFAS leaching. Ultimately, the results may assist in the development of effective PFAS remediation strategies and more stringent regulations.

Session 3b14 orals

Session 3b14 / Abstract title: An approach for diffuse soil contamination in Flanders – development of policy tools

ID: 284

Key words: diffuse soil contamination, soil policy, emerging contaminants

Submitter: Griet Van Gestel

Organization: OVAM - Public Waste Agency of Flanders

Co-authors: Johan Ceenaeme, Dirk Dedecker, Bruno Billiaert, OVAM

Session: 3b14

Abstract

In addition to point source pollution, diffuse soil contamination is increasingly cited as a major threat for soil health. In Flanders, the Soil Decree has been in force since 1995, with the aim of managing and remediating soil contamination. This includes all forms of contamination of soil, sediment and groundwater. However, the legal instruments elaborated in the regulations are primarily aimed at soil contamination that can be directly linked to a clearly identifiable and easily locatable point source or risk activity. This means that diffuse soil contamination is not well covered until recently.

We are developing an approach for diffuse soil contamination. This is desirable for several reasons. Human health risk can arise both in the short and long term, e.g. when the soil is used for food production. Diffuse soil contamination can affect the quality of agricultural land in such a way that a safe food supply will become more difficult in the future. Problems with diffuse soil contamination also occur in practice, e.g. during excavation works, when unexpectedly elevated concentrations of pollutants are found, and questions arise on how to deal with it, who is responsible for investigations and further measures, …

As a first step all existing data on diffuse soil contamination in Flanders have been inventoried: possible sources, measurement data, and other supportive data. Next, the impact was evaluated. Then, based on the inventory and stakeholder discussions, a roadmap was developed for a policy approach on diffuse soil contamination. Key elements are:

- Identification of ‘suspected areas’ where it is highly possible to find diffuse soil contamination. This implies collecting, analyzing and presenting spatial information, and the

production of maps and databases.

- Organization of measuring campaigns to validate inventoried data and to obtain systematically more detailed information. Substances to be analyzed are selected based on the inventoried information. Often emerging contaminants are present as diffuse soil contamination.
- A thematic approach for different categories of diffuse soil contamination, e.g. harbors and surroundings, agricultural land, line trajectories, such as roads, railways, …

To support this policy, tools and applications are under development, in order to make databases publicly available.
The main purpose of the approach is to provide information on the soil quality to land owners and users, supplemented with recommendations on its use. In this way risks and further spreading are avoided. In addition, the same tools can be used to stimulate the circular reuse of excavated soil.

In the presentation, results of the inventory study will be discussed. How are they used for policy development, for designing measurement strategies, …? Which measurement campaigns are ongoing? Also examples of tools and applications will be shown.

<u>Session 3b14 / Abstract title</u>: The fate and uptake of sewage sludge-derived emerging organic contaminants in winter wheat

ID: 325

Key words: Composting, Endocrine Disruptors, Pharmaceuticals, Pyrolysis, Sewage Sludge

Submitter: Niluka Wickramasinghe

Organization: Czech University of Life Sciences

Co-authors: Martina Vítková - Czech University of Life Sciences, Alena Grasserová-Institute of microbiology Czech Academy of Sciences , Tomáš Cajthaml-Institute of microbiology Czech Academy of Sciences, Michael Komárek- Czech University of Life Sciences
Tomáš Cajthaml2, Michael Komárek1

Session: 3b14 backup

Abstract

This study investigated the uptake of sewage sludge-originated emerging organic contaminants (EOCs) in winter wheat. The study aimed to evaluate the potential of using sewage sludge as a source of nutrients in agriculture while minimizing its ecotoxicological impacts. The utilisation of sewage sludge while maintaining its safety for the environment and human health is a high priority for sustainable waste management and the prevention of pollutants entering the soils, water, and crops. Current legislation in the Czech Republic allows only pre-treated sludges in agricultural soils. Therefore, two popular strategies were imposed, i.e., composting and pyrolysis. Five different sludges from the Czech Republic were selected and treated before application to the experimental plots on two contrasting agricultural sites. The dose of the application was five tonnes of dry weight per hectare. Winter wheat (Triticum aestivum) seeds were cultivated immediately after the application and harvested the following year. The collected plant materials were milled separately. Subsequently, EOCs were extracted with methanol and analysed by liquid chromatography-mass spectrometry (LC-MS/MS). In particular, 37 pharmaceuticals and personal care products (PPCPs), and 14 endocrine-disrupting chemicals (EDCs) were considered. Telmisartan and triclosan were the most abundant PPCPs in raw sludges, comprising 62.3% of the total PPCPs. Caffeine is the only detected compound in pyrolyzed sludges, with a 93.5% reduction from the raw sludges. The most found EDCs in raw sludges was bisphenol A, and the average concentration was 632 ng/g with a 71.4% average reduction during the composting process. There were no EDCs found in the pyrolyzed sludges. However, only four PPCPs were found in plant materials from both locations. The accumulation of EOCs has been found in the order of roots > shoots > seeds. Caffeine was the highest accumulated compound in seeds, yielding 12.4 ng/g in plots amended with composed sludges and 4.85 ng/g in plots amended with pyrolyzed sludges. Diclofenac and

carbamazepine were detected only in the seeds with low concentrations of 0.42 and 0.36 ng/g, respectively; due to their high hydrophobicity, these compounds can only be recovered from the areal parts of the plants. These results suggest that the bioavailability of EOCs has been reduced with the treatment strategies. However, further verifications and analyses must be done to confirm the safety of the treatment strategies for using sewage sludge in agriculture.

<u>Session 3b14 / Abstract title</u>: High resolution characterization technology with continuous monitoring of contaminants composition and intensity

ID: 344

Key words: high resolution, contaminant screening, remedial design

Submitter: Eugen Martac

Organization: Fugro Germany Land GmbH

Co-authors: nan

Session: 3b14

Abstract

Joshua Both*, Charline Kaplan**, Olga Vounaki**, Paulo Valle**

Affiliation(s): HMVT*, ERM**

Background: Brownfield redevelopment is a critical requirement if we are to build homes and industrial sites without encroaching on greenland. No matter if former gas stations or refineries, chemical plants or dry-cleaning facilities, regulatory compliance or proceedings with remedial scenarios, choosing the right technology is the key to address the particular issue of each individual site.

Methods/Activities: Volatile contaminants such as fuels or solvents are detected by the Membrane Interface Probe. Along with Hydraulic Profiling, it provides in only one push a high-resolution structuring of the underground to determine contamination, hydraulic, lithology and geotechnical parameters. Fugro coupled the standard system with a high end lab analyser in order to develop a field equipment able to provide additionally the composition of the contaminant cocktail and the concentration of each individual compound.

Results: Besides the typical MIP signals, being able to identify individual compounds and deliver their concentrations in high vertical resolution proved to be a quick, very reliable and inexpensive pre-screening field method. This continuous and rapid survey allows a high-end analysis directly from the screening phase of a site, no matter of hot spots, different source areas or degradation paths. A comparison to the results from conventional soil and groundwater sampling confirmed the results.

Conclusion: This study method further-development illustrates the usefulness of reliable initial screening methods for effective site investigation especially at large contaminated sites. The large-scale application of low-invasive initially screening can be valuable in directing and focusing the subsequent, more expensive methods of soil and groundwater sampling. Moreover, it delivers a

significant added value for a success promising design of remediation strategies and shortens the overall decision chain with associated budget savings.

<u>Session 3b14 / Abstract title</u>: Sustainable Remediation Starts with an Effective Sustainable, High-Resolution Site Characterization Program

ID: 407

Key words: Green Characterization, sustainability, high resolution, site characterization

Submitter: Harry O'Neill

Organization: Beacon Environmental

Co-authors: nan

Session: 3b14 backup

Abstract

Groundwater monitoring wells installed on and adjacent to an industrial manufacturing facility identified chlorinated solvents known to have been used in the facility's operations. Following a traditional investigation approach, soil samples were collected at targeted locations based on available site information to identify if releases of the identified contaminants in groundwater (primarily TCE, PCE and DCEs) had occurred. Soil samples were collected at 11 sample locations strategically located near areas of greatest concern and at multiple depths ranging from near surface to 12 meters below ground surface, which is the depth to groundwater. Results from this soil sampling program were inconclusive, at best, with almost all non-detects except for low-level measurements of TCE and DCE at depths just above the water table. Given that this portion of the facility, which is approximately 1.1 hectares, was known to store and use the identified chlorinated compounds in the groundwater, a highly sensitive and sustainable sampling approach was employed to identify if source areas were present through the use of a high-resolution, minimally invasive soil gas sampling program.

The prior soil sampling program consisted of a focused sampling plan targeting areas of greatest concern, including a metal plating area, a TCE aboveground storage tank area, a hazardous waste storage areas, an on-site wastewater treatment area, and a paint booth. Following industry standard procedures, a PID was used in the field to screen soil cores and guide at what depths to collect soil samples for submittal to a fixed laboratory for analysis. A total of 29 soil samples were collected over a two-day period and were analyzed by EPA Method 8260B. Based on these inconclusive results, a minimally intrusive passive soil gas (PSG) survey was then employed with samples collected in a high-resolution grid pattern with 5 meter spacing in the areas of greatest concern and 12 meter spacing in those area of less concern to assess whether releases may have occurred from past, unknown operations. A total of 60 PSG samples were installed and sealed in 35 cm deep holes through a concrete slab, which required 10 hours of fieldwork using basic hand tools. Following an

approximately 2-week exposure period, the passive sorbent samplers were retrieved, requiring 4 hours of fieldwork, and were shipped to a fixed laboratory for analysis following U.S. EPA Method 8260C.

The passive soil gas survey identified multiple locations with discrete source areas of chlorinated compounds, as well as 1,4-Dioxane, which had not been targeted in prior soil or groundwater samples. The PSG data clearly identified where contaminant releases had occurred and was used to cost-effectively focus the design of a remediation system that included in-situ chemical oxidation. A discussion will be presented on the findings from this investigation, including the advantages of using in-situ adsorbent samplers as a Green Characterization technique that allows for the rapid collection of a high-resolution data set with the requirement of only basic hand tools, reduced carbon footprint during mobiilzation, and no soil waste being generated. Passive soil gas samplers are small and light weight (e.g., 8 cm x 1.2 cm), easy to transport without the requirement for preservatives or ice and are analyzed using thermal desorption techniques that do not require solvents or generate sample waste. Using adsorbents to trap VOCs/SVOCs in soil gas for later analysis via thermal desorption methods (TD-GC/MS) has the additional advantage over traditional approaches of collecting soil samples where organic compounds have a significant risk of volatilizing and being lost before analysis. A discussion will also be provided on the decision process for designing the soil gas investigation, the QA/QC procedures that were employed by the PSG method to provide reliable data, and the range of VOCs and SVOCs that were targete

<u>Session 3b14 / Abstract title</u>: A New UK Approach: Development of Vertical Screening Distances to support more Sustainable Assessment of the Petroleum Vapour Intrusion Pathway

ID: 70

Key words: Hydrocarbon Vapour Biodegradation Screening Empirical-dataset

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Organization: Arcadis

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Session: 3b14

Abstract

Petroleum hydrocarbons are known to be readily biodegraded under aerobic conditions as they migrate through the subsurface. However, under current UK regulatory guidance, biodegradation is not considered in the assessment of the risk to human health via the Petroleum Vapour Intrusion (PVI) pathway in the most frequently used Johnson and Ettinger sub-model. In countries where large-scale and robust empirical datasets assessing the impact of biodegradation on the PVI pathway exist, regulatory and best practice guidance has evolved to account for the significance of this process in developing risk-based assessment thresholds. The absence of a comparable empirical dataset in the UK has led to risk-based thresholds which may be overly conservative for the PVI pathway, in turn leading to land contamination management decision-making which is less sustainable.

A UK research project has been undertaken to compile an empirical dataset to support more robust decision-making for the PVI pathway in the UK, following comparable approaches in the United States (US) and Australia. The compilation of the UK-specific dataset, which required collaboration with multiple stakeholders across the UK, was undertaken using bespoke data collection forms for 144 sites with known petroleum hydrocarbons within soil or groundwater. These forms allowed collection of information on the type of site, geology and soil, groundwater and gas monitoring and were designed to enable the data to be classified as suitable for inclusion in the database as it was received. Of the 144 sites considered, 39 were classified as suitable for insertion into the database with a total of 237 gas datasets to work with. The UK database will in future be available as a public resource.

Preliminary analysis of the dataset was undertaken to understand the significance of biodegradation as a factor affecting concentrations of petroleum hydrocarbons in vapours, versus the impact of other factors such as the presence of Non-Aqueous Phase Liquid

(NAPL), the geology of the unsaturated and the concentration of petroleum hydrocarbons in groundwater. Having completed the preliminary analysis and identified appropriate subsets within the data, the 'Vertical Distance Method' was used to derive vertical screening distances suitable for use in the UK. Following the findings of the preliminary assessment, separate vertical screening distances were developed for sites where dissolved phase only impacts are present, and sites where NAPL is present. Where a vertical screening distance is met or exceeded; a vertical column of clean soil is present between a petroleum hydrocarbon source and a human health receptor at a thickness greater than the vertical screening distance, as such, the risk to human health via the PVI pathway would not be considered significant.

A comparison between the UK dataset, and resulting vertical screening distances, was undertaken against international datasets from the US and Australia. The datasets from all three countries were relatively consistent, with existing US and Australian vertical screening distances comparable to those proposed for the UK.

The results of the research project have been used to develop a best-practice guide for UK practitioners undertaking PVI pathway assessments. The guide includes appropriate application of vertical screening distances, including the need for a robust CSM and the absence of conditions which would preclude biodegradation.

The presentation will be centred around the development of the vertical screening distances and how they should be robustly applied to contaminated land sites to drive more sustainable risk management decisions.

<u>Session 3b14 / Abstract title</u>: Tire-derived compounds from biosolids contaminate soil and might be taken up by edible plants

ID: 74

Key words: Tire wear particles, biosolids, plants, uptake, 6PPD

Submitter: Thorsten Hueffer

Organization: University of Vienna

Co-authors: Anya Sherman, Stephanie Castan, Thorsten Hüffer, University of Vienna

Session: 3b14

Abstract

Tire wear particles are expected to reach agricultural fields via biosolids application, atmospheric deposition, or irrigation with recycled water. On the field, tire wear particles will release a suite of organic additives in the root zone of plants. These compounds are then available for uptake by edible plants, which could be a route for human exposure to tire-derived compounds, as has been previously shown for pharmeceuticals and personal care products. In a hydroponic study, we exposed lettuce plants to five common tire-derived compounds: hexamethoxymethylmelamine (HMMM), benzothiazole (BTZ), 1,3-diphenylguanidine (DPG), N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6PPD) and 6PPD-quinone (6PPD-q), and monitored the concentrations in lettuce roots and leaves. We found that all five compounds were taken up and translocated to lettuce leaves. Translocation was compound dependent, and was hindered by the differential affinity of compounds to lettuce root tissues. This affinity was driven by varying logKow and the charge of the compounds. In ongoing work, we are conducting pot experiments to investigate how partitioning between soil and pore water affects the uptake of these tire-derived compounds. While sorption to soil decreases plant uptake of several compounds, it enhances the stability of other compounds, which leads to a longer-term availability to plants, and thus, more uptake over the longer term. All five tire-derived compounds are metabolized in lettuce plants, and we used untargeted high-resolution mass spectrometry to identify their transformation products. We found that the five compounds were transformed via various metabolic processes within the plants. We identified novel transformation products of several compounds, including HMMM and 6PPD-q. We also found that for all compounds, except 6PPD, the transformation products formed were highly stable in the lettuce leaves. In another set of hydroponic experiments, we exposed lettuce to tire particles and found that the long-term leaching of tire-derived compounds from the particles provided a resupply of these compounds, and was able to overcompensate for the rate of metabolism in plants, leading to continuously increasing concentrations of the tire-derived compounds in the lettuce leaves over the duration of the experiments. Altogether, our findings indicate that if

plants are exposed to tire wear particles during growth, the compounds contained in the tire wear particles may be taken up by plants, and these compounds and their transformation products may be present in the edible parts of the plants up through the time of consumption. This work highlights an important potential route of human exposure to tire-derived compounds.

<u>Session 3b14 / Abstract title</u>: Micro-or nanoplastics do not enhance the relocation of contaminants in agricultural soil

ID: 75

Key words: Microplastic, transport, vector, organic contaminant, soil

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Session: 3b14

Abstract

Insufficient waste management and slow degradation rates contribute to the ubiquitous accumulation of micro-and nanoplastics (MNP) in the environment. Agricultural soils can receive additional MNP input by fertilization with compost or sewage sludge. Mulch films are often poorly recovered and can fragment on-site to ever smaller particles contributing to the plastic load in agricultural soils. MNP can contain additives and contaminants sorbed from the surrounding environment. That MNP could transport associated contaminants into deeper soil layers or even to groundwater is an often raised concern, but experimental evidence is so far not available. This study aimed to compare the transport times of plastic particles with the desorption times of contaminant from the plastics to determine whether or not MNP contribute to the relocation of contaminants to deeper soil layers.

The Damköhler number Da describes the ratio between the transport and desorption time. For Damköhler numbers > 100, MNP are in equilibrium with the soil phases and do not contribute to contaminant relocation. For Damköhler numbers 0.01 there is no significant desorption within the particle transport time and MNP contribute to contaminant relocation.

To calculate reaction rate constants of the contaminant desorption, two diffusion processes need to be considered: the diffusion of the compound through the particle (intraparticle diffusion, IPD) and diffusion through an aqueous boundary layer on the outside of the plastic particle (ABLD). Distribution coefficients between plastic and water and apparent diffusion coefficients were compared with literature values of various polymer-contaminant combinations to estimate whether MNP can transport organic contaminants beyond one meter soil depth.

Considering IPD as the rate-limiting diffusion process, our results show that at a flow velocity of 1 m a-1 contaminants establish equilibrium with the surrounding soil phases too fast to be transported by MNP. Similarly, when considering ABLD, decoupled transport only occurs for

particle size > 1 mm. Nanoparticle research has shown that 1 µm sized particles at a density of 1 g cm-3 have the highest mobility in soil. At this size only for very few polymer-contaminant combinations, ABLD can be slow enough for decoupled contaminant transport. For preferential flow paths, decoupled transport is possible for slightly smaller particles since the time for the contaminants to diffuse from the particle and to establish equilibrium is shorter. Preferential flow paths represent the only scenario under which particle-assisted contaminant transport would occur in soil layers beyond one meter depth. However, such flow paths in agricultural soils are not continuous and rarely extend deeper than one meter.

Organic contaminants can be transported by a multitude of natural colloids in soil, including soil minerals or organic macromolecules. Compared to these, the role of MNP as a contaminant vector is limited. For organic contaminants that come into contact with the plastic in the soil, MNP play a minor role in their transport through soil due to the lower abundance and the comparatively low sorption coefficient of the plastic compared to other soil substituents. However, MNP can add to the flux of organic contaminants like additives to soil and release these in the upper soil layers with negative effects on soil organisms, crops, and ultimately the consumer. This study contributes to a better understanding of MNP interactions with contaminants in soil.

Session 3b15 orals

Session 3b15 / Abstract title: Aerobic biodegradation potential of ETBE in groundwater: Observations and management perspectives

ID: 237

Key words: Groundwater, remediation, management, biodegradation, ETBE

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Session: 3b15

Abstract

Gasoline ether oxygenates (GEO), such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), tert-amyl ethyl ether (TAEE) and diisopropyl ether (DIPE), are added to gasoline formulations to reduce vehicle emissions. Over the last 15 years ETBE has become the dominant ether oxygenate used in European gasoline, mainly because it can be synthesised from biomass and contributes to the requirements of the EU Renewable Energy Directives for use in biofuels.

GEO may enter groundwater through releases during production, distribution and storage, along with other GEOs and gasoline hydrocarbons. While the fate of MTBE in the subsurface environment is well characterised, the knowledge base on the potential for biodegradation of ETBE in groundwater is limited, but essential to develop appropriate management strategies. Evidence from studies on MTBE suggest aerobic pathways may be important for ETBE biodegradation in groundwater, given the similar chemical structure of these compounds.
This presentation summarises research on the potential for aerobic biodegradation of ETBE in groundwater. The purpose of the study was to understand (i) the effect of environmental factors (contaminant exposure history, co-substrates, GEO concentration), and (ii) the distribution of ETBE-degrading microorganisms in the aquifer microbial community on ETBE biodegradation, as a basis to inform risk assessment and remediation strategies at sites with

ETBE-releases to groundwater. Aerobic microcosm experiments and field-based studies were developed using inocula from a number of ETBE-release sites in Europe. Samples of inocula (groundwater and aquifer material) were collected from locations, which had been exposed (previously impacted), and not exposed to ETBE. The microcosm experiments were dosed with either ETBE, or ETBE and MTBE. As sole substrate, ETBE was biodegraded without a lag in ETBE-impacted microcosms but with a lag of up to 66 days in non-impacted microcosms. As co-substrate, ETBE was biodegraded preferentially to MTBE in both non-impacted and impacted microcosms. Further addition of ETBE and MTBE reduced lags and increased biodegradation rates. TBA was produced as a transient metabolite in these experiments. ethB gene copy numbers increased significantly (> 100 fold) after exposure to ETBE, while overall cell numbers remained constant, suggesting that ethB gene-containing microorganisms come to dominate the microbial communities. Aerobic ETBE biodegradation potential (as determined by quantification of the ethB gene) was detected predominantly in the attached microbial communities and was below detection limit in the groundwater at the sites studied.

This study demonstrates (i) the potential for aerobic ETBE biodegradation within the unsaturated and saturated zone in European aquifers, (ii) that this capability is rapidly developed and maintained within the aquifer microbial community over extended timescales, and (iii) this potential can be assessed within the typical groundwater monitoring undertaken at GEO-release sites by analysis of ethB gene copy numbers in samples of mixed groundwater-aquifer material obtained from pumped monitoring wells. The detection of the ethB gene was found to be a more appropriate function-based indicator of ETBE biodegradation potential than taxonomic analysis of the aquifer microbial community. Overall, the study implies that biodegradation of ETBE can be expected to occur under aerobic conditions in mixtures with other GEOs in groundwater at ETBE-release sites. Furthermore, microbiological assessments of aerobic ETBE biodegradation can be achieved using relatively inexpensive field methods integrated within existing (hydrochemical-based) groundwater sampling protocols.

<u>Session 3b15 / Abstract title</u>: Permeable contaminant barriers: A new technology for interrupting exposure pathways while avoiding surface sealing

ID: 243

Key words: Soil protection, permeable barrier, exposure pathways, infrastructure

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Session: 3b15

Abstract

Groundwater is a highly important and scarce common good, which is why high demands are consequently placed on its protection. In many technical guidelines, the legal obligation to maintain high soil and groundwater quality is achieved by specifying sealing systems. The state-of-the-art foresees the sealing of surfaces with concrete, asphalt or geosynthetic barriers to prevent the transport of pollutants into the subsoil. In this way, the transport path of the carrier medium, i.e., the runoff or leachate, is diverted. It is discharged in sewage systems and – in a best-case scenario – the environmentally relevant contents are centrally removed in treatment plants. Certainly, this protects the soil under the sealed surface, but it is no longer available as a habitat, water reservoir, nutrient reservoir, pollutant filter, and carbon sink. Thus, new approaches are needed in which barriers selectively protect the underground from the contaminant while allowing the carrier medium to pass through. The use of permeable contaminant barriers represents such a new approach to groundwater protection by changing the state-of-the-art techniques. While contaminated water percolates through the filter, the transport of the pollutants is stopped, whereas the water can follow its natural flow path into the underground unimpeded. In this way, the subsoil maintains its natural functions and is protected at the same time. Newly developed contaminant filters consist of a carrier layer and a cover layer made of durable geotextiles with a core of amendment material, such as activated carbon, ion exchanger, organophilic clay, or oil binders. The approach offers new ways for groundwater protection in several applications. In different projects and pilot studies it has been tested successfully by the authors together with various partners (i.e., universities, laboratory, consultants) in recent years. For example, permeable contaminant barriers are used to unseal logistics areas for weakly to moderately contaminated railroad construction materials. It stops the contaminant transport from old timber sleepers or railroad gravel into the subsoil while the runoff can enter the underground unhindered. The substitution of asphalt or concrete sealings, which are required by

guidelines, brings monetary as well as ecological advantages, like CO2 emissions. Pilot tests on a logistic area of the German federal railway company Deutsche Bahn was carried out successfully over a period of four years. Another example is the use along roads through water protection areas. Instead of constructing a sealed swale in the roadbed, the treatment measure can be implemented directly along the road body before infiltration. Results carried out at a funded research project with a German university show that suspended solids as well as metals and hydrocarbons were removed with an effectiveness of up to 95%. Moreover, the filter mats offer new solutions for dealing with contaminated soils or sediments. Temporary soil storage yards or structures made of contaminated construction materials can be carried out by installing the filter mat underneath the soil body allowing the open installation of the soil. Due to the targeted infiltration of precipitation, mobile pollutants, such as PFAS are transported to the horizontally installed contaminant barrier and bound there durably. In this way, an improvement of the soil quality takes place while the structure functions as a noise barrier or an infrastructure dam. Lab and outdoor test results are also available for this application, proving the high effectiveness of the pollutant filters. The oral presentation will figure out important design parameters as well as test results from different pilot studies.

<u>Session 3b15 / Abstract title</u>: In Situ Metal Precipitation (ISMP) of heavy metals

ID: 295

Key words: Precipitation heavy metals biological sustainable

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Organization: TAUW Belgium

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Session: 3b15

Abstract

In Situ Metal Precipitation (ISMP) of heavy metals
Background/Objectives: An industrial site in the north of Flanders is contaminated with an historical contamination of a variety of contaminants like heavy metals, sulfate and ammonia due to spills and calamities starting early 20th century.
A cost effective and sustainable remediation technique compared to a traditional pump and treat (P) system was proposed to the problem holder for further investigation.
The technique of in situ metal precipitation (ISMP) was selected and lab and field tests were realized to evaluate not only the feasibility of the technique but also the durability on a longer term, since the polluted plume is also impacted by contaminated groundwater entering the test zone from the upstream zone.
Contamination: Most of the contamination is difficult to reach due to the presence of industrial buildings. In the core zone an extreme high concentration of sulfate (up to 18,000 mg/l) and heavy metals (sum of heavy metals up to 12,000 mg/l) was measured under strong acid conditions (pH of 1).
Local geology: The local geology at the site is a complex of alternating sand and clay layers resulting in a three aquifer system. The top aquifer is a (presumed) perched aquifer. The second aquifer is sandwiched between two clay layers. The two top layers are heavily contaminated with heavy metals (As, Cu, Ni, Pb and Zn ranging into hundreds of mg/l) and a low pH due to a calamity in the thirties. The third aquifer also is impacted with heavy metals though to a lesser extent (hundreds of µg/l). The aquifers are not used for drinking water purposes but water from the third aquifer is used for industrial use.
Labtest: In order to test the feasibility of the technique of ISMP -prior to the field test- a labtest was realised. Two conditions were tested:
1. Precipitation as metal sulphides using a carbon source (protamylasse and sodium lactate)
2. Adsorption of heavy metals on iron(hydr)oxides after using ferrous sulphate.
Field testing: A field test was conducted in the source zone and in the plume area to

investigate the feasibility of the technique of ISMP. ISMP should be capable of controlling the spreading risk from the contaminants of concern (COC's).
The field test was realized in two separate test zones :

1. Zone 1 (core zone): Chemical approach with precipitation of heavy metals as metal sulfides using a solution of Ca-polysulfide.
2. Zone 2 (plume zone): Biological approach with the reduction of sulfates to sulfides using a C-source with a pH correction (potassium bicarbonate)

Results/Lessons learned: The results of the field test indicate that in the core zone a rapid consumption of the injected Ca-polysulfide was observed due to the high concentration of COC's and due to strong oxidative conditions responsible for a fast oxidation of the injected sulphides to sulphates indicating the limits of a technique as ISMP.

In the plume zone also a rapid consumption of TOC was measured. However after the second injection of September 2021, reductive conditions were created with a sharp decline of dissolved heavy metal concentrations.
During the presentation these results will be discussed in more detail.
Costs and sustainability: ISMP is a less costly and a more sustainable approach compared to a classic pump and treat (P) remediation. The injection of a harmless carbon source enhances the biological precipitation process avoiding the huge mobilization costs, the high consumption of energy and production of waste materials caused by a P system making ISMP a more sustainable remediation technique than the more classic remediation techniques.
The environmental conditions were harsh, but maybe nature is stronger and more robust then we think.

<u>Session 3b15 / Abstract title</u>: What about the CO2 Fingerprint of a Successfully Finished In Situ Thermal Remediation (ISTR) of a CHC Source Area after 16 Years of Groundwater Remediation (P)

ID: 332

Key words: In Situ Thermal Remediation, CO2 fingerprint, chlorinated hydrocarbons, technology transfer, full scale remediation

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Session: 3b15 backup

Abstract

How to combine remediation and cost effectiveness with ecological demands?
In 1994 the soil and the upper aquifer system below a former chemical facility (mineral oils, solvents, chlorinated hydrocarbons (PCE)) were highly contaminated with 2,000 kg PCE after a filling accident. The groundwater table is located 2 m bgs., the contamination of the soil extended to 8 m bgs. From 1995 until 2002 a Pump Treat (P) system removed about 1,200 kg of CHC from the saturated and unsaturated zones. In 2002 the local community bought the area and the contamination was investigated in detail between 2008 and 2010. Between 2012 and 2021 the P was continued to remove 200 kg of CHC. During and before that period the remediation planning was focussed on in situ remediation (e.g., ISCO, molasses, in situ thermal remediation (ISTR)) as well as soil exchange and deposition including pilot studies and cost evaluations.
The most promising and cost-effective technology (steam-air injection) was selected to remediate 7,200 tons, around 3,900 m³ of soil. The aim was to reduce the CHC-flux in the groundwater by 75%, allowing a mass flux of 9.4 g/d CHC leaving the site and to reduce the CHC content of the soil to be less than 1 mg/kg.
In April 2021, 31 steam-air injection wells (2”, 7 – 8 m bgs filtered) were installed in a distance of 4 – 5 m. To extract the hot soil vapour 50 wells (2”) were rammed down the unsaturated zone, and 5 combination wells (5”) for the extraction of groundwater and soil vapour were used. From May until August 2021, the remediation plant, consisting of a steam generator (2,000 kW), a compressor station (160 m3/h), a soil vapour extraction and cooling unit (3,000 m³/h air, 1,100 kW cooling power), a groundwater treatment unit (30 m³/h groundwater and condensates) and a two-stage adsorption unit, each 2 m³ GAC to treat the off-gas was established. The temperatures in the soil were monitored at 156 discrete

measurement points, also the mass fluxes of steam-air, soil vapour extraction, and contaminant concentration in the soil vapour.
The ISTR was operated from August 2021 until February 2022. There were 10 remediation areas to be treated sequentially. During 3 – 4 days each of the areas initially heated up to 92°C. The contaminant desorption by evaporation starts at the co-boiling point of 92°C and lasted for about 14 days during which the temperature was maintained at a reduced heat flux to about 900 kW steam power.
In total 195 MWh of electrical energy for the plant's operation and 2,168 MWh of fuel-based heat energy (steam generator) were consumed. This corresponds to a total emission of about 585 to of CO2 and met the design calculations.
The contaminant removal mass from each remediation zone clearly localised the former source zone and the surrounding/downstream area. In total 280 kg of CHC were removed from 7,200 tons of soil by the SVE, and 20 kg CHC were removed from the groundwater leading to a CHC concentration in the groundwater remediation wells of 140 µg/L at the end of the ISTR.
A steam propagation for 250 kW steam power per well resulted in a radius of steam expansion of more than 2.5 m at a depths of 6.5 m bgs.
The total duration of the ISTR was 28 weeks, as long as predicted using the design-tool. Soil sampling indicted a CHC contamination of 1 mg/kg after the cooling phase and a CHC emission of 5.5 g/d. The P was continued for 6 months and then stopped, a monitoring phase for the next 10 years followed. The area is now free for new industrial use.
A replacement of the sandy contaminated soil, washing and treating at a distance of 60 km and re-use it again for construction at the original site might lead to an emission of 822 tons CO2; the site-specific ISTR emitted 29% less CO2, met the energetic design data and reduced the CO2 emissions compared to alternative ex-situ methods.

<u>Session 3b15 / Abstract title</u>: The use of compound-specific isotope analysis (csia) to allocate the potential sources of dissolved chlorinated solvents contaminant in large urban areas: lessons learned from few case studies

ID: 360

Key words: Compound-Specific Isotope Analysis (CSIA), Chlorinated Solvents

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Organization: Environmental research scientist

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Session: 3b15

Abstract

Porpuse of the study: The origin and pathways of frequently detected contaminants in groundwater such for example tetrachloroethylene (PCE) were investigated by coupling isotope, groundwater flow and transport modeling, and statistical analysis at two major cities in the North of Italy (Milano and Pavia) as part of their Water Safety Plans (WSPs). A Water Safety Plan (WSP) ensures safe drinking-water through good water supply practice from catchment to consumer, in order to (i) prevent contamination of source waters, (ii) to treat the water to reduce or remove contamination and (iii) to meet water quality targets. Thus, isotopic data can give crucial insights both in terms of defining hazards and assessing risks and can play a pivotal role in management and monitoring phases consistently ensuring the safety and acceptability of a drinking-water supply. Chlorine and Carbon Compound-Specific Isotope Analysis (37Cl 13C-CSIA) and 2H, 3H, 18O were applied in different hydrogeological settings to infer additional information's for the development of the conceptual model of the contamination, including source apportionment, remediation and containment actions efficacy evaluation and overall to asses the pathways of such contaminants in groundwater, resources which are also used for the water supply systems of tow large cities.
Methodology: With regards case study #1 (Milano), about 60 sampling locations used for water supply purposes (wells and piezometers), were selected among two main aquifers within the Milan Metropolitan area - B (intermediate, below 40 m below ground surface, b.g.s.) and C (deep, below 100 m b.g.s.) while for case study #2 (Pavia) about 30 locations were sampled within the shallowest aquifers (down to 10 m and from 10 to 30 m. b.g.s

approx.). Samples were collected in addition the all chemical analysis also for 3H- 2H-, 18O-H2O, 13C-CSIA and 37Cl-CSIA on chlorinated solvents contaminants. The results were interpreted together with groundwater flow and contaminant transport modeling, and statistical efforts.

Summary of findings/results: The environmental isotopes (2H, 18O – H2O and 3H-H2O) allowed a better understanding of the groundwater flow dynamics mainly in terms of recharge and relationship among different layers/aquifers. 13C-CSIA and 37Cl-CSIA were useful instead for pollution assessment, in particular for perchloroethylene (PCE). Distinct δ13C- and δ37Cl- PCE were found in the proximity of different polluted areas, allowing to discretize responsibilities (sources allocation) and in distinguishing between plumes and background (diffuse) contaminations (in the case of the City of Milano). 13C-CSIA and 37Cl-CSIA results for trichloroethylene (TCE) and dichloroethylene (cis-DCE) better constrained the role of natural attenuation processes in containing and mitigating the contamination. Overall, 13C-CSIA and 37Cl-CSIA results in combination with groundwater flow and contaminant transport modeling and statistical efforts helped in a better understanding of the conceptual model development with regards source and pathways of chlorinated solvents in groundwater under the Milan Metropolitan area and the city of Pavia.

Conclusion: 13C-CSIA and 37Cl-CSIA results in combination with groundwater flow and contaminant transport modeling and statistical efforts helped in a better understanding of the conceptual model development with regards source and pathways of chlorinated solvents in groundwater.

Significance: Only through a correct understanding of the origin together with the assessment of the fate of contaminants, will water practitioners be enabled to successfully manage water resources and to put in place prevention and/or mitigation measures to avoid additional deteriorations. The proposed case studies reveal how isotope applications coupled with hydrogeological investigations can turn in a fine-tuned tool essential in the management and risk assessments within a WSP in urban areas

<u>Session 3b15 / Abstract title</u>: Detection of new organic micropollutants in drinking water supply system using high resolution mass spectrometry

ID: 394

Key words: drinking water, micropollutants, high resolution mass spectrometry

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Session: 3b15

Abstract

Due to climate changes and increasing anthropogenic activity, global sources of drinking water are under threat. Increasing pollution directly endangers the population as it leads to a worsening of the quality of surface water, which is one of the main sources of raw water for drinking water treatment plants (DWTPs). Therefore, legislation norms are tightening all over the world, and the implementation of these norms, together with the improvement of water treatment technologies, ensure the quality of the final product of the drinking water treatment – tap water. With a certain level of knowledge about the prevalent anthropogenic organic compounds (e.g., their production, toxicity, bioaccumulation, and persistence), the most common ones are already routinely monitored. However, the majority of drinking water pollutants remain unmonitored or undiscovered yet. On top of that, a wide range of new chemicals are being synthetized and detected in the environment every day as a replacement to the regulated substances. So far, only the man-made chemicals themselves have been mentioned, but the truth is that their degradation products or metabolites may present an environmental problem as well. Within this work, a new methodological workflow for the identification of new hazardous contaminants in the drinking water supply system and for the evaluation of treatment processes was developed. Using advanced analytical techniques including passive sampling and high-resolution mass spectrometry, untargeted analysis of new water pollutants has been performed. The exposure of passive samplers in 10 drinking water plants to raw and treated water revealed a whole range of anthropogenic pollutants including already known pesticides, pharmaceuticals and derived by-products. Several new organohalogen compounds were described as well. Moreover, our results of a 3 month screening of selected drinking water treatment plants also revealed the potential of such an approach for drinking water treatment technology evaluation.

Session 3b16 orals

Session 3b16 / Abstract title: Case Studies and Analysis of Sustainable Remediation Techniques and Technologies

ID: 219

Key words: sustainable remediation, sustainability assessment, case studies

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Session: 3b16

Abstract

Purpose of study
The concept of sustainable remediation has become well established in the remediation industry and its application has spread around the world. However, there is a recognised gap which is the provision of detailed case studies documenting the practical implementation of sustainable remediation in the real world, particularly in a European context. A consequence of this gap is that the further refinement of guidance is impeded by a lack of knowledge of what aspects work well in practice, versus poorly.
Concawe commissioned a study in 2021 to a) to gather, prepare and publish ten European case studies that demonstrate sustainable remediation techniques and technologies and b) to provide an analysis of the case studies to identify key success factors that facilitated the adoption and success of these projects at different sites.
Methodology
A long-list of twenty case studies was identified. Each case study provider was invited to complete a questionnaire based on the ISO Standard on Sustainable Remediation 18504:2017. This was used to assess the suitability of all potential case studies for inclusion in the study.
Each case study was then scored by the project team on how closely it matched ISO 18504, its relevance to Concawe and its ability to be delivered to time. Ten case studies were recommended for selection, agreed by Concawe and a case study provider contracted. Case study information was then collected in a common template and reviewed by the project team, CL:AIRE's Technology and Research Group and Concawe. A series of ten detailed case study bulletins will be freely available on-line from the CL:AIRE and Concawe

web sites by Summer 2023.
In addition, a cross comparison analysis of the ten case studies has been carried out, seeking to help practitioners compare these case studies to their own projects when they may be considering sustainable remediation techniques and technologies, both in terms of success factors and areas for improvement.

Summary of findings/results

Cross comparison analysis focused on the following attributes:

- Site location
- Type of site (former use)
- Saturated / unsaturated zone etc
- Targeted contaminants
- Risk drivers
- Envisaged land use
- Objectives for sustainability assessment
- Remediation options compared
- Stakeholder engagement
- Boundary conditions
- Scope (environmental, economic, social)
- Key constraints / opportunities
- Assessment type (qualitative, Multi Criteria Decision Analysis etc)

Based on this case study analysis and recently published guidance, a practical approach for deploying sustainable remediation on operational sites has been devised.

Conclusions

This project brought together ten sustainable remediation case studies to help address a critical gap in provision. Sustainable remediation techniques and technologies are being used on sites in Europe, particularly in the UK which has benefitted from the work of SuRF-UK and a pragmatic regulator. Working with a risk-based conceptual site model, effective engagement with stakeholders and a sound understanding of sustainable remediation practices are seen as key success factors from these case studies.

Significance / contributions of study

The value to industry from this study is a greater awareness of sustainable remediation techniques and technologies, and the key enablers that will make these examples more relatable to other sites across Europe and beyond.

<u>Session 3b16 / Abstract title</u>: PFAS in coastal areas – implications of diffuse impact from dispersion via aerosols and sea foam

ID: 236

Key words: PFAS, sea foam, aerosols

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Organization: Central Denmark Region

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Session: 3b16

Abstract

Purpose of study
PFAS was found in shallow groundwater and drainage water at a Danish coastal town by the North Sea at the west coast of the Jutland Peninsula. Due to no obvious point sources a working conceptional hypothesis was: Can PFAS contamination spread by sea spray aerosols (SSA) and sea foams generated during storms? And if so, is this a local or a regional occurrence?

Methodology
The hypothesis was addressed by sampling of soil, sea-, ground-, surface- and drainage water in an area including a reference area located 25 km south of the study area. Sampling was done at different distances from the shoreline up to 1,000 m from the sea. During storm, seafoam was sampled on the beach. Field work also included sampling of grass to address risk of cattle grazing on coastal meadows. The results have led to new investigations farther south and north of the initial coastline study area, and the results have led to considerations, that PFAS in water wells at two public waterworks may have origin from diffuse contamination spread from low level of PFAS in sea water.

Summary of findings/results
Data show that PFAS concentrations in shallow groundwater and surface water can be up to 7,000 ng/l (∑4 PFAS – PFOS, PFOA, PFHxS, PFNA) close to the shoreline (100 m from sea) declining logarithmically with distance to average concentrations of 50 ng/l at 500 m from the shoreline. Fewer samples still show significant concentrations several km from the shoreline. Soil samples do not show a clear correlation with distance to the sea, hence it is considered that soil type, content of water and organic matter may play a role in the soil concentrations.

Results from sampling of sea foam show high concentrations from 2,800 to 1,700,000 ng/l (∑22 PFAS). The main contaminants are PFOS and PFOA in both sea foam, soil, surface- and groundwater. Sea foam also contains long chain PFCAs (PFNA - PFTrA). Short chain PFAS (mostly PFBA) are present in samples of ground- and surface water near the shoreline, though PFBA is not detected in samples of sea foam. The pattern of PFBA is different than PFOS and PFOA, with a lower decline of PFBA with distance to sea. Together with the absence of PFBA in sea foam it is considered, that PFBA have a different spreading pattern than long chain PFAS, where PFBA may primarily spread by SSA.

Conclusion

The results give evidence that low background levels of PFAS in sea water can accumulate in sea foam/SSA and spread during storms to coastal areas. The results show that this process results in diffuse PFAS contamination with risk of contamination of coastal surface water, ground water and meadows leading to hazards of contaminated drinking water and accumulation of PFAS in gamebirds and grazing livestock. It is assessed that the diffuse contamination may be widespread along the shores of the North Sea.

Significance / contributions of study

The Danish EPA have together with the Central Denmark Region and Lemvig Municipality funded a project in order to perform further investigations both on the occurrence of PFAS in coastal areas and in sampling methods to further understand the dispersion mechanisms.

<u>Session 3b16 / Abstract title</u>: Plastics are everywhere, including in the soil. But what are the risks for us?

ID: 292

Key words: plastics, soil, risks, impact

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Organization: Deltares

Co-authors: Stefan Kools, PhD, KWR, scientist and Bas Coolsma, M.Sc., Antea Group, senior manager

Session: 3b16

Abstract

One of the major environmental issues in soil and water management is the presence of plastics. Awareness is growing that pollution of water and soil with plastics must be prevented. For this aim, there are more and more initiatives to limit the increasing plastic pollution. This mainly concerns the visible problems with littering plastics such as plastic bags, bottles and packaging in the environment. However, little is known about the fate and impact of smaller plastic particles (micro- and nanoplastics or MNP). More knowledge about degradation, spread and exposure to MNP is needed to assess the impact on human health and the environment.

Knowledge about plastics in the soil is also still a young branch of science. In addition to the unintentional pollution by plastics, many plastics are also used for infrastructure as building or isolation material, in geotechnical engineering and in agriculture. This deliberately brings them into contact with water and soil. On the one hand, many plastics have been in use for a long time, but the knowledge about their full stability and inertness is very limited. Over a long period of time, plastic particles but also substances (additives) could be released from the plastics and end up in the soil and furthermore, for example, end up in our food chain via plants.

The health risks of MNP are investigated internationally with great relevance. Developing solution routes is key in our research as well as insights into the design and progress of the ongoing research about health and environmental impact will be shared. It also discusses how the sector and policymakers can contribute to the development and application of this knowledge.

Starting points on the adequate risk-oriented action points in relation to potential effects of (micro)plastics in the environment (soil and water) are examined in more detail and

significant insights on the state of affairs will also be shared during this presentation.

Session 3b16 / Abstract title: Current Status and Challenges of, and Preparedness for Sustainable Remediation from Nuclear Disaster

ID: 294

Key words: Sustainable Remediation, Nuclear disaster, contaminated soil and waste

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Session: 3b16

Abstract

In March 2011, the accident at Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant (hereinafter referred to as "Fukushima Daiichi Nuclear Power Plant") occurred following the Great East Japan Earthquake, which caused extensive damage mainly on the Pacific side of the Tohoku region. As a result of the accident, evacuation orders were issued to 13 cities, towns, and villages in Fukushima Prefecture, and 164,865 people were forced to evacuate at the maximum.
On the other hand, more than 11 years have passed since the accident, and radiation doses have significantly decreased due to decontamination measures implemented for environmental remediation from the contamination caused by the nuclear disaster, as well as natural attenuation of radioactive materials. As a result, evacuation orders have been lifted in many areas, and daily life has returned. For example, J Village, a national soccer training center located about 20 km from the Fukushima Daiichi Nuclear Power Plant, which temporarily served as a response base for the accident site, fully reopened on April 20, 2019, and concerts and J-League matches are being held there. Change in the research subjects by the researchers that Horikoshi et al. (2019) revealed through text mining of published papers and research fund reports and finding "as work on radiation and radioactivity in the environment continues, interest in matters related to social life, such as return of evacuated residents and recovery, increases" is also a sign of the progress in environmental remediation and social reconstruction. On the other hand, major issues still remain, such as the lifting of the remaining evacuation orders and the final disposal outside of Fukushima Prefecture of soil and waste of more than 13 million cubic meter generated by decontamination works and currently stored in the interim storage facility.
This presentation will provide an overview of off-site environmental remediation process following nuclear disasters in Japan, and summarize current efforts to reduce the volume of removed soil and recycle it, as well as the issues involved in its final disposal outside of the prefecture. The presentation will also include examples of research and studies on sustainable environmental remediation processes, not only from an environmental and

technological perspective, but also from social and economic perspectives.

<u>Session 3b16 / Abstract title</u>: Non-point source pollution control for farmland by biochar application in agricultural practice

ID: 40

Key words: Non-point source pollution, Chinese leek (Allium tuberosum), nutrient loss model, pollution control

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Session: 3b16 backup

Abstract

Agriculture is an indispensable industry that provides food for human survival. In conventional agricultural practices, fertilizers are employed to ensure nutrient supply for crop growing. Although highly questionable, overdose in fertilization was conducted oftentimes to provide economic benefits after harvest. As a consequence, a considerable amount of residual fertilizer remains in the farmland and these residues would be washed out during rainfall events, causing non-point source pollution to neighboring water bodies. The fertilizer residuals in water would consume dissolved oxygen, impairing water quality and ecological integrity. Therefore, an investigation for the control strategy was deemed necessary to protect the water quality in rural areas. Along with the context, this study aimed to employ biochar as the soil amendment agent to increase the soil holding capacities for the investigated nutrients, thus to control the non-point source pollution in the farmland. In the study area, the Chinese leek (Allium tuberosum) was selected as the target plant. In addition, a control experiment using conventional agricultural practice was conducted for comparison.

The losses of total nitrogen, phosphorus, and potassium in the control group were 5.63, 0.14, and 5.11 g/m2, respectively, while those for the experimental group were 1.13, 0.03, and 2.18 g/m2, respectively. The reductions in the nutrient loss were 79.9% in nitrogen, 78.6% in phosphorus, and 57.3% in potassium. In the condition of using half fertilization with biochar, the crop yield and produce quality could be maintained. Compared to the control group, the experimental group showed a better performance in the mitigation of non-point source pollution. The addition of biochar improves the bulk properties of soil. The biochar (having the characteristics such as porous structure, high surface area, and high negatively-charged surface) increased the cation adsorption. Thus, the biochar-amended soil was able to preserve more ionic nutrients in the soil and the nutrient loss by leaching or runoff-washout decreased as well. The addition of biochar also increased the pH value, nutrient

availabilities, and microorganism activities in the soil. The mass balance of nitrogen in the investigated area was analyzed and the results indicated that the major nitrogen consumption was crop uptake, accounting for more than 50% of the total nitrogen introduced. The loss of nitrogen was reduced by 20.5% through surface runoff. The loss through infiltration water was reduced by 10.2%. As shown from the present study, the source control farming practice using biochar was able to reduce non-point source pollution apparently without impairing the overall growth and yield of crops.

<u>Session 3b16 / Abstract title</u>: How to deal with very Persistent and Mobile Toxins – best strategy to go forward

ID: 428

Key words: None

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Organization: WUR

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Session: 3b16 backup

Abstract

Economic growth and the human-induced impact on our surroundings are the main cause of climate change, biodiversity loss and pollution. The very Persistent and very Mobile and potentially Toxic substances (vPMT) produced and used in our products are detected globally and form an increasing threat for our way of living, natural capital and human health. These substances are not eliminated naturally in the ecosystem which leads to build up of concentrations in water, nutrient and other material cycles.
Maybe PFAS chemicals are best known among the persistent and mobile (PM) substances but new vPMT keep "popping up". Registration of vPMTs and prohibiting use of them via legislation is not preventing them from impacting our world.
Since much is unknown of the behavior and effects of vPMTs (inter)national research projects are being performed which will deliver results on the midterm. But what is the best strategy to go forward?

In our presentation we will present the strategies followed in two research projects:
- The 'Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the Soil-sediment-water system' (PROMISCES) proposal addresses Horizon 2020 (H2020) call LC-GD-8-1-2020: "Innovative, systemic zero pollution solutions to protect health, environment and natural resources from persistent and mobile chemicals", which aims at i) establishing new knowledge, ii) exploring the feasibility of new or improved technologies and iii) demonstrating innovative solutions to protect health, environment and natural resources from persistent and mobile substances.
- 'PFAS degradation purification plant EMK, the Netherlands'.

The PROMISCES project aims to increase the circularity of resources by overcoming barriers associated with the presence of very Persistent, very Mobile and potentially Toxic substances (PM(T)/vPvM) in the soil sediment-water system, to contribute to the zero pollution ambition and to improve human health protection on the path to acceptance and

sustainability of the circular economy.
To achieve this overall objective, the project will: (i) address key knowledge gaps in terms of monitoring and modelling of PM(T)/vPvM substances and sources; (ii) enhance application of circularity to resources in the SSW system through an analysis of associated risks, (iii) promote prevention/mitigation/remediation solutions for these substances in the SSW system; and (iv) co-develop tools and strategies (technical, regulatory, economic) with relevant stakeholders for sustainable management of CE routes in the context of the Zero Pollution Action Plan.
https://cordis.europa.eu/project/id/101036449

EMK is a former industrial site that has known diverse industrial activities since 1884, such as the production of coal tar and asphalt, and waste treatment. As a result, the location is heavily polluted with oil and tar. In 2019 a remediation project involving groundwater extraction and treatment, was initiated, However, PFAS pollution was found in the topsoil, which leaches to the groundwater. Therefore, a project was initiated to study potential remediation options for the location. The options to be investigated in the lab, include the potential immobilization of PFAS on various materials and their chemical or biological degradation. In the projected 2nd phase of the project field scale pilot studies are foreseen, which will also involve phytoremediation schemes, since we have found in parallel projects that several plant species are very efficient in retaining and accumulating PFAS. The overall aim of the project is to significantly reduce the cost of remediation and to provide long-term sustainable and nature-based solutions for existing PFAS pollution.

The sharing of knowledge through a national or international platform is an integral part of the project in order to optimize the efforts undertaken to improve our knowledge regarding the management and policies to prevent emissions of persistent, emerging and other contaminants to soil and water.

<u>Session 3b16 / Abstract title</u>: The IMPEL project "Water and Land Remediation"

ID: 87

Key words: In Situ Chemical Oxidation, Soil Vapour Extraction, Multi Phase Extraction, Phytoremediation, Termal Desorption

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Session: 3b16

Abstract

PURPOSE
The IMPEL Water and Land Remediation project aims to accelerate progress in the management of contaminated sites by focusing on the last step, the application of remediation technologies, which can sometimes be one of the delaying factors. In fact, the application of a technique that is not appropriate for the specific site situation or the contaminants present results in the dispersion of both public and private resources and a delay in returning the site to its legitimate uses. In this series of IMPEL publications, various aspects of different remediation technologies are explored in depth, from applicability, to pilot study, and with several real application cases presented in summary in the appendices.

METHODOLOGY

Soil protection is among the priorities for action of the European Commission. It has recently been approved, the European Soil Strategy with protection and remediation targets set and to be implemented by 2030, and the Soil Health Law is being prepared that will protect even more of the European Union's soils. In Europe, contaminated sites are often listed as one of the priority environmental and health issues according to the WHO, which stresses concern about the impact of these sites. The proper and timely management of contaminated sites becomes an important factor in both reducing the degradation of soil, understood as a non-renewable resource and the potential impact on the environment and health.

The expected outcomes from this project are:

- Share technical expertise needed to move forward with the remediation phase in Europe, in order to enable MS where no procedure is currently underway to have a reference.
- Share knowledge, expertise, and best practices by producing technical guidance and coordinating actions across countries.
- Involve key European networks dealing with contaminated sites, such as COMMON FORUM, EIONET, and NICOLE.

RESULT

In the first phase of the project, documents on In Situ Chemical Oxidation and Soil Vapour Extraction were published and translated into 11 languages, already available on the IMPEL website (https://www.impel.eu/en/projects/water-and-land-remediation). These documents are intended to serve as a primary source of information to link and expand knowledge among European countries and regions. With the goal of supporting an understanding of the potential of the specific remediation technology that is presented. The content reported is based on the relevant bibliography, experience of the authors, and case studies collected. The paper may not extend to all situations where this technology has been or will be applied. The case studies are acknowledged voluntary contributions. Each publication has 15+ case studies attached.

CONCLUSION

The second phase of the project deals with two other technologies as Multi-Phase Extraction and Soil Washing, and they are now published on the IMPEL website, the former in its final version while the latter is still in draft form. The publication of these two documents is expected in Spring 2023 and the translations will follow afterward. The third phase of the project will instead deal with Thermal Desorption and Phytoremediation, for which case studies are still being collected and with publication in draft by Fall 2023.

SIGNIFICANCE

Whereas, these technical documents are NOT intended as a guideline or a reference document as if they were a Best Available Technology in this field. The soil, geological, and hydrogeological contexts of contaminated sites throughout Europe show wide variability. Therefore, site-specific design and implementation is the key to success in contaminated site remediation. Thus, each recommendation reported could be applied, or not applied, after careful consideration. Nonetheless, the documents produced can give context for controls and promote the use of these in situ and onsite technologies toward other more impactful techniques such as dig and pump that are not sustainable in the long term.

Session 3b17 orals

Session 3b17 / Abstract title: The Use of the Combined OIHPT Probe to evaluate the Distribution and Efficiency of a Remediation Agent supplemented with a Fluoresceine Tracer

ID: 134

Key words: remediation, acidic groundwater, fluoresceine, HRSC, OIHPT,

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Session: 3b17

Abstract

Purpose of the study
The purpose of this research is to evaluate further options for the use of High Resolution Site Characterisation (HRSC) tools in remediation projects. In addition to making a valuable contribution in the pre-remediation investigation phase, which usually assists in obtaining an understanding of the extent and characteristics of the contamination, these tools can also be used for the evaluation of the remediation process both during and following treatment.
Methodology
The Combined Optical Image Profiler probe with a Hydraulic Profiling Tool (OIHPT, Geoprobe, USA), which is routinely used for non-aqueous phase liquids (NAPL), can also be employed to detect various tracers. The addition of a fluoresceine sodium salt to the remediation agent ensures the clear visibility of the influenced horizons under short-wave UV light. The data obtained from the Hydraulic Profiling Tool (HPT) is important in terms of capturing changes in the permeability of the aquifer. Two on-site pilot scale tests were performed in 2022 at the site of a dump for the landfilling of residual petrol waste from a former refinery that produced mineral oils. The contamination (in addition to the petroleum residuals) comprised vertically stratified highly-mineralized acidic groudwater that negatively affected the functioning of the underground sealing barrier. Previous remediation attempts at

this site provided unsatisfactory results. The two pilot tests followed previous remediation attempts with the addition of the use of HRSC tools. The tests consisted of the direct-push injection of a Ca(OH)2 solution aimed at enhancing the pH of the aquifer and initiating the precipitation of the minerals.

Summary of the findings/results

The post-injection investigation clearly revealed the various influenced horizons based on the graphical output of the fluorescence. The marking of the influenced horizons with fluoresceine provided two important contributions, i.e. the evaluation of the actual distribution and preferential migration of the agent in the aquifer and the indication of the stability of the influenced horizons with regard to the transition back to acidic conditions. The OIP data revealed the significant rebound effect back to acidic conditions. Only around 10% of the aquifer had been neutralized between 30 and 100 days following injection. Moreover, the HPT data did not reveal changes in the permeability of the aquifer and nor did it confirm the presence of newly-formed crystalline mineral phases via ray powder diffraction and optical microscopy.

Conclusion

The OIHPT tool, combined with a fluoresceine tracer, proved to be a valuable tool for the evaluation of the distribution of the remediation agent in the aquifer, its stability and its impact on remediation. This detailed approach allowed for the clarification of the reasons for the failure of previous remediation efforts, i.e. particularly the application of an insufficient amount and concentration of CaOH2 solution and the limitations of the direct-push injection technique.

Significance/contributions of the study

Pilot testing revealed a further important aspect of the use of HRSC techniques, i.e. the use of such tools for the evaluation of previous in-situ remediation programs.

<u>Session 3b17 / Abstract title</u>: Compound-specific stable isotope analysis to determine sources and sinks of PFAS

ID: 141

Key words: PFAS, CSIA, reductive defluorination, oxydative degradation

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Session: 3b17

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a highly diverse group of xenobiotics with over 5000 different known compounds. PFAS are extremely stable, considered to be nearly non-biodegradable and many PFAS substances are toxic to humans and animals and are suspected of being carcinogenic. Therefore, they are emerging pollutants of very high concern. Successful evaluation of remediation concepts and source identification for PFAS requires appropriate monitoring methods. Compound-specific stable isotope analysis (CSIA) is clearly the most conclusive method to provide a sound source characterization by the isotopic fingerprint as well as for evaluation of contaminant degradation, as changes in isotope ratios are directly linked to this process. We will present first-time developed innovative methods for sensitive carbon and sulfur CSIA of PFAS for sound source identification and degradation assessment of this priority pollutant class.

The biggest challenges for the development of a carbon CSIA (13C/12C) method for PFAS are the limited applicability of gas chromatography isotope ratio mass spectrometry (GC-IRMS), the complete conversion of the thermostable compounds to CO2 as the measuring gas and the formation of unwanted by-products during conversion, e.g. hydrofluoric acid (HF). A methylation of the carboxy group of per- and polyfluorinated carboxylic acids (PFCAs) followed by a complete conversion to CO2 with a catalytic reactor at >1000°C and the simultaneous trapping of unwanted by-products (HF) proved to be the most suitable way for precise and accurate determination of carbon isotope values of a wide set of different PFCAs.
In addition to carbon CSIA, sulfur isotope analysis (34S/32S, 33S/32S) opens up possibilities

for degradation assessment and source identification of PFAS, since initial reaction steps mostly occur at functional sulfur groups of PFAS. Therefore, sulfur CSIA has a high potential for the degradation assessment of sulfur-containing PFAS (e.g. PFOS). We are in the process of developing a highly innovative GC-ICP-MS (gas-chromatography inductively-coupled-plasma mass-spectrometry) method for the sulfur CSIA of PFAS.

Carbon isotope ratios of PFCAs were determined with a standard deviation of ≤0.5 ‰. It was possible to clearly differentiate batches of PFOA from different manufacturers with a range of up to 20 ‰, revealing the applicability for forensic studies. A database with source isotope signatures of highly PFCAs-contaminated field samples was developed.
Furthermore, the applicability of this carbon CSIA method for remediation assessment was demonstrated by degradation tests via reductive defluorination using hydrated electrons as well as by chemical degradation of PFOA using heat/FeS-activated persulfate. In the course of PFOA degradation, their carbon isotope ratios (□13C) became increasingly positive, demonstrating PFOA degradation. Oxidative degradation resulted in more positive isotope values (□13C up to 3.5 ‰), but to a much lesser extent compared to reductive defluorination (□13C up to 20 ‰) proofing the high potential of CSIA to assess remediation concepts for PFAS at contaminated sites.
By using a dry plasma and optimizing the tuning strategy, the formation of spurious isobaric interferences at maximum signal intensity could be almost completely minimized enabling a promising method for sulfur CSIA of PFAS by using GC-MC-ICPMS. With the use of sulfur-containing test standards, a high analytical precision and accuracy of the respective sulfur isotope ratios was shown.
The degradation tests reveal significant carbon isotope fractionation. This method significantly exceeds classical monitoring concepts based on simple concentration measurements. Furthermore, a database of degradation-related changes in isotope ratios and isotopic fingerprints of PFAS enable a reliable success control of sustainable PFAS remediation processes as well as a more precise PFAS source identification.

<u>Session 3b17 / Abstract title</u>: Improvement of the global quantification of PFAS through TF, AOF and EOF measurements: Application to complex environmental matrices (sludge and compost) from wastewater treatment plants

ID: 250

Key words: PFAS; organic fluorine content; biosolids; combustion Ion chromatography

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Session: 3b17

Abstract

More than 4000 Per- and polyfluoroalkyl substances (PFAS) also called forever chemicals are attracting the warning of scientists and public authorities [1]. The application of ion chromatography to environmental matrices allows the global analysis of different halogens including fluorine thanks to initial sample combustion using combustion and ion chromatography coupled (CIC) instrument [2].
Depending on the preparation, different fractions of the sample can be analysed by CIC [3], [4]: TF (total fluorine), EOF (extractable organic fluorine) or AOF (adsorbable organic fluorine). Removal of inorganic fluorine (IF) is needed for discriminating organic fluorine from TF content.
Even though the principle is relatively simple, different methodological issues may arise. Differences in analytical responses related to the forms (inorganic or organic) or chemical structure, and mismatch with standards used for calibration could lead either to under- or over-estimation of the fluorine content [5]. Due to the large range of polarity among PFAS, recoveries during solid phase extraction (SPE) step both on activated carbon or other polymeric cartridges should be assessed to avoid underestimation of OF content. Effect of complex matrices such as compost or sludge for solid samples, or wastewater treatment plant (WWTP) effluent for liquid samples need to be investigated to validate the robustness of the method.
For this study, our objective is to validate robust and reliable methods for measuring global

organic fluorine based on CIC measurements for TF and EOF for complex solid samples and AOF, SPE-AOF, EOF and TF for liquid samples. Methods will be applied on biosolids and recovered fertilizers to evaluate the release of PFAS into the environment through land application of these materials.

Methodology

It was first determined whether the TF measured is in line with the expected quantity from a known added quantity of IF and/or OF. Impact of potential incomplete combustion of some specific chemical structures has been particularly studied. For AOF, the retention efficiency was assessed for PFAS compounds ranging in polarity. The proportion of polar PFAS retained on activated carbon was determined and compared to the proportion removed by the rinsing solution.

A similar approach was implemented with SPE in order to optimize the recovery of polar PFAS. AOF, SPE-AOF and EOF were finally assessed for the potential effects of complex matrices, in particular the organic carbon and suspended particulate matter content during combustion.

For solid samples, different protocols were tested on complex matrices (sludge and compost) to determine the best conditions to remove IF for EOF measurements. In parallel, the estimation of the IF content has been done on several biosolids samples (sludge, compost) to determine the mass balance gap between TF and calculated TOF measurements.

Conclusion

This work has led to a better understanding of the factors influencing the quantification of TF in complex matrices that can contain both IF and OF. It allows for better characterisation of the chemical groups among PFAS considered in the determination of AOF, EOF and TOF.

Significance / contributions of the study

These results allow a more reliable determination of the mass balance and the fate of PFAS during the wastewater treatments and a better understanding on how to limit the transfer of PFAS during fertilizers recovery from sewage sludge. The final goal is to provide a more reliable sustainable remediation of emerging contaminants and prevent spreading of PFAS in the environment towards zero pollution objectives.

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<u>Session 3b17 / Abstract title</u>: A sustainable approach of mercury sequestration in sediments resulting in the reduction in concentration of methylmercury and suppression of mercury bioaccumulation

ID: 361

Key words: Novel amendment, mercury remediation, bioaccumulation

Submitter: Kim Pingree

Organization: Albemarle Corporation

Co-authors: Jon Miller, Albemarle Corp, R advisor

Session: 3b17

Abstract

MercLok™ P-640™, a novel powder-based amendment, has been developed by Albemarle to address soil and groundwater impacts from mercury. Using MercLok P-640, rapid sequestration of multiple mercury species and long-term stability have been validated in bench and in-situ remediation field studies in a wide range of soils and subsurface conditions.

Objectives of these studies were to assess the effectiveness of MercLok P-640 at (1) decreasing the concentration of methylmercury in sediment porewater and (2) reducing bioaccumulation of mercury in exposed biota because of methylmercury suppression in the water system.

Treatment of sediment with MercLok P-640 reduced the fraction of methylmercury relative to total mercury in porewater from 25.4% to less than 1%.

The bioaccumulation exposure experiment was conducted over a 28-day period using freshwater Lumbriculus worms. The concentration of total mercury and lipids were measured in tissues at Day 14 and Day 28. Tissue concentrations of mercury on Day 28 were reduced by 79% and 73% in MercLok P-640-treated sediments compared to unamended sediments (controls), and with total mercury concentrations in sediments of 10 and 100 mg/kg mercury. The relationship between concentrations of methylmercury in the sediments and mercury in worm tissues (Biota to Sediment Accumulation Factors, BSAFs) were also evaluated to directly assess the effectiveness of MercLok P-640 at reducing partitioning of mercury into the worm tissues. BSAF values greater than 1.0 indicate preferential partitioning of methylmercury from the sediment into worm tissues. BSAF values were substantially greater (up to 24x at Day 28) for unamended versus MercLok P-640-amended sediments. BSAF values on Day 28 ranged from 12.6 - 22.9 in unamended sediments and 0.6 - 1.5 in amended sediments.

A notable increase in effectiveness of the MercLok P-640 treatment was also observed over

time with greater BSAF ratios between unamended and amended sediment on Day 28 compared to that observed on Day 14.

<u>Session 3b17 / Abstract title</u>: Development of a robust analytical protocol for PFAS contamination in soil and groundwater by the LIFE Capture project

ID: 390

Key words: total PFAS, analysis, quantification, protocol

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Session: 3b17

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a family of man-made chemicals that have been widely used since the 1950s. PFAS is a class of thousands of substances (>6,000 compounds) characterized by extreme persistence and different behaviors/mobility in the environment. The efforts towards the substitution of old generation PFAS with short-chain and new generation PFAS has brought new concerns as these substitutes are once again poorly known, with similar mobility in the environment, and could lead to relevant health effects.
Up to now, far too little attention has been paid to the methodology for the PFAS analysis. Nowadays, only a very limited number is taken in account (approx. 40) during quantification, leading to sometimes severe underestimations of the PFAS presence in soil, water and other matrices. Therefore, LIFE CAPTURE wants to develop a protocol for any type of PFAS contamination by enlarging the spectrum of the PFAS family that can be identified and analyzed.
LIFE CAPTURE proposes a robust protocol that follows a staggered approach to: quantify whether any kind of PFAS is present; quantify the concentrations of a set group of well researched PFAS; determine if there are significant concentrations of other PFAS present; quantify and qualify those other PFAS.
The foreseen novel analytical approach consists of a sequential analytical approach with three phases.
- In phase 1 the presence/absence of PFAS compounds is determined by using a “Sum parameter”. Due to the large number of PFAS, sum parameters were developed such as the AOF method (adsorbable organic fluorine compounds) for groundwater and the EOF method (extractable organic fluorine compounds) for soil. The method setup and fine tuning are part of the scope of this project.
- In phase 2, analytical procedures using LC/MSMS techniques will be used. These methods

have been implemented so that currently about 30 - 40 PFAS can be commercially analyzed. If the EOF/AOF values significantly exceed the Target analysis there is a risk that a large concentration of non-target PFAS compounds could be present, requiring a third analytical step.

- In the final phase 3, the TOP-assay (Total Oxidizable Precursor) approach is available. The principles of the TOP assay is a worst-case approach where the sample is subject to a chemical oxidation process that converts precursors/polyfluorinated compounds into perfluorinated PFAS. After this chemical oxidation another target analysis is performed, allowing the evaluation of the increase of the Perfluorinated compounds before and after the oxidation step.

The first results applying this three-step method showed that, in more than 90% of cases, when sampling suspected sites, if PFAS were encountered using Target Analysis, concentration increased after applying the three-step quantifying technique. This increase could be both statistically significant or not, but would give information about the pollution either way. Indeed, high increases in concentration are typical for more recent PFAS-pollutions, rich in polyfluorinated compounds that are then converted into perfluorinated PFAS. While a low increase in concentration is more representative of an older, historic pollution in PFAS for which most of the polyfluorinated compounds already had time to degrade into perfluorinated PFAS over time. These results further highlight that the improvement of technologies and the development of new approaches and techniques for the quantification of contaminated sites is of utmost importance.

The aim of LIFE CAPTURE is to enhance existing technologies and to boost non-mature technologies enabling an improved site-specific management approach for PFAS contamination in soil and groundwater.

Session 3b1 orals

Session 3b1 / Abstract title: Biodegradation of B, T and BTEXIeIaN under NO3- and SO4- reducing conditions in column studies

ID: 110

Key words: BTEXIeIaN, biodegradation, continuous reactor, anaerobic, Griftpark

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Session: 3b1

Abstract

Purpose of the study
Former gasworks sites are potential sources of mobile pollutants that pose a risk to the environment and human health. Griftpark, located in Utrecht (The Netherlands) is a former gasworks site, harboring mixtures of aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylenes, indene, indane and naphthalene (BTEXIeIaN). These compounds are still present in the subsurface and groundwater of Griftpark and are a threat for drinking water sources due to them being toxic. Bioremediation is an attractive strategy for their removal and complete aerobic degradation of BTEXIeIaN mixture by the indigenous microorganisms, originating from anoxic environment, was shown previously with batch experiments. On one hand, anaerobic conditions are prevalent in the subsurface, and introduction of oxygen to the aquifer might be challenging. On the other hand, batch experiments under NO3- reducing conditions showed no degradation of BTEXIeIaN mixture. Here, column studies will be presented with sequential addition of single compounds (T/B) and subset of compounds (T+B), as well as the complex BTEXIeIaN mixture. The aim is to investigate the microbial degradation capacity of the Griftpark microbes with single compounds or in mixtures, under anaerobic conditions (NO3- and SO4-) in continuous reactors where similar conditions as in aquifers can be tested.

Methodology
To investigate anaerobic degradation of BTEXIeIaN compounds in a continuous system, four columns were monitored. Columns were filled with sediments from Griftpark (29,5-31 m

below groundwater level) that served as a source of inoculum. All columns were fed with medium containing the electron acceptor(s) of interest and contaminants were spiked continuously via a syringe pump. Liquid samples were taken weekly, throughout the columns and analyzed in HPLC for BTEXIeIaN quantification and for ion chromatographic analysis to monitor NO3-, NO2- and SO4- concentrations. Oxygen was routinely monitored to maintain anaerobic conditions.
Experiments were separated to 3 phases based on the compound added to the columns. Each phase was monitored for 12 weeks; 3 weeks of flow mode and 3 weeks of batch mode, repeated two times. The batch mode allows to biomass growth while the flow mode eliminates the non-degraders by flushing them out of the column.

Results
Toluene was anaerobically degraded by the indigenous microorganisms when present alone. All columns showed faster degradation in the second batch mode proving that an adaptation phase is needed for the removal of toluene. When toluene was present with benzene, it was fully degraded, however when present in the BTEXIeIaN mixture, it was recalcitrant. Benzene degradation was not as significant as toluene degradation when present alone or in a mix (B+T, BTEXIeIaN). Investigation on the biodegradation of toluene, benzene and the mix are on-going for a third alternating period of 6 weeks. The results will be presented.

Conclusion / Significance
Complex mixtures at former gasworks sites often suffer from recalcitrance and not enough focus is given on the investigation of the multi-substrate effect in the degradation of complex mixtures, especially under anaerobic conditions. First, the results will help to understand indigenous microorganism's degradation capacity. Secondly, the strategy of subsequent periods of flow mode and batch mode, which creates an environment that selects for biodegradation of complex mixtures by allowing biomass growth to perform improved conversion of complex aromatic mixtures in anaerobic environments, will be tested. Finally, results from the columns will help to design and optimize better remediation strategies for Griftpark, where laboratory observations can be better extrapolated to the field.

<u>Session 3b1 / Abstract title</u>: Four innovative technologies for in situ bioremediation developed for a range of environmental pollutants (EiCLaR EU-China project)

ID: 207

Key words: Electro-nanobioremediation, Bioaugmentation, Biolectrochemical remediation, Phytoremediation

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Organization: Ecole Centrale de Lyon

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Session: 3b1

Abstract

Bioremediation of contaminated sites has proliferated since the early nineties. Still, the applications of different biotechnologies have levelled off partly because of their inability to deal rapidly and competently with complex environments. The Enhanced Innovative in Situ Biotechnologies for Contaminated Land Remediation (EiCLaR) is a project funded by the EU and China. It is composed of 13 EU and 5 Chinese partners. This project integrates biological and non-biological processes to extend the sustainability and cost-effectiveness benefits of in situ bioremediation (ISBR) to a far more comprehensive range of land contamination problems. These four technologies include:

(1) Electronanobioremediation, combining nano-scale and micro-scale ZVI with applied electrokinetic (EK) treatment for extended lifetimes and microbial degradation for synergistic effects.

(2) Monitor Bioaugmentation, aerobic chloroethene biodegradation for removing contaminants from the subsurface environment and improving groundwater quality.

(3) Bioelectrochemical Remediation, enhanced electron acceptor for anaerobic hydrocarbon degradation, and electron donor for hexavalent chromium and chlorinated solvents reduction in soil and groundwater.

(4) Enhanced phytoremediation: synergistic exploitation of electrokinetics and plants, microorganisms and/or mycorrhizae is used for degrading and/or immobilising contaminants in situ.

The four EiCLaR technologies target difficult and complex contaminant mixtures at different sites in the EU and China. We support this goal by including cross-cutting comprehensive decision support that links to demonstrable risk management and sustainability performance, supported by realistic market entry assessment for each technology and in-depth engagement with remediation practitioners and markets in the EU and China.

EiCLaR project is relevant to Society, economic activity and environmental protection by ensuring our work meets the needs of sustainable and risk-based land management (SRBLM) demanded by critical international regulatory/industry networks and initiatives worldwide and the recent standard ISO 18504:2017 on “sustainable remediation”. We shift four innovative bioremediation technologies from proof-of-concept through scale-up and “market pull” to field demonstrations that provide robust and market-credible evidence that these technologies will treat contaminated sites effectively at lower costs, extending the range of ISBR-treatable problems and do so with a smaller sustainability footprint.

<u>Session 3b1 / Abstract title</u>: Biological degradation of high concentrations of 2,4- and 2,6-DNT on laboratory and field scale

ID: 304

Key words: Dinitrotoluene, anaerobic, reduction, diaminotoluene, bioremediation

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Session: 3b1

Abstract

Purpose of the study.
On a former toluene-di-isocyanate production site in Brazil, a variety of contaminants are present, including nitrotoluenes, chlorobenzenes, BTEX and some chlorinated compounds. The main components of concern are 2,4 and 2,6-dinitrotoluene (DNT). Highest maximum concentrations for DNT that were found were 940 mg/l 2,4-DNT and 540 mg/l 2,6-DNT. Greensoil was given the opportunity to investigate the feasibility of both aerobic and anaerobic biodegradation of the different contaminants with the focus of DNT by means of laboratory degradation tests and a subsequent field test.

Methodology.
Based on scientific literature DNT can be biodegraded both aerobically via removal of the nitro groups, leading to the production of nitrite as degradation product and anaerobically, where the nitro groups are being reduced to amino groups. Since aminotoluenes are considered more recalcitrant under anaerobic conditions, the anaerobic conditions are typically followed by aerobic conditions, to further biodegrade the aminotoluenes. Even though switching from anaerobic to aerobic conditions takes extra effort, costs etc. from a practical point of view, this approach was considered since dichlorobenzene (DCB) was being used as solvent for DNT. In case of aerobic degradation, it is expected that DCB is preferentially degraded over DNT with the potential risk of crystallization of DNT, that has been observed at the site. The feasibility of biological degradation of DNT was investigated both on laboratory and field scale. For the field test, two different layers are investigated in order to be able to potentially test the reduction at different pH's if necessary.

Summary of fundings.
During the laboratory degradation test > 99% DNT degradation was observed under anaerobic conditions. Since the natural pH was ± 6.0, it was decided to also test a buffered condition with neutral pH. At natural pH, the main degradation products in the presence of an electron donor were aminonitrotoluene (ANT) isomers, while at neutral pH they were 2,4-and 2,6-diaminotoluene (DAT). Only at neutral pH, the degradation products were completely further degraded under aerobic conditions.
Under aerobic conditions complete degradation of 2,4-DNT (> 99%) was observed in all biological conditions, including the biological control, however no degradation of 2,6-DNT could be observed under aerobic conditions.
Anaerobic reduction was confirmed by CSIA by demonstrating an isotopic shift on the nitrogen atom. Next Generation Sequencing showed an enrichment in Enterococcus and Dysgonomonas, two groups that are not previous known to be able to reduce DNT.
Based on the degradation tests, a field test was started to further investigate the feasibility of stimulated anaerobic reductive biodegradation under field conditions. So far complete reduction to DAT has been observed and increased in time. After 4 months in the shallow layer with an average pH of 6.6, the average degree of DNT reduction was 82% in a ratio 43:57 ANT/DAT. In the deeper layer with higher concentrations of DNT and an average pH of 6.1, the degree of DNT reduction was on average 3.6% in a ratio 96:4 ANT/DAT so far.

Conclusions
Based on laboratory tests, anaerobic reduction of DNT to ANT and DAT and subsequent degradation of ANT and DAT under aerobic conditions seems appeared to be the most feasible approach for the treatment of high concentrations of both 2,4-DNT and ,2,6-DNT. The approach is being tested in a field study and so far a significant part of the DNT is being reduced to mainly DAT during the anaerobic phase in the more shallow layer with a slightly higher pH and lower DNT concentrations.

Significance
This study proved the value of laboratory testing prior to a field test and showed also high concentrations of DNT can be treated by bioremediation.

<u>Session 3b1 / Abstract title</u>: In Situ Bioaugmentation for Anaerobic Benzene, Toluene and Xylene Remediation

ID: 397

Key words: bioremediation, petroleum hydrocarbons, benzene, anaerobic, molecular biological tools

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Organization: SiREM

Co-authors: Phil Dennis, Sandra Dworatzek, Jennifer Webb (SiREM, Guelph, ON, Canada) Elizabeth Edwards, Nancy Bawa, Shen Guo and Courtney Toth (University of Toronto, Toronto, ON, Canada) Kevin Kuntze and Anko Fischer (Isodetect, Leipzig, Germany)

Session: 3b1

Abstract

Purpose of study:
Anaerobic microbes have been identified that completely degrade benzene, toluene, ethylbenzene and xylene (BTEX) into carbon dioxide and methane. The ability to function in the absence of molecular oxygen is what makes these microbes unique and useful for anoxic field applications where aerobic remediation approaches are impracticable or impossible to implement due to challenges in introduction and distribution of oxygen. SiREM has a consortia of cultures, collectively referred to as DGG-PlusTM which include a methanogenic benzene enrichment culture (DGG-BTM), a toluene degrading culture (DGG-TTM) and an o-xylene degrading culture (DGG-XTM), that have been enriched and scaled up and have been laboratory and field tested. The purpose of this ongoing work was to better understand the mechanisms and take lessons learned from lab studies to maximize field success.
Methodology:
Bench scale treatability studies use site specific materials to evaluate remediation technologies to provide information for field design. Numerous treatability studies were conducted from BTEX sites from around the world to learn more about anaerobic BTEX degradation. Compound specific isotope analysis (CSIA) is a powerful technology used to assess the extent of degradation and quantifies bond breaking processes over non-degradative losses such as sorption and dilution. The microorganisms responsible for benzene, toluene and o-xylene (BTX) transformation in the DGG-PlusTM cultures have been identified and these microorganisms can be tracked and quantified using developed molecular biological tools (MBTs)
Summary of findings/results:
Results from laboratory treatability studies demonstrated enhanced benzene, toluene and o-

xylene biodegradation rates with DGG-Plus bioaugmentation and provided information to aid in field pilot-test design. One field pilot-test initiated in 2019 at a site in Saskatchewan, Canada included three injection points, two of which received up to 10 liters of the DGG-BTM culture. Four additional bioaugmentation points were added to the site in September 2021. Benzene degradation rates were accelerated in situ with up to 90% removal observed in 3 years. Additional bioaugmentation field applications in Canada and the US are also demonstrating promising results and updates will be provided on these projects as applicable.

Conclusions:

These first-to-field projects arel be used to establish a better understanding of dosing requirements, timeframes for obtaining results and ranges of conditions over which the cultures are effective. Bioaugmentation for BTEX compounds has the potential to decrease remediation time frames and increase the range of sites to which bioremediation is applicable providing a much-needed, cost-effective alternative for BTEX remediation in groundwater.

CSIA along with MBTs can be used to confirm that biodegradation is occurring. Furthermore, in situ degradation processes can be quantified (e.g., as first-order degradation constants, half-life distances, etc.) and different degradation mechanisms (e.g. aerobic vs anaerobic biodegradation) can be distinguished with the help of a multi-element CSIA. This presentation will highlight several field applications (both pilot and full-scale) where these anaerobic cultures were used for anaerobic remediation of BTEX.

<u>Session 3b1 / Abstract title</u>: Bio-electrochemical treatment of soil contaminated by petroleum hydrocarbons with biosurfactant obtained from agricultural waste

ID: 425

Key words: biosurfactant, bioslurry, microbial electrochemical treatment, soil washing, bioremediation

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Organization: University of Brescia

Co-authors: Prof. Mentore Vaccari, University of Brescia, environmental engineer

Session: 3b1

Abstract

The utilization of biosurfactants for the bioremediation of contaminated soil is not yet well established because of the high production costs of biosurfactants. Consequently, it is interesting to look for new biosurfactants that can be produced at a large scale and can be employed for the bioremediation of contaminated sites.
In this work, biosurfactants were produced by Burkholderia thailandensis E264 strains by utilizing the olive oil and wine sectors—the valorization of by-products and residues through innovative processes and new business models (CREIAMO)—and applied to the remediation technologies (soil washing, bioslurry, and microbial electrochemical treatment MET) to clean up soil that has been contaminated by petroleum hydrocarbons.
Then, the performance and biodegradation of different remediation technologies (soil washing, bioslurry, and microbial electrochemical treatment) were determined in terms of total petroleum hydrocarbon removal using a gas chromatography GC- FID.
The results show that in both bioslurry and MET, the presence of biosurfactants accelerated the biodegradation of soil polluted with petroleum hydrocarbons. After 10 days of bioslurry treatment, biosurfactants from olive oil and wine reduced the concentration of total petroleum hydrocarbon in the soil to 79.4% in soil charged with 4500 mg/kg of hydrocarbon, whereas after 20 days of MET, 72.5% of the total petroleum hydrocarbon in the soil was biodegraded with the generation of 9.5 Am-2 current density. The results were use to perform an LCA study, which demonstrated that MET is much more sustainable than bioslurry treatment.
In general, our results revealed that nonfermented grape marcs and olive pomace residues, derived from the white winemaking process and olive oil extraction, respectively, could be used as economical substrates to produce biosurfactants (e.g., long-chain RLs), which are in agreement with the CE principles within the agricultural sector. Moreover, the nonpathogenic nature of the selected organism and the RL purity suggested the possible use of these biomolecules directly in industrial practices and soil remediation methodologies.

Hence, the Burkholderia thailandensis E264 strain could be employed in the petroleum industry for the management of contaminated soil and renewable energy production for the development of a sustainable environment.

Session 3b2 orals

Session 3b2 / Abstract title: Remediation of Chlorinated Ethenes Plume in Denmark by Retardation and Enhanced Biodegradation – Lessons Learned

ID: 224

Key words: plume remediation, reactive barrier, chlorinated ethenes

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Organization: Capital Region of Denmark

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Session: 3b2

Abstract

Purpose of study
Remediation of chlorinated solvent plumes is often done in a pump and treat system, which is a very expensive and lengthy task involving many years of operation and maintenance. Therefore, there is a need to find and develop new remedial methods that can reduce concentrations of chlorinated solvents and metabolites to acceptable levels in the groundwater. With this in mind, the Capital Region of Denmark has initiated and completed a technology development project to mitigate contaminated plumes, including a pilot test of Liquid Activated Carbon (LAC, Plumestop) coupled with Enhanced Reductive Dechlorination (ERD).

The aim of the project is to investigate the feasibility of the technology under Danish conditions. To do this, the following 3 main topics have been investigated:

- Distribution of amendments
- Development of a combined set of documentation methods allowing to distinguish between the different remedial processes initiated in the plume
- Efficiency of amendments, i.e. sorption and especially degradation

Methodology
The project included field tests and a variety of controlled laboratory experiments. PlumeStop, donor, and bacteria were injected as a barrier across the contaminant plume at

a depth of 12-21 m bgl. Monitoring wells were established in 3 transects perpendicular to the groundwater flow and one transect following the flow direction. Each well was fitted with 3 screens resulting in approx. 65 screens. Moreover approx. 25 upgradient screens were included to describe the baseline and keep track of contamination passing into the treatment zone from the source area.

Besides monitoring groundwater for the usual parameters (CVOC, ethene, redox parameters, pH, dissolved organic carbon (DOC) etc.) samples were also analysed for microbial parameters (qPCR) and compound specific isotopes (CSIA) to support the interpretation of degradation and sorption processes. In all 12 monitoring events were performed during the test period. To our knowledge this is the most extensively documented field test Of LAC combined with ERD to date, and the first time that CSIA as well as a newly developed sorption capacity test method were included.

Summary of findings/results

The first injection event revealed that of the amendments, donor was easier to distribute than PlumeStop and bacteria. Visual observations of water samples and soil cores sampled from near injection points showed an uneven distribution of PlumeStop. Analyses indicated that degradation stalled at cis-DCE. As a result, a second injection was performed based on a revised design. Monitoring showed a satisfactory distribution of amendments.

Interpretation of the monitoring results cannot rely on decreasing CVOC in water samples alone, so there was a need to develop e.g. sorption capacity analysis as a measure of the distribution of PlumeStop and an application of CSIA to document degradation. Due to transient conditions in the system, the interpretation of these developed methods was not straightforward but was none the less considered essential for understanding the processes taking place.

Monitoring results also showed that in some parts of the injected zone sorption dominated whereas degradation dominated in other parts, and that there were some parts where effects of the amendments were insufficient. Degradation also took place further downgradient from the injection points creating a reactive treatment zone rather than a strict barrier.

Conclusion

The results of the field test show that the technology is suitable in remediating chlorinated ethene plumes when the injection of amendments is designed to be robust. The investigation exposed the diverse conditions that ought to be considered during the design, injection, monitoring and maintenance of the remediation technology.

Significance / contributions of study

The project revealed the complexity of the system and the necessity of employing different analysis and tools to document th

Session 3b2 / Abstract title: Lab studies with field-derived microcosms and stable isotope analysis to evaluate the intrinsic biodegradation potential of lower-chlorinated benzenes in a coastal aquifer

ID: 132

Key words: Aerobic biodegradation, Groundwater, Isotope fractionation, Chlorobenzenes.

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Session: 3b2

Abstract

Monitoring in situ biodegradation processes to demonstrate the occurrence of contaminant degradation is challenging because mass balances are difficult to close. The situation is even worse when pollutants exist as mixtures, as often occurs in groundwaters contaminated with chlorobenzenes. In those scenarios, it is complex to distinguish between precursors and breakdown products. A diagnostic tool used in the last years to determine qualitatively and quantitatively the extent of biodegradation is compound-specific stable isotope analysis (CSIA). However, few CSIA studies were conducted to study the isotope fractionation during lower chlorinated benzenes degradation despite that these compounds are frequently detected in groundwater.

This study was conducted with samples from the subsurface of a former chemical plant located in an industrial area of Barcelona. The production of predominantly pesticides caused the release of a large volume of chlorinated compounds, mostly chlorinated benzenes, into the groundwater. Several wells were installed for sampling and monitoring the hydrochemical parameters of the aquifer (redox potential, T, pH, EC). The assessment of the intrinsic biodegradation potential of lower-chlorinated benzenes in this aquifer was carried out with field-derived microcosms in the laboratory, set up with either water/sediment from the source zone or the contaminant plume. Three wells from each area were sampled and the microcosms were performed for aerobic, anaerobic biostimulation, and natural attenuation treatment strategies. Abiotic controls were also included in this study. In addition,

carbon isotope fractionation during aerobic degradation of monochlorobenzene (MCB) and, for the first time, of 1,4-dichlorobenzene (1,4-DCB) was determined in microcosms from the contaminant plume.
In aerobic microcosms set up with groundwater from the source zone and amended with a mixture of lower chlorinated benzenes, biodegradation of MCB and 1,4-DCB was observed with a net increase of carbon dioxide in the headspace. In the aerobic microcosms established with groundwater samples of the plume, the three isomers of dichlorobenzene (DCB) and MCB were simultaneously degraded. No inhibitory effect was observed on aerobic MCB biodegradation under the presence of DCB isomers. In contrast, the addition of lactate to the anaerobic microcosms (biostimulation) had no effect on enhancing the anaerobic reductive dechlorination.

Compound stable isotope analysis (CSIA) during the aerobic biodegradation of MCB and 1,4-DCB was performed in microcosms from the plume to evaluate whether the carbon isotope fractionation (εC, ‰) could be used to quantify and monitor their biodegradation in the field. The εC values obtained from field-derived microcosms were -0.7 ‰ ± 0.1 ‰ and -1.0 ‰ ± 0.2 ‰ for MCB and 1,4-DCB, respectively. These results show weak carbon isotope fractionation for the aerobic pathway but would allow tracing in situ degradation in aquifers with a high extent of biodegradation.

The interpretation of our field-derived CSIA results suggests that at a low degradation stage, the isotopic fractionation could not be significant according to the EPA criterion to confirm biodegradation. The weak carbon isotopic effect during aerobic degradation of MCB and 1,4-DCB is associated with the initial enzymatic reaction catalyzed by dioxygenases. Nevertheless, based on the carbon isotope effects measured in this and previous studies, relatively high carbon isotope shifts (i.e., Λδ13C > 4.0 ‰) of MCB or 1,4-DCB in contaminated groundwater would suggest that their biodegradation is controlled by anaerobic reductive dechlorination.

In conclusion, the laboratory experiments carried out with field-derived microcosms in this study can be a valuable tool to design and assess biodegradation strategies to remediate aquifers contaminated with multiple chlorinated aromatic hydrocarbons and to interpret the results when monitoring polluted sites.

<u>Session 3b2 / Abstract title</u>: Stimulation of metabolic aerobic TCE degradation by bioaugmentation and in bio-electro-systems

ID: 164

Key words: Bioaugmentation, Trichloroethene, Aerobic metabolic degradation; Bioelectrochemical system; Electrokinetic

Submitter: Steffen Hertle

Organization: TZW:DVGW - Technologiezentrum Wasser

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Session: 3b2

Abstract

1. Introduction

Due to their toxicity and persistence, chloroethenes cause major issues when released into the environment. Aerobic metabolic chloroethene degradation represents a promising concept to remove contaminants from the subsurface environment to improve groundwater quality. In comparison with anaerobic processes, aerobic processes pose no risk of formation of stable hazardous intermediates. Aerobic metabolic processes are not in need of auxiliary substrates. Therefore, the oxygen demand for treatment is significantly lower as compared to co-metabolic processes, enabling to remove approx. 100 times more pollutants with the same amount of oxygen.

Aerobic chloroethene biodegradation can occur under natural conditions or after addition of oxygen both in in situ or in ex situ engineered approaches. At specific sites, where the required microorganisms are not present or in insufficient numbers, enriched cultures can be added to the field site (bioaugmentation) and, therefore, enhance in-situ bioremediation. This study focuses on bioaugmentation approaches to induce aerobic metabolic TCE degradation and electro-supported bioremediation approaches to treat chloroethene contaminations.

2. Experimental investigations

2.1. Bioaugmentation to stimulate aerobic metabolic TCE degradation

Chloroethene contaminated groundwater was extracted from a contaminated site in the Walloon Region, Belgium. Batch experiments were conducted in 2 L-bottles to study the viability of a bioaugmentation approach with varying conditions. The bioaugmentation approach to induce aerobic metabolic TCE degradation can be used to treat TCE

concentrations up to 20 mg/L at room temperature as well as at groundwater temperature (12°C). Chloride formation was consistent with complete TCE degradation.
Experiments conducted at room temperature showed successful biodegradation after enrichment addition after 27 days. While natural attenuation approaches showed intrinsic potential for aerobic TCE degradation after 147 days.
At groundwater temperatures, bioaugmentation with the lab enrichment showed successful TCE-degradation after 105 days. Using groundwater from a site where aerobic metabolic TCE degradation had been stimulated, degradation started 78 days after inoculation.

2.2. Aerobic TCE degradation in a bio-electro-system

Due to microbial activity and reduced organic substrates, contaminated sites tend to turn anoxic over time. In order to facilitate aerobic processes, replenishing dissolved oxygen is crucial. Failure to provide oxygen results in the limitation of the electron acceptor and interruption of the aerobic biodegradation. In this combined bio-electro approach, oxygen is provided in the bioactive zone by electrolysis.
A bioaugmentation culture was circulated through column systems in order to establish the microbiota on sand. The columns mineralized ~20 mg/L of TCE in a single passage with ~ 8 mg/L oxygen. Application of low strength direct current resulted in an immediate increase in TCE degradation. Results demonstrate proof of concept for this combined technology.

3. Conclusion

Aerobic metabolic TCE degradation is a new and promising process. The use in bioaugmentation approaches, as well as combined bio-electro-approaches were successfully demonstrated.

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<u>Session 3b2 / Abstract title</u>: Biogeochemically Enhanced In Situ Treatment of Chlorinated Organics and Metals

ID: 206

Key words: Groundwater, Chlorinated, Metals, Reductive, Biogeochemical

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Session: 3b2

Abstract

Background/Objectives: For over two decades, biotic (enhanced reductive dechlorination; (ERD) and abiotic (in situ chemical reduction; ISCR) processes have been applied to degrade chlorinated volatile organic compounds (CVOCs) in situ. Recently, biogeochemical reduction (BGCR), a process which combines natural biological and chemical processes, has been combined with ERD and ISCR to provide an additional mechanism to more aggressively degrade CVOCs and to sequester toxic metals.
Approach/Activities: During ERD and ISCR, highly reducing conditions are established which are favorable to the reduction of ferric iron (Fe[III]) to ferrous (Fe[II]) and sulfate (SO4) to sulfide (HS-). These reduced forms are highly soluble and rapidly combine to produce insoluble iron-sulfide minerals such as mackinawite (FeS), and pyrite (FeS2). The newly formed minerals precipitate throughout the aquifer in various forms such as distinct euhedral crystals, framboidal agglomerates, and as very fine coatings on the aquifer matrix. These biologically generated iron-sulfed minerals have been demonstrated to abiotically degrade CVOCs on contact by the β elimination pathway. This additional biogeochemical degradation pathway minimizes the generation of toxic degradation products such as vinyl chloride, thereby minimizing risk and substantially reducing the time to achieve remedial goals.
In addition to degrading CVOCs, iron and sulfide remove toxic metals from solution as iron-sulfide minerals such as arsenopyrite (FeAsS2), or as sulfides such as sphalerite (ZnS). These minerals have very low solubility in water and have been demonstrated to be very stable following formation. In addition to forming reactive minerals, the generated sulfide will precipitate on zero valent iron (ZVI) if present. This sulfidation of zero valent iron (ZVI) has been demonstrated to substantially enhance reactivity and reduce passivation of the ZVI.
Bench tests, and full-scale treatment were conducted at multiple sites affected by CVOCs and metals to evaluate the effectiveness a BGCR enhancing reagents (Geoform® Extended Release; (Geoform® ER), and Geoform® Soluble) for in situ remediation of CVOCs and metals. Contaminants at the CVOCs sites included chlorinated ethenes, ethanes, and methanes, both individually and mixed. Separately, bench tests and full-scale treatment

were conducted to sequester elevated concentrations of arsenic in groundwater. At each site, full-scale treatment was conducted by distribution of the reagents into the affected aquifer by high-pressure injection (Geoform® ER) or by low pressure injection through wells (Geoform® Soluble). Groundwater monitoring was conducted to confirm and quantify treatment.

Results/Lessons Learned: The bench tests at demonstrated that BGCR significantly increased the reactivity of the ZVI containing ISCR reagents for treatment of CVOCs. The field tests demonstrated that the application of both Geoform® ER and Geoform® Soluble, established highly reducing conditions and enhanced the biological reduction of the supplied sulfate to sulfide. Simultaneously, the CVOCS in the mixed plumes were rapidly degraded by both biotic and abiotic processes to below regulatory goals. Bench tests for the arsenic site demonstrated that soluble arsenic was rapidly removed from solution using Geoform® ER and a clear dose response for treatment was observed. A description of the BGCR processes applied, and the methods and results of the bench tests and full-scale application of biogeochemical reduction for treatment of CVOCs; and for sequestration of arsenic will be presented.

<u>Session 3b2 / Abstract title</u>: Outlining the best remediation strategy at a multi-focus site where both shallow and deep aquifers are contaminated by chlorinated ethenes: hydrogeological characterization, treatability studies and in situ pilot tests.

ID: 217

Key words: chlorinated ethenes; groundwater contamination; biodegradation; chemical reduction; organohalide-respiring bacteria.

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Organization: LITOCLEAN, SL

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Session: 3b2

Abstract

The shallow aquifer of a historical multi-industrial area in northern Spain is severely contaminated with the chlorinated ethenes PCE, TCE, cis-DCE and VC. Due to its location and characteristics, the area is of strategic importance: it is really close to the coast, belongs to a protected area, and the deep aquifer, also contaminated, is exploited for water supply. Thus, the aim of this project is, firstly, to improve the hydrogeological characterization of the site and the conceptual site model (CSM) and, secondly, to carry out laboratory treatability studies and in situ pilot tests to outline the best remediation strategy.
The new CSM was obtained after performing 1) a thorough historical background study, which identified two differentiated north and south contamination plumes; 2) several rotational probes of different depths (aiming at the shallow or deep aquifer, separately) with continuous sample extraction and habilitated as piezometers; 3) an extensive and periodic groundwater sampling from the existing and the recently installed piezometers to monitor geochemical variations and the migration of the two plumes; and 4) in situ hydraulic and tracer tests in order to investigate the connectivity between the shallow and deep aquifers. These works evidenced two different hydrological units: the upper one, of silts and clays, corresponding to the shallow aquifer; and the lower one, constituted by a layer of alluvial base gravels and the deep aquifer. Thus, the vertical migration of leaked contaminants from the upper to the exploited lower hydrological unit mainly occurs through the gravels, in the instances where the silts and clays are, naturally or artificially, connected to them.

Furthermore, it is also through the alluvial gravels that contaminants migrate horizontally towards the installed and active groundwater exploitation wells.
Based on the new CSM, six groundwater samples, derived from the north and south shallow and deep aquifers, were used for the characterization of the natural hydrochemical conditions, and the preparation of treatability studies to assess the intrinsic biodegradation potential at the site. For this, several techniques were used, including 1) the acquisition of hydrogeochemical data; 2) microcosms experiments; 3) molecular techniques (qPCR and metabarcoding), and 4) stable carbon (δ13C) and chlorine (δ37Cl) isotope analyses. The microcosms confirmed the feasibility of a biostimulation treatment with organic fermentable substrates at the shallow aquifer in both the north and south plumes to transform contaminants to non-toxic end-products. This was also confirmed via qPCR with primers targeting Dehalococcoides sp. and Dehalogenimonas sp. 16S rRNA, and the TceA, VcrA and BvcA reductive dehalogenase genes. The gene copies of the targeted biomarkers notably increased in the north and south shallow aquifers. qPCR also confirmed the presence of native dechlorinating bacteria in the south deep aquifer. Conversely, biodegradation was not observed in the field-derived microcosms with concentrations that were indicative of DNAPL (dense non-aqueous phase liquid), nor in the microcosms derived from the north deep aquifer (MW-5). In the latter case, pH was moderately alkaline and qPCR results evidenced very poor increase in the gene copies of the biomarkers, which could explain the obtained results.
Following the beforementioned results and a similar methodology, the next steps (currently ongoing) were planned: 1) additional laboratory studies with groundwater from MW-5 testing for chemical reduction (ISCR); 2) two biostimulation in situ pilot tests to be implemented at the north and south shallow aquifers; and 3) the implementation of an ISCR in situ pilot test for the north deep aquifer, which hopefully will provide evidence of an effective remediation strategy for this aquifer. The results and conclusions obtained throughout the totality of the project will be presented at the conference.

Session 3b3 orals

Session 3b3 / Abstract title: Solid Phase Colloidal Organic Amendments Promote Sustained In-Situ Biodegradation of Groundwater Contaminants Within Permeable Barriers

ID: 225

Key words: In Situ, Biodegradation, Groundwater, Remediation, permeable barrier

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Organization: REGENESIS

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Session: 3b3

Abstract

Purpose of Study:
In-ground permeable reactive barriers composed of colloidal scale activated carbon coated aquifer material or granular activated carbon are effective at intercepting groundwater plumes and retarding downgradient contaminant migration. However, activated carbon does not directly promote contaminant degradation. In high contaminant flux environments, the carbon particle surfaces can become contaminant saturated resulting in diminished barrier performance. Barrier longevity can be extended by adding complimentary remediation amendments that promote contaminant biodegradation. Commonly used soluble fermentable remediation amendments have limited persistence (sodium lactate), and longer acting products (emulsified vegetable oil) competitively sorb to the carbon particles displacing target contaminants. This work describes the development, modeling, and field demonstration of a novel plant-based, sub-micron fermentable remediation amendment. This is the first solid-phase colloidal material that can be co-injected with activated carbon at low pressures to promote sustained in-situ bioremediation in permeable reactive barriers.

Methodology:
Several plant-based products were investigated to identify a material that could be reduced in size to about one micrometer and slowly degrade to support bioremediation. To inhibit the agglomeration that naturally occurs in small particle size suspensions, several food-grade dispersants were investigated. This work was followed by experiments to optimize the

particle size with the goal of producing a material that could be co-applied with similarly sized colloidal activated carbon. Particle transport through sand was verified using column studies. The ability to promote biodegradation was studied using closed bottle treatability studies with chlorinated ethenes. A pilot study was then performed by direct push injection at low pressures with and without activated carbon. Monitoring well data was used to measure degradation rates and degradation pathways of chlorinated ethenes, geochemical parameters, and the generation of gaseous reaction products such as ethane and methane.

Summary of Findings/Significance:
After numerous iterations, a stable colloidal suspension of a biodegradable plant-based material was produced. The median particle size was about 1 micrometer with 99% of the particles less than 5 micrometers. This particle size and product appearance compares favorably to commercially available emulsified vegetable oil products. Treatability studies verified the ability to degrade TCE to ethene via reductive dechlorination. The pilot studies successfully demonstrated the ability to co-apply the product at low injection pressures with and without colloidal activated carbon. Monitoring data verified the occurrence of reductive dechlorination with ethene production continuing more than two years after product application.

<u>Session 3b3 / Abstract title</u>: Remediation of Chlorinated Solvents in a Chalk Aquifer used for Public Water Supply

ID: 234

Key words: Chalk, TCE, ISCR, Potable Water Supply, EHC Plus

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Session: 3b3

Abstract

Purpose of Study: Trichloroethene (TCE) concentrations in groundwater indicative of Non-Aqueous Phase Liquid (NAPL) were identified in an important Chalk Aquifer system (within a source protection zone for a public water supply well). Delineation of the source area dissolved phase plume was required followed by development and implementation of a remediation strategy to protect and restore the groundwater resource as well as enabling regeneration of the former manufacturing site where the source had been identified.
Methodology: Due to initial uncertainties on the conceptual site model (CSM) (unknown source, source / plume extent, deep groundwater, potential for high conductivity fracture flow within bedrock) the investigation strategy had to be agile to ensure a robust CSM could be developed.
Site investigation comprised:
•In field data collection using
  oMembrane Interface Probe enabling rapid delineation of soil source (unsaturated zone was 10 m thick and subject site was 10,000m2).
  oGeophysical assessment of chalk aquifer to 50 metres below ground level to assess groundwater flow through dual porosity system, including detailed mapping of fractures and high hydraulic conductivities in the down gradient plume.
•Nested wells used to vertically laterally delineate groundwater plume.
•Soil gas assessment to determine potential risk to off site human health receptors (residential properties and school located within 50m of site).
•Liaison with the operator of the Public Water Supply Well to confirm testing of abstraction well and determine if chlorinated solvents had been identified.
The site works confirmed a concentrated source in the unsaturated zone (10m thick) extending to depth of 35m bgl in the chalk aquifer and extent / direction of the dissolved phase plume. Liaison with the operator of the public water supply well confirmed an absence of detectable CVOC concentrations at the public water abstraction. The data from the site investigation was used to complete a robust risk assessment which confirmed an absence of

risk to existing receptors and enabled remediation criteria based on a 250m remediation compliance point to be agreed with the Regulators.
Remediation strategy was developed in line with SuRF-UK methodology, and recommended application of:
•Soil Vapour Extraction to address unsaturated soil / soil gas;
•Enhanced Reductive Dechlorination (ERD) / In Situ Chemical Reduction (ISCR) through the injection of EHC® Plus reagent using packers in open boreholes into bedrock.
Remediation injections of EHC® Plus were focus to target remediation on zones where bulk mass and mass flux were present. Targeting of these zones could only be completed successfully due to the high resolution delineation of the source zone and associated dissolved phase plume.
Summary of findings/results: Proactive engagement with Regulators enabled remediation to be completed on a voluntary basis. Environment Agency and Local Authority accepted remediation thresholds based on a 250m compliance point from the Site .
Remediation works achieved:
•88% reduction average sum VOC concentrations in soil gas over a 10 month period, with the SVE system removing 0.42T of equivalent TCE from the unsaturated source zone.
•Application of EHC® Plus resulted in a >98% reduction of maximum TCE concentrations from approximately 30,000 µg/l to 400 µg/l over an 18 month period.
•Verification monitoring (6 months) confirmed that concentrations of TCE and degradation products (e.g. cis 1,2 dichloroethene and vinyl chloride) remained below agreed remediation thresholds.
Conclusion: Application of SVE combined with EHC® Plus can significantly reduce concentrations of chlorinated solvents rapidly in aerobic chalk aquifers.
Significance / contributions of study: Application high resolution site investigation and remediation technologies has enabled an important aquifer system to be protected continue to supply potable water to the local community.

<u>Session 3b3 / Abstract title</u>: Use of a bioreactor for the continuous cultivation of DHC bacteria for the complete dechlorination of a CHC-contaminated site

ID: 249

Key words: Sustainable, Anaerobic bioreactor, DHC-inoculation, Complete dechlorination, Chlorinated ethenes

Submitter: Lukas Scholz

Organization: NTP Umwelt

Co-authors: nan

Session: 3b3

Abstract

Use of a bioreactor for the continuous cultivation of DHC bacteria for the complete dechlorination of a CHC-contaminated site

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Theoretical background

One of the most common pollutants on contaminated urban sites are chlorinated hydrocarbons such as perchlorethene and trichlorethene. Conventional, longstanding remediation methods like pump treat are characterized by high energy consumption, which, in addition to high costs, also leads to high CO2 emissions.

In principle, CHC show good biodegradability. Only the right conditions need to be created in the groundwater. Under anaerobic conditions there is the possibility of completely biological dechlorination if the right bacteria are present in high concentration. Both perchlorethene (PCE) and trichlorethene (TCE) are degradable by sulfate-reducing bacteria. However, most often no further degradation can be observed which is problematic, because the forming metabolites dichloroethene (DCE) and vinyl chloride (VC) are characterized by higher mobility and higher toxicity. Therefore, the presence of a high population of Dehalococcoides mccartyi (DHC) is required for sustainable and successful biological treatment of these sites. DHC is to date the best known organism capable of a complete dechlorination of CHC. Due to their susceptibility, the natural concentration of this species is not sufficient for the complete dechlorination in most cases, so DHC-inoculation must be performed.

Innovative in-situ technology in practice

The oral presentation is to present the implementation and the results of a remediation project in Rheine (Germany) where an on-site bioreactor was used for the continuous cultivation and infiltration of DHC bacteria. The site, located in an urban area, was mainly contaminated with perchlorethene and had a maximum concentration of 10.000 µg/l. During the preliminary study no DHC-bacteria at all could be found. The innovative use of this bioreactor resulted in high concentrations of DHC-bacteria throughout the groundwater cubature being remediated (35.000 m^3). This led to a massive decrease in contaminant levels in the entire source area due to complete dechlorination in less than 6 months. In most monitoring wells the CHC concentration was found to be about the detection limit. The progress of the remediation was monitored by chemical analyzes and qPCR analyzes to quantify the bacterial population and online measurements of pH and redox.

Sustainable remediation

Since the concept aims to use the efficient metabolism of specialized bacteria, the energy consumption is very low. The high level of automation and remote maintenance of the system also play their part in sustainability.

The advantages in a row:

- Relatively short remediation period;
- Contamination is completely converted;
- The system can be applied in urban areas. All potholes and pipes can be underground; this results in minimal nuisance for the surroundings;
- Very low energy use, the degradation itself is energy neutral;
- Cheaper than non biological methods.

<u>Session 3b3 / Abstract title</u>: NATURE BASED REMEDIATION APPROACH FOR THE CVOC CONTAMINATION UNDERNEATH AN ELECTRONIC MANUFACTURER SITE

ID: 356

Key words: sustainable remediation, complex sites

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Organization: GreenSoil Group

Co-authors: M. de Camillis, GreenSoil Group, Projectengineer, M. Slooijer, GreenSoil Group, CEO

Session: 3b3

Abstract

Purpose of Study
Soil and groundwater of an electronic manufacturer site was impacted with cVOC due to site activities. Three main contaminated areas have been identified: A, B and C. Zones A and C are located mainly outside the current production buildings, whereas zone B is located underneath a building in which a very sensitive production area (cleanroom) is present.
Due to the complex site conditions, the client (previous owner and operator) was told that remediation could only be conducted when the buildings would be demolished. This would leave the client an uncontrolled long-term liability. As this is an orphan site to the client, Greensoil was asked to develop a plan to complete this challenging cVOC remediation in a reasonable time, despite very difficult logistical conditions. The proposed strategy involved several techniques with the overarching goal of using mainly bio-based technologies.
Methodology
A “source driven concept” was the strategy selected by the client. To address this concept, GreenSoil proposed a phased approach:
1. Zone A: excavation of the shallow source area and in-situ bioremediation system to stimulate the anaerobic biological degradation (ERD) of chlorinated compounds using a combination of direct push and groundwater circulation with dosing of the electron donor Dehalo-GS.
2. Zone B:
- installation of a biobarrier to prevent further off-site migration.
- source delineation inside the building.

Based on the outcome of these investigations, a full-scale remedial strategy was designed:
- multiphase extraction (MPE) until 4 m-gl, and stimulation of ERD until 10 m-bgl inside the operational building.
- Installation of 2 deep wells connected to 3 horizontal segmented drains placed at

different depths to stimulate anerobic biodegradation by ERD.
GreenSoil installed the entire in-situ remediation system underneath the building complying with the requirements of the client (dust and vibration free environment).

3. Zone C: after additional investigation was performed, excavation and in-situ ERD were carried out.

Summary of findings/results

During remediation, groundwater quality is being closely monitored by sampling monitoring wells on site. Within 2 years, the remediation of Area A and C reached the target values and are in aftercare monitoring. Further decreasing trends have been reported with no rebounds. The biobarrier at the site boundary was operated with a high efficiency (> 95%) to date. The first phase of the Area B source remediation by MPE was operated for 1 year and reduced initial soil cVOC concentration levels from >2,100 mg/kg to 2mg/kg in average (removal efficiency 99.5%). The second phase of Area B by bioremediation is currently operational.

Conclusion

The project shows the effectiveness of bioremediation in combination with other techniques to treat an extensive cVOC soil / groundwater contamination. In which 2 of the areas are close to completion and the last one is still on going but showing great results. Despite that this project was historically assessed as impossible to conduct by in situ remediation due to the logistical conditions and the complexity.

Significance / contributions of study

This project shows the flexibility and potentials of bio-based technologies, and that in-situ remediation can be a successful strategy to be applied in difficult conditions without disturbing site operations.

<u>Session 3b3 / Abstract title</u>: Remediation of residual PCE Impact in Groundwater: Enhanced bioremediation approach to facilitate remediation in a complex hydrogeological setting

ID: 393

Key words: sustainable remediation, enhanced bioremediation, ERD

Submitter: Diderik Göschel

Organization: Ramboll Iberia

Co-authors: Diderik Göschel, Irene Moreno, Victor Bahillo, Peter Wouters (Ramboll Iberia, Spain), Mark M. Mejac (Ramboll, Milwaukee, Wisconsin, USA)

Session: 3b3

Abstract

The site covers approximately 1ha and consists of several adjoining industrial properties located in Spain. PCE and daughter compounds impacted groundwater associated with a former degreasing installation has been identified at several discrete locations within shallow overburden soils, and also the top of underlying weathered limestone bedrock. Groundwater flow and contaminant migration are strongly conditioned by the site's hydrogeological setting and the physico-chemical properties of the contaminants. Remedial objectives include reduction of CVOC concentrations in site groundwater to facilitate downgradient compliance with applicable GW Criteria. A plume of CVOC-impacted groundwater has been identified mostly at the base of the shallow overburden and to a limited extend in the top of the bedrock, to depths of approximately 10 m. Initial investigations suggested that deeper groundwater impact existed affecting the bedrock.

As a first step the contaminant distribution in the site subsurface was reexamined. Discrete-interval sampling showed that deeper groundwater impacts did not exist and were indeed only associated with deficiently installed monitoring wells. Therefore, the remedial efforts could be focused on more localized shallow groundwater impacts. However, substantial heterogeneities within the overburden (including outcrop of limestone) and nearby surface water receptors posed significant challenges to effective distribution of injected amendments. Following a feasibility study, groundwater remediation using in-situ enhanced reductive dechlorination (ERD) technologies has been conducted starting in 2022 to address the CVOC-impacted groundwater. This approach replaced an earlier remedial concept that was initially suggested by the Authorities based on a pump-and-treat approach. The change in methodology took into account both the effectiveness and the sustainability of the remedial system. Based on varying hydrogeologic conditions and contaminant distributions throughout the site, specific amendments and injection approaches were tailored to enhance distribution and flexible injection to facilitate the integrated approaches to effectively

stimulate ERD. Slow-release carbon (large droplet and fine droplets Emulsified Vegetable Oils -EVO- depending local conditions) substrate was applied via injection wells to biostimulate CVOC-impacted shallow overburden, and bioaugmentation using commercially available microbial cultures was also conducted to further enhance rates of biotic dichlorination.

The results of post-injection overburden groundwater monitoring revealed effective electron donor distribution based on total organic carbon concentrations, establishment of reducing conditions based on manganese, nitrate, ferrous iron, sulfate, and methane data, and substantial reductive dechlorination based on evaluation of CVOC molar fractions. After one injection rounds of substrate focused on impacted shallow overburden groundwater, significant changes in CVOC concentrations were observed.

Post-injection groundwater monitoring data interpretation will be presented, along with discussions of rationales regarding injection approach and next steps.

Conclusions A detailed Site Conceptual Model should be developed and the contaminant distribution should be thoroughly established prior to any site remediation. Site data showed that in-situ enhanced reductive dichlorination has proven to be effective for the degradation of PCE and TCE, even under the site's complex hydrogeological setting.

Contribution of the study It was shown that deeper groundwater contamination did not exist. This significantly improved the relations between the site and external stakeholders. It also allowed to select a more sustainable remedial technology.

Session 3b4 orals

Session 3b4 / Abstract title: Sequential dechlorination of chloroform to dichloromethane and acetate bioelectrochemically assisted

ID: 174

Key words: Dehalobacter, Dehalobacterium, Chloroform, Bioelectrochemistry, Bioremediation

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Session: 3b4

Abstract

Sequential dechlorination of chloroform to dichloromethane and acetate bioelectrochemically assisted.

D. Fernández-Verdejo, P. Cortés, A. Guisasola, E. Marco-Urrea, P. Blánquez.

Using bioelectrochemical systems (BESs) to provide electrochemically generated hydrogen is a promising technology to provide electron donors for reductive dechlorination by organohalide-respiring bacteria. This study aims to assess the feasibility of coupling the dechlorination potential of two mixed cultures, one containing Dehalobacter and the other Dehalobacterium, in the cathodic chamber of a BES to transform chloroform (CF) into non-toxic final products. The sequential dechlorination proceeds through the organohalide respiration of CF to dichloromethane (DCM) via Dehalobacter, followed by the fermentation of DCM to acetate and formate via Dehalobacterium.
The BES used consisted of two glass vessels with 165 mL of total volume separated by a

cation-exchange membrane with an aperture diameter of 4 cm. A titanium sheet and a graphite brush were used as the anodic and cathodic electrodes, respectively. The enriched cultures containing Dehalobacter used in this study were derived from groundwater contaminated with CF. The inoculum of the Dehalobacterium-containing consortia was obtained from slurry samples of a membrane bioreactor from a wastewater plant and subsequently enriched in the laboratory.

CF was not bioelectrochemically transformed in BESs operating at the non-hydrogen producing potential of −0.3 V, discarding direct electron transfer from the graphite brush electrode surface to Dehalobacter. The dechlorination of CF was almost immediately detected when the cathode was poised at −0.6 V, with the concomitant production of DCM. The BESs were sequentially operated at −0.6, −0.7, and −0.8 V after the consumption of three doses of CF (500 μM) per cathodic potential. The decrease of the poised cathodic potential showed a significant increase in both the CF degradation rate and the DCM production rate. CF degradation and DCM production rates increased one order of magnitude when moving from −0.6 V to −0.8 V, reaching values of 10.3 ± 7.3 and 10.1 ± 8.5 μM d−1 (at −0.6 V cathodic potential) and 131.6 ± 64.9 and 125.2 ± 58.9 μM d−1 (at −0.8V cathodic potential), respectively.

After the degradation of nine CF doses, the experimental BESs were inoculated with an enriched culture containing Dehalobacterium on day 83 of operation. At this point, the DCM accumulated in the BES (1128 ± 616 μM) was completely degraded in the following seven days at a degradation rate of 481 ± 141 μM d−1. Once DCM was degraded, CF was spiked at increasing concentrations of approximately 200, 400, 600 and 800 μM to couple both Dehalobacter and Dehalobacterium dechlorination capabilities.

The Dehalobacter 16S rRNA gene copies increased four orders of magnitude during the whole period. The coulombic efficiencies associated with the degradation of CF reached values > 60% at a cathodic potential of ¬−0.8 V when the degradation rate of CF achieved the highest values.

This study shows the advantages of combining syntrophic bacteria to fully detoxify chlorinated compounds in BESs and further expands the use of this technology for treating water bodies impacted with pollutants, providing a basis to use BESs as on-site bioreactors to deliver enriched OHRB and hydrogen in contaminated groundwater requiring biostimulation and bioaugmentation.

<u>Session 3b4 / Abstract title</u>: Treatment of groundwater polluted with DNAPL by electrochemical oxidation

ID: 177

Key words: DNAPL, lindane, electrolysis, diamond, groundwater

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Organization: Complutense University of Madrid

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Session: 3b4

Abstract

Abstract

The occurrence of chlorinated organic compounds (COCs) from dense non-aqueous phase liquids (DNAPLs) in groundwater is a major concern for the scientific community due to the hazardous nature of these compounds. DNAPLs come from accidental spills, leakages, or uncontrolled discharges in different industrial activities. As a particular case, groundwater contaminated by chlorinated compounds in two industrial landfills (Bailin and Sardas) in Sabiñanigo (Spain) is considered here. During several decades of the 20th century, large amounts of DNAPLs from lindane (γ-hexachlorocyclohexane, γ-HCH) production were dumped in unlined landfills located in northeastern Spain (Sabiñánigo). This DNAPL contains 28 different COCs, including different isomers of hexachlorocyclohexane (HCH), being these compounds solubilized in groundwater. For this reason, it is necessary to develop clean and efficient technologies that allow to remove COCs from groundwater. Advanced Oxidation Processes (AOPs) can be considered a suitable alternative for the degradation of these organic pollutants.

Among the different AOPs, this work focuses on applying electrochemical oxidation to treat groundwater from the Bailin and Sardas landfills polluted with DNAPL. The proposed technology is based on the in-situ production of powerful oxidants (chlorine, persulfate, peroxodiphosphate…) and free radicals (hydroxyl, sulfate…) from the oxidation of the ions naturally contained in the effluents and from water oxidation. These species significantly contribute to the degradation of organic pollutants. Hence, the addition of reagents or

catalysts is not required. The efficiency of oxidant generation strongly depends on the electrode material and the applied current density. Mixed Metal Oxides (MMO) electrodes based on ruthenium and/or iridium oxides over titanium substrates have been employed for the electrochemical production of chlorine and wastewater treatment. More recently, Boron Doped Diamond (BDD) electrodes have emerged as excellent electrocatalytic materials for removing organic pollutants from liquid phases. The production of hydroxyl radicals from water oxidation takes place over both electrodes. However, these radicals are chemisorbed over the MMO anode, whereas they are physisorbed over the BDD anode. This promotes different degradation mechanisms with each material, and for this reason, MMO and BBD anodes are classified as active and non-active electrodes, respectively. The main advantage of non-active electrodes is that electrogenerated radicals are available to attack the organic pollutants (direct oxidation) or react with inorganic species to form powerful oxidants, favouring the indirect oxidation processes. With this background, BDD and MMO anodes have been tested for treating groundwater polluted with DNAPL. The influence of the current density (0-30 mA cm-2) on the removal of COCs contained in DNAPL-polluted groundwater has been evaluated, paying special attention to the elimination of hexachlorocyclohexanes (HCHs).

Acknowledgements

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<u>Session 3b4 / Abstract title</u>: Bench Test Evaluation of Arsenic Immobilization in Shallow Soils at Collstrop-Grunden, Hillerød, Denmark

ID: 279

Key words: Arsenic Immobilization, Lumber preservation, Bench treatability study,

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Session: 3b4

Abstract

Purpose of Study. Collstrop is a large former wood treatment facility where soil, groundwater, and surface water are contaminated by arsenic (As) from historical application of chromated copper arsenate (CCA) for lumber preservation. The majority of the As mass occurs in the vadose zone and serves as a primary source for As contamination in ground water and surface water. As there is limited knowledge regarding the long-term stability of As immobilization methods in soil (i.e., over decades to centuries), a bench treatability study is being performed to evaluate the effectiveness of various stabilization technologies Collstrop site soil. A primary goal is to identify one more treatment agent capable of stabilizing As permanently, over a period >100 years, throughout a period anticipated to be impacted by extreme weather conditions induced by climate change. Specific criteria being evaluated in the bench test include ability to reduce porewater As (Cu and Cr) concentrations, longevity of treatment under stressed (variable redox) conditions, sustainability of the various agents, and cost, feasibility, and risks of field application. This study is funded by the Capital Region of Denmark/Danish EPA and performed by a project team consisting of COWI A/S, Geosyntec Consultants, the Geological Survey of Denmark and Greenland (GEUS), Copenhagen University, and Columbia University.

Methodology. The experimental design involves successive phases of testing in which the best performing treatments are retained for subsequent phases of testing, and weaker performing treatments are screened out of the study. In Phase 1, six in-situ treatment technologies are being evaluated in batch reactors consisting of As-contaminated site soil

and synthetic groundwater representative of site groundwater: electrochemical precipitation of magnetite, flushing with a Fe(II) solution, flushing with a green rust suspension, biological precipitation of magnetite, flushing with an Al(III) solution, and stabilization with MetaFix®, a commercial material containing a carbon and ZVI composite. In Phase 2, the four best performing treatment technologies from Phase 1 will be tested in batch reactor treatment stability tests in which conditions will be stressed via saturation/desaturation cycles to create dynamic redox conditions, and application of heat to accelerate reactions. In Phase 3, the two best performing treatment technologies from Phase 2 will be tested in column tests designed to evaluate As stabilization longevity in scaled-up, flowing reactor systems over a range of redox conditions.

Summary of Findings. Preliminary data have been generated from Phase 1 batch reactors of electrochemical precipitation of magnetite and in-situ flushing with Fe(II) and Al(III) solutions, which are currently being evaluated to improve the performance. An early observation is that flushing with Fe(II) generates acidity that can solubilize As, necessitating application of NaOH to improve stabilization. Complete results from Phases 1 and 2 of the study, and partial results from the Phase 3 column study, will be presented at the AquaConSoil conference.

Conclusion. The ongoing batch tests are expected to provide data to further select the best performing technology for a field pilot test based on consideration of As concentration reduction, treatment longevity, dosage, and feasibility of field application. Conclusions will be updated upon bench test completion later in 2023.
Significance. These bench studies support development of efficient and cost-effective technologies for long-term in situ stabilization of As in vadose zone soils. If successful, these studies pose the potential to both identify a viable and sustainable solution to the As leaching problem at the Collstrop site, as well as advance the state-of-the-science in general regarding effective approaches for stabilizing CCA sites throughout varying redox conditions, over durations of decades to centuries.

<u>Session 3b4 / Abstract title</u>: Pragmatic approach to upscale a macrophyte based metal(loid)s phytoremediation to treat polluted ground water

ID: 281

Key words: Macrophytes; Phytoremediation; Bio-electrochemical system; Heavy metals; Nature based solutions.

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Session: 3b4

Abstract

Heavy metal concentrations in water bodies are a global concern that affect human health. Phytoremediation is a sustainable and eco-friendly alternative treatment relaying on natural ability of plants that accumulate, reduce, and/or degrade the pollutants. Understanding of underlying plants' biochemical and molecular mechanisms involved in phytoremediation are the key to better for potential for its application. This can be done by studying the genomic and transcriptomic profile to identify the potential tolerant species. Further, for the upscaling of phytoremediation and its implementation as a nature-based solution, the consideration related to the treatment time, removal efficiency, and possibility to be upgraded, upscaled, and coupled with other remediation methods are extremely important. At this regard, the capacity of emergent macrophytes, including Phragmites australis, Scirpus holoschoenus, and Typha angustifolia was explored. The macrophyte selection was based on their tolerance to an industrially metal(loid)s´ contaminated groundwater, that was assessed by studying the physicochemical characterization of plants. The heavy metals compartmentalization in plants leads to alterations in the phenotype, biomass, chlorophyll pigment concentration, total soluble proteins, and relevant antioxidant enzyme activities of the ascorbate-glutathione cycle. Specifically, P. australis and S. holoschoenus showed improved fresh and dried aerial biomass, while carotenoids content of T. angustifolia showed significant fluctuation. The catalase activity decreased in plant exposed to metal(loid)s, compared to control conditions in the three species, while for ascorbate peroxidase there

was a significant increase from the beginning. Based on these results, P. australis, S. holoschoenus, as T. angustifolia were subjected to study focused on the identification of design and hydraulic retention time needed for upscaling. In this study plants were subjected to 2 different scenarios, i.e, i) phytoremediation individually, and ii) Bio-electrochemical system coupled with phytoremediation. Both scenarios were provided with 2 different HRTs (15 and 30 days) to assess the optimal metal(loid)s´ removal and to study the changes in treated ground water toxicity, using Vibrio fischeri bioluminescence microtox assay. P. australis and S. holoschoenus showed no change in physiology and biomass compared to plants cultivated in control conditions. The impact of HRT was found on T. angustifolia, which showed less impacted plant physiological response at HRT of 30 days, than in HRT of 15 days. Considerable As, Cd, Fe, and Pb reduction occurred with phytoremediation, when compared with the non-treated ground water. However, the reduction in toxicity of the treated ground water to V. fischeri between non-treated and treated polluted groundwater was not significantly different, at 15-day HRT. However, at 30 days HRT the toxicity of treated groundwater using P. angustifolia and S. holoschoenus was significantly lower than the non-treated water and was very similar to controlled conditions. Hence, it can be concluded that metal(loid)s in groundwater can be treated using macrophytes. Nevertheless, it is important to find the potential macrophyte as the acute stress due to exposure results in the generation of less biomass, and the treatment time (HRT) needed for metal(loid)s removal should be identified as it can limit the benefit of the phytoremediation system. To make this work holistic and data driven it is important to decode and identity the specific molecular mechanisms utilized by plants to remove the heavy metals and to reduce their toxicity. Currently, in BIOSYSMO project, we aim to investigate these pathways involved in the HMs removal and tolerance in macrophyte plants, and how the integration of multiple green and NBS technologies can be improved.

<u>Session 3b4 / Abstract title</u>: Testing Electro-Nano-Bioremediation of chlorinated hydrocarbons at medium and large scale under ideally controlled boundary conditions

ID: 362

Key words: Zerovalent Iron, Direct Current, Perchloroethylene, Reductive Dechlorination

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Session: 3b4

Abstract

Sustainable land remediation has been the focus of intense research. In-situ injection of zerovalent Iron (ZVI) particles to remediate contaminated groundwater is a widely applied approach. However, because of the high reactivity and thus limited lifespan of ZVI particles contaminant reduction is often not performed sufficiently. Bioremediation involves the stimulation of a microbial community for contaminant degradation. The technique requires specific boundary conditions such as physicochemical groundwater parameters and moderate contaminant concentrations. Furthermore, experiments have shown that the application of direct current is a promising method to increase longevity and remediation efficiency of ZVI particles. Additionally, a suitable environment for bioremediation can be created. Thus, a sequential remediation of first reducing the main contaminant load with ZVI and second microbial degradation of the residual contaminant and metabolites with applied direct current during both stages shows a promising combined approach.

In a first step, column experiments were conducted to assess the influence of direct current on the reductive dechlorination of perchloroethylene (PCE) with nano ZVI particles (Nanofer Star). Columns with a volume of 2 dm^3 were packed with medium sand (Quartz, Dorsilit 8) and a reactive ZVI zone (Nanofer Star). A fixed amount of PCE was injected in the reactive zone at the start of the experiment. The columns were equipped with Titanium/Mixed Metal

Oxide (Ti/MMO) electrodes and a mean current of 1.2 mA was applied. Initial results show that an increase in the current intensity leads to a pH increase (mean pH of 10.7) which in turn increases stability and longevity of ZVI particles.

In a second step, a large-scale experiment (L/W/H = 3m/1m/1m) was set up at ideally controlled boundary conditions. The aquifer was unconfined, with constant flux (inflow) and constant head (outflow) and filled with medium sand from the Rhine valley. The reactive iron zone consisted of a mixture of nano ZVI particles (Nanofer Star) and micro ZVI particles (Atomet) and was emplaced during the packing in order to ensure a homogenous iron distribution in the subsurface. A constant PCE concentration (200 mg/L) was introduced to the experiment with the injected degassed water. Application of direct current (60 V) was ensured by stainless-steel power electrodes in flow direction. A control experiment set up in the same manner as described above was set up without the application of direct current. Throughout the experiment, physicochemical groundwater parameters (electrical conductivity, pH and oxidation reduction potential), voltage, and the concentration of PCE and its degradation products as well as chloride and hydrogen are monitored at the inlet and outlet and at several sampling positions within the box. In the course of the experiment, microbially enriched water will be injected to induce the bioremediation phase.

The talk will give insight into the efficiency of ZVI-bioremediation in combination with an electric field at medium and large scale by presenting latest experimental results and findings. The investigations were conducted within the EU research project “Enhanced Innovative In Situ Biotechnologies for Contaminated Land Remediation (EiCLaR)”. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N°965945.

Session 3b5 orals

Session 3b5 / Abstract title: Sequential Reductive/Oxidative Bioelectrochemical Process For Chlorinated Aliphatic Hydrocarbons Removal In Contaminated Groundwaters: The Scaled-Up Field Test

ID: 133

Key words: Chlorinated Solvents, Bioremediation, Bioelectrochemical Systems, Reductive Dechlorination, Oxidative Dechlorination

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Session: 3b5

Abstract

Purpose of study: Chlorinated aliphatic hydrocarbons (CAHs) are common groundwater contaminant due to their improper use in the past. In recent years, more sustainable remediation and cost-effective technologies involves groundwater's indigenous microorganism. Dehalorespiring microrganisms are able to reduce CAHs as trichloroethylene (TCE) to ethylene through reductive dechlorination (RD) while aerobic dechlorinating microorganisms oxidized low chlorinated compounds such as cis-dichloroethylene (cDCE) and vinyl chloride (VC) into non harmful products. The integration of reductive dechlorination and aerobic dechlorination results an efficient approach for the complete mineralization of high chlorinated compounds. A sequential reductive/oxidative environment can be easily create by a bioelectrochemical systems (BES) which allow to the control of dechlorinating microorganisms activity simply by an electrochemical device. The BES avoid the use fermentable substrates or other chemicals in groundwater to stimulate the RD.
Methodology: The study presents the development of a 420 L pilot scale sequential reductive/oxidative bioelectrochemical process in which four microbial electrolysis cells (MECs) were connected in series. In the first two MECs, named reductive reactors, a graphite granular cathode has been used as working electrode while in the second two oxidative MECs, a titanium MMO anode was used as working electrode. In the reductive

reactors, the cathode chamber supplies the reducing power necessary to the dechlorinating biomass to perform the reductive dechlorination reaction while in the oxidative reactors, the titanium-metal mixed oxides anode ensured the oxygen evolution necessary for the aerobic dechlorination. Both reactors were equipped with a graphite internal counterelectrode which allowed for a simple, flexible and cost-effective configuration of the process. The sequential bioelectrochemical process has been fed by a CAHs contaminated groundwater.
Summary of findings/results: The pilot plant was operated at three different flow rates, corresponding to three different overall hydraulic retention time (HRT) of 0.89, 2.06 and 5.45 days (referred to the volume of 4 units). After the start-up period, the most abundant contaminant in the groundwater was Tetrachloroethane (TeCA) which follows different dechlorination pathways as reported in literature. The TeCA is partially removed in the reductive reactors in correspondence to an accumulation of cDCE, which suggests the removal through the biological □-dichloroelimination pathway, in all the explored conditions. The formed cDCE and the VC were removed in the oxidative units partially. During the different operational periods, the sulphate reduction reaction also was monitored but can be explained due to the presence in the aquifer of soluble organic carbon that can stimulate the heterotrophic reduction thanks to the restored redox condition.
Conclusion: The pilot scale performances were partially achieved, indeed while the removal capacity, the coulombic efficiency and the energy consumption resulted in line with the laboratory scale performance input which resulted like the results obtained under laboratory scale. The presence of low chlorinated by-products in the effluent indicated the insufficient dechlorinating capacity of the pilot. The main reason that affected the pilot plant performance was the TeCA inhibitory effect on the dechlorinating consortium utilized for the pilot inoculum.
Significance/contributions of study: The pilot scale sequential reductive/oxidative bioelectrochemical plant represents the largest attempt to scale up a bioelectrochemical process

<u>Session 3b5 / Abstract title</u>: Electroreductive defluorination of unsaturated PFAS by a quaternary ammonium surfactant-modified cathode via direct cathodic reduction

ID: 241

Key words: electrochemical reduction, quaternary ammonium surfactants, adsorption, defluorination pathway, direct electron transfer

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Session: 3b5

Abstract

Purpose of study
Per- and polyfluoroalkyl substances (PFAS) have been widely used in fast-food containers, surfactants, polymer additives, and aqueous film-forming foams. Due to their widespread use and chemical stability (C–F bond strength of 485 kJ/mol), PFAS have been persistent and commonly detected in the environment. Groundwater as the drinking water source of at least half the global population is also threatened by PFAS. Despite the ubiquity of PFAS, common remediation procedures of these compounds in groundwater have been limited by their trace concentrations and the strength of the C–F bonds. Therefore, an efficient removal and defluorination treatment method for PFAS-contaminated groundwater is desired. Electrochemical reduction approach has been considered as an environmentally friendly and low-cost approach for the remediation of groundwater contaminated by persistent halogenated organic pollutants and employed in the field. When treating anionic PFAS, which is the most commonly detected PFAS in groundwater, the difficulty lies in the electrostatic repulsions between these compounds and the cathode. Quaternary ammonium surfactant modification of the cathode improved the adsorption of anionic PFOS molecules. However, the role of quaternary ammonium surfactants in PFAS electrochemical adsorption and degradation induced by electron transfer is not yet clear. To this end, an electroreductive system with a quaternary ammonium surfactant-modified cathode was built to degrade unsaturated PFAS and to explore the C–F bond breakage in Unsaturated PFAS through direct cathodic reduction. In addition, the function of quaternary ammonium surfactants in the electrochemical activities was discussed.

Methodology

Fluoride was measured by an ion-selective electrode (ISE) connected to a meter. The parent compound concentration was measured by ultra-high-performance liquid chromatography. High-performance liquid chromatography quadrupole time-of-flight mass spectrometry (HPLC-QTOF-MS/MS) was used for intermediate analysis. The electron paramagnetic resonance (EPR) signals of radicals by spin-trap reagent DMPO were detected on an EPR spectrometer. Molecular dynamics (MD) simulations were carried out using the Forcite module in Materials Studio 2018 (BIOAccelrys).

Summary of findings/results

The removal and defluorination efficiencies by the surfactant-modified cathode reached 99.81% and 78.67%, respectively. The overall degradation procedure started with the adsorption of PFAS onto the cathode. This adsorption process was promoted by hydrophobic and electrostatic interactions between the surfactants and PFAS. Meanwhile, C-F bond breaking with direct electron transfer only was achieved for the first time in this study, which also showed that the C=C bond structure of PFAS facilitates the C–F cleavage. Quaternary ammonium surfactants modifying the cathode not only enhanced the effective adsorption of PFAS on the cathode but also improved interfacial charge transfer and mass transfer.

Conclusion

The cathode modified by quaternary ammonium surfactant enriched the anionic PFAS on the electrode surface through electrostatic and hydrophobic interactions, overcoming the treatment limitations of trace PFAS concentrations. At a low potential, the removal and defluorination efficiencies by the surfactant-modified cathode reached 99.81% and 78.67%, respectively. C–F bond breakage with only direct electron transfer was achieved for the first time in this study.

Significance / contributions of study

Electrochemical technology was shown to be a clean method without any further amendment, giving it promising potential as a sustainable and low-cost PFAS remediation solution. This study promotes an electroreductive defluorination system coupled with a quaternary ammonium surfactant-modified cathode, in which complete degradation of unsaturated parent PFAS was achieved. Such electroreductive approach with c

<u>Session 3b5 / Abstract title</u>: Global first trial and assessment of In-situ electrochemically enhanced nanoremediation for PFAS removal

ID: 318

Key words: PFAS, in-situ remediation, novel technology, proof of technology, physiochemical conditions

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Session: 3b5

Abstract

The unique stability and surfactant properties of PFAS in combination with its extensive industrial adoption, have created an environmental remediation challenge. The urgency to immobilise, remove and destroy PFAS in support of traditional and limited ex-situ field technologies has emerged. An innovative combination of technically and commercially synergistic approaches will be required. Development of effective in-situ technologies, with a focus on potable and groundwater contamination may support broader PFAS remediation approaches.

The objective of this field study was to empirically demonstrate Photon Energy Group's electrochemically enhanced nanoremediation as an effective technology for removal of PFAS in groundwater. The Australian field trial site, a contamination hotspot, featured an upper aquifer into which a combination of electrokinetics and nanoparticle injection was undertaken. Extensive data obtained from real-time and discrete sampling examined physiochemical properties, standard water analytes and PFAS. Data processing and statistical analysis was also undertaken.

This significant trial site demonstrated evidence of reduction for PFAS (sum n=30) concentrations compared to pre-trial values. At the time of writing, peer review and verification is underway.

As a consequence of the in-situ technology, changes in groundwater pH, oxidation reduction potential and electrical conductivity were noted with statistical significance, correlating to the observed PFAS reduction.

While the scope of this study did not extend to the destruction mechanisms, initial pre-site trial auxiliary lab scale reactor tests supported onsite findings. Additional University laboratory studies are currently underway to further quantify the fate of PFAS species, volatiles, and partitioning/phase transfer.

Results discussed demonstrate electrochemically enhanced nano-remediation as a safe tool for efficient management and reduction of PFAS in-situ within groundwater. While continued site verification and assessment of degradation pathways will be required, these site-based findings should support Photon's in-situ remediation technology from a developing, limited application solution to a recognised and verified field implemented technology, applicable for PFAS contaminated water sources.

<u>Session 3b5 / Abstract title</u>: Electrosorption for enhancing adsorption of short-chain perfluoroalkyl acids on activated carbon and on-site regeneration of the adsorbent

ID: 347

Key words: Short-chain perfluroalkyl acids, Electrosorption, Activated carbon, Adsorption enhancement, On site regeneration.

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Session: 3b5

Abstract

Short-chain perfluoroalkyl acids (PFAAs) are a major topic in environmental studies today 1. Adsorption by activated carbon (AC) as the most commonly used technique for removing PFAAs from water 2 is able to effectively eliminate long-chain PFAAs 3. However, for short-chain PFAAs including perfluorobutanoic acid (PFBA) the removal efficiency is much lower due to the higher hydrophilicity of PFBA (log DOW (at pH 7) = -1.22) 4 and thus lower adsorption affinity. As a consequence, early breakthrough and/or no removal of PFBA in AC filtration has been frequently reported 2. More importantly, continued operation of the AC adsorbers to achieve breakthrough of other PFAAs leads to desorption of PFBA as a result of displacement by other PFAAs as well as other co-adsorbates. Displaced PFBA may elute together with the non-adsorbed PFBA and thus even exceed the PFBA concentration in the influent. Our strategies to avoid these undesirable effects in mixed adsorption of PFAAs of various chain length are: 1. improving the adsorption affinity of PFBA by exploiting the charge-induced attractive forces between adsorbate and adsorbent, and 2. regenerating the PFBA-loaded adsorbent on site by electrodesorption before the displacement phenomena takes effect.

Therefore, this work is aimed at applying electrosorption to mitigate the above mentioned challenges. We used conductive activated carbon felts (ACFs) as electrode materials in batch and then continuous electrochemical cells. Various types of ACFs were characterized to evaluate their textural, surface chemical and electrochemical properties. Our intention was to mitigate carbon attrition from applied harsh electric potential by a proper material selection allowing charge-reversal already at mild positive or negative potentials. In this respect, the potential of zero charge (EPZC) of the ACF electrodes was considered as important selection criterion 5, 6. A set of electrosorption batch experiments were then performed to determine the best experimental condition for achieving a strong enhancement in

(electro)adsorption of PFBA and a reversible and strong electrochemical-induced desorption of it within a narrow electric potential window (i.e., applied potential for electrodesorption EPZC of ACF as working electrode WE applied potential for electroadsorption). Based on adsorption isotherm data for PFBA at positively and negatively charged ACFs, we provide a first estimation of the concentration factor as high as 50 that is theoretically achievable in a continuous electrosorption unit. The output of batch experiments was applied to design and run an effective electrosorption of PFBA in continuous mode by a symmetric electrochemical flow cell. The results of electrosorption in the flow cell showed significant enhancement in adsorption loading of PFBA on anodically polarized ACF. A full regeneration of ACF exhausted by PFBA using electrodesorption (cathodic potential on ACF) was also observed. This electroadsorption/electrodesorption was studied in cyclic experiments. Finally, the results showed that an enrichment of the pollutant in the outflow with a concentration factor of 10-20 by swinging potential in the flow cell was achieved.
The results of this study show that electrosorption is a promising novel approach for effective remediation of water contaminated with hydrophilic organic compounds including short-chain PFAAs.

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<u>Session 3b5 / Abstract title</u>: Advanced industrially influenced wastewater treatment scheme for agricultural water reuse

ID: 96

Key words: Water reuse, PFAS, micropollutants, electro-peroxone, constructed wetland

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Session: 3b5

Abstract

The European Green Deal, which recognizes the urgency to enhance the European Union (EU) natural capital and to protect health and well-being of its citizens from environment-related risks and impacts, includes a commitment to a zero-pollution ambition for a toxic-free environment. In this context, is highly necessary that the European research ecosystem provides innovative approaches to prevent and manage the occurrence of persistent, mobile and toxic (PMT) substances in the environment. Thus, one of the objectives of the European funded project PROMISCES is to deliver innovative strategies to move forward towards a non-toxic environment and safe reuse of resources with a particular focus on the soil-sediment-water system.

The aim of this investigation, part of PROMISCES, is to obtain a source of reclaimed water via treatment of industrially influenced wastewater for irrigation of food crops which does not pose a risk for human health. The targeted pollutant limits are set by a risk-based approach determined by means of a human health exposure assessment. The wastewater comes from the secondary treatment of a wastewater treatment plant (WWTP) located in Montornès del Vallès, Barcelona Province, in the Besòs river basin. This WWTP has a treatment capacity of 206,000 PE and 40,000 m3/d, with a 60/40 share of industrial/urban influent. Treated water is discharged to the Besòs river basin, which influences the sources of drinking water of the Barcelona metropolitan area. The amount of treated wastewater in the total flow of the

Besòs river and its tributaries is between 60-80%. The industrial sectors that generate the highest amounts of wastewater in this basin are mainly chemical, pharmaceutical, food, leather and textile, among others. Industrially sourced PMTs found in the secondary effluents of this WWTP from greatest to least abundance are: benzotriazole and derivatives, melamine, 2-aminophenol, tris(2-butoxyethyl) phosphate, 2,4-diaminotoluene, N,N'-diphenylguanidine, perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA) and perfluorohexane sulfonic acid (PFHxS).

One of the main challenges in the implementation of water reuse schemes is to find cost-effective and appropriate water treatment technologies to remove a large number of different micropollutants. To treat a large quantity of water per time unit, very reactive oxidants such as ozone, hydroxyl (OH) radicals, chlorine, or permanganate, among others, or high-capacity adsorbents such as activated carbon, or membrane separation processes are required. However, certain pollutants are highly recalcitrant to these processes, such as 1,4-dioxane, oxalic acid, and 4-chlorobenzoic acid, among others. For this reason, the present study tested a hybrid system, combining an electrochemical process based on electro-peroxone with a wetland. The electro-peroxone enhances the ·OH production by electrocatalytically producing hydrogen peroxide (H2O2) from oxygen and reacting with ozone. It has been shown that E-peroxone can considerably accelerate organic pollutant degradation, especially for these recalcitrant contaminants. Another advantage is that this process avoids or reduces the formation of by-products such as perchlorate, bromate or trihalomethanes. The rationale of a hybrid system is to find out if a post-treatment by means of a nature-based solution can shorten times and doses of the electrooxidation stage, and thus makes the solution more cost-effective.

To date, the electrochemical process based on E-peroxone has been tested at bench-scale with synthetic water to assess the abatement of industrial PMT as well as the formation of degradation by-products. Degradation rates up to 89%, 67%, and 39% for PFHxA, PFBS, and PFHxS, respectively, with a 4 ppm O3 dose, current of 30A, and 120 min have been achieved. Bench-scale and pilot testing with the real secondary WWTP effluent is planned for the upcoming months.

Session 3b6 orals

Session 3b6 / Abstract title: In situ flushing of multilayer DNAPL contaminated soils using a polymer/alcohol/surfactant mixture

ID: 123

Key words: DNAPL, biopolymer, alcohol, multilayer, mobilization, solubilization

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Organization: BRGM (French Geological Survey)

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Session: 3b6

Abstract

Purpose of study
Chlorinated Dense non-aqueous phase liquid (DNAPL) spills are a significant environmental concern, particularly for groundwater. One method of addressing this issue is to use in situ flushing of the contaminated aquifer with a polymer or surfactant solution. However, after the primary flushing with these methods, there will be some residual DNAPL ganglia trapped in porous media that cannot be mobilized anymore. Post-injection of alcohol-surfactant emulsion can result in higher recovery of DNAPL by solubilization or mobilization mechanisms. In the case of a multilayer system, it can be challenging to recover the residual DNAPL from all layers after primary flushing. In this work, we show how the injection of a mixture of alcohol, surfactant, and polymer can improve the recovery of residual DNAPL in a multilayer system.
Methodology
1-propanol and 1-hexanol, soluble and insoluble in water respectively, were used as two biodegradable alcohols in the mixture. Xanthan was selected as a biopolymer exhibiting a non-Newtonian behavior in solution form. Sodium dodecylbenzene sulfonate (SDBS) was used as a biodegradable and non-toxic surfactant to stabilize the mixture of alcohol and polymer. Batch experiments were conducted at various concentrations of surfactant and volume fractions of alcohols, water, DNAPL. The alcohol/surfactant solutions were mixed

with DNAPLs in polypropylene small tubes using a shaker for 24 hours, then separated by centrifugation at 10,000 rpm. To evaluate the performance of the alcohol/polymer mixtures on the recovery of the residual DNAPL, 1D-columns were used. The performance of these mixtures on the improvement of DNAPL recovery in multilayer systems was evaluated using a confined, decimetric-scale 2D tank.

Summary of findings/results

The analysis of batch experiments shows that when only 1-propanol is used as the remediating fluid, the volume of DNAPL decreases; therefore, the main washing mechanism is solubilization. On contrary, when 1-hexanol is added regardless of the presence of 1-propanol, the volume of DNAPL increases. It shows that the presence of 1-hexanol in the mixture influences the partitioning behavior of the 1-propanol and results in a mobilization mechanism. The results show that when 1-propanol is the only alcohol present in the mixture, DNAPL is recovered by dissolution through the aqueous phase. When 1-hexanol is also present, the alcohol is partitioned into the organic phase. The density analysis shows that by using the mobilization mechanism the recovery efficiency can be improved from 91% (by primary flushing) to 99%, and from 86% to 94% for single-layer and multilayer experiments respectively. The images obtained from 2D experiments show that when the solubilization mechanism is active, the remediated layers appear brighter as the black DNAPL is more dissolved in the aqueous phase. In the case of the mobilization mechanism, a contaminant bank is formed in front of the alcoholic mixture in flushed zone in the soil.

Conclusion

Secondary flushing with a non-Newtonian viscous washing solution is needed to remove residual pollutants, especially in multi-layered systems. Our results show that a mixture of alcohol, surfactant, and polymer can effectively remove DNAPL in these systems.

Significance / contributions of study

Chlorinated DNAPL contamination near groundwater is common and requires a sustainable and efficient solution. Primary flushing by a polymer/surfactant mixture can displace DNAPL but some droplets remain in pore spaces. A post-flushing by an alcoholic mixture can properly remediate the residual pollutant; however, in the multilayer zones, it is challenging to recover the residual contamination from all layers. The literature is bereft of a comprehensive study of the remediation of residual DNAPL in the multilayer system by flushing solutions. In this study, we address this challenge by introducing a mixture composed of alcohols, surfactant, and polymer.

<u>Session 3b6 / Abstract title</u>: Mobilization of PFAS from heterogeneous soils: Desorption by ethanol/xanthan gum mixture

ID: 137

Key words: Poly- and perfluoroalkyl substances (PFAS), Non-Newtonian fluids (NNF), Desorption, Alcohol, In-situ soil flushing

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Organization: BRGM

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Session: 3b6

Abstract

Purpose of study
Poly- and perfluoroalkyl substances (PFAS) have been manufactured since the 1950s. One of the main application of PFAS is in aqueous film-forming foam (AFFF) as a low-viscosity sealant to extinguish hydrocarbon fires. The use of AFFF in firefighting activities sites has contaminated many soil and water systems, leading a serious and complex sanitary and environmental risk. It is therefore important to improve PFAS remediation technologies. The conventional remediation techniques might not be functioning effectively because of the strong C-F bonds, surfactant properties, solubility, and adsorption capacity of these substances. However, some studies showed that in-situ soil flushing with solvent is a successful method for PFAS mobilization. Despite their high desorption performance in removing PFAS, their effectiveness in soils with heterogeneous pore sizes may be constrained. In this context, the use of a non-Newtonian fluid (NNF) can improve the solvent flow in heterogeneous soils and consequently the PFAS desorption. In this study, we show the efficiency of the mixture of polymer and alcohol on PFAS mobilization in heterogeneous soils.
Methodology
The flushing solution to solubilize PFAS is an aqueous ethanol solution at a fixed volume fraction of 50%. Xanthan gum as a biopolymer was added to this solution at different concentrations to induce a shear-thinning behavior of the mixtures. The rheometer was used

to examine the ethanol-xanthan rheological behavior of the mixtures. The soil was a blend of 3% of organic materials, 92% of silica sand, and 5% of clay with the same range of grain sizes as representatives of the soil layers usually reported for real polluted sites. At a fixed concentration of PFOS, PFOA, PFBS, and PFHxS, batch studies for understanding the adsorption and desorption behavior were conducted. An aqueous PFAS stock solution containing $CaCl_2$ was added to the soil. The mixture was then stirred and centrifuged. The remaining contaminated soil was used for desorption experiments by adding various solutions such as water, ethanol, and a mixture of ethanol-xanthan with different concentrations of xanthan. To assess the polymer performance in transporting alcohol to solubilize PFAS, 1D column experiments were carried out for two different soil permeabilities.

Summary of findings/results

The ethanol-xanthan mixtures homogeneity was confirmed by rheological analyses, which revealed that the addition of ethanol reduces the bulk viscosity of the mixture while maintaining a similar shear thinning behavior. Batch analysis revealed that the longer the PFAS chain, the greater the adsorption capacity, which corresponds to the solubility of each component. The main reason for adsorption is hydrophobic interactions with soil organic matter. In addition, ethanol desorbed more than 85% of the four PFAS components. Furthermore, the presence of xanthan in the mixture has a minor effect on the extraction capacity of ethanol. The efficacy of the injection of the ethanol-xanthan mixture on PFAS desorption and mobilization for various soil grain sizes was assessed using 1D-column experiments.

Conclusion

Depending on the length of the PFAS carbon chain, each component exhibits a different adsorption behavior. Ethanol flushing, as a promising method, has the potential to improve PFAS-contaminated soil remediation. In heterogeneous soils, the presence of xanthan in the flushing solution improves PFAS removal.

Significance/contributions of the study

PFAS contamination is frequently reported due to its applications in various fields. This study fills a gap in existing research by investigating the use of a mixture of ethanol and xanthan as a non-Newtonian fluid for in situ solvent flushing method aiming at removing PFAS from heterogeneous soils. While other PFAS desorption methods have been investigated, this is the first comprehensive study to evaluate the efficiency of this method in heterogeneous soils.

<u>Session 3b6 / Abstract title</u>: Evaluation of stability and performance of foam composed of complex mixtures of surfactants, nanoparticles and polymer for in-situ remediation of LNAPL

ID: 147

Key words: Foam, foam stability, in-situ soil remediation, LNAPL

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Session: 3b6

Abstract

Purpose of study:
Light Non-Aqueous Phase Liquids (LNAPL: gasoline, diesel, motor oil, etc.) - immiscible organic liquids which are one of the most common sources of groundwater pollution. The presence of LNAPL in the subsurface is mainly associated with accidental spills and leaks during storage and transportation. As a result of the low mass removal efficiency of pump-and-treat, in-situ environmental remediation (ER) methods are receiving more attention. Moreover, even more advanced recovery methods like in-situ surfactant flushing reach their technical limits due to the heterogeneity of the soil. Injection of non-Newtonian fluids can be beneficial to overcome this issue.
Among the increasing interest in shear-thinning fluids for in-situ ER, foam is a promising displacing agent. However, it is worth noting the main challenge of using foam for ER: when foam gets in contact with LNAPL (e.g. diesel), its stability deteriorates dramatically, which leads to poor sweeping efficiency. A current focus among many foam studies is on methods to enhance stability of foam using a variety of additives, such as co-surfactants, polymers, and nanoparticles (NPs). It should be noted that the majority of these studies are focused on foam application in EOR. Thus, the main objectives of our study are: (i) to determine the destructive effect of LNAPL on foam properties, (ii) to study the stability of foam composed of two or more additives in the presence of diesel, both in bulk and in the porous medium, (iii) to evaluate the recovery yield of each of the foaming compositions.
Methodology:
All foaming components used in our study were environmentally friendly. Pure nitrogen was used as a gas phase. Two highly biodegradable surfactants: sodium dodecyl sulfate (SDS)

and cocamidopropyl hydroxysultaine (CAHS), and their mixture were used for the foaming liquids. A drop-shape analyzer was used to determine the interfacial properties of the surfactants. Silica NPs (SiO2) and Xanthan Gum (XG) biopolymer were employed as foam-stabilizing additives. All prepared foaming liquids were experimentally investigated for foaming ability and stability (half-life) in the presence of diesel using the bulk foam screening method. The rheological properties of the foaming liquids were also studied using a rheometer.

Two 1D columns filled with sand and connected in series (i.e. foam generator and highly permeable diesel saturated sandpack) were used: (i) to generate a fully developed foam flow, (ii) to assess the foam Resistance Factor (RF) (i.e. foam strength) and (iii) to quantify the remediation yields of diesel. Each injection experiment included monitoring differential pressure and mass balance.

Results:

Our results show a significant destruction effect of diesel on foam stability. For instance, for SDS surfactant, the half-life of the bulk foam decreased 8 times in the presence of LNAPL, while the stability parameter (RF) decreased by more than 2.5 times in the porous medium. However, stability assessments in our study clearly demonstrated an increase in foam stability in the presence of diesel, both in bulk and porous media, when complex foaming liquids were employed. The bulk foam analysis showed that in contrast to SDS alone, the mixture of SDS+CAHS (SC), SC+NPs, and SC+XG improved foam stability at least more than 7.5 times. From 1D column experiments, we observed foam stability enhancements of 2.2, 2.5, and 2.8 times for SC, SC+NPs, and SC+XG, respectively. Moreover, for all these complex foaming fluids there is a significant LNAPL recovery efficiency (more than 90%).

Conclusion/contributions of study:

Additional studies are being carried out to deeply characterize how the presence of NPs and polymer impacts diesel recovery. Nevertheless, based on our results we can conclude that advanced foam formulations clearly exhibited promising perspectives to develop efficient in-situ remediation technology for highly permeable soils contaminated by LNAPL.

<u>Session 3b6 / Abstract title</u>: Successful treatment of PFAS-contaminated soils on large scale: practical experience with soil washing

ID: 200

Key words: soil washing, PFAS, large-scale remediation project

Submitter: Benjamin Faigle

Organization: Züblin Umwelttechnik GmbH

Co-authors: Thomas Meyer, Benjamin Faigle, Bernhard Volz, Hans-Georg Edel -> all Züblin Umwelttechnik GmbH

Session: 3b6

Abstract

Successful treatment of PFAS-contaminated soils on large scale: practical experience with soil washing

presenter: Anke Wiener, Thomas Meyer,
co-authors: Benjamin Faigle, Bernhard Volz, Hans-Georg Edel

The method of soil washing is currently the only economically feasible cleaning method for PFAS-contaminated soils on large scale.
A total of about 430,000 t of soil contaminated with PFAS and HCs was washed from August 2018 to October 2021 at the site of a former refinery in Bavaria. The cleaned soil could then be reinstalled at site-specific costs of about EUR 50 per ton.
Since September 2022, Züblin Umwelttechnik GmbH has been operating another soil washing plant in Northern Germany, which was specially designed to treat soils contaminated with PFAS. Several hundred thousand tons of sandy soil with around 10% fines will be washed and refilled on site.
Data obtained from these two large-scale remediation projects are presented. The technical concept and challenges to treat 1,000 to 3,000 t of material per day are discussed, along with regulatory obstacles and the boundary conditions to process these quantities while limiting emissions. A special focus lies on the heterogeneous nature of input material, with varying contaminant load, soil quality and soil structure as well as affiliated contaminants. In both attempts, the washing water is circulated in a closed water cycle, therefore intensive treatment of sludge and polluted water is required.
One of the critical issues in soil washing is to optimise the washing process so that the washing liquid serves as the predominant contaminant sink. In this way, steady washing results are achieved, and all output fractions can be successfully processed while water

consumption is kept to a minimum.
The complex nature of the contaminant itself, the multitude of singular PFAS substances and precursors, further complicate operation and controlling. Progress shows that soil washing can even be a viable tool to treat the fine fraction, and various strategies in different treatment steps have been tested on multiple scales, including several washing agents. Since after treatment, the washed soils can be safely reused on site, large emissions from transportation and properly disposing the PFAS-materials is avoided while ever limited landfill space is maintained.
Future research is required for ever expanding the applicability of the method to highly challenging materials such as high fines and/or high organic content. Further projects for washing of PFAS contaminated soils in Europe are already in the planning stage.

<u>Session 3b6 / Abstract title</u>: The hybrid soil washing system for the treatment of PFAS contaminated soils

ID: 63

Key words: PFAS PFOS soil washing

Submitter: Stany Pensaert

Organization: DEME Environmental

Co-authors: nan

Session: 3b6

Abstract

About ten years ago the group of PFAS compounds were seen as the emerging contaminants on the European continent. PFAS, in particular PFOS, was found back in the soil and groundwater at fire fighting locations on numerous airports all over Europe, and massive volumes of PFOS contaminated groundwater were identified threatening drinking water productions.
Since 2016 DEME Environmental started developing a soil washing process specifically for PFAS contaminated soils. Compared to 'ordinary' pollutants there are two large differences in washing PFAS contaminated soils: first of all the initial concentrations and remediation levels are at least 1000 times lower (µg/kg versus mg/kg), secondly PFAS are quite soluble in the process water phase. The first difference requires that the PFAS fraction that is anyhow adsorbed to certain soil particles (clay, silt, organic matter,…) has to be removed extremely well by a thorough separation of these specific particles. The second difference demands a continuous process water treatment system that keeps PFAS concentrations in the water low and in addition requires an after-washing step of washed sands and gravel with ultra-pure water (PFAS 100 ng/l) to avoid any trace of PFAS in the outputs' adherent water phase. As the developed process initially consisted of two consecutive washing steps that were later merged into one it was named the 'hybrid soil washing process'.

The delicate soil washing process was first developed at lab scale. In 2020 it was implemented at full scale in DEME's soil treatment centre in Antwerp. This fixed soil wash plant, which operates since 1994 and was one of the first soil washing plants in Europe, was adapted to the hybrid soil washing process. This included a special arrangement of hydrocyclones and upstream density classifiers to optimally remove fine and organic particles, next to a process water treatment system based on granulated activated carbon filtration. In addition, an internal production of ultra-pure water combined with a rinsing step of the washed sand was added.

Over 50000 tons of PFAS contaminated soils from various origins in Belgium and the Netherlands have been treated since 2020. Most of the soil came from fire fighting activities (airports and large industrial sites) with PFOS as the major compound. Other projects entailed complex PFAS blends from PFAS production sites. Soils with ranges between 10 to 500 µg/kg DM of PFAS were treated to below the treatment targets (levels for free reuse in Flanders), being 3 µg/kg DM for PFOS, 2 µg/kg DM for PFOA and 8 µg/kg DM for the sum of PFAS. The washed sands and gravels are being used in the construction industry.

The process has two residues: the fines and organics removed from the soil are dewatered and result in a filter cake that is disposed in a dedicated cell at a hazardous waste landfill. The spent activated carbon can be treated and reactivated by the supplier. During reactivation and subsequent off gas treatment all PFAS are destroyed.

In addition to the full scale treatment projects various lab scale research projects have been carried out in the DEME research lab. Interestingly we learned that the effectiveness of PFAS removal by washing is very dependant on the mineral composition of the soil, its particle size distribution, and the nature and amount of the organic matter in the soil. It was found that for some soils low target levels could not be achieved, and that the washing efficiency can only be assessed by lab scale trials. Although a set of characterisation analyses (PFAS concentrations, organic matter content, particle size distribution) can give a first idea of treatability, it is not sufficient. Therefore a lab testing protocol was developed that allows to gather sufficient information for evaluating treatment feasibility but also the design and dimensioning of a full-scale process.

Session 3b7 orals

Session 3b7 / Abstract title: Thermal Treatment of PFAS Impacted Soil – Field Demonstration and Scale-Up Considerations

ID: 191

Key words: thermal treatment, PFAS impacted soil, field-scale study, U.S. Air Force Base

Submitter: Gorm Heron

Organization: TRS Group

Co-authors: Gorm Heron Ph.D., TRS Group, Chief Technology Officer, environmental engineer

Session: 3b7

Abstract

Soils contaminated by per- and polyfluoroalkyl substances (PFAS) present a unique challenge because the options for treatment are extremely limited. Excavation and off-site disposal/treatment is problematic because of the inherent liability for the PFAS contaminants present in the soil. Even thermal destruction in soil burners may be problematic due to the potential formation of byproducts.

Laboratory-scale thermal treatment studies using PFAS-impacted solids at temperatures between 350 and 400oC have shown great promise; all 28 targeted PFAS compounds were effectively removed to near non-detect concentrations. These findings are consistent between studies performed by TRS Group, Jacobs Engineering, and Kruger.

TRS completed the first field-scale thermal treatment of PFAS in soil demonstration in December 2021 at Eielson Air Force Base in Alaska.

This U.S. Air Force Base has approximately 150,000 cubic yards of PFAS-laden soils stored in 52 above-grade piles. With funding from the U.S. Department of Defense's Environmental Security Technology Certification Program, TRS treated one of the piles on site. Activities included:

• Laboratory soil heating studies – including experiments designed to look for non-targeted compounds and potential by-products formed during heating

• Field demonstration of thermal treatment of one stockpile using 48 heaters and nine soil vapor extraction wells – a three-month-long operation which brought the soil to temperatures above 350oC

• Extraction of vapors and on-site treatment using cooling, condensation, and granular activated carbon

• Soil sampling and determination of PFAS concentrations before and after treatment

To our knowledge, this is the first field-scale PFAS soil thermal treatment demonstration that focuses on providing a detailed understanding of the process. The detailed sampling and analysis demonstrated PFAS reductions and served to identify the fate of precursors and by-products. As part of the off-gas sampling effort, the new U.S. Environmental Protection Agency OTM-45 vapor sampling method was deployed.

The presentation will focus on lessons learned from the field demonstration, PFAS behavior and fate, and considerations for scaling up the process to treat large volumes of PFAS-laden soil piles.

<u>Session 3b7 / Abstract title</u>: Thermal Conductive Heating (TCH)

ID: 226

Key words: Soil, TCH technology, Population safety, Urban regeneration, Target concentrations

Submitter: Rodolfo Costa

Organization: Arcadis Italia

Co-authors: nan

Session: 3b7

Abstract

This work describes the executive phases of an in situ Thermal Conductive Heating (TCH) of an area of 32400 m2 in Northern Italy.
The purpose of the intervention was to bring the concentrations of pollutants present in the saturated soil to the source areas (NE and SW), within the Limit Risk Concentrations defined through the site-specific risk analysis.
The main contaminants are Chlorinated Solvents (mainly Monochlorobenzene, Trichloromentane), BTEX (mainly Benzene and Toluene) and Hydrocarbons.
The choice of the methodology was based on technical-economic feasibility, environmental risk management and sustainability criteria, minimizing the impacts associated with the transport of contaminated soil and to achieve the target concentrations of the project in the shortest possible to safeguard the population.
TCH technology is particularly suitable for the treatment of volatile (VOC) and semi-volatile compounds even in soils with low permeability; it provides for the input of energy into the subsoil to increase the temperature of the soil and interstitial water, resulting in an increase in the volatility of VOCs and the desorption of the separated phase from the soil matrix.
Once volatilized in the pores of the soil, the VOCs are transported through a special extraction system which guarantees the migration of the pollutants towards the treatment unit.
For heating the ground, 120 heaters were installed in the NE area and 220 in the SW area, arranged according to a regular grid to guarantee a homogeneous distribution of heat.
After heating, effluents generated were captured by a ventilation system designed to avoid both emissions into the atmosphere and fugitive emissions.
For this purpose, 8 MPE wells were therefore installed in the NE area and 15 MPE wells in the SW area for the capture of both the vapors and the liquid phase, and 33 SVE wells in the NE area and 49 in the SW area for aspiration of vapors alone.
The effluents were subsequently conveyed to the treatment plant consisting of catalytic oxidation and consequent basic washing.
To verify the heating of the land, 14 wells were built in the NE area and 29 in the SW area,

equipped with probes able to continuously monitor the vertical distribution of temperatures. The entire system was managed in parallel on site and remotely. The data were processed in real time and made it possible to modulate the heating to optimize the input of thermal energy and protect the safety of the operators and of the near inhabitants, guaranteeing the optimal treatment of the effluents.

Approximately 14 tons of contaminants consisting mainly of Monochlorobenzene were recovered in the NE treatment area.

During heating, daily extraction peaks (max around 350 kg/day) occurred due to evaporation of DNAPL pockets. Peaks of 40% of LeL were detected at the inlet sensors of the treatment plant which caused safety blocks to the catalytic oxidation plants.

To ensure continuity of treatment, the intervention was modulated to split the main peak into two peaks of lower intensity, such as not to cause blockage of the oxidizers; once this change was made, the intervention continued as planned.

The NE area has been reclaimed as emerged from the results of the land verification surveys in June 2020.

In the SW area, almost 12 tons of contaminants were recovered, mainly consisting of Monochlorobenzene.

In the light of what occurred in the NE area, the intervention strategy in the SW area was immediately oriented to avoid excessively high daily extraction peaks: the heating was distributed in such a way as to treat areas in portions, by applying higher temperatures in correspondence with the most contaminated areas and lower temperatures in correspondence with the less contaminated areas. This strategy was efficient and made it possible to distribute the contaminant extraction peak and extract the contaminants and subsequently treat them to the catalytic oxidation plants in complete safety.

<u>Session 3b7 / Abstract title</u>: CAN LOW TEMPERATURE THERMAL DESORPTION BE CONVERTED TO DESTRUCTION AND BE MORE SUSTAINABLE THAN TRADITIONAL INCINERATION

ID: 276

Key words: Persistant organic Pollutants, PFAS, Pesticides. Dioxins

Submitter: Søren Eriksen

Organization: Krüger A/S

Co-authors: Niels Ploug, Krüger A/S, Soeborg, Denmark Steffen Griepke Nielsen, TerraTherm, Gardner, MA, US

Session: 3b7

Abstract

Can thermal remediation be designed to be more than a simple separation of contaminants from soil?
High temperature thermal conductive heating (TCH) remediation at 300 - 350 ˚C has been utilised for decades to remediate contaminated soils both in situ and ex situ. TCH has a documented effect for a range of persistent organic pollutants like Dioxin, PCBs, Lindane and PFAS as well as mercury and PAHs. A literature study suggests that DDT can also be treated successfully.
Tailoring the remediation process to favour thermal degradation of contaminants can greatly reduce the risk of operation, simplify the treatment system and associated costs and limit the need for disposal of waste products like spent activated carbon.
Full scale remediation projects have demonstrated significant thermal degradation of the contaminants in the soil during the heat treatment process, e.g. dioxins (99%) even where thermal degradation processes were not believed to be a major removal mechanism.

In order to reduce operator risk arising from the highly toxic pesticide parathion, a 40 ton pilot scale project was designed to optimise thermal degradation. During operation 99.99% destruction of parathion in the soil was achieved.

Recently a lab scale study has implemented a similar approach to PFOS remediation and has demonstrated near complete conversion of PFOS to inorganic (water soluble) fluoride 25% and insoluble species (75%) with only 0.05% left as PFOS. The investigation of the reactions and the insoluble fluorine species formed is ongoing.
A common feature of the high temperature processes is that the thermal degradation forms more volatile degradation byproducts that more easily can be removed by simple evaporation. The chemical reactions need to be controlled and monitored, to ensure that all

reaction products are accounted for and included in the monitoring program. The degradation reactions can potentially be optimised to result in complete degradation or even mineralization if sufficient reaction time at elevated temperature is obtained.
The presentation will show examples of how in-situ or on-site thermal desorption can be operated towards thermal destruction in a far more sustainable way than traditional incineration consuming 5 to 8 times more energy due to the soil having no caloric value. Using this approach it is likely to ease the stress on fixed incineration facilities as well as avoiding long and sometimes cross bordering transports of highly toxic substances.
Some sites will contain high mass pure substances where a combination of handling pure chemicals combined with in-situ or on-site thermal desorption/destruction of contaminated soils will be a safe and sustainable approach.

<u>Session 3b7 / Abstract title</u>: Validation of the applicability of In Situ Thermal Desorption (ISTD) for the remediation of a site contaminated with mercury beads

ID: 333

Key words: Mercury Beads in soil; Laboratory trials; venting; In-Situ Thermal Desorption

Submitter: Pierre-Louis Guillerm

Organization: Ramboll

Co-authors: Pierre Guibert, Ramboll, Principal Consultant

Session: 3b7

Abstract

Purpose of Study
Pilot studies were undertaken to assess the feasibility of the remediation of highly impacted soils containing mercury (Hg) beads.
Two options were evaluated:
Option 1: Excavation, on-site pre-treatment by stabilization before off-site disposal
Option 2: In-Situ Thermal Desorption (ISTD) and off-site disposal of Hg condensates

Methodology
For the excavation option, the following studies were undertaken:
- Stabilization tests in laboratory. Soil samples were mixed with chemical agents (cement, Na2S, CaS5, FeCl3 and TMT15). Leachable Hg was tested for each stabilization recipe and compared to the control
- Vibration tests in laboratory. Soil samples were placed in a vertical column and constant vibration was applied. Hg was then analysed at different column's depths to check for potential Hg vertical migration consecutive to vibrations
- Geotechnical investigations and dimensioning of reinforcement

For the ISTD option, the following studies were undertaken:
- Soil thermal capacity test in laboratory to know how the soil would react to heating and how much energy would be needed
- Thermal desorption trials in laboratory on batch to determine the optimal temperature (T) and exposure time (t). Soil samples were heated in an oven at 250, 350 and 450°C and during 24, 48 and 168h
- A desorption trial in laboratory at the optimal conditions (T and t) with an additional air flow. Hg repartition and mass balance was estimated by measuring Hg on different media (soil, water and air effluents and condensate)

- In-situ venting trial in the vicinity of the Hg hotspot. Four extraction flows were tested on site. Depression, CO_2 and O_2 were monitored on three standpipes located at different distances from the extraction well

Results

The test results for the excavation option demonstrate that:

- the best chemical agents for the stabilization are CaS5 and TMT 15 with a reduction of more than 80% of leachable Hg
- no migration of Hg is observed in soils subjected to vibration
- Berlin walls are applicable on site

The test results for the ISTD option indicate:

- a relatively low soil thermal capacity (0,7 to 1,1 kJ/kg/°C). This means less energy will be consumed to heat the ground in comparison to “average” soil
- a greater depletion of Hg concentrations when the soil is heated up to 450°C (Batch test in laboratory) reaching 99,8% after 48h
- Most of the volatilised Hg is condensed as elemental Hg (> 97%), and only traces of Hg are detected in gas effluent (1,3%) and water effluent (1,5 %). Thus almost no additional costs for the treatment of gas emission or water would be required
- an effective 5,5 m radius of influence for the venting, with an air flow rate of 100 m3/h. Only 8 extraction wells would be required for full-scale implementation

Conclusion

Pilot trials validated the applicability of both remedial options to treat the Hg pollution on the subject site. Compared to the excavation solution, ISTD will reduce Hg exposure time for the future workers and avoid permanent installation (berlin walls) in soil. Additionally, the volume of waste produced will be drastically reduced. It is currently estimated that 10 to 20 tons of Hg condensate will be recovered with ISTD versus 2 000 tons of soil to be excavated, stabilized and disposed of in salt mines in Germany. Finally, the costs for ISTD were estimated to be slightly cheaper than the excavation works and this solution was chosen for the remediation of the site.

Contributions of study

In-situ thermal desorption has only been scarcely implemented around the world for the treatment of Hg-impacted sites. The results of the pilot tests undertaken during this study, demonstrate the applicability of this technology for the subject site. Data collected provide interesting information on Hg speciation and recoverability and allow interesting comparison with standard remediation technologies. A full scale ISTD treatment will be implemented in Autumn 2023 on this site.

<u>Session 3b7 / Abstract title</u>: State of the art for PFAS-impacted soils. What are the available remediation technologies?

ID: 51

Key words: PFAS, remediation technologies, sustainable

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Session: 3b7

Abstract

Per- and polyfluoroalkyl substances (PFAS) are a group of highly persistent chemicals that have been widely used in industrial and consumer products. Due to their mobility and ability to leach into soil and groundwater, these chemicals can pose a significant threat to human health and the environment. PFAS can enter soil through various pathways, such as industrial discharges, landfills, and agricultural use, and once in soil, they can migrate into groundwater and potentially contaminate drinking water sources. Additionally, they can be taken up by plants grown in contaminated soil and enter the food chain through consumption. Long-term exposure to these chemicals can cause adverse effects on human health and the environment, including increased risk of cancer, thyroid disease, developmental problems, and damage to liver and immune systems.
Given that removing all PFAS to zero is practically impossible, addressing the source-zone areas is crucial. This means addressing contaminated soils, in the vadose zone, containing high levels of PFAS and treating them to eliminate the PFAS they contain. However, not many technologies are available to handle these chemicals in soil, given their nature and the specificalities of porous media such as soil. Among the different technologies that can be used to address soil contamination, Soil Washing and Thermal Desorption have been found to be particularly effective in removing PFAS from soil.
Soil washing is a process that involves physically removing the contaminants from the soil using a combination of mechanical and chemical processes. It has been found to be effective in removing PFAS, but it can be costly and may not be suitable for all types of soil. On the other hand, Thermal Desorption is a thermal treatment process that uses heat to separate and remove contaminants from soil. It has been found to be effective in removing PFAS from soil, but it can be energy-intensive and may not be suitable for all types of soil. A combination of these technologies can also be used to optimize costs and achieve the

highest possible treatment efficiency.
It's important to note that these technologies have advantages and limitations, and the results can vary depending on the specific case and PFAS compounds present. Additionally, it's important to consider the potential risks and benefits of each method, as well as the costs, before selecting a treatment approach.
This paper presents the different technologies that can be used to address soil contamination, namely: Containment (landfilling or on-site containment), Stabilization (on-site or at landfill sites), Soil Washing, Thermal Desorption, and Incineration, with a particular focus on combining soil washing and thermal desorption, to optimize costs and achieve the highest possible treatment efficiency. The technologies are compared on the RECAP level scoring, i.e. scoring individually the 5 components of Sustainable Remediation: Rapidity, Effectiveness, Climate-Friendly, Affordability and Predictability.

Session 3b8 orals

Session 3b8 / Abstract title: INVESTIGATING THE USE OF ZERO-VALENT BIMETALS FOR THE DEGRADATION OF CHLORINATED SOLVENTS VAPORS IN THE SUBSOIL

ID: 129

Key words: Chlorinated solvent vapors; Diffuse contamination; Vapor Intrusion; Risk management strategies; ZVI bimetals.

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Session: 3b8

Abstract

In the past decades chlorinated solvents, such as trichloroethylene (TCE), have been used for various civil and industrial applications in a massive and uncontrollable way, contaminating a large number of sites. Indeed, once released in the subsoil, chlorinated solvents are characterized by high mobility and low biodegradability at the same time, with consequent persistence in the environment. For these reasons, many groundwater bodies in industrial and civil areas are affected by diffuse contamination by chlorinated compounds, which can cause potential long-term risks to human health. In particular, the presence of these contaminants in groundwater is challenging for the management of the migration pathway of chlorinated solvents vapors to ambient air or into buildings (i.e. vapor intrusion). Indeed, in sites characterized by diffuse contamination by chlorinated solvents, traditional remediation techniques are not technically and economically sustainable as they typically require high amounts of energy or reagents. In this situation, it is more indicated to adopt risk management strategies to interrupt the migration pathways of contaminated vapors. Recently, it was proposed to use horizontal permeable reactive barriers (HPRBS) placed in the unsaturated zone to degrade chlorinated solvents vapors. Namely, Zero-valent iron (ZVI) was proposed as filling material for HPRBs and tested for TCE degradation in the vapor phase through abiotic reductive dehalogenation. In the last years, ZVI bimetals based on iron and a secondary transition metal have also been widely investigated for the enhancement of chlorinated compounds degradation in the aqueous phase. In particular, the

addition of a secondary transition metal (e.g. Cu or Ni) to iron increases the rate of reduction of chlorinated contaminants, as these metals are catalysts of iron corrosion reaction and of the dissociation of molecular hydrogen on the surface of the material. However, such bimetals have been so far poorly investigated for the treatment of chlorinated solvents in the vapor phase. In this study, we investigate the use of zero-valent Fe-Cu ad Fe-Ni bimetals for the degradation of TCE in the vapor phase at partially saturated conditions. Different bimetals were synthesized by mixing Fe and Ni or Cu powders at different weight percentages (i.e. 1%, 5%, 20%) using disc milling and then characterized. Afterward, the produced bimetals were involved in anaerobic batch degradation tests of TCE in the vapor phase at different reaction times to evaluate their reactivity towards dechlorination. From the characterization analyses, the disc-milled bimetals produced presented particles with micrometric size and homogenous distribution of Cu or Ni in the iron phase. In all the tests, complete degradation of TCE vapors was achieved in maximum 4 days with zero-order degradation kinetics. Fe-Ni bimetals have shown better performances in terms of TCE removal compared to Fe-Cu ones leading to complete TCE degradation in the vapor phase after 2 days of reaction. These results showed a significant enhancement in TCE removal compared to using ZVI alone, which was found to entirely degrade TCE vapors after minimum 2 weeks of reaction in previous works. The only detectable reaction byproducts in the tested conditions were C3–C6 hydrocarbons, with no presence of vinyl chloride (VC) or dichloroethylene (DCE). In view of using the tested bimetals as constituents for HPRBs to treat chlorinated solvent vapors in the subsoil, the experimental results achieved were integrated into an analytical model to simulate the reactive transport of contaminated vapors through the barrier. From this model, it was found that an HPRB of approximately 20 cm could ensure a complete degradation of TCE in the vapor phase.

<u>Session 3b8 / Abstract title</u>: Evaluation of chlorinated ethene degradation by an integrated approach in the risk assessment of a contaminant plume influenced by source and barrier remediation

ID: 152

Key words: Chlorinated ethenes, risk assesment, degradation, CSIA, molecular microbial tools

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Session: 3b8

Abstract

Purpose of Study Remediation of severe source zone contamination with chlorinated ethenes at a former gas regulator production site has included excavation, NAPL pumping and thermal treatment with steam and installation of a ZVI funnel and gate reactive barrier intercepting the plume at the site in early 2000's. However, the primary flow of groundwater and the plume pass by (not through the barrier) resulting in the plume heading for the town Hedensted. The heating and the ZVI installation has changed conditions in the plume and increasing levels of vinyl chloride (VC) reveals ongoing reductive dechlorination. The purpose of the current study is to evaluate the natural/stimulated attenuation of the plume for evaluation of the current risk associated with the contamination. An integrated approach including CSIA and molecular biological tools is applied to identify and document biogeochemical processes in the plume.

Methodology 4 transects of each 8-10 boreholes with depths until 10 m below surface have been established with a distance of 25, 50 and 60 meters respectively across the plume flow line downstream the source area. Concentrations of chlorinated ethenes, degradation products, redox conditions and NVOC have been measured in the groundwater samples from all boreholes. CSIA of C and Cl and molecular microbial tools have been used on selected samples both along the groundwater flow line in the plume and in representative samples in each of the transects. Groundwater flow rates and contaminant mass discharge across transects has been established.

Summary of findings/results The source area is still highly contaminated with chlorinated ethenes. Downstream the source area two plumes are observed in the groundwater; one where primary TCE is present representing water from the source area (thin plume 10 m)

and another where degradation products are present representing back diffusion from the clay till matrix (wider plume 20 m). In the central part of the plume chlorinated ethenes and degradation products are observed up to 3 m into the clay till matrix. Groundwater will therefore be affected both by contaminants from the source area and by back diffusion from the clay till matrix for many years to come. The microbial analysis revealed widespread presence of the specific degraders Dehalococcoides and of the genes responsible for VC degradation. This indicates a good potential for complete dechlorination of the chlorinated ethenes in (parts of) the plume. C-CSIA (analytical results pending) is expected to document degradation of chlorinated ethenes, including VC, and dual CSIA may help in differentiating biotic and abiotic processes (potentially induced by ZVI). From transect 3-4 a significant reduction in the concentration of VC in the groundwater is observed possibly caused by degradation and/or dilution as water from the top of the flow till layer seem to runoff here. Degradation is sought documented based on microbial data and CSIA.

Conclusions Natural degradation processes stimulated by heating and ZVI have resulted in ongoing dechlorination of chlorinated ethenes in the plume. However, degradation processes in the low permeable clay till also influence the contaminant composition in the plume. Better understanding of the ongoing processes are expected to lead to understanding of the effect of current processes on the risk and to identify beneficial approaches to remediation of the plume.

Significance of study The study illustrates that an integrated approach combining concentration measurements, CSIA and molecular microbial tools is a valuable method to document complex processes at a site contaminated with chlorinated ethenes. In the present study documented processes are crucial in the planning of future plume remediation as documented processes have high impact the risk assessment today but also how it will evolve in the future.

<u>Session 3b8 / Abstract title</u>: Effect of zero-valent iron on anaerobic dechlorinating bacteria for remediation of chlorinated methanes and 1,2-dichloroethane

ID: 170

Key words: Nanoscale zero-valent iron, organohalide respiring bacteria, Dehalobacterium, Dehalogenimonas, chlorinated organic pollutants.

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Session: 3b8

Abstract

Nanoscale zero-valent iron (nZVI) has the potential to degrade a diversity of chlorinated compounds and it is widely used for remediation of contaminated groundwaters. However, some frequently detected contaminants such as dichloromethane (DCM) and 1,2-dichloroethane (1,2-DCA) have shown nearly no reactivity with nZVI. Here, we assessed the effect of nZVI on two anaerobic dechlorinating bacteria, Dehalobacterium and Dehalogenimonas, capable of transforming DCM and 1,2-DCA, respectively.
Experiments for this study were developed at lab scale in anaerobic microcosms. Three different treatments were included for each experiment: (i) abiotic controls containing an anaerobic-defined medium and nZVI, (ii) biotic controls containing an anaerobic-defined medium and the corresponding bacterium, and (iii) biotic-abiotic treatments containing an anaerobic defined medium, nZVI and the corresponding bacterium.
An abiotic source of DCM in groundwaters is the hydrogenolysis of chloroform (CF) by nZVI, which accumulates in the medium with no further degradation. In this scenario, the approach of coupling nZVI treatments with functional anaerobic dechlorinating bacteria is promising to fully detoxify such chlorinated compounds, but the effect of nZVI on bacterial degraders has been poorly explored yet. In our study, CF (500 µM) was fully degraded by 1 g/L nZVI to DCM as a major byproduct. The reaction rate was slower when vitamins or sulfur-cysteine lacked in the culture medium , suggesting that they can act as electron shuttling compounds, hence enhancing electron transfer from nZVI to CF. However, there was no significant reactivity of nZVI towards DCM. Our results indicate that nZVI caused an

inhibitory impact on DCM dechlorination by Dehalobacterium activity, but the dechlorination activity was recovered when transferred to a fresh medium without nZVI. The effect of the partial pressure of H2 and pH was studied as potential inhibitors using microcosm tests, but indeed our results pointed to soluble inhibitory compounds released by nZVI as inhibitors. Similarly, a Dehalogenimonas-containing culture was unable to dichloroeliminate 1,2-DCA when exposed to 1 g/L nZVI, but dechlorinating activity was also recovered when transferred to nZVI-free media.

The recovery of the dechlorinating activity after the exposure of bacteria to nZVI suggests that a combination of nZVI and bioremediation techniques can be feasible under field conditions, where dilution processes can alleviate the impact of the potential inhibitory soluble compounds.

These findings have implications for remediation strategies aiming to combine both abiotic and biotic treatments to decontaminate aquifers with mixtures of chlorinated compounds. In particular, our study suggests that factors such as the buffering capacity of groundwaters and dilution processes can play crucial roles in the viability of this combined strategy in bioremediation treatments.

Throughout these experiments, a morphological characterization and the oxidation state of nZVI were studied with a Zeiss Merlin Field-Emission Scanning Electron Microscope (SEM) and a Transmission Electron Microscopy (TEM), respectively. SEM also permitted to visualize the interaction between nZVI and bacterial cells.

<u>Session 3b8 / Abstract title</u>: Technologies options for Rebound control and rapid site closure for ISCO/ISCR treatments

ID: 384

Key words: Rebound Control, Site Closure, ISCO, Injectable Carbons, ISCO

Submitter: Lorenzo Sacchetti

Organization: Carus LLC

Co-authors: nan

Session: 3b8

Abstract

Purpose of Study
To identify In Situ technologies options for rebound control and to achieve site closure.

Methodology
Evaluted esperiences with several clients to understand best practiced to treat rebound from residual NAPL or adsorbed contaminants.

In Situ Chemical Oxidation (ISCO) technologies originated in the 90s of the twentieth century for the removal of organic contaminants (or CoCs: Contaminants of Concern) from soil and groundwater. One of the major challenge to site closure is contaminants rebound that occurs when, after ISCO reagents have been depleted, there is a new release of contaminants from secondary sources.
In recent years, technologies have been developed to reduce rebound through the use of persistent products, surfactants or combinations of adsorption and oxidation/reduction.

A brief description and application cases of these technologies will be presented.
Such technologies allows to reduce the amount of reagents required for site closure and to increase sustainability of remediation actions.

Fidnigs/Conclusion
Several technolgies or combination of technologies showed effectiveness in reducing rebouds and allowinf site closure, in details:

Colloidal Carbons and ZVI: have been designed for a two step action: adosrption of dissolved CoCs to the to colloidal carbons and degradation by ZVI (Zero Valent Iron) embedded into the colloidal carbons. Colloidal Carbons are applied as off-site migration prevention action or after an ISCO treatment. This results in very rapid decrease of dissolved

contaminants (almost below detection limit) and long term adsorption on CoCs released over the time by secondary/poor treated sources to allow rebound control. Injections can be carried out into existing wells, valved pipes or by direct push. Colloidal Carbons can be prepared also without ZVI for non chlorinated CoCs treatment.

Surfactant for remediation applications that has a good resistance to ISCO agents allowing the reduction of surface tension with the consequent pseudo-solubilization and treatment of secondary sources reducing the mass that originates the rebound. Surfactants are applicable to any hydrophobic organic contaminants (TPH, PAH, chlorinated, pesticides...) with a physical and non-chemical effect so it does not react with contaminants and does not generate reaction products/by-products.

Fe-Zeolithes with a modified Fenton technology that involves the injection of Iron Zeolites followed by injection of hydrogen peroxide (hydrogen peroxide) that generates Fenton radicals at the active sites of zeolites. No pH control is required. The temporary adsorption effect on zeolites reduces groundwater concentrations during treatment by reducing rebound. Fenton-type technology is effective on a wide range of contaminants,

<u>Session 3b8 / Abstract title</u>: Biochemical Destruction of Chlorinated Pesticides and Organic Explosive Compounds with Sustainable Organic Carbon/ZVI Reagents

ID: 413

Key words: soil remediation, pesticides, explosives, sustainability

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Organization: Evonik Corporation

Co-authors: Dan Leigh, Evonik Corporation, hydrogeologist; Mike Mueller, Evonik Operations GmbH, business manager

Session: 3b8

Abstract

Introduction and Objectives:
Agricultural, industrial, and military applications of chlorinated pesticides (OCPs), and organic explosive compounds (OE) have resulted in contamination of soil in many countries. Many of these compounds are not adequately degraded using traditional bioremediation approaches. This prompted research on alternate remediation methods and led to discovery of a novel biochemical treatment using reagents formulated using microscale elemental iron (Fe0 or ZVI) and process plant material (Daramend®). A key finding was that greater degradation of OCPs, and OE, was achieved when soil was treated with ZVI plus organic carbon than when ZVI alone or organic carbon alone were used. Over the past 25 years, many soils contaminated with OCPs and OE have been remediated using this reagent and a variety of soil mixing approaches. This carbon/iron approach to soil remediation is a form of in situ biochemical reduction and results in destruction of the targeted contaminants, rather than adsorption and immobilization. It has enabled reliable attainment of common industrial and residential remediation standards, provides a more environmentally sustainable and economical alternative to excavation and off-site soil disposal or thermal treatment.

Methodology and Scope of Work:
Bench-scale research on the organic carbon/ZVI reagents was initiated in 1992 and focused on evaluating various types of organic carbon and ZVI for their influence on soil pH, ORP, and pesticide degradation. Dosage response studies were also conducted at bench-scale. Pilot-scale demonstrations on pesticides and herbicides were completed in 1996 and 1997, and on organic explosive compounds in 1998. Full-scale soil treatment projects using the iron/carbon reagents have been successfully completed in Brazil, Canada, China, Colombia, El Salvador, Europe, Republic of Korea, and the United States. Treatment has been conducted in situ (i.e., without excavation) as well as on excavated soil. Findings from

bench-scale research, pilot-scale demonstrations, and full-scale projects will be presented and discussed from the perspectives of performance and cost.

Results and Conclusions:
The organic carbon/ZVI approach has proven broadly effective in treatment of pesticides, herbicides, and organic explosive compounds in soil. Among the chlorinated herbicides and pesticides successfully treated are 2,4-D, 2,4,5-T, Aldrin, Heptachlor, Metolachlor, Chlordane, Dieldrin, DDD, DDE, DDT, Lindane, and Toxaphene. Treatment has reliably achieved between 90% and 95% reduction in concentrations of chlorinated pesticides with attainment of both industrial and residential land use criteria. As an example the average concentration of Toxaphene in soil at an industrial site in California was reduced from 150 mg/kg to less than 2.0 mg/kg. The organic explosive compounds successfully treated include TNT, DNT, amino-nitrotoluenes, RDX, HMX, Tetryl, and nitrocellulose. Treatment has reliably achieved between 95% and 99% reduction in concentrations of organic explosive compounds with attainment of both industrial and residential land use criteria. As an example the average concentration of TNT in soil at a military site in Virginia was reduced from over 15,300 mg/kg to less than 6.0 mg/kg. The observed rate and extent of OCP and OE destruction was influenced by a variety of factors including physical and chemical soil characteristics, contaminant concentration and solubility, and site conditions. Results from completed projects will be used to illustrate attainable performance as well as recognized limitations to the organic carbon/ZVI treatment approach for chlorinated pesticides and organic explosive compounds.

Session 3b9 orals

Session 3b9 / Abstract title: In-situ soil remediation at low-permeability sites using the hydraulic/pneumatic fracturing (FRAC-IN) approach

ID: 125

Key words: fracturing; hydraulic; pneumatic; ISCO; ISCR

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Session: 3b9

Abstract

- Purpose of the study

The issue of minimal spreading of injected remedial agents at sites with low permeability can be overcome by fracturing of the geological formations. However, the fracturing technology currently employed in Europe is unsuitable for the injection of remedial agents. The so-called Frac-In method combines direct-push drilling with pneumatic/hydraulic fracturing and the subsequent hydraulic emplacement of the remediation agents so as to enable the remediation of low permeable aquifers. The technology has been tested in the Czech Republic at 2 differ-ent sites and was used in the full-scale remediation of one of the sites.

- Methodology

The initial pilot testing of the technology was conducted at a site with a complicated hetero-geneous geology that was contaminated with chlorinated ethenes. The contamination was fixed in low-permeable sandy clays in both the saturated and unsaturated zones. The aquifer at the site shows low permeability (ranging from 10-5 to 10-6 m/s) with preferential flow paths. The pilot test remediation technology consisted of ISCR (using milled cast iron and sulfidated nanoscale zerovalent iron) combined with ERD (using dried whey).

The second pilot test was conducted at the site with groundwater that was contaminated with a mixture of solvents, predominantly 1,2-DCA, chloroform and dichloromethane. The aquifer at this site is developed in poorly permeable loamy soils. The remediation technology used at the site consisted of ISCO using a mixture of sodium and potassium persulphate with differ-ing activation processes.

Full-scale remediation using the Frac-In technology was conducted at the Duchcov site at which a heterogeneous poorly permeable quaternary aquifer was contaminated mainly with hexavalent chromium and chlorinated ethenes. In a similar way to the first pilot test, ISCR (using milled cast iron, microscale iron and sulfidated nanoscale zerovalent iron) combined with ERD (using glycerol) was utilised as the remediation technology.

- Summary of the findings/results

Concerning the first pilot test, the long-term monitoring of the groundwater revealed that ISCR was the dominant degradation process during the first few months after injection. This was followed by a significant increase in the amount of dechlorinating bacteria and the degra-dation of the majority of the contamination in both the saturated and unsaturated zones.

A significant increase in the hydraulic permeability of the aquifer together with the good distribution of the injected remediation agents were observed at the second site. A mean decrease of 62% in the sum of the volatile organic compound concentration was observed via the monitoring of boreholes 4 months following the injection campaign. It was also proved that the injection of highly reactive and corrosive remediation agents is possible using the Frac-In technology.

The injections at the Duchcov site triggered the inorganic chemical reduction of both the hexavalent chromium and chlorinated ethenes as well as a gradual increase in the amount of dechlorinating bacteria. The full-scale application of the Frac-In technology proved to provide a viable solution for the remediation of the site.

- Conclusion/significance/contributions of the study

The Frac-In technology enables in situ remediation of the soil at low-permeability sites that are difficult to remediate using conventional technologies via the application of hydraulic/pneumatic fracturing. It can be used for the injection of strong chemical oxidants in combination with oxygen release compounds so as to enhance the rate of aerobic biodegradation, as well as the injection of chemical reductants in combination with organic substrates so as to enhance the rate of anaerobic biodegradation.

<u>Session 3b9 / Abstract title</u>: LNAPL Recovery from low permeability strata by means of sand layer injection using i-SAV© technology and non-ionic surfactant application

ID: 166

Key words: surfactants, sand injection, LNAPL removal

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Session: 3b9

Abstract

Purpose of study
The herein described pilot test was aimed at assessing the effect of sand layers in combination with a surfactant addition for extraction of the mobile available gasoline phase from a low-permeable strata.
Methodology
Sand layers with a total of 8.5 tons of sand were emplaced in the contaminated subsoil by means of hydraulic stimulation (i-SAV© technology) at one injection bore. Nine sand layers in a depth section between 16.6 m and 19.6 m were successively constructed at vertical depth intervals between 30 and 50 cm distance. The subsurface site strata in which the sand layers were emplaced consists of low-permeable partially fissured fine sediments such as silts, clays and sands as wells as carbonates, and residual sulphates (gypsum).
A viscous suspension of drinking water, carrier medium and sand were injected. The injection pressure exceeds the cohesion forces of the silty/clayey rock allowing the suspension to penetrate the rock as a dedicated layer.
The addition of non-ionic surfactants sourced from Ivey Inc. at concentrations below the critical micelle concentration improve the extraction of the gasoline phase (LNAPL) by mobilization while reducing the interfacial tension (IFT) of the water-oil system and changing the wettability. As a consequence, the reduction of the IFT leads to a reduction in entry pressure. A reduction of the IFT has a particular effect on the continuous mobile LNAPL as it reduces the capillary forces. Therefore, the sand-gel was coated with a surfactant-water mixture immediately after injection thereby making available the gasoline phase to the sand layers.
Results of the pilot test
The areal coverage of the sand layers and their 3D orientation were recorded by means of tiltmeter measurements. In summary, a maximum radius of influence (ROI) of 6 m was recorded for most of the nine fracs.

The removal of the gasoline phase in the area of the pilot test was carried out after the placement of the sand layers by vacuum enhanced recovery and dual phase extraction (DPE). From the extraction well placed at the location of the injection borehole approximately 1,230 L of gasoline phase could be extracted over a period of 3 months. The output was far above the predicted extractable volume in the pilot test area.

In order to answer the question of whether a detectable increase in permeability of the sedimentary rock for the extraction of the mobile gasoline phase was made possible by the sand injections, existing data from CPT soundings and results from the groundwater potential measurements were evaluated.

The sand layers injected have a permeability K of 2E-4 m/s to 1E-3 m/s and are significantly more permeable compared to the formation (K=1E-6 m/s to 1E-7 m/s). The injection of sand layers increased the average rock permeability by a factor of 6 compared to the initial situation, allowing an LNAPL extraction rate of more than 40 L/d. Furthermore, the effective porosity increased by 50% by the introduction of nine layers of sand with a cumulative thickness of 10 cm.

The additional effective porosities generated by the sand layers in the order of 2 m^3 act like a macropore enabling the passive penetration of mobile LNAPL into this macropore/sand layers. This means that up to 2,000 litres of LNAPL can theoretically be stored in the sand layers.

By adding surfactants to the permeable sand layers, the entry pressure into the coarsely porous and permeable sand layers is reduced allowing the LNAPL to be extracted through DPE.

Conclusion

We conclude that a significant LNAPL recovery can be achieved from low permeability strata by means of sand layer emplacement using i-SAV© injection technology and non-ionic surfactant application.

Significance / contributions of study

Permeability enhancements through sand injections coupled with the application of modern non-ionic surfactants provide a realistic remediation methodology for LNAPL removal from low permeability strata.

<u>Session 3b9 / Abstract title</u>: LIFE Frac In: Enabling in situ soil remediation on low-permeability sites through hydraulic and pneumatic fracturing

ID: 412

Key words: remediation, In-situ, fracturing, injection

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Session: 3b9

Abstract

The pattern of ground remediation practices is altering from traditional excavation and 'ex-situ' treatment toward in-situ treatment technologies. This shift is caused by increased regulatory control of landfill operations and associated rising costs, combined with the requirements on sustainability and the ongoing improvement of in-situ ground remediation techniques. In the case of in situ chemical or biological treatments (ISCO, ISCR, biodegradation, stabilization, sorption, etc.), different remediation agents are injected into the soil for contaminant removal/breakdown. Successful treatment of the soil depends on direct contact between the remediation agents and the contaminant. Therefore, proper distribution of the remediation agents into the contaminated matrices is crucial.

Direct push (DP) is an innovative delivery method used for injection of soil remediation agents in situ, while omitting the need for permanent wells. This reduces material and operational costs and makes it possible to achieve higher treatment efficacies. A variety of remediation agents (oxidants, reduction agents, nutrients etc.,) both in liquid and solid (suspension) form can be injected via DP. The main limitation of DP is poor applicability for sites with a low permeability (permeability below 10-5 m/s). While proven successful for highly permeable soils, this limitation is currently hampering the application of in situ chemical or biological treatment in low permeable soils.

The problem of minimal spreading of injected remedial agents in low permeability soils can be overcome through soil fracturing (hydraulic, pneumatic or blasting). However, the existing fracturing technology is not suitable for a remediating agents' injection without the installation of special wells. The FRAC-IN technology combines Direct-Push drilling with pneumatic and hydraulic fracturing to inject remediation agents in low permeable contaminated soils , thus enabling in situ treatment. The injected suspension consists of a water-sand-guar gum mixture, containing tailor-made remediation agents such as coarse milled iron filings

(recycled waste material) and/or other chemical reductants or oxidants, and carbon/oxygen sources to enhance bacterial activity.

Several contaminated sites (5 in Belgium, 2 in Czechia) have been selected for pilot testing of the FRAC-IN technology. Thus a wide range of geological and contamination conditions are represented. On 1 Belgian site, Cr(VI) contamination is present in the banks of a motorway, due to waste from a chromate plant. A direct push injection pilot failed because of the low permeability of the sandy clay soil. At another Belgian site, chlorinated solvents are present in groundwater due to historical meal works activities (degreasing). The soil consists of sandy and loamy clays and hence is poorly permeable; limiting the available remediation solutions. Overall, 12 to 36 injections will be performed per site with various remediation agents injected at regular intervals.

The objective of the proposed LIFE project is to validate the FRAC-IN technology in different field conditions and soil types, to provide a list of reference projects for potential customers and to speed up the wider implementation of the technology for full scale applications. Verifying the optimal operating conditions, the vertical working ranges and the compatibility of FRAC-IN with established remediation agents will result in operational guidelines. The first pilot tests were initiated in 2018. At the conference, the application of the FRAC-IN technology at several pilot test sites, as well as the achieved clean-up of each encountered contaminant, will be presented.

<u>Session 3b9 / Abstract title</u>: CROSS-BOREHOLE ELECTRICAL MONITORING IN GROUNDWATER REMEDIATION PROJECTS: UNDERSTANDING THE FLOW PATH OF REMEDIATION AGENTS

ID: 50

Key words: in-situ remediation; ZVI; ISCO; electrical resistivity tomography

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Session: 3b9

Abstract

Industrial application of environmentally hazardous substances have led to contamination of important groundwater aquifers worldwide. Several remediation techniques exist, such as excavation, pump-and-treat, and in-situ remediation. Excavation is effective but it is associated with significant pollution and resource use, especially below a couple of meters depth. In situ remediation technologies, considered less invasive, are discussed here. They rely on the installation of a treatment zone, where a reactive agent is injected to chemically and/or biologically degrade the contamination.

Adequate delivery in the target volume is a major challenge for in-situ remediation. Preferential pathways, and more generally permeability contrasts, might lead to incomplete contact between contamination and reagent. This increases the risk of insufficient treatment followed by rebound effect, where contamination starts diffusing back into more permeable zones after remediation, resulting in an aquifer still contaminated in the long-term. In order to identify incomplete treatment and take appropriate action, it is essential to monitor the reagent distribution during the injection program. Sampling-based approaches provide accurate information at a given location, but yield limited spatial and temporal resolution. This limitation can be overcome by geophysical imaging techniques, such as electrical resistivity tomography (ERT). ERT imaging uses the electrical signature of reagents to provide a spatially continuous assessment of the reagent distribution. The cross-borehole

ERT method (XB-ERT), which significantly improves data quality and spatial resolution at the relevant depths compared to surface ERT, is particularly useful in remediation contexts. It has recently been applied to monitoring full-scale and pilot-scale remediation campaigns in Denmark.
Kærgård Plantation is one of the 20,000 Megasites identified among the 2.8 million contaminated sites in Europe, with over 300.000 tons of pharmaceutical waste dumped in sand dunes between 1956 and 1973. Two full-scale remediation campaigns were carried out in 2019 and 2021, involving 100 wells for injection of peroxide activated persulfate and 30 electrode-boreholes for XB-ERT monitoring. The chemical oxidation mostly targets hydrocarbons in the contamination hot spots, in the top eight meters below ground surface, where the geology consists of sand and gravel layers. We show that resistivity monitoring quantitatively reflects the spreading of sulfate ions related to reagent injection. Reagent transport caused by groundwater flow and density sinking is assessed thanks to regularly repeated profiles. Using standard instruments and geophysical inversion, we also provide 3D visualizations of reagent spreading that allow identification of untreated zones.

Farum contaminated site is located on a paved parking lot in the suburb of Copenhagen. Waste from a packaging and plastic factory active in the period 1959-1989, led to several groundwater contamination hotspots. The chemical reduction agent Provect-IR®, contains micro-scale zero valent iron, targets chlorinated solvents, in the range 10-20 m below ground surface. Geology consists of quaternary sandy till in the top 3-5 m of the investigated volume, underlain by glacio-fluvial meltwater sands. The treatment zone installation at this ZVI pilot site was more challenging: two injection rounds were attempted with different strategies and both led to heterogeneous spreading, as well as significant upstream leakage and surface spills. Based on time-lapse XB-ERT results, chemical monitoring, as well as solid iron analyses in core sediments, we suspect the creation of preferential pathways during injection, due to the high viscosity of the product and the high pressure used for the injection. We explore to what extent these engineered preferential pathways may play a role on the long-term contaminant and amendment transport properties.

<u>Session 3b9 / Abstract title</u>: Injection of colloidal reagents for in situ soil remediation: lessons learned on more than 100 projects over Europe

ID: 93

Key words: Colloidal, direct injection, efficient, in situ soil remediation

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Session: 3b9

Abstract

Purpose of study
In the last decades, in situ soil remediation with injection of reagents became more and more accepted and applied as a sustainable and efficient remediation technique. Different injection techniques are suitable for the injection of soluble and liquid reagents depending on the geology of the site; injection wells and recirculation systems are ideal for homogeneous sandy aquifers, whereas soil mixing and direct injection techniques suit best in heterogeneous and low permeability aquifers or soil layers. For these kind of reagents, the injection pressure (IP) is the key parameter to be controlled. The injection of colloidal or emulsified reagents, on the other hand, needs more knowledge and understanding to achieve a homogeneous distribution within the aquifer material. In recent years, Injectis performed multiple injection projects with colloidal or emulsified reagents using the patented SPIN® injection technology and bundled these experiences in order to optimize their injection working procedures.
Methodology
The field experiences on multiple sites and with different colloidal reagents (CR) were used as most valuable input to develop a decision tree for the working procedures as a manual for the injection of this type of reagents.
Summary of findings
Injection of colloidal or particulate reagents in different aquifer materials resulted in varying findings:
The precipitation of particles can be overcome by thorough mixing, high flow and pumping rates and/or addition of a thickening agent to increase the viscosity of the mixture. These high flow rates and thorough mixing of the colloidal mixtures makes them act as the perfect “scouring powder", resulting in abrasion of all equipment in contact. The abrasion severity is function of the size and hardness of the particles and the sensitivity of the materials. The

gradual increase in IP with increasing volume injected clearly seemed to be a result of the sieving/filtering out of the particles near the injection point. This filtering effect gives rise to clogging of the natural porosity of the aquifer material resulting in a significantly lowered hydraulic conductivity. To maintain the injection flow rate, IP increases. In most cases, higher IP were needed to inject colloidal mixtures, partly due to this clogging effect and/or the use of a thickening agent. These higher IP frequently resulted in a unintended exceedance of the fracturing pressure. This unintended (micro-)fracturing gives rise to arrival of the reagents in artificial fractures/cavities in the aquifer and hence not in homogeneous distribution in the natural soil porosity. For some reagents, this might not be an issue, but for reagents stimulating a reaction (e.g. sorption) where physical contact between reagent and pollution is crucial, this fracturing might be problematic.

In another case, it was observed that the CR was flushed out from the injection zone within a relatively short period of time. Groundwater velocity in combination with the ratio particle size/pore size seemed to be on the basis of this phenomenon.

Conclusions

The principal cause of most of the above experienced problems/limitations find its origin in a bad (or no) matching of the particle size of the reagents with the pore size distribution of the aquifer material. Additionally, the use of a thickening agent should be kept to a minimum.

Significance / contributions of study

Zero Valent Iron (ZVI) products are frequently used to treat chlorinated solvents, iron oxyhydroxide and iron sulfide minerals for heavy metals immobilization, colloidal activated carbon for sorption of all type of organic pollutants and different types of colloidal sorbents for in situ PFAS immobilization. All these reagents have colloidal properties and need thorough knowledge, understanding and experience to achieve homogeneous distribution in the aquifer material for an optimal remediation result.

Session 3b orals

Session 3b / Abstract title: Pilot test of PCE sources mobilization in the transition zone to aquitards by combining ISCO and biostimulation techniques

ID: 115

Key words: DNAPL pools; remediation field pilot test; combined remediation method; abiotic reduction with mZVI; biostimulation with lactate

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Organization: University of Barcelona

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Session: 3b backup

Abstract

The potential toxic and carcinogenic effects of chlorinated solvents in groundwater on human health and aquatic ecosystems require very effective remediation strategies of groundwater contaminated to achieve the low legal cleanup targets required.
The main objective of the present work is to analyze at the field scale the combined use of microparticle Zero Valent Iron (mZVI) and lactate biostimulation in the form of lactic acid (LA), to favor the mobilization of the recalcitrant Dense Non Aquose Phase Liquid (DNAPL) sources located in the transition zones between aquifers and aquitards.
In order to develop the remediation technology, a field site contaminated by PCE, located in Vilafant, about 140 km northeast of Barcelona near the border between Spain and France, was chosen.
Once the contamination source architecture was characterized, in which PCE pools were detected in the transition zone, sediment and groundwater samples were obtained for microcosm tests. The potential efficiency of combined techniques of insitu chemical reduction, with micro zero valent iron (mZVI), and biostimulation, with lactic acid, was tested. Once tested at laboratory scale, a pilot test a combined strategy using ZVI in microparticles and biostimulation with lactate in the form of lactic acid was conducted. To check the efficiency of the technology, we were monitored the pilot test for 504 days. Groundwater samples were used to analyze the evolution of the redox conditions, chloroethenes and microbiological communities in the subsoil. This has made it possible to characterize the main biotic and abiotic processes that favor the total degradation of the original PCE pool in

the transition zone and to evaluate the degradation rates that have taken place.
Following the activation of pilot test, a rapid enhanced degradation-dissolution PCE DNAPL process initiated that led to the mobilization of the DNAPL pool.
The LA biostimulation of the halorespiring activity of genera of chlorinated solvents reducing microorganisms of the medium (Dehalococcoides, Geobacter, Sulfurospirillum and Treponema) promoted the incomplete biotic reductive dechlorination of PCE.
The occurrence of genera of chlorinated solvents oxidizing microorganisms under the oxic conditions generated by the oxygen supply during the recharge periods of part of the rainfall (Nocardiodes, Aciditerrimonas, Phenylobacterium, and Nitrosospira) enabled the oxidation of metabolites products. This would be comparable to a certain coupling between biotic reductive and oxidative degradation processes.
The mZVI injected abiotically degraded PCE and the other products from its biotic degradation transforming them into chloroacetylenes. The latter were converted into the harmless acetylene.
After 500 days removal efficiencies ranging from 83.4% to 96.3% of the PCE from the PCE pool.
The pilot test has shown that a coupling and interdependence between biotic and abiotic processes has occurred. This has allowed the generation of the necessary synergies for the efficient mobilization of recalcitrant pools in transition zones from the aquifer to the bottom aquitard, which is the main novelty of the current research.
Our contribution has been the development of a technology, that is patent, for the remediation of DNAPL pools located in the transition zones.

<u>Session 3b / Abstract title</u>: The conceptual model of a persistent chlorinated solvent plume must include the consideration of micro DNAPL far from the source release area

ID: 136

Key words: DNAPL, remediation, mercury tracer, oxidation

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Session: 3b backup

Abstract

In performing in situ remediation of hundreds of large and persistent chlorinated plumes, we have often found response inconsistent with the commonly held belief that matrix back diffusion is the primary driver of long-term, high-concentration contamination. A primary aim of our field study was to confirm the presence of remote DNAPL using a novel, opportunistic NAPL tracer (metallic mercury) as well as a chlorine balance after oxidants were injected in a small area of a plume more than 650 m from the source release area. If NAPL is the primary driver of contamination rather than back diffusion, as we found in our field test, there is a higher potential for faster, cost-effective remediation.

At the U.S. Department of Energy's Savannah River Site (SRS), 1.7 million kilograms of chlorinated solvents were released to the subsurface as DNAPLs in a settling basin and through leaks in a sewer line connecting the manufacturing area to the basin for 35 years until 1985. Despite the installation of hundreds of wells, DNAPL was only collected from one well adjacent to the settling basin. However high aqueous concentrations were found in wells along a tortuous path consistent with density travel along fine grain strata more than a kilometer west of the basin and not consistent with groundwater flow. These observations led to the SRS conceptual model of long-distance DNAPL transport which conflicts with the common assumption of limited DNAPL travel, dissolution into groundwater near the source release, aqueous transport over long distance to create extensive plumes, and remote plume persistence due exclusively to matrix diffusion. Although multiphase transport theory clearly allows for DNAPL movement over large distances through porous media, available literature generally presumes that chlorinated solvent DNAPL transport and deposition is limited to "near" the release area in most contaminated site scenarios, especially when the

contaminant release was not recent. Until this field test was performed, a plethora of both conventional and innovative high-resolution characterization techniques could not definitively determine if the persistent, high aqueous concentrations found in the distant plume were due to groundwater transport from the release area, matrix diffusion, or localized, lingering DNAPL.

In addition to chlorinated solvents as DNAPLs, other constituents including oils and elemental mercury were released to the unlined SRS settling basin. Elemental mercury can dissolve in NAPL but essentially not in water. When elemental mercury is converted to an ionic form, such as by injections of chemical oxidants, it is much more soluble in water. Therefore if aqueous mercury concentrations significantly higher than background are measured after oxidant injection in an area far from the source release, mercury must have been transported there in DNAPL. We found chloride concentrations higher than can be explained by oxidation of dissolved solvents and statistically significant higher concentrations of mercury after oxidant injections, which proves that DNAPL traveled far from the source release area but was not detected by other characterization methods.

The determination of DNAPL far from the source area suggests a conceptual model that requires consideration of alternatives to contaminant persistence in this area solely as a result of dissolved phase transport from the release area and local matrix diffusion. It also may suggest different remediation strategies that could reduce cleanup time since DNAPL has more than 1,000 times the contamination potential of a similar mass/volume of aqueous phase contaminant. The reduction of that potent source will reduce the persistence and magnitude of aqueous contaminant concentrations. The identification of a remote DNAPL rather than a large-scale matrix diffusion contaminant source scenario may allow the conversion of a technically impracticable site to one that can be effectively remediated.

<u>Session 3b / Abstract title</u>: Adsorption and biodegradation modelling of TCE on biochar, enhanced by PHA addition

ID: 212

Key words: Biological reductive dechlorination, electron donors, biochar, modelling, chlorinated solvents.

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Session: 3b backup

Abstract

Biological reductive dechlorination (BRD) achieves the degradation of chlorinated compounds by microorganisms. The main scope of BRD is reducing toxic chlorinated compounds to non-toxic compounds, such as the BRD of trichloroethylene (TCE) to produce ethene (ETH) as the final product. BRD involves multi-step anaerobic reactions enhanced by the injection of slow-release sources of electron donors [1], such as polyhydroxyalkanoates (PHAs) [2].

This work studies the BDR of TCE in batch mode using an aqueous solution (125 mL) containing the microorganism (Dehalococcoides mccartyi), a synthetic mineral medium with TCE (58 mg/L) and in the presence (0.125 mg) or absence of PHAs. Cis-dichloroethene (DCE), vinyl chloride (VC), and ETH were identified and quantified over time as product intermedia of the DBR. It was found that the microorganism could promote the complete dechlorination of TCE after 170h in the experiments using PHAs. The concentrations of the compounds in the aqueous phase inferred that the microorganism first removed the TCE to produce DCE. The DCE dechlorination to VC started after TCE was utterly consumed. In the same way, the VC generated ETH when the DCE dechlorination was accomplished. The experimental profiles of the compounds involved with time were used to obtain a kinetic model according to a serial reaction mechanism.

In a second set of experiments, a semi-pilot structured column with microorganisms inoculated was used. The improvement in the TCE abatement was investigated using a system composed of PHAs and biochar. The column (1.4 m high and 0.1 m in diameter) was divided into two sections. The bottom section was a mixture of commercial sand with 4%w

biochar and PHA, produced from a microbial culture of urban biowastes. The second section was composed of sand with 4%w biochar. The column was inoculated with the microorganism, and a TCE solution (13.1 mg/L) was continuously fed at 2 mL/min. It was observed that the presence of biochar increased TCE dechlorination by the microorganisms due to the adsorption of TCE on the biochar surface. This experimental setup could treat large volumes of polluted water with TCE reaching its complete dichlorination to ETH.

The fluid dynamics of the column was modelled with an advective-dispersive model using a conservative tracer (NaCl) experiment. This model, coupled with the kinetic model obtained in the batch experiments and the adsorption of TCE on the biochar, was used to predict the experimental results obtained in the column output using Eq.1. A good fit between with and without PHA addition was obtained.

$$dC/dt=[(1+k_L\cdot C)^2/(R_{WL}\cdot q_L\cdot k_L+(1+k_L\cdot C)^2)]\cdot[D\cdot(d^2 C)/(dl^2)-u\cdot dC/dl]-k\cdot C \qquad (1)$$

Acknowledgements

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<u>Session 3b / Abstract title</u>: The full-scale remediation of an impregnation facility polluted with creosote oil using on-site co-composting

ID: 28

Key words: PAHs, full-scale remediation, co-composting, creosote oil

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Session: 3b backup

Abstract

Purpose of the study
The origin of this “old ecological burden” comprised the impregnation of wood using creosote oil during the 20th century near to the town of Česká Lípa, Czech Republic. Although creosote oil has not been used for around 50 years, the contamination remains in both the unsaturated and saturated zones and poses significant risks to the local drinking water source. The creosote that dripped into the sandy soils beneath the facility has been partially degraded and, today, oil substances and, mainly, heavy PAHs that are difficult to biodegrade via conventional bacterial-based technologies represent the majority of the contamination mass of the top soils. The risk analysis of the site estimated the quantity of the contamination at 300 t of PAHs and 400 t of oil substances in the unsaturated zone. Risk-based remediation targets were determined of 2 g/kg for the sum of the monitored PAHs and 60 mg/kg for the individual heavy PAHs. Currently, a full-scale remediation project is underway co-funded by the EU Operational Programme Environment (2019 – 2023).

Methodology
The contaminated sand is treated via so called co-composting technology, which consists of the mixing of the polluted sand with an organic substrate (min. 15 wt. %) provided by a local composting facility on a purpose-built insulated paved area with runoff collection. The mixture is moistened and regularly aerated employing mechanical re-digging. The microbial consortia that develop naturally during the process act to break down the organic matter and degrade the various contaminants. The co-composting process is monitored based on gas and temperature measurements and regular sampling. The contaminated sand is excavated in segments and treated on site in the form of several rows of piles. Each year, 1/3 of the total volume is treated and later returned to the excavation pit. Although co-composting technology has previously been used for remediation purposes, this is the first time it has

been applied at such a scale for the on-site decontamination of PAHs.

Summary of the results

Almost 13 000 m3 of contaminated sand has been excavated and treated on-site via a total of 5 active co-composting campaigns. Each campaign involves the mixing of 2,600 m3/4,420 tonnes of contaminated soil with 2,600 m3/1,033 tonnes of organic substrate on average followed by active treatment over a period of around 120 days. The mixture is subsequently left unmanaged in the form of one large heap for an additional 120 days and later returned to the excavation pit. The average degradation of the monitored PAHs was determined at 85% (a decrease in the mean concentration from 2,100 mg/kg to 0.320 mg/kg) and the degradation of individual heavy PAHs varied from 70% for benzo(b)fluoranthene (a decrease in the mean concentration from 80 mg/kg to 24 mg/kg) to 90% for benzo(a)anthracene (a decrease in the mean concentration from 252 mg/kg to 26 mg/kg). In the case of bezo(a)pyrene, the degradation rate was 75% (a decrease in the mean concentration from 59 mg/kg to 15 mg/kg). The measured temperatures (max. 34°C) inside the piles roughly corresponds to that of mesophilic organisms.

Conclusion

The vast majority of the bioavailable and, thus, potentially mobile and toxic portion of the contamination has been degraded and the residual contamination is now well below the remediation targets. The treated soil is stable and free of odour and has been returned to the excavation pit.

Contributions of the study

The co-composting method proved the ability to degrade heavy PAHs that are difficult to biodegrade via conventional bacterial-based technologies. The feasibility study showed that the cost of the ex-situ landfilling of the soil would have been approximately 3 times higher than on-site treatment. In addition, the ex-situ approach would have been significantly less environmentally and socially sustainable due to the need for the transportation of large amounts of hazardous waste.

<u>Session 3b / Abstract title</u>: Application of an All-In-One ISCO Technology for the treatment of Hydrocarbons, BTEX and MTBE at a Former Retail Petrol Station in Italy

ID: 32

Key words: groundwater, remediation, hydrocarbons, mtbe, ISCO

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Session: 3b backup

Abstract

Background/Objective.
Klozur® CR is a combined remedy treatment technology consisting of Klozur® SP (sodium persulfate) and PermeOx® Ultra (extended release calcium peroxide). Klozur CR is a single, all-in-one formulated product that can be readily applied to either source areas or plumes impacted with a wide range of contaminants, e.g. TPHs co-mingled with CVOCs. Klozur CR destroys contaminants in both soil and groundwater by promoting three modes of action: activated persulfate chemical oxidation, aerobic bioremediation, and anaerobic oxidation. This thermodynamically powerful reagent provides self-activating sodium persulfate oxidation technology, utilizing the alkalinity generated by the calcium peroxide component. High pH, or alkaline, activated persulfate is capable of destroying a wide range of contaminants, including PAHs, BTEX, TPHs, phenols, chlorinated solvents, chlorobenzenes, haloalkanes, pesticides, energetics, and many others. Following the initial chemical oxidation phase, Klozur CR will continue to release oxygen (used as an electron receptor for aerobic bioremediation) for up to a year. This as a result of the slow hydration of the engineered calcium peroxide. Diffusion and transport of oxygen downgradient will support contaminant reductions in plume areas, treating the contaminants of concern (COCs). As a result of the persulfate oxidation with organic compounds, generated sulfate ions can be utilized by sulfate reducing bacteria as an electron acceptor under anaerobic conditions to degrade COCs via a process called anaerobic oxidation.

Approach/Activities.
This technology was successfully applied at a densely populated urban area site in the northern Italy. The site was characterized by historical contamination of various toxic compounds. The site, a dismantled former petrol station, was impacted by the storage of fuels which has resulted in the groundwater contamination, including hydrocarbons (C12 ~

2000 µg/L), benzene (~ 500 µg/L), ethylbenzene (~ 380 µg/L) and MtBE (~ 13000 µg/L). Two injection campaigns were carried out 15 months apart, and a total of 4800 kg of Klozur CR (in a 25% aqueous solution) was injected onsite.

Results/Lessons Learned.
Following 18 months after the first application, the concentrations of contaminants had reached and maintained concentrations below the remediation goals in all monitoring piezometers in the treatment area. TPHs were reduced by greater than 80 percent, while MtBE was reduced by greater than 90 percent. Monitoring data confirmed sustained elevation of oxidation-reduction potential (ORP) and dissolved oxygen (DO) as necessary subsurface conditions to support treatment.

<u>Session 3b / Abstract title</u>: Accumulation and tolerance appraisal of Phragmites australis L. for the treatment of textile processing effluents in a constructed wetland blended with oxalic acid

ID: 35

Key words: Wastewater, Phragmites australis, antioxidant enzymes, oxalic acid, macrophyte, photosynthesis

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Session: 3b backup

Abstract

Water contamination containing metals at various levels elevates major environmental issues. Heavy metals (HMs) causing modifications in plant bodies and mitigations emphasize the significance of implementing specific environmental protection measures. Cadmium (Cd), lead (Pb), and chromium (Cr) are among the most threatening toxins owing to their high accumulation potency. Toxic metal removal efficiencies could be enhanced by phytoremediation augmented by oxalic acid (OA). This constructed wetland experiment was conducted to assess the consequence of the single and combined application of wastewater (WW) effluents with oxalic acid on morpho-physiological attributes, antioxidant enzyme activities, oxidative stress, and HMs accumulation in Phragmites australis. Plants were subjected to various treatments containing OA (10 mM) and textile wastewater (25, 50, 75, and 100%), with triplicate of each treatment. WW stress inhibiting growth parameters, chlorophyll content, and carotenoid content, HMs absorption also increases antioxidant enzyme activities. Constructed wetland experiment setup containing OA enhances antioxidant defense mechanisms and reduces HM-induced toxicity. Results reveal the Cr, Pb, and Cd concentrations in different parts of plants were found to be higher in the OA medium. The concentration of Cr, Pb, and Cd was found in leaves at 164, 447 350%, in stem 213, 247 219%, and in roots at 155, 238 195% at 100 % WW with OA (10 mM). The contaminants toxicity reduces in plants by using the amino acid chelator oxalic acid. Ultimately, the findings demonstrate that P. australis can tolerate elevated concentrations of WW stress and can be an eco-friendly source for industrial effluent remediation. This plant is effective at restoring contaminants in textile effluents. Moreover, oxalic acid could be a beneficial agent for the phytoextraction of HMs.

<u>Session 3b / Abstract title</u>: Understanding nanoparticle transport and retention from the pore scale up with X-ray µ-CT

ID: 400

Key words: S-nZVI, in-situ remediation, transport, retention, pore scale, tomography

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Session: 3b backup

Abstract

We present our work on the usage of X-ray micro computed tomography (µ-CT) to spatially resolve the retention of sulfidized nanoscale zerovalent iron (S-nZVI) particles in granular porous media (PM) at the pore scale. The purpose of our study is to obtain a better understanding of the elusive mechanisms and dynamics during substrate delivery under field like conditions, which lead to poor distribution and clogging of the porous media. The initial study is a proof of concept to showcase the type of information that can be obtained via this method.
We injected 10 g/L of carboxymethylcellulose stabilized S-nZVI under 3 flow rates comparable to field site application and imaged the S-nZVI distribution after 1, or up to 3 injection pulses. Our data show that initial retention is heavily dependent on narrow features in the PM, implying that retention might be described as a function of pore geometry. Variation of the injection rate suggests enhanced ripening dynamics under lower flow regimes. Imaging after repeated pulses allows to partially access the time domain and reveals that the retained S-nZVI mass is often not stationary, but that entire patches of retained S-nZVI are displaced during multiple injection, which is opposed to the single colloid release mechanism typically employed in modelling. The retained structure size growth is best fit using an exponential, rather than the typically used power model and overall an entirely new quality of information is being obtained. We since performed true in-situ experiments in sandy PM and spherical glass beads to further proof the relevance of pore geometry. We plan to share preliminary results of this latest work as they come in.
The presented work opens new pathways for a better understanding of the limitations encountered during in-situ remediation using nanoparticles. Such basic research can allow to develop new approaches and strategies to identify and overcome the bottlenecks in particle delivery. Especially understanding the retention dynamics as a function pore

geometry might allow, in the future, to optimize injection conditions, i.e. rate and concentration, for the porous matrix encountered at a particular field site.

<u>Session 3b / Abstract title</u>: PFAS – Danish Guidelines for investigation and Remediation

ID: 403

Key words: PFAS guidelines investigation remediation characteristics

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Session: 3b backup

Abstract

Purpose of study
Pollution with PFAS is widespread and there is a growing need to investigate and remediate soil and groundwater contaminated with PFAS. PFAS is a group of chemicals with very different and unique characteristics that empathizes the importance of setting up a strategy for the extent and scope of activities required when investigating soil and groundwater contamination at sites where PFAS have been used. In 2018 the Danish Regions therefore initiated the preparation of a handbook on soil investigations and remedial actions at sites polluted with PFAS. The handbook has been updated in 2022 and establishes guidelines for conceptual site models and for preliminary and supplementary site investigations and provides an overview and status for remedial methods.

- Methodology

The updated guidelines are based on a review of the newest available data on PFAS composition, characteristics, sources, environmental fate and toxicity. Analytical possibilities and possible cross contamination during sampling has also been reviewed. The review furthermore includes an overview of background values for PFAS including an extensive appendix on PFAS in air, and a status of findings of PFAS in soil, groundwater, surface water, biota and air in Northern Europe.
Newer literature has also been reviewed to update the availability and maturity of remediation technologies that can be applied for soil and water.

- Summary of findings/results

Based on collected chemical and physical characteristics of PFAS an approach to assessing the distribution of PFAS in soil, water and air is described.
Based on PFAS characteristics, a conceptual model for transport and mobility of PFAS in

soil, groundwater and surface water is set up for hot-spot sources, unidentified sources at landfills and diffuse sources. The conceptual site models form the basis for elaborating strategies for preliminary and supplementary site investigations depending on the source of PFAS and for risk assessment. These models are also used to describe different investigative techniques relevant for assessing the extent of contamination, flux in groundwater plumes etc. Moreover, the need for sampling of different environmental media is increasing and requirements for sampling of these different media have been supplied in order to plan the sampling strategy and to prevent cross contamination. Pros and cons of available analytical methods are described including considerations for quantification of precursors.
State of the art for remediation methods towards soil and groundwater is described and assessed. Only a few technologies are at present available for soil remediation in Europe. In contrast, technologies for treating PFAS in water are more mature and some such as sorption by granular active carbon (GAC) have already been applied during the last decade, while ion exchange with polymeric resins is growing in popularity due to a higher treatment efficiency compared to GAC. These two treatment technologies require a destruction technology to remove PFAS from the waste products. The assessment of pros and cons includes cost, removal efficiency, suitability towards different PFAS depending on chain length, besides availability and maturity.

- Conclusion

The handbook gives a structured and invaluable overview of existing data on PFAS contamination in soil and groundwater, assesses the data and supplies guidelines for investigation and remediation.

- Significance / contributions of study

The guidelines describe pitfalls and gives advice on successful investigative and remedial approaches for anyone working with PFAS contaminations.

<u>Session 3b / Abstract title</u>: Enhanced PFAS Removal From Soil and Groundwater Via Surfactant Flushing

ID: 418

Key words: PFAS, Surfactant, Remediation, Research, Sustainable

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Session: 3b backup

Abstract

Background/objectives
Removal of PFAS from aquifers depends on groundwater pump and treat (P). Groundwater is recovered and PFAS is removed, most often by filtration and granular activated carbon (GAC), with ion-exchange resins having increasing usage. P can take decades to complete as the efficacy of the process is limited by contaminant sorption (i.e. adsorption and absorption) to soils, hydraulic conductivity (K), and the relative low concentrations of PFAS in groundwater, even when the PFAS source zone is relatively close by.

Enhanced recovery of contaminants from source-zone areas has been demonstrated to be more cost-effective that using P alone. Operational time frames are lowered, in some cases, from years to months, or months to weeks, but to-date they have not been used for PFAS source zones. This work represents the first attempt to understand the potential of solvents and surfactants to increase the removal rates of PFAS, at a scale using reagent concentrations that are environmentally applicable.

Approach/Activities
Tests were designed to measure the effectiveness of a specifically-developed surfactant PFAS-SOL to increase the concentration of PFAS compounds in water in a simulated enhanced recovery experiment. Methanol and surfactant extraction were compared. The experiments were run at the University of Greenwich, UK in the summer of 2022.

A series of column experiments were carried out using 75 cm high and 14 cm diameter columns. A mineral sand was used in the first instance, followed by the addition of 10% by mass activated carbon to show the impact of organic material. The columns filled with mineral sand and were saturated from the base and spiked with high concentrations of PFOA and PFOS to mimic a source zone. They were then drained and the effluent sampled.

They were filled again, one with methanol at 50% concentration and the other with PFAS-SOL at 4% concentration, drained and the effluent sampled. The columns were then deconstructed and a moisture profile was measured, with soil samples taken to measure the retained PFAS.

Further samples of the same soil were then mixed with activated carbon and the columns were set up again. The same procedures were followed, with an additional drainage carried out. A moisture profile was again taken during column deconstruction with soil samples taken to measure retained PFAS.

Results/Lessons Learned

The experiments showed the effect of both solvent-enhanced extraction and surfactant-enhanced extraction, as well as the mass of PFOA and PFOS retained following the drainage tests. Furthermore, the moisture profiles at the conclusion of the tests showed the positive effects of surfactant on the unsaturated soils. The addition of surfactant was demonstrated to lower the moisture content of soils, allowing more water to be drained and therefore greater mass removal of any liberated contaminant – including PFAS – in the drained layers.

These experiments represented a novel approach for PFAS source zone treatment at an environmentally relevant scale, using around 12 L of specimen and reagent concentrations that are applicable to field-application.

<u>Session 3b / Abstract title</u>: Removal of long- and short-chain PFAS, hydrocarbons and heavy metal compounds from contaminated groundwater by advanced groundwater treatment technologies

ID: 423

Key words: groundwater treatment, landfill leachate treatment, foam fractionation, PFAS treatment

Submitter: Sylvie Braekevelt

Organization: Ramboll

Co-authors: Dorte Harrekilde, Ramboll, Senior Chief Consultant Contaminated Soil and Groundwater

Session: 3b backup

Abstract

At many locations in Denmark, environmentally hazardous contaminants are found in groundwater,
originating from human, industrial or agricultural land use. Contamination with e.g. PFAS substances
can occur on many different sites with industrial activities, such as fire training sites, landfills, textile and paper industries and paint industry. Since these persistent substances do not decompose in nature and have negative effects on living creatures, their presence in groundwaters is of major concern. European authorities have already set environmental quality standards for one PFAS compound, PFOS, at 0,13 ng/l in marine and 0,65 in freshwater. The current groundwater standards for PFAS22 in Europe are 0,5 µg/l and in Denmark 0,1 µg/l PFAS22 is the standard. With PFAS concentrations in extracted groundwater exceeding those limits comes a large need for the development and upscaling of advanced removal technologies.

The polluted groundwater is either permanently extracted to protect the quality of our groundwater aquifers, e.g. from landfills (leachate), or temporarily extracted from construction sites to prevent water from leaking into the excavated area. In both cases, PFAS pollution typically occurs in a complex matrix of other pollutants, ranging from biodegradable organics to heavy metals as well as persistent organic pollutants. Specifically, landfill leachate contains significant amounts of organic pollutants and heavy metals. Former gas plants can cause other groundwater contamination with polyaromatic hydrocarbons (PAHs), hydrocarbons, phenols, heavy metals and cyanide. How specific PFAS removal technologies affect the full pollution profile beyond PFAS compounds is not well understood today.

The Danish Environmental Protection Agency's Technology Development Programme for Soil and Groundwater (TUP) has supported Ramboll A/S in helping their clients identify the most suitable treatment technology for cleaning groundwater contaminated with PFAS compounds and monitor the behaviour of PAHs, hydrocarbons, phenols, heavy metals and cyanide in these technologies.

Since the effectiveness of most advanced PFAS removal technologies is dependent on the type of PFAS compound prevailing, the technologies are selected after an assessment of the PFAS content in the groundwater samples. With this, the ratio of long- and short-chain PFAS compounds as well as a specific PFAS fingerprint analysis (on compound level for 22 PFAS species) is performed on polluted groundwater samples from different locations. Subsequently, lab-scale treatment tests are carried out for groundwater samples from at least one groundwater extraction site in Denmark with at least two different technologies, including foam fractionation. The removal efficiency of 22 PFAS compounds as well as PAHs, hydrocarbons, phenols, lead, cadmium, chromium, copper, nickel, zinc and arsenic is measured for the different technologies. The results elucidate how effective the PFAS removal technologies are in removing long- and short-chain PFAS, as well as non-PFAS pollutants. The work contributes to establishing Best Available Technologies (BAT) for PFAS removal from polluted groundwater and aims to highlight the technical challenges and economic consequences for various industries and waste management utilities.

<u>Session 3b / Abstract title</u>: Rapid remediation of a chlorinated solvent plume using an injectable barrier combining in situ sorption, biological degradation and chemical reduction

ID: 47

Key words: Chlorinated, CAC, remediation, sorption, ISCR

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Co-authors: nan

Session: 3b backup

Abstract

Purpose: This is a case study of combined-approach in situ remediation works completed at a former manufacturing site contaminated with chlorinated solvents in a high flux aquifer. The site is located in a major city in Central Italy and is to be redevelopment to create residential housing. The redeveloping company had a strict timeline in which the remediation would be completed, as they wanted to achieve the remediation goals ('site closure'), prior to the sale of any properties, in order to maximize their return of investment. The selection of the remediation strategy needed to focus on a very fast solution that could avoid the installation of active equipment on site and that would cause minimal interference with the ongoing construction activities.

Methodology: An in situ injectable permeable reactive barrier was installed along the site's downgradient boundary to prevent offsite migration and protect external sensitive receptors. Colloidal activated carbon, colloidal sulfidated zero-valent iron, and an organic long-term release electron donor were co-injected. The synergy between in situ sorption, chemical reduction and biological degradation of chlorinated compounds optimizes remediation efficiency in terms both of timing and minimising daughter product production. A single direct push injection application was performed, co-applying the different products, using small, mobile equipment without leaving any fixed installations or treatment plants on site. Performance and price were guaranteed to the client.

Results: Post-application monitoring showed a very rapid reduction of PCE and TCE with stringent remediation targets achieved already at the first monitoring campaign. The daughter products DCE and VC reduced to below their own very stringent target levels after few months (0.5 µg/L for VC). Validation monitoring continued following this and confirmed the stable and complete compliance to remediation targets over the long term. This allowed the site to obtain formal closure as planned and the redeveloper to release to market the

residential properties built in parallel to the remediation activities.

Conclusion: In situ remediation was a viable option for this site with highly demanding timeline and stringent performance targets. It removed uncertainty for the client by providing a guarantee of achieving targets within a given budget.

Significance: This case study demonstrates the effectiveness of in situ remediation for sites with strict timing requirements and stringent performance targets. It also highlights the value of using a combination of physical, chemical, and biological processes to optimize remediation efficiency.

Session 3c1 orals

Session 3c1 / Abstract title: GreenCat - Green Catalysis for Groundwater Remediation: A Sandbox Experiment for Evaluating the Degradation of Chlorinated Solvents with a Catalyst Made from Waste Materials in an artificial confined aquifer.

ID: 213

Key words: Remediation, Sustainability, Experimental Aquifer, Chlorinated Compounds, Iron-Biochar

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Session: 3c1

Abstract

The purpose of this study was to assess the effectiveness of a new sustainable iron-biochar composite (IBC) technology for the in-situ remediation of sites contaminated with chlorinated compounds. The IBC mainly consists of green rust (layered Fe(II) and Fe(III) hydroxides) and biochar made from organic waste materials such as wheat straw, bone meal, and wastewater sludge. In the 3 years the GreenCat project has been running, extensive laboratory testing of the iron-biochar composite technology was conducted to evaluate its reactivity, stability, and longevity in groundwater and sediments. Additionally, the usability of IBC injection and the extent of its impact (radius of influence) was evaluated and modeled to aid in the planning and sizing of aquifer remediation efforts.
This study used a 2 m3 pressurized tank, with trichloroethylene (TCE) contaminated

groundwater flowing through a sand-box, to simulate a confined anaerobic groundwater reservoir. The tank was designed to have a flexible hydraulic gradient controlled by the difference in groundwater-pressure in the inlet and outlet. The experiment simulate the groundwater flow realistic to an artificial aquifer in fine sand, making the residence time for the particles to be between 2-4 days with a groundwater flow on approx. 0,2-0,4 l/min. The experiments will take place during the early spring 2023 where we monitor the tank in 117 small 12 mm wells in 3 levels, which are installed for sampling of the flow-through water. Initially the hydrodynamic properties of the tank will be determined by modelling and sampling the flow of a tracer through the tank. These results make the foundation for the following discharge and by that the sampling program, when adding the TCE contaminated groundwater and the IBC. The IBC catalyst is injected into the TCE-contaminated groundwater through an injection well upstream in the tank. The tank will be tightly monitored throughout the experiment to follow the extent of the IBC injection and the degradation of TCE to find out the reactivity, mobility and longevity of the IBC Catalyst.
This presentation will show the results as well as the conclusions drawn from the experiment conducted in the spring 2023. The detailed sampling and analysis allow the authors to observe the progress of the IBC injection and the accompanying degradation of TCE in the tank. We will share our experiences of building the confined tank and provide insights into the sampling and testing process as well as the flow-through/injection results. Furthermore, the observations and results of the following excavation and analysis from the sediment in the box will be presented.

<u>Session 3c1 / Abstract title</u>: Measurements for chlorinated solvents in sewer gas is not that simple, do we use the best sampling methods?

ID: 289

Key words: Sewer gas, chlorinated solvents, sampling methods, vapor intrusion, risk assesment

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Organization: Central Region Denmark

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Session: 3c1

Abstract

Purpose of study
The purpose of this presentation has been to examine the temporal variability of chlorinated solvents in sewer gas, and whether the methods for sewer gas sampling used today are reliable.

Methodology
Central Denmark Region has carried out a study of the temporal variability of chlorinated solvents in sewer gas and of different sampling methods for sewer gas sampling to determine the concentration of chlorinated solvents.

The study was carried out in Central Denmark Regions test-house. The test-house is a single-storey house of 144 m², former dry cleaner, where chlorinated solvents, including vinyl chloride, have been found in the sewer system. The house is now unoccupied; hence the sewer systems were not used in the test-periods. Drains from the bathroom and kitchen are connected to two separate sewer manholes and therefore represent two different sewer systems.

The test-period has been 2 x 14 days. In each 14-day period these sampling methods were performed:
• ORSA tube over 14 days (passive sampling)
• Beacon tube over 14 days (passive sampling)
• Canisters with time control over 14 days (passive sampling)
• Carbon tube sampling (100 minutes active sampling), 6 times in each test period

Each measurement is carried out both in the sewer manhole and "behind the water trap", in each of the two sewer systems – a total of 4 sampling points and 2 sampling periods. There are thus a total of 8 samples with each passive sampling method and 48 active carbon tube samples. Each sample is analyzed for chlorinated solvents (PCE and TCE) and degradation products (DCE and vinyl chloride)

Results

The results show very high temporal variability for the active (100 minutes) carbon tube sampling.

For vinyl chloride 15 out of 48 samples is below detection limit (LD) (0,4 µg/m3). The highest concentration is 140 µg/m3, which is 350 times LD. The passive sampling methods all show concentrations above 5 times the LD for active carbon sampling.

For PCE 5 out of 48 samples is below detection limit (LD) (1 µg/m3). The highest concentration is 92 µg/m3. The passive sampling methods all show concentrations above the LD for active carbon sampling.

For TCE 9 out of 48 samples is below detection limit (LD) (1 µg/m3). The highest concentration is 36 µg/m3. The passive sampling methods all show concentrations above the LD for active carbon sampling.

For the passive methods, Canister gives the highest concentrations of vinyl chloride, and ORSA tubes the lowest, with a few exceptions.

Conclusion

This study found a high temporal variability of chlorinated solvents in sewer gas for active sampling on carbon tubes, for PCE and vinyl chloride up to over a factor 100 in the same sampling point. For TCE up to a factor 20.

Different sampling methods gives different results when sampling in sewer gas.
For passive sampling for PCE and TCE, ORSA tubes give the highest (and most accurate) concentrations.

For passive sampling for vinyl chloride, Canisters provide the highest (and most accurate) concentrations, while ORSA tubes significantly underestimate the concentration.

There is a high risk of significant under- or overestimation of the average concentration of chlorinated solvents in sewer systems with active sampling on carbon tubes (100 minutes).

Contributions of study

In recent years, it has been recognized in the literature that chlorinated solvents contamination in sewer systems can have a significant impact on indoor air in homes. In order to assess the risk of vapor intrusion from the sewer system, measurements must be made in the sewer system.

This study has led to a better understanding of the complexity while investigating the content

of chlorinated solvents in sewer gas. On the basic of the study Central Region Denmark has made some changes while assess the risk of impact from contaminated sewer gas.

<u>Session 3c1 / Abstract title</u>: Removal of chlorinated solvents in air by Vacuum UV

ID: 296

Key words: Air treatment; Vacuum UV; Chlorinated solvents; MIMS

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Session: 3c1

Abstract

1. Purpose of study

Previously a “Proof-of-concept” project has been completed. It showed that Vacuum UV-technology (VUV-technology) can be used to remove chlorinated solvents and degradation products in the air phase. The project was completed with promising results which leads to the assessment that VUV-technology has a high potential for replacing activated carbon filters as air purification units in remediation systems. Especially the decomposition of Vinyl Chloride, which is challenging to retain in activated carbon filters, showed a reduction of nearly a 100%. The results also showed an average removal of almost 95% and 60% of the industrial solvents trichlorethylene and tetrachlorethylene. An excerpt of the results is shown in the graphs below this form.

Based on the promising results, a phase 2 has been initiated and the results hereof will be available early summer 2023.

The objective of phase 2 is to assess whether VUV-technology can be used as a prevention system for air purification of chlorinated solvents including degradation products that are difficult to remove using activated carbon filters. Additional assessments include:

- Optimize the VUV-reactor design to different location-specific conditions
- Assess whether the results show the predicted degradation and/or a higher/lower degree of degradation products when the conditions are changed
- Compare UV-reactor to the same air flow as an existing, known activated carbon filter prevention system regarding effectivity, consumption and sustainability.

The presentation will provide insight into e.g. further development of the method regarding modelling, construction of a reactor, risk assessment of potential degradation products as well as the possibility of an alternative remediation technique for air with chlorinated

solvents.

2. Methodology

The beginning of the project has been focused on a literary review of the chemical process the air exposed to UV-light goes through as well as a risk assessment of the degradation products. Based on the experiments carried out in 2021 a prototype VUV-reactor with a capacity of 100 m3/h is produced. This VUV-reactor will during spring 2023 be tested full scale on polluted air from an existing remediation system. During the test factors related to air pollution (e.g. temperature and absolute atmospheric humidity) and UV-dosage (e.g. flow and light intensity) are varied. An Eco-Efficiency assessment of the UV-reactor compared to activated carbon filters will also be made.

3. Summary of findings/results

“Proof-of-concept” studies have shown VUV-technology to be able to remove chlorinated solvents and degradation products in the air phase. Steady removal rates have been shown during the full 3 weeks test period. The following reduction has been proven

- Tetrachlorethylene: 55%
- Trichlorethylene: 94%
- Vinyl Chloride: 99%

Reviewing the literature indicates that the use of UV-light can cause some undesired degradation products. Work to concretize/evaluate this problem is a part phase 2 conducted spring 2023.

4. Conclusion

Vacuum UV-technology has shown its potential of as a remediation method to remove chlorinated solvents and degradation products from air phase. Furthermore, undesired degradation products will undergo risk assessment. Depending on the results, possible applications of VUV-systems will be discussed.

Impact on UN Sustainable Development Goals and a sustainability comparison (eco-efficiency model) on VUV-systems against existing activated carbon filter solutions will be made.

5. Significance/contributions of study

This study can contribute with a new way to use UV as an air remediation system on sites contaminated with chlorinated solvents. The presentation will show results, deal with possible challenges (e.g. degradation products) and compare the method with today’s preferred method.

<u>Session 3c1 / Abstract title</u>: A fungal biostimulation and biaugmentation orientation study for the bioremediation of a PCE and TCE contaminated loamy sand soil

ID: 315

Key words: chlorinated solvents, mycoremediation, bioremediation, feasibility

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Organization: NOVOBIOM

Co-authors: Dr. Ilaria Chicca, Novobiom, microbiologist, Dr. Caroline Zaoui, Novobiom, microbiologist

Session: 3c1

Abstract

Purpose of the study. The present work is part of an ongoing site rehabilitation project based in Herstal (Belgium), and coordinated by SPI, the economic development agency for the Liège province. This site is facing heavy trichloroethylene (TCE) and tetrachloroethylene (PCE) soil contaminations, implying soil excavation and subsequent offsite treatment. Aiming at implementing a circular environmentaly-friendly approach at each step of the rehabilitation process, soil biological remediation solutions have been investigated to propose cost-efficient and effective soil treatment alternatives. The purpose of this study is thus to assess the feasibility of TCE and PCE biodegradation in soil, adopting fungal bioaugmentation and biostimulation approaches.

Methodology. Soil from the site was spiked with PCE and TCE to reach the highest pollution spots detected (830 and 29 mg/kg, respectively). A fungal screening was performed to determine the best strains able to grow on that soil environment and to be used in the fungal bioaugmentation microcosms tests. In a second phase, soil was either inoculated with the chosen fungal specimens in two different configurations (mixed to soil and in layers), or supplemented with a non-inoculated and pasteurized ligno-cellulosic amendment. The soil supplementation rate (inoculated and non-inoculated conditions) was 10%, in sealed filter boxes containing 1 kg of soil. Nitrogen was added to obtain the C:N:P ratio for soil bioremediation (100:10:1). The experiments were run for 4 months, in static condition.

Summary of results. Despite the presence of a significant amount of heavy metals (Cd, Cr, Cu, Pb, Zn) in the soil, 3 isolates of the same Basidiomycete species were chosen to perform soil microcosms (isolates A, B, and C). Final concentrations after soil spiking reached 200mg/kg and 130mg/kg for PCE and 7.9mg/kg and 5.8mg/kg for TCE in control conditions for layer and mixed respectively, showing the high volatility of the compounds.

After 13 weeks of treatment, TCE concentration decreased to 0.62mg/kg for strain B in a mixed configuration. Similarly, soil bioaugmentation with strain C in a mixed configuration led to a final PCE concentration of 1.2mg/kg. Finally, soil biostimulation with aligno-cellulosic amendment mixed to the soil led to a PCE end concentration of 1.2mg/kg.

Conclusions. Altogether, those values are compatible with future industrial activities on the treated soil, according to the Walloon Décret Sol. Both biostimulation and bioaugmentation approaches led to significant decrease of the contaminants, although no individual strain could tackle both compounds and bring their concentration levels below the legal thresholds.

Significance/ contributions of study. These results are opening up the way to design and propose successful (onsite) soil bioremediation solutions to tackle severe chlorinated volatile compounds soil contamination, such as TCE and PCE, as alternatives to conventional methods.

<u>Session 3c1 / Abstract title</u>: Experimental upscaling to develop a remediation design for surfactant-enhanced in-situ chemical oxidation (S-ISCO)

ID: 373

Key words: groundwater remediation, DNAPL, experiments, upscaling, S-ISCO

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Organization: Research Facility for Subsurface Remediation (VEGAS) - University of Stuttgart

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Session: 3c1

Abstract

Soil and groundwater contaminations by dense non-aqueous liquids (DNAPLs) still are a present challenge we need to address. A variety of technologies, such as in-situ chemical oxidation (ISCO), has been developed to remediate contaminated sites. Surfactant-enhanced in-situ chemical oxidation (S-ISCO) is an emerging innovative remediation technology for the treatment of DNAPLs. S-ISCO combines contaminant solubilization by surfactants with chemical oxidation by oxidants. This combination aims at potentially increasing the efficiency of the state-of-the-art ISCO. However, further investigations are required to transfer this technology from the lab to the field and to develop a suitable remediation design.

Experimental upscaling analyses were performed at the research facility for subsurface remediation (VEGAS). First, the oxidation of a selected surfactant by activated persulfate (Na-PS) was investigated in batch experiments. These showed that the solubilization of contaminants (1,4-DCB, naphthalene, and PCE) was significantly reduced. Thus, it is beneficial to temporally and spatially separate the solubilization and degradation in the remediation design. Second, the developed S-ISCO remediation design was tested in a medium-scale experiment (LxHxW: 100 cm x 70 cm x 12.5 cm) with a DNAPL contamination of 1,2-DCB. A 60 g/L Na-PS solution was injected via a groundwater circulation well (GCW) to degrade the contaminant. Extensive sampling of the outflow during and soil material after the S-ISCO application showed that neither a concentration rebound occurred nor residual mass loadings on the soil material were found.

In the next step, we uspcaled the S-ISCO remediation design to field-like conditions and performed a large-scale experiment in the big flume of VEGAS (LxHxW: 6 m x 3 m x 1 m). This setup still allows for controlled boundary conditions and extensive sampling to monitor the relevant processes on such a scale. The S-ISCO application proved an efficient

contaminant removal from the source zone by surfactant solubilization down to a concentration of 5 mg/L 1,2-DCB. However, the experiment revealed a heterogeneously distributed contaminant degradation due to density-induced migration processes that resulted in suboptimal reaction conditions. Eventually, the designed operation of the three-filter GCW was not able to distribute the oxidant optimally. We compared the experimental results with numerical simulations and were able to adequately match the observations by employing a density-dependent transport model. Finally, comparing different simulation scenarios led to an improved operation of the GCW that provides a more efficient distribution of the density-influenced oxidant injection. Thereby, a more efficient remediation design was developed to foster the application of S-ISCO in the field.
This talk will present the experimental investigations and numerical simulations and highlights the findings and implications relevant for a remediation design of an S-ISCO application. We will invite the audience to discuss the findings and find potential knowledge gaps that have to be addressed in future investigations.

Session 3c2 orals

Session 3c2 / Abstract title: Effects of per- and polyfluoroalkyl substances (PFASs) and chlorinated aliphatic hydrocarbons (CAHs) co-contamination on the native microbial community in the field and associated biodegradation potential for PFASs

ID: 165

Key words: PFASs, CAHs, Groundwater, Microbial community, Biodefluorination

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Organization: Institue of Soil Science, Chinese Academy of Sciences

Co-authors: Dr. Xin Song, Institue of Soil Science, Doctoral Supervisor

Session: 3c2

Abstract

 Purpose of study: The purpose of this study was to explore the effects of per- and polyfluoroalkyl substances (PFASs) and chlorinated aliphatic hydrocarbons (CAHs) co-contamination on the native microbial community in the field. In addition, the biodegradation potential of PFASs, represented by trifluoroacetate (TFA), perfluorooctanoic acid (PFOA) and hexafluoropropylene oxide dimer acid (HFPO-DA), by the native microbial community was investigated.

 Methodology: We evaluated the presence of PFASs and CAHs in groundwater samples collected from a fluorochemical plant (FCP), and carried out Illumina MiSeq sequencing to understand the impact of mixed PFASs and CAHs on the indigenous microbial community. A series of microcosm incubation studies using the native microbial consortium were carried out for a period of 10 months to assess the biodegradability of TFA, POFA and HFPO-DA.

 Summary of findings and results: The sum concentrations of 20 PFASs in groundwater samples collected in the FCP ranged from 2.05-317.40 μg/L, and the highest PFOA concentration was observed in the deep aquifer (60m below ground surface), co-contaminated by CAHs in the form of dense non-aqueous-phase liquids (DNAPLs). The existence of PFASs and CAHs co-contamination in groundwater resulted in a considerable decrease in the diversity of microbial communities, while the abundance of metabolisms associated with contaminants biodegradation has increased significantly compared to the background wells. Furthermore, Acinetobacter, Pseudomonas and Arthrobacter were the dominant genera in PFASs and CAHs co-contaminated groundwater. And geochemical

parameters, such as ORP, sulfate and nitrate were the key factors to shape up the structure of the microbial community and enrich the abundance of the potential functional bacteria. Finally, it was found in the microcosm studies that the defluorination rates based on the theoretical maximum fluorine content for TFA, PFOA, and HFPO-DA were 3.32 %, 3.46 %, and 2.15 %, respectively. And the corresponding removal rates of TFA, PFOA, and HFPO-DA by the consortium were 8.03 (±3.03) %, 13.52 (±4.96) %, and 2.38 (±0.49) %, respectively. The co-occurrence network analysis based on the Illumina MiSeq sequencing showed that the functional modules of the microbial consortium mainly composed of Bacteroidetes, Nitrospirae, Acidobacteria and Chloroflexi, which might be responsible for the defluorination and biodegradation of representative PFASs.

- Conclusions: The exposure to PFASs and CAHs led to a significant decrease in the diversity of microbial communities, while the abundance of metabolisms related to pollutants biodegradation has increased significantly. The mixed contaminants, as well as ORP, sulfate and nitrate, were shown to have significant influences on the organization of the microbial community and the number of potential functional microorganisms. The biodegradation, and defluorination of TFA, PFOA, and HFPO-DA by the native microbial consortium were observed and verified in the microcosm studies.
- Significance/contributions of study: These findings further shed lights on our knowledge in understanding the intrinsic relationship between microbial communities and relevant environmental factors, to further develop bioremediation strategies for the mixed contaminants of PFASs and CAHs in soil and groundwater.

<u>Session 3c2 / Abstract title</u>: PFAS behavior in the unsaturated subsurface

ID: 173

Key words: PFAS, PFOS, PFOA, unsaturated subsurface, transport behavior, air-water interphase, adsorption

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Organization: KWR

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Session: 3c2

Abstract

Purpose of the Study
Per- and polyfluoralkyl compounds (PFAS) are man made so called ‘forever chemicals’ invented in the 1930s and subsequently applied in consumer goods by the industry. Currently more than 6000 PFAS compounds have come to life. Due to their stability they are persistent and accumulate in our environment. Scientific studies revealed toxic effects on animals and humas, such as neuro-, hepa- and immunotoxicity, tumor development and others. Unlike conventional contaminants PFAS compounds can be hydrophobic and hydrophilic at the same time depending on their molecular composition. This implicates besides adsorption to the soil solid soil phase, also adsorption to the air water-interphase (AWI), occurs in the unsaturated zone of the subsurface. The effects on transport phenomena due to adsorption to the air water-interphase is a relatively limited studied and understood topic currently. However, for prediction of future soil and groundwater quality it is important to understand the sensitivity of involved parameters for PFAS transport in the vadose zone. In this modeling study we focused on transport behavior and more specific retardation effects of PFAS compounds in the unsaturated zone towards the groundwater fringe.
Methodology
From scientific literature two modelcodes have been selected that are able to simulate PFAS transport in the unsaturated zone:
- PFAS LEACH Screening tool. An analytical python modelcode, developed by dr. Bo Guo (Arizona State University, Phoenix Arizona).
- Hydrus 5(version 5, 2022), a commercial software package for waterflow and transport of chemical compounds and heat in the unsaturated zone. Including the PFAS

module (Simunek et al., 2022).
As a first step both models have been tested and explored and results from literature have been reproduced, subsequently Dutch soil types and climate conditions have been simulated.

Summary of findings / results

Results for a Dutch sandy soil type (staring B01) applying semi-arid climate conditions, show more retardation for PFOS than PFOA. PFOS leach approximately 75 cm in 40 years, while PFOA leach 300 cm in the same time frame. In Dutch climate conditions the leaching effect increases to 400 cm for PFOA and 100 cm for PFOS at semi-arid conditions. These results were similar using the python and Hydrus module. Besides sandy soil, the processes were simulated in a Dutch peaty soil (staring O17). In peaty soil conditions PFOS showed, like in sandy conditions, more retardation for PFOS than PFOA, and Dutch larger leaching effect at Dutch climate conditions than semi-arid. The largest leaching effect was shown for PFOA approximately 75 cm.

In earlier studies relatively large starting concentrations were used in the order of tens of milligrams per kilo of dry soil. In this study we also used norm concentrations of 1.9 and 1.4 ug/kg.ds which are set for areas with agricultural or nature land use in the Netherlands. Results show that also at these relatively low concentrations leaching effects are shown in a couple of decades towards the groundwater fringe.

Conclusions

According to our study using a python modelcode and Hydrus 5, it was concluded that PFOA potentially leach towards the groundwater fringe, within a timeframe of one or two decades, in sandy as well as a peaty soil type. This was concluded for relatively high (tens of milligrams per kg of dry weight soil) as well as low concentrations (several micrograms per kg dry weight soil). The same conclusions apply for PFOS, although over a longer time span of around four decades.

Significance / contributions of study

This study shows that PFOS and PFOA potentially leach towards the groundwater fringe within a generation. Moreover, results show not only the importance of adsorption to the solid soil phase, but also on the air-water interface. Furthermore, other parameters are discussed such as possible influence of varying water content in the soil or how heterogeneity could influence leaching

<u>Session 3c2 / Abstract title</u>: Long Term Performance of a Carbon Barrier Evaluated Through Integrated Use of Aspect Ratio, Passive Flux and Modelling Analytical Tools

ID: 350

Key words: Iniectable Colloidal Activated Carbon Performance

Submitter: Jeremy Birnstingl

Organization: Regenesis

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Session: 3c2

Abstract

Injectable colloidal activated carbon (CAC) barriers are increasingly used in plume management. Their purpose can be to retard plume migration per se as in the case of non-degradable species such as PFAS, or to increase residence time of degradable species in a treatment zone. Historic solvent releases on a site in the eastern US have resulted in a solvent plume extending 1,700 feet (500 m). The plume principally comprises TCE at concentrations exceeding 10,000 µg/L. Migration of the plume has been mitigated by a sequence of CAC barriers co-applied with an electron donor to combine retardation and biodegradation. The full-scale application was preceded by pilot study in 2014, conducted in an area of the plume spatially separate from the full-scale barrier application that followed. This has allowed long-term performance without subsequent intervention to be evaluated.

Barrier performance is determined by the combined contributions of contaminant retardation and destruction. A CAC barrier represents a localized adjustment of the soil adsorption coefficient (Kd) which is typically increased by several orders of magnitude. This results in plume retardation to a corresponding degree. Since Kd is fundamental to all fate and transport models, CAC applications naturally lend themselves to modelling. The PlumeForce™ modelling software was used to unwrap and interrogate field performance data over the period 2014 to present. The software accommodates mass-conservative dialog between multiple compartments, dynamic competitive interactions of mixed solutes, and biotic and abiotic transformations of amenable species. Model inputs were supported by velocity estimation by plume aspect-ratio analysis and deployment of passive flux measurement devices. In addition to barrier performance evaluation, the overall exercise served as a means of cross checking the respective tools to evaluate consistency.

Initial model fits suggested the presence of significant TCE mass in lower transmissivity

‘storage’ units. These represented the largest component of plume mass pre-application and a source of anticipated back-diffusion. Aspect ratio analysis of plume dimension indicated the governing seepage velocity to be significantly faster than the 60 ft/year (18 m/year) estimated at the time of design. Based on the known plume history and its measured present extent, the natural retardation of the TCE was calculated from the new velocity estimate. The magnitude of the storage compartments indicated by modelling closely matched the overall matrix Kd (taken as immobile/mobile mass) inferred by the calculated retardation. The desktop estimates were then confirmed by direct measurement of contaminant and Darcy flux by passive flux units. Convergence of independent lines of evidence from the three approaches supports confidence in their individual use. Collectively, their integrated application can be of great value to the establishment of a robust conceptual site model. Suitable modelling, calibrated to field performance using combined lines of evidence, can be used to project barrier longevity under different management scenarios including ‘leave-alone’, donor-based bio-regeneration (as employed) and ZVI-based ferro-regeneration. The merits and efficacy of different approaches or combinations can therefore be explored such that a strategy optimal for the project may be identified, refined and communicated.

<u>Session 3c2 / Abstract title</u>: How the Site Remedial Setting Drives the PFAS Remedial Response

ID: 45

Key words: PFAS, behavior, remediation, storage, transport

Submitter: Jim Fenstermacher

Organization: Ramboll

Co-authors: nan

Session: 3c2

Abstract

Discussion around PFAS is maturing from an evaluation of an emerging contaminant to an evaluation of emerging treatment technologies. In other words, how do we successfully treat this broad class of compounds that possess characteristics like very low surface energy, elevated physical, chemical and thermal stability, and amphiphilicity (possessing water-soluble and hydrophobic ends), among other useful but hard-to-treat properties? And how do these properties affect transport, storage, and treatment of PFAS in ways that are unique from other “classical” contaminants?

This presentation will reach back to some of the same concepts that were key to advancing our understanding of classic contaminant transport, behavior, and remediation (e.g., ITRC 2015, Integrated DNAPL Site Characterization) and apply those concepts towards evaluation of treatment technologies for PFAS. Because classic cleanup of a site to low numeric standards will likely be difficult to attain with most PFAS releases, understanding of PFAS behaviors such as storage in the vadose zone and at capillary air-water interfaces will be imperative to allocation of resources towards remedy implementation and ensuring remedial efforts are truly addressing risks to sensitive receptors. For instance, the properties that make PFAS a unique contaminant class affect how PFAS mass storage and mass transport change with time in subsurface systems, and these changes will influence both current and future remedy effectiveness as well as receptor risk. This presentation will seek to address the critical questions raised above and inform participants on how to practically address PFAS releases in light of their unique properties and behaviors.

Session 3c3 orals

Session 3c3 / Abstract title: Immobilisation of PFAS - What happens under stress?

ID: 88

Key words: PFAS, immobilidation, stressing conditions, ageing

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Organization: Cornelsen Umwelttechnologie GmbH

Co-authors: Dr. Hans Ulrich Dahme, Eurofins Umweltanalytik GmbH, Hamburg, chemist

Session: 3c3

Abstract

Purpose of Study
On an industrial site, soil had to be excavated that showed PFAS contamination. Landfilling was chosen as the main disposal route, but immobilisation of the PFASs was planned for part of the soil. The intention of this supplementary measure was to subsequently subject samples of the immobilised soil to extensive stress tests in laboratories. These tests should clarify whether certain factors can reduce or eliminate the sorption of PFASs over time.

Methodology
The process of immobilisation of the PFAS in that soil was first simulated in a bench test. That was done in a technical lab. Different amounts of the immobilising substance were added to a representative sample of the soil. Treated samples went to an external laboratory where they determined the corresponding eluate values of PFAS were in an analytical laboratory. The immobilisation proved to be effective. The measure was implemented and after immobilisation was completed, samples of the soil were again taken on site. These were sent to different institutions to test the elution behaviour during simulated ageing of the material. The investigations considered, for example: Freeze-thaw stress, different water-solid ratios, biological stress (activated sludge), wet-dry changes and chemical stress.

Result
In the untreated soil, 2.3 µg/l PFAS could be determined in the eluate (65% PFOS and 21% PFHxS). The simulation of the immobilisation process itself showed that already with an addition of only 0.5 wt.% of the immobilising powder no PFAS above the determination limit of 0.01 µg/l per individual parameter were present.

The simulations of the treated samples under stressing conditions resulted in the following findings. Activated sludge as well as wet-drying changes have no influence on the binding of PFAS. Only chemical stress carried out as accelerated solvent extraction (ASE) at 10 bar and 100°C was able to dissolve a few PFAS to a small extent.

Conclusions

As a general result of the investigations of the treated soil, it was found that most ageing tests cannot achieve mobilisation of the PFAS.

<u>Session 3c3 / Abstract title</u>: TESTING INNOVATIVE TECHNOLOGIES TO ENHANCE PFAS POLLUTED GROUNDWATER TREATMENT – LIFE SOURCE PROJECT

ID: 105

Key words: PFAS, phytoremediation, boron doped diamond electrode, Surface Active Foam Fractionation, anion exchange filters

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Organization: Eurecat

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Session: 3c3

Abstract

LIFE SOuRCE (Demonstration and evaluation of Sustainable On-site Remediation technologies for PFAS-ContaminatEd groundwater) is a European project funded by the EU LIFE Programme, which objective is to develop a cost-effective solution for on-site remediation of PFAS (per- and polyfluoroalkyl substances) polluted groundwater.
Despite the risk posed by PFAS, traditional treatment technologies like granular activated carbon (GAC) are still relatively expensive and not fully effective for all PFAS. The LIFE SOuRCE modular treatment train should reduce costs, increase efficiency (>99% reduction of long-chain PFAS and 95% of short-chain PFAS) and result in complete destruction of PFAS. The solution is based on a pump-and-treat scheme and the combination of four on-site PFAS remediation technologies: Surface Active Foam Fractionation (SAFF), anion

exchange filter (AEX), electrochemical oxidation (EO), and phytoremediation (PHYTO). The solution, combining the SAFF with PHYTO and EO, will be assessed at a landfill in Sweden, where groundwater is polluted by multiple compounds, among them PFAS. The solution, combining SAFF, AEX and EO, will be tested at a PFAS-polluted site in Spain. But before bench scale tests were done to optimize each individual technology obtaining the necessary parameters for the design of the pilot scale configuration. The results from these bench tests are presented.

Three bench tests were done with the AEX to find out: i) the best of three different resins from Purolite (PFA694, A532E and A592EBF), ii) the adsorption capacity of the most suitable resin was estimated; iii) the most efficient regeneration solution for the selected resin was selected. All experiments were done using groundwater collected from the Spanish site and spiked for the three most-abundant PFAS. Nine experiments were done with EO boron doped diamond electrodes (BDD) treating the three AEX regeneration solutions at 5, 15 and 25 A. A bench scale version of the SAFF was tested with water from the Swedish site. Two trials were done, firstly at a constant frequency of 54 hz, and a secondly, with decreasing frequency from 40 to 50 hz. To test the PHYTO technology, batch and pre-pilot scale tests were done, aiming to select the best performing plant species and the best performing substrate. Batch sorption tests were done with a mixture of peat, biochar, and dolomite lime to investigate the sorption capacity for PFAS. They were compared with the same test carried out with peat, biochar, LECA, and GAC as reference. At the pre-pilot scale, four plant species were investigated including a combination of Salix Wilhelm and Salix Loden, Carez elata (tufted sedge), and Cannabis sativa (industrial fibre hemp). The tests were performed in duplicate plus a control without a plant species.

Results from the batch tests conducted with the AEX resins showed that PFA694 is the best performing resin. This was successfully regenerated using either ethanol or methanol-based solutions. Results from the PHYTO tests showed that the 1:1 biochar and peat mixture is the best option, as Biochar showed high affinity for PFAS. Unfortunately, there were no significant different uptake of PFAS between plant species due to the short vegetation time, thus PFAS uptake will be further investigated. Results from the EO experiment concluded the best regeneration strategy involves an ethanol-based solution treated at an intensity around 20A for 4 hours. Electric consumption is maintained between 1.4 and 2.5 W·h/Δppb AOF, ensuring a destruction above 90%. Finally, the miniSAFF® showed high removal efficiencies (>90%) for longer chain PFAS, but lower for the short chain PFAS.

Individual tests confirmed the capacity of each technology to treat PFAS and to overcome the limitations of each other if combined properly. Beginning of 2023, the Spanish pilot treatment train is starting to operate with the optimized configuration based on these results.

<u>Session 3c3 / Abstract title</u>: The In Situ Treatment of PFAS at the Air-Water Interface in a Source Zone Using Colloidal Activated Carbon

ID: 13

Key words: PFAS, in situ remediation, colloidal activated carbon

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Organization: InSitu Remediation Services Ltd

Co-authors: Leticia Benevenuto, Aquifer Servicos de Remediacao, Brazil, biologist

Session: 3c3

Abstract

The treatment of PFAS within soil and groundwater is an emerging topic with various technologies being researched and tested. Currently PFAS-impacted groundwater is typically treated ex situ using sorptive media such as activated carbon and ion exchange resin. Proven in situ remedial approaches for groundwater have been limited to colloidal activated carbon with plumes down gradient of the source zones being treated successfully for greater than seven years. However, treatment of groundwater within the source zones has not been shown to be feasible. This study looked at using colloidal activated carbon to treat dissolved PFAS at the air-water within the PFAS source zone. Studies has shown that PFAS tends to preferentially accumulate at the air-water interface due to the chemical properties of various PFAS. This accumulation can act as a long-term source for dissolved phase d PFAS thus making down gradient treatment of the groundwater a long-term requirement.

A solution of colloidal activated carbon was injected into the source zone using direct push technology delivered on a dense grid that targeted the interface between the air and groundwater. Concentrations of PFAS within the pore and groundwater were collected using a series of 9 lysimeters installed within the vadoze and saturated water columns. A total of six PFAS were detected in the pore and groundwater including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA). Detectable concentrations of PFAS within the pore and groundwater prior to treatment ranged from greater than 300 µg/L for PFPeA to less than 3 µg/L for PFNA. Following the injection of the colloidal activated carbon, monitoring of the pore and groundwater for PFAS was conducted approximately 3-, 6-, 9-, 12-, 18-, and 24-months post injection. The results indicated that the PFAS within the pore and groundwater at and near the air-water interface was effectively attenuated over the 2-year monitoring program with

PFAS concentrations being below the method detection limits of approximately 10 ng/L with the exception of PFPeA which is a 5-carbon chained PFAS which has been shown to have a lower affinity for sorption onto activated carbon compared to the longer carbon chained PFAS such as PFOA.

Examination of aquifer cores in the zone of injection indicated that the foc concentration of the aquifer increased by two orders of magnitude post injection with 100 percent of the samples collected within the target injection area containing activated carbon indicating that the colloidal activated carbon was successfully delivered into the source zone.

The results of the field study indicate that sorptive media such as colloidal activated carbon can be effectively used to attenuate PFAS within a source zone over a short and moderate time frame. Long term monitoring of the field site coupled with laboratory and numerical modelling will provide additional data to determine if this approach can be effective over the long term.

<u>Session 3c3 / Abstract title</u>: Flexible and sustainable in situ solutions for PFAS source-plume systems using a variety of colloidal activated carbon application methods

ID: 46

Key words: PFAS, source, plume, CAC, remediation

Submitter: Jack Shore

Organization: REGENESIS

Co-authors: nan

Session: 3c3

Abstract

Purpose: To introduce and explain the processes through which PFAS source and plume zones can be remediated using application of Colloidal Activated Carbon (CAC).

Methodology: Contamination of soils and groundwater with Per- and polyfluoroalkyl substances (PFAS) can result from the historic use of Aqueous Film Forming Foams (AFFF), particularly associated with fire training facilities. Accumulation of PFAS in the soil creates significant reservoirs of contaminant mass. Further vertical movement of PFAS may occur through leaching of sorbed mass into infiltrating precipitation. Eventually this may result in discharge to groundwater, plume propagation and risk to downgradient environmental or human receptors. The mobility of PFAS, combined with the toxicity of longer chain compounds, means that these source areas can create and maintain widespread environmental risk long after the discharge event has occurred. Treatment of both source and plume zones has been considered problematic due to the recalcitrant nature of PFAS compounds. Waste management facilities increasingly do not want to receive PFAS impacted soils excavated from the site. Extraction and treatment of impacted groundwater is inefficient and needs a large volume of water to be removed and filtered over many years – requiring high energy use, waste production and an uncertain treatment end-point. In situ sequestration of the PFAS compounds provides a sustainable and long-term alternative solution that has now been used on 40 sites worldwide. This comprises the application of Colloidal Activated Carbon ((CAC), a liquid comprising 1-2µm particles of activated carbon suspended in water) in a range of locations within the source-plume. In the impacted vadose zone soils, CAC is mixed with the soil and other sorption modifiers to reduce the leachability of the PFAS. A horizontal barrier of CAC is emplaced just under the treated soils to remove residual PFAS infiltration and prevent further discharge to the groundwater. In the source area groundwater, injection of CAC in a grid pattern is used to target the lateral and vertical extent of high concentrations of dissolved PFAS. The CAC attaches to the aquifer material

and removes the PFAS from the groundwater through sorption, preventing further migration into the plume body.

Results: The combination of prevention of PFAS discharge into the groundwater with adsorption of contaminant mass already in the source area groundwater, will allow the enhanced attenuation of the residual plume. Site treatment can be further enhanced by combining these source-treatments with a plume application. This is achieved through the low-pressure injection of CAC into flux zones using Direct Push Technology (DPT) at the site boundary or upgradient of a receptor. This creates a treatment zone comprising a 1-2µm layer of activated carbon on the aquifer material, without affecting groundwater flow, while acting as a purifying filter, immediately removing the PFAS influx from the groundwater through adsorption, thereby eliminating the risk to downgradient receptors.

Conclusion: In situ treatment of PFAS using CAC is a sustainable solution as the installation takes only a few weeks of site activity, after which the treatment will continue without need for further energy use or onsite machinery and no waste is created at the surface. This talk will introduce CAC technology and explain the processes through which it can be used to treat source and plume zones and how designs are tailored to each site. Lab data will demonstrate sorption efficacy and leachability reduction. Practical application and validation will be discussed. Case studies and treatment results will be shown of source treatment at a military base in the USA and full-scale plume treatment at two airport sites in the UK.

Significance: This talk will be of interest to practitioners, site operators and regulators interested in how to practically sustainably manage PFAS contamination.

<u>Session 3c3 / Abstract title</u>: Experience with PFAS as secondary component in pump-and-treat plants

ID: 82

Key words: PFAS, groundwater, pump-and-treat, data analysis,

Submitter: Niels Døssing Overheu

Organization: Capital Region of Denmark

Co-authors: Line Mørkebjerg Fischer, Capital Region of Denmark, chief consultant; Liselotte Clausen, HOFOR - Greater Copenhagen Utility, chief consultant

Session: 3c3

Abstract

Background and Purpose
The Capital Region of Denmark operates 55 pump-and-treat (P) plants that protect groundwater resources from the impact of orphan contaminated sites. These plants were built to treat traditional contaminants like chlorinated solvents, usually by adsorption in granular activated carbon (GAC) vessels.

Since PFAS have emerged as widespread contaminants of concern, we have set out to investigate if they pose a problem in our P plants. Our concern is whether concentrations in the outlet water after treatment exceeds quality limits, since the majority of the water is discharged to surface waters or back to the groundwater zone. And then what to do if concentrations exceed quality limits.

Added benefits of the study have been to
- Get an overview of the level of PFAS in untreated groundwater
- To evaluate the reproducibility of PFAS analyses
- To assess the treatment efficiency of PFAS compounds in existing GAC plants
- And to gain operational experience before we build our first dedicated plants for cutting off PFAS plumes.

Methodology
Inlet and outlet water from 55 P plants was sampled and analyzed for 22 PFAS compounds at an accredited lab. Samples were taken in duplicates separated by a month to examine reproducibility. Results were compared to Danish EPA quality limits for surface waters and groundwater. At the same time, we measured concentrations of the pesticide degradation product N-N dimethylsulfamide (DMS); another diffuse contaminant present in most of our secondary groundwater resources.

Where the outlet concentrations of PFAS were above quality limits, we have evaluated and implemented additional treatment, including supplemental GAC vessels and ion exchange (IX) resins.

Results

PFAS compounds were found in the inlet at most of the P plants (0-100 ng/L sum of 22 PFAS), which supports our assumption of a widespread PFAS load in secondary aquifers around Copenhagen.

Most of the GAC filters manage to treat the PFAS compounds to below quality limits, in addition to treating the original contaminant of concern, e.g. chlorinated solvents. A tentative range of possible treated GAC bed volumes is in the order of 5,000-8,000. As expected, GAC treatment is most effective for the longer chain PFAS. However, results indicate remarkably high retention of some short-chain sulfonic acids like PFBS.

Duplicate sampling showed good reproducibility on samples taken at in-plant sampling taps, even at ng/L levels.

Full scale treatment with ion exchange resins has been implemented at one plant with PFAS concentrations above quality limits, and in Winter/Spring 2023 other alternatives to GAC will be tested at one or two plants with concerning PFAS levels.

Conclusion

It is generally possible to remove PFAS compounds in existing GAC vessels, where PFAS are present as secondary contaminants in low to midrange concentrations, with little or no treatment modifications.

The study also showed that it is possible to sample and analyze ng/L levels of PFAS from in-plant taps with good reproducibility.

Experience with long term operation helps us evaluate the cost-efficiency and practical challenges of different treatment methods. Good pre-treatment of other compounds (like iron) is essential for effective use of sorbents or IX material. In September 2023 we can hopefully share mid- to long-term experience with efficiency and costs of different methods.

Significance

The large data set acquired is relevant for many actors in the remediation and drinking water sector. In Jan. 2023 we have entered a collaboration with the largest Danish water utility companies to expand on the data collection and interpretation to further examine the cost-efficiency of different PFAS treatment methods. The collaboration will include facilities for testing and comparing novel treatment methods. Hopefully we can share some insights into this collaboration in Sep. 2023.

Session 3c4 orals

Session 3c4 / Abstract title: Applicability of different iron and persulfate-based oxidation processes for the elimination of PFAS compounds in groundwater

ID: 193

Key words: Groundwater PFAS oxidation ferrateVI nZVI

Submitter: Leonidas Perez-Estrada

Organization: EURECAT

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Session: 3c4

Abstract

The intense Industrial activity in large metropolitan areas, has impacted urban groundwater (GW) introducing industrial contaminants in the soil and GW. The Besòs and Tordera river basing are some of these sensitive and impacted areas of concern due to the various industrial parks, which partially discharge their effluents into municipal wastewater treatment plants located by the riverbed. The project PROMISCES (GA-101036449) is a EU funded project within the European Green Deal program, which aims to understand the origins, routes and fate of these pollutants with the goal of moving forward to a zero-pollution circular economy. The soil-groundwater continuum route is one of the important pollutants introduction routes that are being investigating within the project. This research work is focused on an impacted site, located in Barcelona province, with an aquifer contaminated by PFAS used during fire-fighting activities, this site was selected as a case study for the aforementioned project.
Investigated treatments were done based on GW quality characterization and include persulfate, (n)ZVI, and Ferrate (VI), all in different combinations. This research is focus on evaluate the degradation of major compounds identified in the GW's site, synthetic GW was

used as the matrix based on deionized water. Catalyst concentration was used in a low/high scheme of 1 mM and 10 mM targeting an order of magnitude difference; thus, significant differences might be noticed in a reduced period of time. Samples were collected at 1, 2.5 and 5 hours, additionally controls and blanks were taken. Perfluoro hexanoic acid (PFHxA) was selected as a target PFAS for this series of experiments, it was spiked at 100 micro-g/L in solution and its concentration was followed by means of a liquid chromatography coupled to a high-resolution mass spectrometry. Lab-scale oxidation treatments were applied in column tests simulating the soil and groundwater conditions to assess the physicochemical alteration of the aquifer.

Based on the PFHxA degradation results, the best treatment processes were Ferrate (FeVI), Ferrate-Persulfate mix, and Ferrate-Persulfate-nZVI mix. PFHxA degradation using low catalyst/oxidant concentrations showed an average of 85% reduction with no significant difference between 1 and 5 hours of exposure. Contrary, high catalyst/oxidant concentrations caused that the PFHxA levels were below the limit of quantification (suggesting 100% degradation). The rest of catalyst/oxidant combinations reflect different concentration behaviors, ranging between 5 and 70% degradation. The use of Ferrate (VI) and nZVI produced an interesting oxidant environment behavior, confirming previously reported oxidation effects. Moreover, an important synergistic effect was observed when these two iron-based catalysts were combined with persulfate. The complex redox system that was formed increased the observable rate of degradation, falling this below quantification limits of the target's PFAS method used.

Based on degradation rate, by-product formation, reagent consumption and associated costs, as well as in situ applicability, the most efficient treatment will be chosen for up-scaling. However, previous to the treatment selection, a comprehensive study on degradation by-products will be done to assess the efficiency of the best catalysts and oxidant combinations. Additionally, a preconcentration of samples is planned to clarify if the limit of quantification was an impediment to recognize formed by-products. Although, these first stage results have to be scrutinized by a further and more in-depth analytical study, a clear trend could be seen, and they are a significant contribution to achieve the first tasks and objectives of the PROMISCES project.

<u>Session 3c4 / Abstract title</u>: Remediation of water from per- and poly-fluoroalkyl substances (PFAS) with advanced oxidation processes: a comparative study of ozonation and photocatalysis

ID: 214

Key words: PFAS, water treatment, photocatalysis, ozonation, inverse modeling

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Session: 3c4

Abstract

In the last decade, per- and poly-fluoroalkyl substances (PFAS) have become part of the list of persistent organic pollutants (POPs) as they are environmentally persistent, potentially carcinogens and display a high bioaccumulation rate. Currently, PFAS are detected in multiple environmental matrices (e.g. soil, sediment, biota, air dust, food, drinking water) corroborating their high persistence and mobility in the environment. Due to their recalcitrance, advanced oxidation methods are foreseen as effective methods for the treatment of PFAS-polluted water.
Synthetic aqueous solutions of perfluorooctanoic acid (PFOA) and perfluorodecanoic acid (PFDA) were prepared and used in the tests. Experimental setups were developed to investigate the potential to destruct the PFAS in aqueous solutions through: (i) their treatment in annular photo-reactors; (ii) their ozonation (oxidation by ozone-rich gases) in bubble flow reactors. ZnO photocatalytic nanoparticles were synthesized and immobilized on various non-porous Duranit (80 % SiO_2-20% Al_2O_3) beads by dip-coating in aqueous solutions of salts and thermal annealing. Photocatalyst-coated beads were packed into the annular area of the reactor, and a UV lamp (375 or 254 nm) was installed within a glass protective container that was positioned vertically along the central axis of the reactor. For the photocatalytic degradation of PFAS, the aqueous solution was recirculating between the photo-reactor and an external tank with the aid of a peristaltic pump. The temperature, pH, and redox potential were measured on-line with sensors placed inside the external tank. From time to time, liquid samples were collected from the external tank and the PFAS concentration was measured with the methylene blue active substances (MBAS) method

and UV-Vis spectrophotometry. A one-dimensional advection-dispersion-sorption-reaction model was used to estimate the kinetic parameters of PFAS sorption on catalyst and surface reaction, with inverse modeling.

The bubble flow (ozonation) reactor was a stainless steel cylindrical column occupied with the PFAS-solution. The ozone was produced by injecting oxygen or air into an ozone generator (high voltage corona discharge plasma) at flow rate 0.1-1.0 L/min, with the aid of a mass gas flow controller. The ozone concentration was monitored on-line with a PC-controlled ozone analyzer, and then was bubbled in the column through a porous cylindrical diffuser. During the experiment, the following parameters were measured on-line with sensors, and transmitted to computer for storage via a data-acquisition system: inlet and outlet gas pressure, pH, temperature, and redox potential. The outflowing gas passed through a silica column to remove moisture and then through an ozone destructor to decompose the residual ozone. Occasionally, liquid samples were collected from side gates for chemical analyses. A simplified tank-in-series model with backflow was developed by coupling the mass-transfer with reactive processes in gas and liquid phases, and used to estimate the PFAS degradation kinetics with inverse modeling.

The transient response of PFAS removal efficiency was correlated with the recirculation rate and treated volume for photocatalytic tests, and with inlet ozone concentration and gas flow rate for ozonation tests. The comparative analysis between the two methods was based on the estimated kinetic parameter values, and the values of energy efficiency index, regarded as the total energy consumed per unit mass of remediated PFAS.

<u>Session 3c4 / Abstract title</u>: Foam Fractionation of PFAS with Combined Air / Ozone

ID: 230

Key words: PFAS Wastewater Treatment Foam Fractionation

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Session: 3c4

Abstract

Purpose of study

Increasing pubic awareness, scientific understanding and regulatory drivers around Per- and Polyfluoroalkyl Substances (PFAS) is resulting in a greater number of PFAS are being regulated to increasingly lower threshold limits within environmental matrices and industrial discharges.

In particular, wastewater containing high concentrations of PFAS are generated from landfills, firefighting foam release areas and a range of industrial processes which are difficult to treat but increasingly subject to tightening discharge conditions to minimise the impact on downstream municipal wastewater treatment works (WWTW) and the environment. In addition, increased remediation and decontamination of PFAS (e.g. Reverse Osmosis (RO) rejectate, Ion Exchange Resin (IER) regenerant, foam system cleanout reagents) can generate complex waste streams which require treatment.

Concerns have been raised regarding the effectiveness, sustainability and capacity of High Temperature Incineration (HTI) to address PFAS liquid wastes so there is a need for novel technologies to concentrate PFAS, minmise waste volumes and hence reduce the cost and environmental impact of subsequent destruction. There is also a need for continued optimisation of novel technologies to address wider range of PFAS compounds now subject to regulation and improve cost and efficiency.

This presentation provides an overview of Foam Fractionation optimised to employ multiple gases (air and ozone), showcasing multiple case studies and highlighting new delivery capability within the European market.

Methodology

The presentation will first summarise the ‘concentrate then destroy’ approach to PFAS treatment and demonstrate the urgent need for more sustainable, effective treatment technologies for low volume, high concentration, complex PFAS waste streams.

Foam Fractionation involves sparging wastewater with fine gas bubbles within a series of columns to concentrate and separate PFAS within a small, fractionate volume for destruction. The technology will be described including the mechanisms of removal, how these take advantage of innate PFAS properties, system components treatment process and how it may be combined with other technologies.

Several full-scale case studies and optimisation trials will be presented describing the matrix treated, flow rates, waste minimisation achieved and PFAS removal performance including of short chain PFAS and precursors compounds. Use of TOP Assay to demonstrate comprehensive PFAS removal.

Summary of findings/results

Foam Fractionation is an effective PFAS treatment technology demonstrated to reduce PFAS like PFOS and PFOA by >99% in landfill leachates and other complex wastewaters. Recent optimisation works using combined air/ozone approaches have shown improved removal of short chain PFAS and precursors compared to air only fractionation systems. Work to further concentrate separated foam fractionate will also be described.

Ozone also provides additional benefits and cost savings by addressing co-contaminants such as metals, BOD COD, ammonia, odours colours without extra system components. The technology can be combined with a secondary polish such as GAC, RO or IER.

Conclusion

There is a need for novel technologies to concentrate PFAS, minmise waste volumes and hence reduce the cost and environmental impact of subsequent destruction. Foam Fractionation employing multiple gases provide sustainable waste minimisation offer improved performance against a range of PFAS compared with air only systems as well as provide co-contaminant treatment.

Significance / contributions of study

The presentation provides insight into an important field-tested technology for PFAS treatment of complex wastewater to reduce reliance on incineration and is of importance to all environmental practitioners and PFAS waste holders. Recent optimisation to employ multiple gases is important to meet increasing demands for comprehensive PFA

<u>Session 3c4 / Abstract title</u>: Iron minerals as catalytic activators for persulfate for in-situ oxidation of PFAS in aquifers - From laboratory to field application.

ID: 80

Key words: PFOA degradation, Persulfate activation, Sulfate radicals, in-situ oxidation

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Session: 3c4

Abstract

Purpose of study:
Existing contaminated sites and newly discovered aquifer contaminations, together with growing environmental awareness and improved analytical techniques, have led to a variety of new remediation methods based to a large extend on advanced oxidation processes (AOPs). Recent developments focus on the destruction of persistent contaminants by oxidation with sulfate radicals generated by activation of peroxydisulfate (PS) and peroxymonosulfate (PMS). Sulfate radicals also appear attractive for in-situ remediation strategies for aquifers contaminated with perfluorinated alkyl substances (PFAS).
Unlike hydroxyl radicals, sulfate radicals are capable of attacking the carboxylate group in a whole range of PFAS. Our main focus is on the heterogeneous activation of PS to generate sulfate radicals to exploit contaminant accumulation on active surfaces in an integrated sorption-oxidation approach.

Methodology and summary of results:
In the present study, the activation of PS with various iron minerals was investigated. From the pool of iron minerals tested, one of the iron(II) sulfide (FeS) mineral proved to be a strong activator for PS. A more detailed investigation of the FeS/PS system (e.g., pH dependence of the reaction, long-term behavior of FeS as an activator for PS, and determination of radical yield and activation energy) led to the hypothesis of an activation mechanism via homolytic bond cleavage and to the assumption that this FeS acts as a true catalyst with considerable lifetime and not, as would be expected, as a reagent.
Based on the experience gained, the FeS/PS system was optimized and specifically designed for the degradation of PFOA (perfluorooctanoic acid), one of the most prominent PFAS representatives in the focus of regulatory authorities. Due to surface-mediated processes, the target reaction, PFOA degradation, can be performed in real groundwater

samples, even in the presence of typical water constituents, such as salts and dissolved organic matter (DOM). These results are remarkable because it is known that not only dissolved iron salts, but also chloride and DOM effectively quench free sulfate radicals, i.e. react with radicals much faster than PFOA. The presentation will provide information on reaction products, yields and pathways under different reaction conditions. By providing mechanistic insight into the activation of PS through heterogeneous activation, this work paves new pathways for novel remediation approaches using PS for in-situ and ex-situ water treatment.
Based on the promising laboratory results, a field trial of the FeS/PS system as part of the Intraplex® technology was conducted at a PFAS-contaminated site in western Germany. The main contaminants were the perfluorinated carboxylic acids with a total concentration of about 600 ng/L. Using a combination of permanent injection points and direct-push injections, an injection transect was inserted to deliver the material across the main flow direction of the PFAS plume. The effects of the pilot test were studied through an intensive monitoring program that determined concentrations of contaminants, transformation products, and hydrogeochemical parameters.

Conclusion and significance:
As a result, several indications were found that in-situ oxidation of the perfluorinated carboxylic acids had occurred. Relative concentration patterns of different pollutant classes were accompanied by a decrease in pH in the effluent evidenced PS activation and a degradation of our main contaminant class perfluorinated carboxylic acids.
This opens the prospect of developing this approach into a remediation technology that can effectively eliminate these specific PFAS contaminants in groundwater in situ.

Session 3c5 orals

Session 3c5 / Abstract title: RECOVERY OF SURFACTANS AND ADSORBENTS IN SELECTIVE POLLUTANTS ABATEMENT IN POLLUTED SOIL FLUSHING EMULSIONS

ID: 211

Key words: granular activated carbon, persulfate, regeneration, Cholobenzenes, pilot study

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Session: 3c5

Abstract

Bad practices in the disposal of wastes from obsolete and toxic pesticide production caused significant environmental risks in many parts of Europe. An example is the dumping in unlined landfills of residues from the lindane (γ-hexachlorocyclohexane, γ-HCH) manufacturing process [1]. The liquid residuum was a dense non-aqueous liquid phase (DNAPL) of hydrophobic nature comprising more than 28 Chlorinated Organic Compounds (COCs) [2]. This DNAPL percolated through the subsurface and accumulated in the non-permeable layers polluting soil and groundwater.
Residual DNAPL in the saturated zone caused a plume of contaminated groundwater. The injection of aqueous emulsions of biodegradable surfactants in the subsurface with further extraction of polluted fluids (SEAR) can be applied to remove the residual DNAPL in shorter times. The contamination is transferred from the subsurface to the extracted emulsion containing surfactant and organic pollutants. This highly contaminated emulsion must be treated on-site to remove the extracted DNAPL and, if possible, to recover the surfactant. This work studied the management of polluted emulsions by selective adsorption of pollutants in granular activated carbon (GAC) and regeneration of the spent GAC. The adsorbent regeneration is carried out at mild conditions, with hydrogen peroxide as oxidant

and immobilized iron on GAC as catalyst (heterogeneous Fenton reaction). A commercial GAC employed in the wastewater treatment plant of the landfill was used. Surfactant selected was a non-ionic biodegradable one produced by EthicalChem (E-Mulse 3®). The operation was performed on a laboratory scale using batch and column experiments. Adsorption isotherms of surfactant and COCs were obtained in batch runs. Column experiments were carried out to study the adsorption-regeneration cycles of the adsorbent. The glass column (50 mm in length and 28 mm in diameter) was filled with 20 g of commercial GAG.

Firstly, iron was immobilized on GAG (62.7 mgFe/gGAC). Following, 280 mL of a contaminated emulsion composed of 9.1 g/L COCs and 12 g/L of surfactant was recirculated through the GAC column for 144h. The concentration of COCs and E-mulse 3 in GAG after the first adsorption cycle were 100.32 mgCOCs/gGAC and 154.41 mgE3/gGAC, respectively. The regeneration of the spent GAC was carried out by passing a solution of H_2O_2 at a flow rate of 2 mL/min. The amount of H_2O_2 required was varied under the stoichiometric ratio required for the mineralization of COCs adsorbed. The evolution of pH in the column outlet, iron leachates and by-products were analyzed in each regeneration. The adsorbent capacity recovery was studied by successive adsorption cycles after GAG regeneration. Three adsorption-regeneration cycles were carried out.l

After each regeneration cycle, it was found that the surfactant adsorption decreased, but the COCs adsorption kept almost constant. This way, selective COCs adsorption was efficiently achieved with surfactant and adsorbent recovery, improving the circular economy without generating secondary wastes.

Acknowledgements

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<u>Session 3c5 / Abstract title</u>: Biological degradation of high concentrations of 1,4-dioxane: from laboratory to field and back

ID: 265

Key words: 1,4-dioxane, biodegradation, microbial community, bioreactor, pH

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Session: 3c5

Abstract

Purpose of the study:
Investigate the feasibility of bioremediation for the treatment of (high) concentrations of dioxane and get further insight into the degradation pathway and microorganisms involved.

Methodology
Laboratory degradation tests and a field test which consisted of an in-situ field test with groundwater circulation and biosparging and a bioreactor to treat extracted groundwater, which was re-infiltrated after treatment.

Summary of findings
In 2017 a laboratory degradation study was conducted to investigate the feasibility of biodegradation for the treatment of a 1,4-dioxane contamination in a source zone. The test demonstrated that high concentrations of 1,4-dioxane could be biodegraded relatively easily in all tested biological conditions.
In 2021 a field study on the site was conducted. During the field tests two crucial challenges were encountered, namely an increased pH up to about 8.9 as a result of aeration and no clear signs of biodegradation for at least 6 months.
Based on these observations additional laboratory tests were performed to gain more insight in process and effect of the increased pH, the dioxane degradation process and the involved microorganisms. Next generation sequencing (NGS) was performed to characterize the microbial community and identify the dioxane degrading microorganisms.
Laboratory tests could confirm biodegradation, but the results were different from the first degradation test, that might be explained by a different abundance and ratio of the two most likely dioxane degrading microorganisms. The Wageningen University is currently further

looking into the microbial community and the effect of different factors like pH and dissolved oxygen concentrations on the composition of the microbial community.
Laboratory test also confirmed that already within 30 minutes of active aeration, the pH of the groundwater increased from neutral values to around 8.7 likely due to the stripping of carbon dioxide. However, it was found that an active dioxane degrading culture was not inhibited by a short term exposure to an elevated pH and the pH decreased in about a week to neutral values again, likely due to the production of carbon dioxide.
Based on these findings the bioreactor was started up with a passive aeration, and once biological active switched to an active aeration. In this way a long-term stable bioreactor with an removal efficiency of 99% was established. Based on NGS analyses it was also found that inoculation of the bioreactor with an active dioxane-degrading culture was not necessary and the dominant dioxane degraders were native microorganisms from the source zone.
Currently also on-site (biopiles) and in-situ treatment is further investigated for treatment of the source zone.

Conclusions
Biodegradation of high concentrations of dioxane was demonstrated, although the biodegradation process was different than initially thought and required more insight.
Challenges in the field were overcome by additional laboratory testing and molecular analyses gave more insight into the biodegradation process and microorganisms involved.
After several challenges like a high pH and the absence of clear signs of biodegradation were overcome, eventually a stable bioreactor with 99% removal efficiency was established.
Significance
Laboratory tests and molecular analyses proved to be very valuable for a better understanding and control of the application of biodegradation on a field scale.

<u>Session 3c5 / Abstract title</u>: Nature-based solution for water treatment using Biologically Enhanced Biochar

ID: 27

Key words: Biologically Enhanced Biochar, Nature-based solution, Climate change mitigation, Waste valorisation

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Session: 3c5

Abstract

Purpose of the study: Our study demonstrates the use of Biologically Enhanced Biochar as a nature-based, economical, and sustainable solution to the global shortage of safe clean drinking water. Biochar has gained wide attention due to its carbon-sequestration potential and multi-functional nature, leading to its use in several energy and environment applications. Biochar is a carbon-rich product of thermochemical conversion of biomass produced under oxygen-deficient conditions and is a great microbial inoculum carrier. Biochar immobilised with microbial communities, referred to as BEB, can facilitate the removal of several organic-inorganic contaminants via a combined adsorption and biodegradation process.

Methodology: We produced biologically enhanced coconut shell biochar, a low-cost porous support immobilized with naturally occurring microbial communities for degrading cyanotoxins in fresh water. We used pyrolysis, a type of thermochemical conversion in oxygen-deficient conditions, to produce coconut shell biochar. To allow for the optimization for microbial colonization and evaluate the scalability of the proposed solution, coconut shell biochar was produced using batch-scale and continuous scale pyrolysers under three pyrolysis temperatures (450, 550 and 700□C), which were then extensively characterized. Microcystins were used as highly toxic, commonly occurring cyanotoxins to influence the

selection of the initial microbial community from natural lake water immobilizing on the biochar, forming BEB. The toxin removal efficiency of the BEBs were then assessed for several complex environments, together with the evaluation of the microbial community structure.

Summary of findings/results: The abundance of microcystin-degrading microbes and richer species diversity in biologically enhanced biochar (BEB) were associated with rapid (as fast as 24 h) degradation of these cyanotoxins. While the differences in properties in coconut shell biochar produced at different temperatures led to different microbial community structures in the BEBs, they all had similar community function evidenced by similar average toxin degradation rates, even for various complex environments. The scalability of the proposed solution was ensured by evaluating the efficacy of BEB from batch-scale, continuous-scale pyrolysis as well as from field-scale low-cost pyrolysis kilns. This method was also assessed to be safe by making sure that any toxic impurities in the produced biochar are within acceptable limits, as well as ensuring that the degradation by-products are non-toxic. These BEB could then be transferred to contaminated water to achieve toxin removal as a scalable water treatment strategy.

Conclusion: This study demonstrates low cost, simple, scalable, nature-based water treatment systems for elimination of commonly occurring toxins from cyanobacteria and shows the potential of BEBs to eliminate several freshwater pollutants of emerging concern such as pharmaceuticals and pesticides making it a technology to improve the quality of water for safe human consumption.

Significance/contributions of the study: BEB is a cost-effective, sustainable option for water treatment rooted in effective waste valorisation, especially in agrarian economies with easy access to abundant biomass in the form of crop residue and organic wastes. In addition, local communities will benefit from better use of agricultural waste to produce biochar, which apart from using in water treatment can be used as a soil fertiliser at its end-of-life in water filtration, indirectly helping in N, P, K recovery. The gas produced during biochar production can also be used for drying and heating purposes. This water treatment solution will have wide application, and will contribute to achieving UN SDG6, while embracing the philosophy of 'Nature-Based Solutions for Water.'

Reference: Jayakumar et.al, Science of The Total Environment, Volume 796, 2021, 148977

<u>Session 3c5 / Abstract title</u>: DNAPL Extraction and Oxidation enhanced by Surfactant addition: LIFE SURFING PROJECT

ID: 273

Key words: Lindane, DNAPL, Fractured Aquifer, SEAR, S-ISCO

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Session: 3c5

Abstract

Surfactant Enhanced Aquifer Remediation (SEAR) and In Situ Chemical Oxidation enhanced by Surfactant addition (S-ISCO) have been successfully tested in the Bailin Landfill (Sabiñanigo, Spain) during the LIFE SURFING Project (SURFactant enhanced chemical oxidation for remediatING DNAPL). DNAPL (comprising 28 Chlorinated Organic Compounds, COCs) was produced as residuum in the lindane manufacturer nearby [1] and dumped in the landfill. It was retained in the permeable sandstone layer (M) fractures, resulting in a plume of highly contaminated groundwater with the associated risk for the Gallego river and the population. After 16 years of pumping the dense phase (DNAPL) in the Bailín landfill aquifer, physical extraction is already inefficient, and advanced techniques are required to remove the residual DNAPL.

LIFE SURFING pilot test was executed from 2020 to 2022 in a test cell about 60 m in length located in the M layer of the old landfill, where most DNAPL was dumped. SEAR and S-ISCO applied ensured enough contact time between reagents and pollutants and prevented surfactant and solubilised COCs from reaching the river.

In SEAR and S-ISCO events, the groundwater composition was monitored in 29 wells in the M layer, from the cell to the river. The injection and extraction strategy in the cell and the implementation of a barrier zone between the cell and the river required a detailed previous characterisation of the groundwater flow in the fractures, carried out in 2020 and 2021. The barrier zone comprises the dosage of NaOH solution to the base of the aquifer to reach pH 12, aeration and vapour extraction and dosing $Na_2S_2O_8$ with alkaline activation downstream of the test cell.

Two SEAR tests were applied in the spring of 2022. E-Mulse 3® was selected as the surfactant in laboratory tests [2]. About 16 m3 of a solution of 20 g L-1 of the surfactant was injected into the test cell (bromide 190 mg L-1 was added as a conservative tracer). Injected fluids were recirculated during the injection. Groundwater was extracted when injection ended with a recovery of 55-60% of the tracer and 30-40% of the surfactant injected in the first and second SEAR tests, respectively, with solubilised COCs up to 3 g L-1, Two weeks after the second SEAR test, 12 m3 of leachate and fines were extracted with approximately 10 kg of DNAPL in solution and 90 kg of DNAPL mixed with the fines. About 130 kg of DNAPL has been removed with the two SEAR events (ratio mass of surfactant injected/mass of DNAPL recovered about 2.5).
S-ISCO was carried out in September 2022. Oxidant (persulfate) and activator (NaOH) were selected in the previous LIFE Discovered project. The effectiveness of this oxidant and E-Mulse 3 ® with this DNAPL was also proved at the lab scale [3]. A volume of 21.6 m3 of a persulfate solution (40 g L-1), surfactant (E-Mulse 3 ®, 4 g/l) and NaOH (10 g L-1) was injected in pulses of 1 m3 each hour in two wells. The groundwater is pumped downstream and recirculated back to the cell during the injection. In addition, a foam barrier has been generated downstream to minimise the flow of injected fluids escaping from the cell. The injected fluid that escaped from the test cell reached the barrier zone without a dense organic phase, without surfactants and with low solubilised COCs. About 20 kg of DNAPL were oxidised in the S-ISCO event. Three months after the end of S-ISCO, the concentrations of COCs in the test cell remain very low, and no rebound has been noticed in the saturated zone. However, rebounds will be monitored during the following months.

<u>Session 3c5 / Abstract title</u>: Removal of halogenated compounds in water by persulfate and peroxymonosulfate activated by iron-copper bimetals and zero-valent iron

ID: 274

Key words: advanced oxidation processes; halogenated compounds; persulfate; peroxymonosulfate; ZVI bimetals;

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Session: 3c5 backup

Abstract

Advanced oxidation processes (AOPs) proved to be efficient and sustainable technologies for the removal of recalcitrant organic compounds from soil and water systems, including emerging contaminants. In this context, persulfate (PS) and peroxymonosulfate (PMS) are considered advanced oxidants because they can be activated to generate highly reactive species, such as sulfate radical (SO4•-), characterized by a longer half-life and higher selectivity towards organic contaminants, rather than hydroxyl radical (OH•) typically produced by conventional AOPs based on hydrogen peroxide. Among the different activation methods, those relying on iron have been particularly appreciated because they are cost-effective, environmentally friendly, and non-toxic. Although Fe2+ is a commonly used activator, zero-valent iron (ZVI) has also been applied to activate PS and PMS, showing better performance regarding the control of the system and generation of undesirable side reactions. Recently, iron-based bimetallic materials were also tested and proved to be more reactive than ZVI promoting electron transfer and overcoming some limitations of ZVI (e.g. its passivation). Bimetals are typically produced by chemical methods, such as chemical solution deposition, and physical methods, such as ball milling. Further investigation is needed to assess the performance of bimetallic materials in combination with PS and PMS and to identify the reaction mechanisms. This work aims to investigate PS and PMS, activated by different ZVI, and disc milled zero-valent iron-copper (Fe-Cu) bimetals for the removal of halogenated compounds in water. Namely, 4-chlorophenol (4-CP) was chosen as model compound of this class of contaminants due to its strong resistance to chemical and biological remediation. To the best of our knowledge, this is the first time that bimetals

prepared by disc milling have been used in the field of AOPs. In this context, a systematic study was carried out, using PS and PMS activated with ZVI (particle size 63 μm), or disc milled zero-valent iron-copper (Fe-Cu) bimetals, in order to find the best operating conditions in terms of 4-CP removal. Batch tests in lab-scale PTFE reactors were carried out to study the efficiency of the different system, which were compared to the ones achieved using Fe^{2+} as activator. The effect of the following operating parameters has also been evaluated: i) reagent concentrations (oxidant and activator), ii) weight percentages of Cu in the bimetals (1%, 5% and 50%), and iii) milling of the activator. The highest 4-CP removal rate was obtained using Fe-Cu bimetals as activators of PMS, followed by bimetals with PS and ZVI with PS. A higher removal of 4-CP at the end of the reaction time interval considered (i.e. 120 min) was obtained using bimetals with higher Cu content in the case of PMS, thus suggesting a better synergy of this oxidant with bimetals than ZVI. Fe^{2+} was the worst activator for both PS and PMS. Additionally, quenching tests were carried out to understand the contribution to 4-CP removal of the main reactive species produced in selected systems, respectively, PS and PMS activated by ZVI and disc milled bimetals. The results obtained confirm the production of both $SO_4^{\bullet -}$ and $OH^{\bullet}$ radicals by PS and PMS activated by ZVI and Fe-Cu bimetals. To address the different possible mechanisms of activation, the concentrations of Fe and Cu in water were measured. Moreover, the activator at the end of the tests was analyzed by SEM and XRD and compared to the initial material. In summary, disc milling has emerged as an effective technique for producing bimetals that can efficiently activate PS and PMS for the removal of 4-CP in water. The results of this study suggest that Fe-Cu bimetals, especially in combination with PMS, can be considered promising activators for the sustainable treatment of halogenated compounds.

<u>Session 3c5 / Abstract title</u>: Study of sorption of micropollutants to microplastics under field conditions

ID: 408

Key words: Microplastics, micropollutants, sorption, field experiment.

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Session: 3c5

Abstract

Microplastics and emerging contaminants are a relatively new and pressing environmental concern in river ecosystems. These contaminants have the potential to cause significant harm to both the ecological health of rivers and the human communities that rely on them for drinking water, recreation, and other uses. The coexistence of these two groups of pollutants raises the question of their interaction, which is currently the subject of active scientific research. However, most of the scientific work investigates this question under laboratory conditions using microplastics that are not environmentally relevant. Thus, there was a need for more environmentally relevant research.
The aim of this work was to expose manually produced microplastic particles, close to those found in nature, to a real river environment to study the sorption of micropollutants on microplastics. Great efforts were made to create microplastics that mimic those found in the environment as closely as possible. Pellets of three types of plastics (PVC, LDPE, PET) were ground on a centrifugal mill and then particles of 150-300 µm were separated. Half of the particles were then subjected to the process of accelerated aging by UV irradiation, elevated temperature and water scraping. The particles were then characterized by FTIR spectroscopy and surface area analysis (BET). Several samplers containing different types of microplastics were installed in a river near a water treatment plant. Passive POCIS

samplers were also installed as a positive control, and passive samplers containing sand particles of the same size as the microplastics were installed as a negative control. After two weeks, the samplers were collected and analyzed. The micropollutants studied included pesticides, pharmaceuticals and personal care products (PPCPs), and per- and polyfluoroalkyl substances (PFASs).

The results of the experiment showed that microplastics have the ability to sorb micropollutants on their surface under natural conditions. For example, PPCPs were the most abundant group of analytes adsorbed on microplastics. While on the surface of sand particles the sum of the averages of PPCPs was 1.5 ng/g, in the case of microplastics these concentrations were in the range of 102 - 337 ng/g depending on the plastic used. Furthermore, different sorption behaviors of contaminants were observed depending on whether the microplastics were artificially aged. For example, in the case of the highly hydrophobic antihypertensive drug telmisartan (log KOW = 7.7), a decrease in the concentration of substances captured on microplastics was observed when aged microplastics were used. However, an increase in the absorbed concentration of aged substances was observed for less hydrophobic substances. This is the first study to monitor the sorption of pesticides, pharmaceuticals and personal care products (PPCPs) and per- and polyfluoroalkyl substances (PFASs) on the surface of microplastic particles placed under real freshwater conditions in nature.

Session 3c6 orals

Session 3c6 / Abstract title: Innovative reactive liner technology for delineating chlorinated solvents in fractured bedrock and determining sustainable remediation methods

ID: 101

Key words: chlorinated solvents, reactive liners, sustainable

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Co-authors: nan

Session: 3c6

Abstract

Chlorinated solvent DNAPL sinks through soil and groundwater. Once past the overburden, it flows along the bedrock topography through gravity, meaning it can migrate along, perpendicular to, or even against the groundwater flow direction. The DNAPL may pool in a depression on top of bedrock, or it may find its way down into open fractures. Once in the fractures, the DNAPL will likely continue to follow the strike and down dip direction of the fractures and can thus migrate far. Accurately delineating solvents in fractures is therefore important, but difficult with traditional methods. This problem can be overcome using the innovative FLUT™ Technologies system.

The FLUTe™-system is based on an impermeable nylon “blank” FLUTe™ liner that is everted down into an open bedrock borehole and filled with water to above the groundwater level of the borehole. This additional weight will ensure the liner is pressed tightly in place against the inner walls of the borehole, effectively sealing it and preventing DNAPL or dissolved phase contaminants from entering the borehole or migrating along the liner.

A blank FLUTe liner™ fitted with a NAPL FLUTe™ reactive textile detects chlorinated solvent DNAPL as this will wick to and stain the textile by dissolving the imprinted dye at the point of contact. Dissolved phase solvents and their breakdown products will not stain but be absorbed by the FACT™ strip, a felt fabric treated with activated carbon, where this crosses a fracture with impacted water. The liner is hauled out, the NAPL FLUTe inspected and the FACT™ strip is sectioned into appropriate lengths for analysis to produce a qualitative profile of the vertical contaminant distribution in fractures transected by the bedrock borehole.

Once fractures carrying contaminants have been identified, another type of liner, a Cased Hole Sampler (CHS), can be installed to draw water from specific fractures or zones through

nipples from the inside of the liners at predetermined depths. Actual concentrations, breakdown products and other parameters can now be determined, while ensuring that no water is drawn from the borehole at higher or lower levels as the whole borehole is effectively sealed by the water column.

This method is a robust tool for mapping solvent migration in fractured bedrock and is used on many projects in Sweden, from granitic/gneissic bedrock to limestone. By understanding the depth and concentration of solvents in fractures, coupled with ATV/OTV filming and level-specific sampling of the groundwater, transport modelling can be performed of the source area and plume(s).

The blank liners can also be used to accurately calculate the transmissivity of the fractures across the length of the borehole using FLUTes “T-profiling” method. Simplified, the evertion rate of the liner is directly dependent on how fast it can displace the water in the open borehole beneath the liner back into the fractured bedrock. The maximum transmissivity of a borehole is right at the start when all fractures are uncovered, and the velocity of the liner descent will thus be the highest. As the liner descends down the borehole, it will successively cover more and more of the fractures and the velocity will therefore reduce. This continues until the liner stops due to no more fractures and the transmissivity is calculated.

Combining the knowledge of DNAPL source, dissolved phase solvent concentrations, migration direction(s!), physical parameters, and fracture transmissivity, sufficient information is available to determine whether the impacted bedrock is suitable for bio- or chemical remediation methods instead of relying on, for example, a thermal treatment system, thus making it an indispensable tool for sustainable remediation. The DEIL system (Direct Extraction-Injection Liner), a tougher version of the CHS, can then be set up in an array around the source and plume and used to inject or draw amendment into the chosen fractures under pressure/vacuum.

<u>Session 3c6 / Abstract title</u>: Evaluation of the applicability of the radon deficit technique in soil gas for quantifying residual LNAPL contamination

ID: 151

Key words: Hydrocarbon contamination; NAPL delineation; Soil gas monitoring; Radon deficit technique

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Session: 3c6

Abstract

The presence of light non-aqueous phase liquids (LNAPL) in hydrocarbon-contaminated sites is typically monitored by analysing the apparent thickness of the free product in the piezometric network. This approach, however, does not provide information on the distribution of LNAPL in residual form, which is essential for a proper design of remediation activities. In the last few decades, the use of radon (Rn) has been proposed as an alternative approach. Due to its proven tendency to preferentially partition into oily phases, it is considered a natural tracer for the presence of LNAPL in the subsurface in both residual and mobile form. It has been shown that in the areas contaminated by LNAPL, there is a local decrease of Rn concentration in the soil gas compared to the background value detected in the subsurface not impacted by LNAPL. By monitoring the Rn in the soil gas, it is possible to determine a Rn deficit between the two zones, which can be used for identifying and quantifying LNAPL in the subsurface. In this paper, the feasibility of using Rn monitoring data in soil gas for this purpose is analysed on a modelling and experimental level. To this end, an analytical model was developed to describe the expected Rn behaviour in the presence of separate phases in the subsurface. Using the developed solution, the vertical Rn concentration profiles in the soil gas expected above the source zone and in the area not impacted by LNAPL were evaluated under different conditions. Based on the simulations performed, it was observed that the parameter that most influences the effectiveness of the use of Rn as a tracer for LNAPL is the vertical distance of the soil gas probe from the source zone. In particular, at distances greater than 2 m, the method appears to be no longer sensitive to the presence of LNAPL. Therefore, using soil gas probes to apply the Rn-deficit

technique for estimating LNAPL would only be applicable if the probes are installed in proximity of the source zone. As an alternative, Rn can be monitored in the headspace of groundwater monitoring wells, typically screened in the portion affected by the presence of LNAPL (saturated zone and capillary fringe). In order to verify the performance of the method, a series of tests were conducted at two gasoline stations owned by Eni, where the concentrations of Rn and other markers (O2, CO2, CH4 e VOC) were analysed using portable instrumentation in the headspace of monitoring wells installed at the sites. In all the tests carried out, Rn concentrations in the hydrocarbon-impacted zones were lower than in the background areas, thus indicating that the method is applicable for the determination of the presence of residual phase in the unsaturated zone, which is not possible with the sole monitoring of the free product in monitoring wells or with water sampling. The method was also effective for estimating the expected concentrations in the investigated area, with results consistent with those available from the characterisation phase. In the application of the method, some uncertainties were found related to the presence of heterogeneities in the subsurface (which may affect the estimation of the Rn deficit) and to the temporal variabilities (daily and seasonal) of Rn emissions from the subsurface, suggesting that in such cases these estimates should be considered semi-quantitative. Following the results obtained, it is believed that Rn monitoring in the piezometer headspace is a rapid and minimally invasive method for the identification of mobile and residual phase LNAPL, which can prove additional information to that typically available from the piezometric network monitoring alone.

<u>Session 3c6 / Abstract title</u>: Comparison of different methods for investigating indoor air quality and vapor intrusion at a chlorinated solvent site. Dynamics between groundwater, drainage system and indoor air.

ID: 154

Key words: Indoor air, chlorinated solvents, vinyl chloride, sampling methods, conceptual model

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Session: 3c6

Abstract

Purpose
At a former dry-cleaning site in Denmark contaminated soil was excavated and three apartment blocks were built in 1991. Years after, site investigations at the neighboring site showed a significant contamination in the groundwater with concentrations of chlorinated solvents over 5000 µg/l originating from the former drycleaner, including high levels of vinyl chloride. It was then crucial to determine how this contamination affected indoor air in the apartment blocks.

The purpose of the site investigation was to investigate the migration pathways and risk to the indoor air. Further objectives included:

- Mapping the contamination of chlorinated solvents and the degradation products in the shallow groundwater under and around the buildings
- Measuring indoor air concentrations of chlorinated solvents using different methods
- Developing a conceptual understanding of how the dynamics between the groundwater, drainage system and the buildings constructions influence indoor air concentrations

Methodology
An extensive site investigation was carried out and a large data set was collected including:

- Repetitive measurements during the year (three sampling campaigns).
- 14 days-sampling of indoor air with different methods for comparison: 700x SKC Charcoal Sorbent Tubes, 600x Beacon tubes and 22x Canisters.

- Water samples from 36x boreholes and additional water samples from sewers and the drainage system.
- Instant measurement of soil gas and sewer gas.
- 14 days of datalogging of indoor air quality and pressure.
- 30 days of datalogging of groundwater levels in boreholes and water levels in the sewers- and drainage system.
- Collection of all data and observations in a conceptual model for the site.
- All samples were analyzed for chlorinated solvents and their degradation products.

Results

The contamination in groundwater at different depths was mapped. Concentrations up to 38 µg/L PCE, 53 µg/L TCE, 5700 µg/L cis-DCE and 580 µg/L VC were detected in the shallow groundwater, mainly between 7-14 m b.g.l.

In the sewer- and drainage system up to 1,8 µg/L PCE, 1,3 µg/L TCE, 200 µg/L cis-DCE and 27 µg/L VC was detected.

In the basements of the apartment blocks and in selected apartments concentrations above the legal standards were detected. An indoor air risk was confirmed because of the high levels, highest concentrations were 8,64 µg/m3 PCE, 5,13 µg/m3 TCE, 32 µg/ m3 cis-DCE and 4,25 µg/ m3 VC.

Very good agreement between the different indoor air sampling methods and during different campaigns over the year was observed, with small variations for vinyl chloride. Specifically, VC was underestimated by SKC Charcoal Sorbent Tubes compared to e.g. Beacon tubes.

Based on the different methods and technologies, a conceptual model was developed.

The last sampling campaign was carried out in December 2022. Currently we are studying the interactions between groundwater, drainage system, basement, and movement to the apartments, and these results are expected to be available in spring 2023.

Conclusion

14 days of sampling with different methods made it possible:

- to obtain two weeks average concentration of contaminants in indoor air which gives a more accurate evaluation of the indoor air risk,
- to get a better understanding of the dynamics between the contamination of chlorinated solvents and degradation products in groundwater, the buildings including the sewers- and drainage system and indoor air,
- to evaluate which sampling method of indoor air are feasible and most reliable.

Contributions

The presentation will give new insights into how a large data set based on different medias (e.g., groundwater, soil gas, indoor air), different technologies (e.g., sampling, data logging) and methods (SKC Charcoal Sorbent Tubes, Beacon tubes and Canisters) contribute to a robust conceptual model. Based on a robust conceptual model, the risk and decisions of remediation can be evaluated with a higher certainty.

<u>Session 3c6 / Abstract title</u>: Mechanisms of long-term leaching of persistent and mobile chemicals (PMOCs) from clayey till to groundwater aquifers

ID: 189

Key words: Persistent and mobile organic chemicals; Pesticides; Long-term leaching; Fractured clayey till; N,N-dimethylsulfamide

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Session: 3c6

Abstract

This study looked at the retention of the fungicide metabolite N,N-dimethylsulfamide (DMS) in clayey till. DMS, along with several other pesticide metabolites are examples of anthropogenic contaminants that can be classified as Persistent and Mobile Organic Compounds (PMOC). This designation is similar to the EU REACH classification “vPvM” substances, which are very Persistent (vP) and very Mobile (vM). These chemicals have received little attention so far due to rather low toxicity. However, their widespread occurrence in the environment is a course for concern and constitutes a risk to groundwater resources.

Understanding the processes affecting the release of pesticides and metabolites from soils and the unsaturated zone is crucial to predicting the duration of contamination in groundwater systems, including groundwater catchment areas for groundwater supply well fields. The mobile nature of DMS suggests that sorption alone does not fully explain the observed retention time in clayey till. A numerical model was built in COMSOL Multiphysics to test the significance af fracture-matrix interactions in clayey till and the effects of fracture aperture and input concentration.

Properties affecting the environmental fate of DMS were investigated in laboratory studies, which included sorption and degradation experiments with different sediement types and redox conditions. The distribution of DMS in the unsaturated zone and groundwater was

aquired from porewater samples and level specific groundwater samples. The former were obtained from suction cells installed in a former strawberry field at 3, 5, and 9 m bgs, and the bottom of the clay at 10-12 m bgs. Groundwater samples were collected at specific depths by a direct push method employing a 1 m-screen.

Laboratory results indicated that DMS can degrade slowly in topsoil ($t_{½}$ = 63-494 d) and aerobic clay ($t_{½}$ = 653-2990 d), while degradation under anaerobic conditions (clay/aquifer material) could not be detected. Regarding sorption, the coefficient was too low to be determined in 10 soils tested, including topsoil, clayey till, meltwater sand, and limestone (Kd 0.1 L/kg). These results confirm the PMOC designation of DMS but with the refinement that a minor degree of degradation can occur under aerobic conditions.

Porewater data gave the current vertical distribution of DMS in unsaturated clay till below the former strawberry field. The concentration was seen to increase over depth with 0.02-0.2 µg/L at 3 m bgs and up to 26 µg/L at 11 m bgs. The bulk of mass seemed to be distributed in the bottom 3 m of clayey till (9-12 m bgs). Numerical modelling was able to replicate the concentration profile in clay if fractures were included to slow the vertical transport by diffusion of DMS between the fracture and the matrix.

The results indicate that even very mobile substances can be retained during vertical transport in unsaturated clayey till by mechanisms of fracture-matrix interactions. This implies that a stop in application of a contaminant/parent compound is followed by a long-term leaching for decades. This has major implications for the longevity of PMOCs in groundwater systems and management of pesticide metabolites. A tool for estimation of the duration of PMOCs in well fields is under development. This provides planning horizons for water utilities facing contamination with PMOCs, which is key for investments and long-term planning.

<u>Session 3c6 / Abstract title</u>: The Utilisation of Innovative Site Survey and Remediation Methods at the Duchcov Site with Complex Conditions and Geology

ID: 29

Key words: Site survey, HRSC; phytoscreening; direct-push; Frac-In

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Session: 3c6

Abstract

• Purpose of the study

A factory that produced prams, scooters, tricycles, cars, swings, furniture and other products was operational at the Duchcov site from 1907 to 1989. Electroplating and degreasing plants were identified as the main sources of the contamination of a heterogeneous low permeable quaternary aquifer mainly in the form of toxic metals and chlorinated ethenes. Initially, only limited information was available on the spatial distribution of the contamination in the soil and groundwater since the presence of heaps of rubble from the demolished buildings prevented a thorough site investigation. The limited results available indicated the presence of chlorinated ethenes in low permeable sediments that vary from solid claystone and plastic clays to fine sands with clay admixtures. The aquifer has a filtration coefficient in the range of 2.6 x 10-6 to 2.8 x 10-5 m/s, which presents a major challenge in terms of its remediation.

• Methodology

Soil gas sampling followed by the so-called phytoscreening sampling of 10-15-year-old trees that grew on the rubble heaps were employed as the initial investigation methods followed by an initial limited MIP investigation and core sampling. The contamination sources were identi-fied and the obstructing rubble was removed. Further MIP, HPT and core sampling was then employed to delineate the contamination, and the contaminated unsaturated zone was exca-vated. So called Frac-In injection that combines direct-push drilling with pneumatic fracturing and the subsequent hydraulic emplacement of the remediation agents was utilised in order to remediate the low permeable aquifer. Based on previous laboratory experiments, ISCR com-bined with ERD was used as the remediation technology. Milled waste cast iron was used as the main chemical reducing agent partly combined with microscale zerovalent iron (mZVI) C100.29 provided by Höganäs and sulphidised nanoscale zerovalent iron (SnZVI) provided by Nano Iron. Glycerol was used as the carbon source in order to enhance

the microbial reduc-tive dechlorination.

- Summary of the findings/results

The phytoscreening and the soil gas sampling provided a good initial insight into the distribution of the contaminants at the site. The results were later confirmed via a combination of MIP, direct-push drilling and groundwater sampling. The site was covered by 96 Frac-In injection points with more than 430 injection horizons; 2 injection campaigns were performed at the site involving the injection of 86.4 m3 of a remediation suspension that contained 10 t of milled cast iron, 3 t of mZVI and 100 kg of SnZVI together with 115.2 m3 of a 50 g/L glycer-ol solution. The results of the monitoring obtained to date serve to prove that the injections triggered both the inorganic chemical reduction of the chlorinated ethenes and the gradual growth of a specific anaerobic bacteria that is capable of the full reductive dechlorination of the chlorinated ethenes. Data on the further development of the groundwater contamination and microbial biomass at the site will be available at the time of the presentation.

- Conclusion

Thanks to the utilisation of innovative site survey methods, it was possible to quickly identify the contamination source zones without the need for the removal of the majority of the obstructing rubble. The combined use of direct-push drilling and pneumatic fracturing and the subsequent hydraulic emplacement of the remediation agents allowed for the injection of a large volume of the reducing agents in the low permeable heterogenous aquifer in a cheap, fast and sustainable way.

- Significance/contributions of the study

The results of this study proved that the use of innovative methods provides an ideal solution to the remediation of complex sites with challenging geological conditions.

Session 3c7 orals

Session 3c7 / Abstract title: Utilizing 3D Geophysics for Detailed Mapping of a Deep Landfill Leachate Plume

ID: 268

Key words: Landfill, tTEM, Pharmaceuticals, Chlorinated solvents

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Session: 3c7

Abstract

Purpose of study. Grindsted landfill (DK) is an old landfill without leachate collection system. In the early 1990s this site was used as a case study for landfill leachate and is well described e.g., /3,4/. It consists of approx. 500.000 m3 household and construction waste deposited from 1930s to 1977 as well as sludge from a pharmaceutical plant deposited from the 1962 to 1977. A leachate plume containing chlorinated solvents and pharmaceutical compounds has developed downstream the landfill /3/. Groundwater is present 2 m below ground and the nearly homogenous sandy quaternary and tertiary aquifer extends 70 m below ground lined by a tertiary clay aquitard. Both land use (farmland), geology and a high conductivity plume makes it an ideal site for geophysical investigations. The geophysical mapping of the plume was part of a larger investigation with the focus to map if the plume has reached downstream surface water.

Methodology. Non-intrusive methods like geophysics provide cost effective knowledge of the geological setting and are widely used for mapping groundwater resources and their vulnerability towards pollutants. Aarhus University has developed a novel geophysical instrument which provides 3D images of geology in a cost-effective manner. Their towed ground based transient electromagnetic (tTEM) instrument is designed to map the shallow subsurface (0-80 m) by employing a fast data repetition and hence enabling a dense measurement sampling of 5-10 meters on mapping lines, and line spacing of down to 10-20 m. The instrument is towed by an all-terrain vehicle (ATV) permitting mapping speeds of up

to 5 m/s and hence hundreds of hectares can be mapped in detail in one day. The tTEM has successfully been used for investigations of landfill plumes /1, 2/, where the high conductivity of the leachate can be identified as a low resistivity area and mapped in great details.

Summary of findings. Using an ATV driven tTEM system, we managed to find and map the leachate plume of Grindsted landfill in a detailed 3D model. We managed to collect approximately 50 km of tTEM lines with a measurement spacing of 15 to 50 m during just 3 days of fieldwork. Our area of investigation covered approx. 300 ha. Ultimately, 5 monitoring wells to a depth of 75 m and 6 monitoring wells to a depth of 40 m with 48 ground water sampling points in total were installed to confirm the geophysical signal indicating the plume and to investigate the development of the plume.

Conclusion. Our detailed 3D mapping shows the plume to extend more than 2.000 m away from Grindsted Landfill and significantly off from the expected pathway suggested by an earlier numerical hydrogeological model. We identified a leachate plume with the strongest signal 30 to 40 m below ground, at its deepest. The plume resurfaces into Grindsted Stream more than 2.000 m downstream. Groundwater samples confirmed the position of the plume as indicated by geophysics with a high conductivity in the same depth. We found plume ionic strengths of 3-9 meq/L and approx. 2 meq/L in pristine groundwater. The plume contained chlorinated solvents (primary VC (up to 4,3 µg/L)) and up to 6.900 µg/L of pharmaceutical components (namely sulfanilic acid and acetyl sulfanilic acid).

Significance. Results from tTEM mapping helped placing monitoring wells with much higher chance of intakes placed directly in the plume. The use of tTEM provides a cost-effective and extremely fast alternative to the traditional trial-and-error strategy for placing monitoring wells downstream a large landfill.

/1/ Høyer et al. 2019 https://doi.org/10.1016/j.enggeo.2018.12.015 /2/ Maurya et al. 2017 https://doi.org/10.1016/j.jappgeo.2017.01.019 /3/ Holm et al. 1995 https://doi.org/10.1021/es00005a039 /4/ Bjerg et al. 1995 https://doi.org/10.1021/es00005a035

<u>Session 3c7 / Abstract title</u>: In-situ Soil Washing as Lead-out for more effective ISCO and ISCR. Full-scale Implementation For Chlorinated Solvents

ID: 365

Key words: surfactant, VOCl, Soilwashing, in-situ, Belgium

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Session: 3c7

Abstract

In-situ Soil Washing as Lead-out for more effective ISCO and ISCR
Full-scale Implementation For Chlorinated Solvents
By: Glenn Heernaert, TerraCorrect bv and Hilde Decuyper , A+E Consult bv

Abstract
In-situ remediation is typically viewed as challenging. This due to the natural sorption of hydrophobic contaminants, that at increasingly higher concentrations, they phase partition to form globules, and floating, or sinking, non-aqueous phase liquids (NAPL). NAPL can become entrained in the soil and groundwater, with limited availability for physical, biological and chemical remediation, due to inhibition of mobility caused by interfacial tension. The limited availability of contamination in soil and groundwater inhibits conventional remediation processes, such as ISCO, ISCR, which are stoichiometrically unfeasibly for site with high concentrations, resulting is repeated chemical applications failures, in what are characteristically known to be very long and very costly in-situ remediation projects, due to the inherent limitations of single remediation technology applications.
With prevailing regulatory and market mandates for more environmentally sustainable remediation of contaminated sites in Europe, this has challenged remediation practitioners to be more innovative. This pressure has driven a recent trend to pursue novel ways to overcome the conventional limits of contaminant availability for physical, biological and chemical remediation. This has been characterized by site remediation employing innovative technology, and the synergistic combinations of technologies, to realize what is to become a new sustainable paradigm in soil and groundwater remediation, regardless of soil texture and contaminant concentration.
An example of this innovative trend that breaks from conventional remediation, employs the use of non-emulsifying surfactants as the lead-out step, for more effective ISCO or ISCR, or in-situ soil washing. The principle objective of the surfactant injections are to enhance

contaminant mass removal, via desorption and resolving interfacial tension. Once the bulk of contamination has been removed, then the remaining residual contaminant, in the soil and groundwater can be more effectively treated with ISCO or ISCR, with the choice oxidant or reductant depending upon the contamination to be treated, and prevailing site conditions (pH, redox-potential, conductivity, etc.).

Depending on the degree of contamination, a minimum removal of 70% of the bulk contaminant mass is pursued with the in-situ soil washing, before moving on to other in-situ techniques.

Results will be given from a full-scale application at a formal textile factory in Tielt (Belgium)

<u>Session 3c7 / Abstract title</u>: Development of biogeofilters to remediate intensive horticultural ecosystems polluted with antibiotics

ID: 383

Key words: antibiotic residues, emergent pollutants, ligninolytic fungi, nanostructured geomaterials, agro-food wastes, circular economy

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Session: 3c7

Abstract

Development of biogeofilters to remediate intensive horticultural ecosystems polluted with antibiotics
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Keywords: antibiotic residues, emergent pollutants, ligninolytic fungi, nanostructured geomaterials, agro-food wastes, circular economy
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In countries that have water scarcity and soils with little organic matter, the use of wastewater for irrigation and the use of organic amendments are common practices. These waters and some fertilizers of animal origin can contain small amounts of antibiotics. Until now, there is not legislation of maximum levels of antibiotics in vegetable food, in contrast to animal food products. Nevertheless, because of the potential risk due to subclinical doses found of these drugs it is clear the need to minimize the levels of antibiotics in vegetable food and regulate their maximum levels.

Different technologies are under development to reach removal of antibiotics and other

pollutants from wastewater such as adsorption, biodegradation, advanced oxidation processes and UV radiations. Hybrid technologies by combination of different strategies seem to be promising such as chemical and biological treatment processes like the case of the proposal presented here, combination of biochemical and adsorption treatment.

In present contribution, a family of biogeofilters have been generated friendly to the environment and with the concepts of circular economy. The pillars of its composition, phyllosilicates based on special clays with a high specific surface area and the residues generated in the production of edible mushrooms.
Biogeofilters designed take advantage of the enzymes obtained from the spent edible mushrooms substrates (waste materials from the post-cultivation substrate of ligninolytic fungi), immobilized onto nanostructured geomaterials with the aid of other adsorbing waste materials, to reduce and/or eliminate antibiotics present in irrigation waters, fertilizers, organic amendments, and leachates.

Results obtained show that some of the geomaterials have been demonstrated to be effective materials for antibiotics (tetracycline family) adsorption which increases as pH increases from 2 to a range of 6–7.5, in contrast to previous natural clays studied as adsorbents. Other devices designed can remove sulfonamides at rates higher than 90% from real wastewater by combining adsorption and mycodegradation processes.

Acknowledgements: this project has received funding from the European Union’s Next GenerationEU: Recovery, Transformation and Resilience Plan. Spanish Science and Innovation Ministery under the grant contract num. PDC2021-120744-I00.

<u>Session 3c7 / Abstract title</u>: Sequenced S-ISCO® , ISCO and Bioremediation for Treatment of a Pharmaceutical Waste Mixture – Full Scale Application

ID: 385

Key words: ISCO, groundwater, bioremediation, surfactant, DNAPL

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Session: 3c7

Abstract

Background/Purpose. The Kaergaard Plantation megasite on the western coast of Denmark represents one of the most difficult remediation challenges in Scandinavia. Disposal of an estimated 280,000 metric tons of pharmaceutical wastes at the site from 1956 to 1973 resulted in the development of a complex mixture of contaminants in soil and groundwater, including sulfonamides, barbiturates, aniline, pyridine, chlorinated solvents (chloroethenes), fuel hydrocarbons, mercury, cyanide, lithium and other compounds. Although the waste pits were excavated down to the water table, residual dense non-aqueous phase liquid (DNAPL) beneath the water table continues to dissolve an impact underlying groundwater. Contaminants in groundwater are estimated to discharge into the ocean, and public health concerns have prompted the closing of a 1.4-kilometer section of beach at the site. A series of bench and field pilot testing programs were previously completed, which were used to select and design remediation programs for each of the waste pits. The primary remedial goal for the site is to substantially reduce the mass flux of chlorinated solvents migrating from four of the waste pits to downgradient areas.

Methodology/Results. A detailed evaluation of the hydrogeology and mass distribution in each waste pit was used as a basis for evaluating six remedial options for each waste pit, to find the most cost-effective solution. This process identified sequenced application of in situ chemical oxidation (ISCO) using peroxide activated persulfate (ASP) for areas with significant DNAPL, followed by enhanced reductive dechlorination (ERD) for areas with less contaminant mass and/or for polishing following ISCO. One waste pit was used to demonstrate the full-scale application and confirmatory monitoring approaches. This was initiated with a series of ISCO injection events in the shallow intervals of the waste pit, along

with an ERD amendment injection event in the deeper zone. This approach was intended to initiate treatment in both the shallow and deep intervals of the waste pit. Multiple lines of evidence have been used to evaluate the performance of each technology, including evaluating initial distribution of amendments, changes in geochemical conditions and bacterial populations, and changes in contaminant mass, mass flux and dissolved phase COC mixture as evidence for DNAPL treatment. With each subsequent injection event the approach has been optimized based on the performance results. Based on the performance results, Surfactant-enhanced In Situ Chemical Oxidation (1) (S-ISCO®) has also been incorporated into the remedy to enhance DNAPL treatment. In 2021, following success of ISCO/S-ISCO in the first waste pit, ERD was initiated in that pit and S-ISCO was applied in the other three waste pits in 2021. Additional ERD and S-ISCO injections are planned in 2023 to continue the remedy.

Contributions of Study. This presentation will describe the approach used to implement the ISCO, S-ISCO and ERD technologies in rapid succession, observations and lessons learned from implementation including evaluation of reagent distribution and the treatment performance of each of these technologies. Overall, this demonstration project has shown the importance of a flexible approach in remediation and demonstrated the success of a multi-component remedy in treating a complex DNAPL source using ISCO, S-ISCO and ERD.

(1) S-ISCO is a patented, proprietary technology owned by Ethical Solutions LLC (EthicalChem).

Session 3c8 orals

Session 3c8 / Abstract title: International comparison of antibiotic resistance surveillance and reduction by wastewater treatment

ID: 161

Key words: antibiotic resistance; surface water; wastewater; indicators; surveilance

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Session: 3c8

Abstract

Antibiotic resistance is a major threat to human-health and wellbeing. Antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARGs) are environmental contaminants that circulate among humans, animals and the environment. A major route of entry into the environment is wastewater. Wastewater treatment plants (WWTPs) are designed to reduce the concentration of organic pollutants and to avoid the direct discharge of wastewater into rivers and oceans. However, conventional wastewater treatment is not sufficient to entirely remove biological contaminants such as ARB and ARGs. ARB can self-replicate and disseminate ARGs through horizontal gene transfer. Current knowledge of the impact of antibiotic resistance on environmental pollution and human health risks, as well as advances in wastewater treatment technology and antibiotic resistance quantification methods, demonstrate the need for guiding parameters for antibiotic resistance surveillance. The establishment of minimum requirements and integrated surveillance are essential to address antibiotic resistance at temporal and spatial scales and to design and implement measures.

The international research project SARA within the AquaticPollutants Joint Transnational Call 2020 will determine the prevalence of ARB and ARGs in wastewater, WWTP effluents and surface water.
As a first step, uniform test parameters were defined for all study sites. Beside the classical fecal indicator bacteria Escherichia coli and coliforms, extended spectrum beta-lactamases (ESBL) producing E. coli are detected using CHROMagar plates. ESBL Enterobacteriaceae are on the list of top-priority pathogens from the World Health Organization. Based on the results of the qPCR analyses, key ARGs for a PCR-based monitoring were selected. After an initial screening, ARGs were grouped into three categories: 1) Frequently detected in high concentration: sul1, blaTEM, tetC, ermB; 2) frequently detected in medium concentration: blaCMY-2, blaOXA-48, blaCTX-M-32, tetM; and 3) not detected or detected with low frequency in low concentration: blaNDM-1, blaKPC-3, mcr-1, vanA. For the comprehensive monitoring at least one ARG from each category was selected.

Results from first campaigns show that the number of E. coli and ESBL E. coli in the influent of the WWTPs are comparable for Germany, Uganda, Israel, Spain, Portugal, Sweden and France (7.0 ± 0.8 and 5.9 ± 1.3 log per 100 mL). In surface water upstream from the WWTP discharge, an average of 6.5 ×·101 ESBL E. coli per 100 mL were detected, while downstream the average concentration was 6.3 × 102 ESBL E. coli per 100 mL. The reduction of antimicrobial resistance by wastewater treatment was investigated. For example, in Uganda, the treatment is based on a pond system, which led to a limited reduction of the indicator bacteria and ESBL E. coli (1.6-2.0 log levels). In Germany, a reduction by 4.7 log levels was measured after wastewater treatment. The genes sul1, blaTEM, and tetC were reduced by 2.4, 2.0, and 3.1 log levels, respectively, in the German treatment plant, whereas no decrease of these ARGs after wastewater treatment was observed in Uganda.

In conclusion, application of harmonized methods for the detection of the selected key ARGs and ARB provides the basis for the comparison of surveillance data. Results demonstrate that WWTP effluents are important sources of ARB and ARGs in the aquatic environment. In the further course of the project, the monitoring will be continued under inclusion of extreme events. PCR analysis of key ARGs will be extended, and assembly-based approaches will be used to associate ARGs to their associated ARB and plasmids.

The SARA project is funded under the 2020 AquaticPollutants Joint call of the AquaticPollutants ERA-NET Cofund (GA Nº 869178). This ERA-NET is an integral part of the activities developed by the Water, Oceans and AMR JPIs.

<u>Session 3c8 / Abstract title</u>: FDOM as a field screening technique for fluorescent pharmaceuticals in a contaminant plume

ID: 168

Key words: groundwater pharmaceuticals fluorescence-screening-method

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Session: 3c8

Abstract

Purpose of study. A former pharmaceutical production facility has led to contamination of the subsurface with the pharmaceuticals sulfonamides and barbiturates, as well as hydrocarbons and chlorinated solvents. A large contaminant plume with complex composition has spread in groundwater and impacts a large portion of the down-gradient Grindsted stream. Contrary to chlorinated solvents and hydrocarbons, there are no common screening methods for the pharmaceuticals and the costs for quantitative analysis are high. We have found that several of the contaminants are fluorescent and their signal can be distinguished from background fluorescence of natural dissolved organic matter. We apply this to develop a field screening tool for tracing path and extent of the pharmaceuticals plume and its discharge to the stream.
Methodology. The fluorescence properties of a number of known plume contaminants were characterized using excitation-emission matrices (EEMs). Contaminants included aromatic hydrocarbons and chlorinated ethenes as well as sulfonamides and a barbiturate. For selected sulfonamides and sulfanilic acid, detection levels were determined and effects of mixtures of pharmaceuticals were tested. Groundwater, streambed/hyporheic water and stream water was sampled and analyzed for both bulk fluorescence properties and specific contaminant concentrations to investigate the potential of bulk fluorescence measurements (referred to as FDOM (fluorescent dissolved organic matter) analysis) as a screening method for the pharmaceuticals in the strongly contaminated plume. Based on the EEMs a FDOM sensor with em/ex wavelengths appropriate for sulfonamides was identified, tested and set up for field application. Both field sensor and laboratory EEM measurements method were applied (and compared to quantitative analysis) in large screening campaigns along the stream with drive-point probe sampling at multiple locations and depths (2.5 km's long section and to about 20 m bgs) to delineate plume discharge locations.

Summary of findings/results. Sulfanilic acid, sulfanilamide and some other sulfonamides are highly fluorescent having a characteristic signal around excitation 260 nm and emission 350 nm. This enabled detection of these compounds, which are present in high concentrations in the plume, despite the presence of background natural organic matter fluorescence. Detection in stream water requires pre-concentration due to rapid dilution of contaminant concentrations in the stream and the higher content of natural organic matter. The FDOM sensor provided on-site measurements in real time.
Conclusion. The quick and relatively simple fluorescence analysis is a cost-effective screening tool for prioritization of samples for more expensive targeted analysis of pharmaceutical compounds. The laboratory FDOM (EEMs) analysis - pending site specific calibration - provided an opportunity for evaluation of relative concentration as a supplement to quantitative analysis. The FDOM sensor provided a tool for on-site measurements in real time at the field site allowing for selection of sampling points for quantitative analysis.
Significance / contributions of study. The new tools provides an opportunity to derive detailed cross-sectional concentration profiles for cost-effective evaluation of mass discharge of sulfonamide pharmaceuticals to the stream. Future perspective: The sensor may potentially be built into a probe (similar to UVOST or OIP) for direct measurements during drive point probing to identify locations for water sampling.

<u>Session 3c8 / Abstract title</u>: Fate of sulfonamides in a complex plume discharging to a stream – a multiple line of evidence approach in the hyporheic zone

ID: 203

Key words: Groundwater, Sulfonamides, degradation, hyporheic zone

Submitter: Josefine Gram Hansen

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Session: 3c8

Abstract

Purpose of study: A complex plume consisting of pharmaceutical compounds (sulfonamides and barbiturates), chlorinated ethenes, and BTEX from former activities migrates, negatively affecting a stream (Grindsted, Denmark). Understanding the degradation of sulfonamides, including the degradation pathway is crucial to assess the natural degradation, and hereby the impact on the stream and the exposure to humans and biota. Knowledge concerning the degradation of sulfonamides in groundwater and freshwater systems is limited. The aim of this project is to contribute to this understanding, evaluate the degradation and the potential for monitored natural attenuation (MNA) and stimulated natural degradation as part of remediation technics in the discharge zone to the stream. The plume affects more than 2 km of Grindsted Å, but the focus area for this presentation is a meander part of the stream with significant discharge.

Methodology: The extent and composition of sulfonamides discharging into the stream is mapped based on a comprehensive field campaign and previous investigations. Field investigations included measurements of sulfonamides and redox-sensitive compounds from diffusion cells (peepers) creating high resolution depth discrete measuring points, piezometers, and monitoring wells near the stream bank. Head measurements, hydraulic properties and geological information from sediment cores were used to assess the groundwater flow pattern. In addition to the investigations on site, an aerobic degradation experiment consisting of 13 microcosms (including sterile controls) spiked with either sulfadiazine (SDZ), sulfanilamide (SAD), or sulfanilic acid (SAC) to a concentration of 500 µg/L in the water phase was carried out at 10°C. The microcosms contained sediment and groundwater from the area.

Summary of findings/results: Results from the peepers helped to identify areas with an almost complete reduction of sulfonamides in bioreactive transition zones where redox conditions changed from anaerobic to aerobic conditions. Vertical profiles showed how a slow inflow of groundwater to the hyporheic zone made a shift in redox conditions possible, and thereby created optimal conditions for biodegradation. The degradation experiment with sediment from the bioreactive zone supports that biodegradation of sulfonamides takes place in the hyporheic zone. All three compounds were degraded within a few weeks in the bioactive microcosms, and no degradation was seen in the sterile microcosms. No accumulation of the mother compound or the aerobic metabolites were observed. Based on the results of the contaminant distribution, hydrogeology, and findings in the degradation experiment, a conceptual model for sulfonamide transport and degradation in the discharge zone was developed.

Conclusion: The results from the field investigations have contributed to the understanding of the interaction between chemical and hydrological processes in the hyporheic zone and the factors that enable favorable conditions for biodegradation of sulfonamides. The degradation experiment and results from the peepers indicates a good potential for aerobic degradation in the hyporheic zone, and in the fringe of the plume where aerobic conditions are present. Due to the high vertical flow and reducing conditions in the hyporheic zone and in most part of the plume, MNA is not recommended as remediation strategy for sulfonamides. Further investigations are needed in order to assess whether stimulated natural degradation will be a suitable remediation strategy.

Significance /contributions of study: The degradation experiment contribute to the understanding of the degradation of sulfonamides in groundwater/surface water systems that is not widely understood yet. The study showed the potential of an integrated line of evidence approach combining detailed field characterization of hydrogeology with high-resolution water sampling and laboratory experiments.

<u>Session 3c8 / Abstract title</u>: Natural attenuation of sulfonamides in contaminated groundwater – Assessment of monitoring techniques

ID: 242

Key words: In situ monitoring tools; Compound-specific stable isotopes; Molecular diagnostic tools; Multiple lines of evidence; degradation of pharmaceuticals

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Session: 3c8

Abstract

Purpose of study: Sulfonamides are emerging organic contaminants that are widespread in the aquatic environment and pose severe risks. The ubiquity of and risk related to sulfonamides necessitates actions to treat these contaminants. While prevention of emissions to soil and water is to wish for, their current ubiquity in the environment also requires in situ remedial actions. One such viable action is elimination through degradation, thus the aim of this study was to assess if natural attenuation is a viable option for remediation in a groundwater system contaminated with sulfonamides. Furthermore, to assess whether the required monitoring tools to assess degradation processes are accessible.

Methodology: The investigation was conducted at a field site in Denmark, where spills from a former pharmaceutical production site have led to a large-scale complex contaminant plume in the aquifer, which ultimately discharges to a stream. High resolution sampling was conducted. We applied state of the art techniques in an integrated approach focusing on hydrogeology, chemistry and microbiology in order to assess the natural attenuation of sulfonamides. Next generation sequencing was conducted in order to assess the microbial community. Compound specific stable isotope analysis (CSIA) for selected sulfonamides and sample clean-up and up-concentration methods were developed. Analysis of selected

metabolites have also been conducted. At the current state, most data have been collected, and data treatment is ongoing.

Summary of findings/results: Preliminary results demonstrate spatial variations in sulfonamide concentrations in transects perpendicular to the plume and along a flowline. Several possible sulfonamide degradation products have been found in the contaminant plume. Furthermore, bacteria (e.g. Pseudomonas) and genes (sadA and sadB) potentially related to sulfonamide biodegradation have been found through next generation sequencing of groundwater samples along the plume. Moreover, a literature study aided the assessment of the monitoring techniques applicability in these settings.

Conclusion: The investigations can be used in order to obtain a conceptualization of the sulfonamide distribution in the aquifer system, in the assessment of natural attenuation and degradation potential, and finally in the evaluation of monitoring techniques' advantages and limitations.

Significance / contributions of study: The study contributes to an improved understanding of sulfonamides fate in groundwater systems and highlights important knowledge gaps towards application of monitoring tools in order to use natural attenuation as a remediation strategy.

<u>Session 3c8 / Abstract title</u>: Use of outdoor pilot-scale photobioreactor and cork-wood pellet-based biofilter for simultaneous nitrate and micropollutant removal in polluted groundwater

ID: 391

Key words: Emerging contaminants, antibiotics, microalgae, wood pellets, denitrification

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Session: 3c8

Abstract

Purpose of the study
Groundwater contamination poses a great threat to human health as groundwater is the main source of safe drinking water. Approximately 13% of groundwater monitoring stations across Europe exceed the 50 mg NO3/L limit (91/676/EEC), while 7% of them reported excessive levels of pesticides. In addition, antibiotics, and antibiotic resistance genes (ARGs) occurrence in groundwater derived from manure application in agriculture is a raising public health concern across Europe.
The main aim of this study is to assess both at bench and pilot scale the pollution removal capacity (nitrates/ pesticides/ antibiotics/ ARGs) of a combined treatment with microalgae photobioreactor and a biofilter, and to assess the microbial communities implied in the removal of pollutants.

Methodology
An outdoor pilot plant was built and operated for 1 year, in continuous mode since spring 2022 under field environmental conditions, with a treatment capacity of 1-5 m3/d. The pilot plant, had a treatment capacity of 1-5 m3/d and includes: i) a continuously stirred photobioreactor (PBR) of 18 m3; 8-16 days of hydraulic retention time (HRT), built with floating sunlight-pits; ii) a clarification step within a dissolved air flotation (DAF) unit, and iii) a cork-wood biofilter unit (CWF) of 5 m3, with 2 days of HRT. A diversified approach encompassing a deep physicochemical (COD, nitrates, antibiotics, ARGs, and pesticides) and microbial assessment (16S/ITS/18S metabarcoding, total genes (16S rRNA and ITS1), and functional genes (nosZ) linked to denitrifying bacteria) was performed throughout time (four seasons, from spring 2022 to winter 2023).

Results
In the pilot plant operation (summer-autumn 2022), inflow polluted groundwater had a high content of nitrate (162-290 mg/L), and lower content of 8 antibiotics (sulfonamides and fluoroquinolones, each at 0,5-98 ng/L), ARGs (intl1 and sul1 genes at 10e+4-10e+5 copies/L), and pesticides below 20 ng/L. A nitrate removal of 19-16% (4 g NO3-/m3d) was depicted in the PBR, whereas the most nitrate removal was observed in CWF, accounting for 83-69% of nitrate depletion (20-28 g NO3-/m3d). Regarding microcontaminants, the whole pilot was effective for reducing 73-78% of the 8 detected antibiotics (ciprofloxacin, sulfamethoxazole, sulfathiazole, sulfadiazine, sulfacetamide, sulfapyridine, sulfamethazine, and sulfamethizole), reaching a final concentration 10 ng/L in the effluent.

Microbial diversity assessment of CWF biomass (16S/ITS metabarcoding and qPCR of ITS1/16S showed an enrichment of lignocellulolytic bacteria and fungi, fermenting and denitrifying bacteria on the bead material, whereas Tetradesmus and Chlorella where the main microalgae in the mixed microalgae-bacterial consortium in the PBR. Although nosZ gene population were high in PBR and CWF biofilms (10e+9-10e+10 nosZ copies/g), the gene expression of nosZ mainly active in CWF.

Conclusion
The high content of nitrates and the presence of micropollutants, such as antibiotics in the GW, was highly depleted by the pilot plant running under environmental conditions, reaching water quality standards for drinking water in livestock. Active growth of suspended

microalgae in PBR, and the metabolically active denitrifying community in CWF, are crucial to ensure an efficient removal of nitrates and antibiotics.

Significance of study

A long-term operation of a nature based solution to generate drinking water from polluted rural GW for livestock at farm level, at pilot scale under real environmental conditions is presented. A deep microbial assessment to identify those key microbial populations implied on nitrate and micropollutants is also included.

Acknowledgements

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Session 3sps1 orals

Session 3sps1 / Abstract title: Integrating Green Remediation Practices in Superfund Cleanups: A United States Environmental Protection Agency Perspective

ID: 307

Key words: green energy, remediation technologies, best management practices, reduced emissions, high resolution site characterization

Submitter: Lucila Dunnington

Organization: United States Environmental Protection Agency

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Session: 3sps1

Abstract

In the last decade, shifting paradigms in the United States Environmental Protection Agency (USEPA) Superfund Program have driven the development and deployment of green remediation best management practices (BMPs). The process of cleaning up a hazardous waste site requires energy, water and other natural or material resources. This process places demands on the environment and creates an environmental “footprint” of its own. A greener cleanup strategy looks at this footprint closely and finds ways to reduce it throughout the life of a project, while achieving cleanup goals and preserving site reuse options. Early consideration of the environmental footprint of a cleanup also can help lead to sustainable reuse or redevelopment of the site.

Green remediation BMPs focused on air quality, for example, can reduce the environmental footprints of cleanup projects while improving their public health outcomes and mitigating climate change. The use of fossil fuels to power equipment at site cleanups can increase production of ground-level ozone that negatively impacts human health. Airborne pollutants are among the impacts that disproportionally affect communities with environmental justice concerns, including those near Superfunds sites. The deployment of air quality related BMPs can help address such environmental justice concerns by achieving emissions reductions in air pollutants.

In this session we will share information on the updates in Green Remediation Best Management Practices, as well as case study lessons learned and success stories from over 40 remediation sites where a broad suite of creative BMPs have been implemented. Featured site profiles include the use of waste cooking oil as a carbon source for a biogeochemical reactor, local mushroom compost for an engineered wetland at an abandoned mining site (in lieu of an energy intensive rotating cylinder treatment system), and deployment of direct-push equipment for sampling, rather than hollow-stem auger, to minimize land disturbance.

The interactive portion of this session will involve knowledge checks throughout the technical presentation and breakout groups following the presentation. The breakout groups will be given an example remediation site and will work together to identify green remediation best management practices to reduce the project's environmental footprint. Afterwards, they will then report back to session participants for a larger group discussion

Session 3sps2 orals

Session 3sps2 / Abstract title: Towards optimized risk-based aftercare at tar sites

ID: 257

Key words: municipal gas plants, tar-DNAPL, site closure, natural attenuation, nature based solutions

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Organization: Tauw bv

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Session: 3sps2

Abstract

Tar-contaminated sites, such as at former manufactured gas plants (MGP) and creosote plants are among the first sites where soil and groundwater contaminations have been addressed. With excavation being the only feasible remedial option at that time, the more complex sites with deep contaminations all have large residual contaminations with tar-DNAPLs. The total number of former MGPs in Europe amounts to over 6,500, of which 1,700 in Germany, 228 in The Netherlands, and 151 in Belgium. At a significant number of these MGP sites, the contaminations are being contained and the stakeholders are faced with potentially infinite aftercare.
25-35 Years later, containment systems are reaching the end of their lifetime, which is often a reason to reassess the containment approach. Practical experiences, scientific insights in contaminant behavior, new technologies, and changing needs have resulted in the development of new risk-based strategies for these sites, including the realistic option of site closure.
The scope of the proposed session is to stimulate risk-based aftercare at tar sites by sharing our experiences in case studies an discussing the results with the audience. We will start the session with an overview of the problems associated with tar contaminations and of new developments, insights, and technologies that allow us to deal with them. After this, we will present case studies of tar sites where the aftercare is being optimized or even completely terminated:

- MGP Kralingen, Rotterdam (Municipality of Rotterdam). In the period 1995-2000 this large MGP site was excavated and since then a hydraulic containment is in place. In the framework of the MGP program of Rotterdam, a conceptual site model including a reactive transport model has been developed. Natural attenuation of the tar constituents in the anaerobic aquifer underlying the site was found to be sufficient to prevent unwanted migration, allowing the implementation of a containment strategy based on monitored natural attenuation (MNA).
- MGP Griftpark Utrecht (Deltares) Here, a hydraulic containment including bentonite walls to 55 m -bgl and a groundwater extraction system were installed as early as 1995. In 2016, a scientific consortium was established, focusing on characterization of the residual contamination, MNA, enhanced natural attenuation (ENA), and the development of a 3D reactive transport model. Pilot studies are planned to select the best approach for the residual contamination.
- A former coal gasification plant in southern Germany (Isodetect). Besides excavation and groundwater treatment by a pump and treat, natural attenuation of PAH was investigated. Combining in situ and laboratory microcosms allowed a comprehensive evaluation of PAH biodegradation at the investigated field. Sustainable in situ biodegradation of naphthalene and fluorene was demonstrated in the aquifer under oxic and microaerophilic conditions allowing the implementation of a MNA strategy.
- Former tar and carbon-black production plant Lumco, Ghent, (TAUW, OVAM/Interreg). After excavation, a large residual contamination was left behind. The site has been redeveloped, but contaminated groundwater drains into canal the ‘Lieve’. This leads to unacceptable risks and here a nature-based solution, (a permeable reactive mat) is applied as a low-cost, long-term approach to protect the surface water.

We will end the presentations with an overview of the similarities and differences of these and other cases, and the lessons we learned from them. This overview is the basis for a panel discussion with the speakers and the audience:

- Are there similar or different experiences at other sites?
- How do these new insights change current practices for tar-contaminated and similar sites?
- How can we increase the acceptance of approaches based on MNA and ENA?
- Can we come to a framework/decision tool for aftercare at tar sites?
- How can we pool and disseminate knowledge?

Session 3sps3 orals

Session 3sps3 / Abstract title: Best Practices for Applying In Situ Chemical Oxidation (ISCO) in 2023

ID: 381

Key words: ISCO Persulfate Oxidation Remediation

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Session: 3sps3

Abstract

In situ chemical oxidation (ISCO) has been used to treat organic contaminants of concern (COCs) at thousands of sites around the world. This technology originated in the 1980's with the application of unstabilized hydrogen peroxide. Over time ISCO has evolved to include several different chemistries including those based on hydrogen peroxide, ozone, sodium and potassium permanganate and sodium and potassium persulfate. As ISCO has become a standard tool used to remediate contaminated sites much effort has been put into learning and optimizing the technologies with the chemistries, design strategies, application methods, and monitoring programs have all evolved in the past decades.

Current best practices consider key site and/or contaminant characteristics, remedial objectives and how each of those interact with the selection of the proper ISCO chemistry and application method. Best practices have matured beyond only treatment efficacy but also evaluate proper dose, rate of release of the oxidant, best methods for establishing contact, application method and monitoring programs.

Key points of evolution include:

- Identification of reductive pathway with activated persulfate and hydrogen peroxide chemistries that were attributed to the superoxide radical allowing ISCO technologies to be used to treat even completely oxidized compounds such as carbon tetrachloride.
- The use of low solubility oxidants for extended release allowing for treatment over a

longer period of time (extended release)

- Understanding of key contaminant characteristics such as solubility and partitioning and how they relate to availability for treatment
- Strategies for low permeable matrixes
- The use of solid slurry emplacement to inject the extended release oxidants.
- Updates in injection strategies including injecting into a larger percentage of an effective pore volume.
- The use of soil mixing to overcome issues with site heterogeneity issues including site geology and contaminant distribution.
- Combined remedies including ISCO with bioremediation and ISCO with ISS

This session will incorporate these key evolution points and discuss the current best practices for matching oxidant characteristics with contaminant/site, design strategy, application methods, interpretation of monitoring results, and combining ISCO with other technologies in a combined remedy. Several site specific examples illustrating how these concepts were used to optimize remediation at the site will be provided.

The session will be divided into four primary sections:

- ISCO Chemistry
- Matching application method and chemistry with contaminant and site conditions
- Best methods for establishing contact
- Combined remedies and monitoring. Multiple paths to achieve goals.

Those attending this session should obtain an understanding of how critical design elements, oxidant characteristics, application method, and monitoring program are all interrelated and must be considered in conjunction with each other and the site/contaminant specifics in order to design the most appropriate remedy for the site.

The session will allow for open discussion with the presenters including the decisions made on actual sites.

Session 3sps4 orals

Session 3sps4 / Abstract title: Decision support framework for risk management of persistent, mobile and toxic chemicals in a circular economy.

ID: 297

Key words: Decision support framework; Circular economy; Persistent, Mobile and Toxic chemicals; risk management; stakeholder involvement

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Session: 3sps4

Abstract

The European Commission’s zero pollution vision for 2050 means reducing air, water and soil pollution to levels no longer considered harmful to health and natural ecosystems, that respect the boundaries with which our planet can cope, thereby creating a toxic-free environment. One critical aspect in making this vision a reality is the transition to a circular economy (CE), which will reduce pressure on natural resources. Although environmental pollution can be decreased by moving towards a CE, environmental pollution can also prevent the deployment of a CE. One specific class of emerging contaminants that is gaining

more and more attention from scientists and policy makers in this respect are persistent, mobile and potentially toxic (PM(T)) chemicals. PM(T) chemicals, such as some per- and polyfluoroalkyl substances (PFAS), are of concern due to their high persistence in environmental compartments, mobility in water and soil and toxicity to humans and/or ecosystems. Due to their physical-chemical properties, PM(T) chemicals are known to be an issue for specific CE routes, including (i) semi-closed water cycles for drinking water supply at urban and catchment scale; (ii) wastewater reuse for irrigation in agriculture; (iii) nutrient recovery from sewage sludge; (iv) material recovery from dredged sediment and (v) land remediation for safe reuse in urban areas.

To ensure safe reuse and recovery of resources, stakeholders (e.g., drinking water utilities, water authorities, producers of PMT substances, polluted sites owners) need to make informed decisions on prevention and reduction of (critical) PM(T) substances in the environment and on the possible reuse of resources for the development of a toxic-free CE. To this end, a decision support framework (DSF) is currently being developed. The DSF is a product of the PROMISCES Project, which runs from November 2021 until April 2025 and is funded by the European Union under the Horizon 2020 Framework Programme to support Europe's Green Deal.

The DSF: maps the PM(T) chemical space to identify the most critical endpoints and PM(T) groups hindering the transition towards a CE; offers solutions at different places in the PM(T) life cycle, for different PM(T) groups according to their characteristics, addressing factors relevant to stakeholders; assesses different solution scenarios for PM(T) reduction in time and the associated reduction of risks to ecosystems and human health, with a specific focus on opportunities for reuse of resources; addresses stakeholders' concerns using a transdisciplinary approach with regard to feasibility, expected effectiveness and possible barriers to the implementation of solutions; supports co-creation of risk management strategies for different PM(T)-use combinations.

As many stakeholders for whom the DSF is developed are expected to attend AquaConSoil, we propose a session focusing on risk management of PMT chemicals in a CE. During this session a prototype of the DSF will be presented. Session attendees will have a first chance to see what kind of information is included in the DSF and will be invited to provide feedback. Feedback may include 1) the suggestion of additional information on PM(T) substances to the DSF (e.g., new data sources) or 2) input on extra information required by stakeholders on PM(T) substances which are not yet met by the DSF. The session will therefore be highly interactive. The preliminary schedule for the session is: 1) Introduction to the DSF (20 min, 10 min questions), 2) Interactive session on a prototype of the DSF with sessions attendees using guided discussion rounds, flip-overs and possibly online tools (45 min), 3) Session closing, including possibility for session attendees to give final recommendations to improve the DSF and ensure that the final product will meet the needs of the users, again using flip-overs and online tools (15 min).

This session is organized by RIVM, INERIS, DECHEMA, EURECAT, KWB BRGM.