

IAP2022

Interfaces Against Pollution: Chemical and Biological Perspectives

Antwerpen, Belgium

18 – 21 September 2022



Program and Abstracts



Welcome to IAP2022

Welcome to the 12th International Conference on Interfaces Against Pollution (IAP). In broad scope, the IAP conferences (www.iapconferences.org) provide a forum for interdisciplinary research in environmental science. More specifically, the conferences address the key role played by (bio)interfaces and (bio)colloids in complex environmental processes and media. The focus is on connecting fundamental aspects of colloid and interface science to environmental issues. The IAP series was initiated in 1997 in Wageningen, The Netherlands, followed by conferences in Miskolc, Hungary (2002), Jülich, Germany (2004), Granada, Spain (2006), Kyoto, Japan (2008), Beijing, China (2010), Nancy, France (2012), Leeuwarden, The Netherlands (2014), Lleida, Spain (2016), La Grande Motte, France (2018), and Wuhan, China (2021).

IAP2022 is hosted by the ECOSPHERE group at Universiteit Antwerpen, Belgium. In this edition of the conference series, we pay particular attention to bringing together chemical and biological perspectives. The invited plenary and keynote lectures reflect this ambition, and we are pleased to have attracted contributions across diverse topics within the overall scope of IAP which comprise both fundamental and solution-oriented research.

We hope that all participants enjoy the stimulating scientific atmosphere and the rich social environment of Antwerpen.

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Program

Sunday 18 September, Antwerpen Stadhuis, Grote Markt 1, 2000 Antwerpen	
17:00 – 19:00	<i>Welcome reception</i>
Monday 19 September, s.KS building, Kattenstraat 10, 2000 Antwerpen	
	s.KS, first floor
08:30 – 09:15	<i>welcome coffee, set up posters</i>
	s.KS.203
	<i>Chair: Raewyn M. Town</i>
09:15 – 09:30	Opening of IAP2022
09:30 – 10:15	PN1: Tamar Kohn, EPFL, CH Aerosol pH is an overlooked driver of airborne influenza- and coronaviruses inactivation
10:15 – 10:45	KN1: Vera Slaveykova, Université de Genève, CH Effect of titanium oxide nanoparticles on the bioaccumulation of mercury species by crustacean <i>Daphnia magna</i>
10:45 – 11:05	<i>coffee break, first floor s.KS</i>
	<i>Chair: Vera Slaveykova</i>
11:05 – 11:25	OM1: Gunter Flipkens, Universiteit Antwerpen, BE Deriving nickel (Ni(II)) and chromium (Cr(III)) based environmentally safe olivine guidelines for coastal enhanced silicate weathering
11:25 – 11:45	OM2: Takumi Saito, University of Tokyo, JP Origin and ion binding properties of dissolved organic matters in deep sedimentary groundwater
11:45 – 12:05	OM3: Chunlan Ni, Huazhong Agricultural University, CN Effect of land use pattern on the bioavailability of heavy metals: a case study with a multi-surface model.
12:05 – 14:00	<i>lunch, first floor s.KS</i>
	<i>Chair: Jose-Paulo Pinheiro</i>
14:00 – 14:20	OM7: Kento Murota, University of Tokyo, JP Unique sorption of Cs and Sr onto mesoporous silicas
	<i>Chair: Jérôme F.L. Duval</i>
	OM4: Nirrit Cohen, Technion, IL Retention and abrasion of microplastic fibers in sandy soil
	OM5: Michael Sander, ETH, CH Enzymatic hydrolysis of biodegradable polyester as assessed by co-hydrolysis of an embedded fluorogenic probe
	OM6: Ali Dhaini, University of Montpellier/CNRS, FR Hydrophobic dyes removal from effluent wastewater using selective cavity of hybrid imogolite
	OM11: Neriya Perez-Lapid, Technion, IL Amorphous iron-oxide montmorillonite composite for phosphate adsorption and reuse

14:20– 14:40	OM8: Andreas Voegelin, EAWAG, CH Thallium adsorption onto phyllosilicate minerals in soils and sediments	OM12: Bram Geysels, Wageningen University and Research, NL Glyphosate adsorption to ferrihydrite: batch experiments and interpretation with CD-Music modelling
14:40 – 15:00	OM9: Anil Can Yildirim, University of Tokyo, JP Modelling of Cs ⁺ , Sr ²⁺ and Eu ³⁺ sorption to sodium-activated metakaolin-based geopolymers	OM13: Mikhail Borisover, The Volcani Center, IL The concept of gate-sorption site coupling for understanding time-independent desorption hysteresis observed in solution experiments
15:00 – 15:20	OM10: Angel Delgado, University of Granada, ES Electrokinetics and stability of silica/clay mixtures at high copper concentration. Environmental and technical implications.	
15:30 – 16:30	Poster session with refreshments, first floor s.KS	
Tuesday 20 September, s.KS building, Kattenstraat 10, 2000 Antwerpen		
	s.KS.203	s.KS.204
	<i>Chair: Takumi Saito</i>	
09:00 – 09:45	PN2: Guillaume Morin, IMPMC, FR Chemical speciation changes in the environmental cycles of metal contaminants. Inputs from field studies	
09:45 – 10:15	KN2 (via MS Teams): Songhu Yuan, China University of Geosciences, CN Ligand facilitates electron extraction from solid Fe(II) for hydroxyl radical production and contaminant attenuation CTRL+click to join online	
10:15 – 10:35	<i>coffee break, first floor s.KS</i>	
	<i>Chair: Michael Sander</i>	<i>Chair: Raewyn M. Town</i> MS Teams session, CTRL+click to join online
10:35 – 10:55	OT1: Szimona Zorzsevskej, Czech University of Life Sciences, CZ The use of composted sewage sludge in brownfield soil remediation	OT6: Jingtao Hou, Huazhong Agricultural University, CN Observing higher As(III) adsorption on ferrihydrite than As(V): a non-ignorable role of micropore sites
10:55 – 11:15	OT2: Veronica Baldasso, University of Reims, FR Sorption of metformin and lamotrigine in a digestate-amended soil in the presence of metal contamination	OT7: Juan Xiong, Huazhong Agricultural University, CN Quantitative characterization of the site density and charged state of functional groups on biochar
11:15 – 11:35	OT3: Ville Nenonen, EAWAG/ETH, CH Effects of dissolved organic compounds on the structure, colloidal stability and phosphate uptake of Fe(III)-precipitates formed by Fe(II) oxidation in oxygenated anoxic groundwater	OT8: Zhenglun Yang, Huazhong Agricultural University, CN Assessment of cadmium bioavailability and stabilization strategies guidance in rice-soil system based on multi-surface speciation

11:35 – 11:55	OT4: Kyle Chardi, University of Vienna, AT The role of competing cations in ligand-induced U mobilization: comparisons from biogenic non-crystalline U(IV) and a bio-reduced field sediment	OT9: Jiezi Jin, Huazhong Agricultural University, CN Generic CD-MUSIC-eSGC model parameters for proton binding by iron (hydr)oxides
11:55 – 12:15	OT5: Mingkai Ma, Utrecht University, NL Kinetic model development for coupled processes: a study of phosphate release during sulfidation of iron (hydr)oxides	OT10: Wenfeng Tan, Huazhong Agricultural University, CN Impact of soil active components on heavy metal speciation and an advanced model through soil-plant continuum model.
12:15 – 13:45	<i>lunch, first floor s.KS</i>	
	<i>Chair: Josep Galceran</i>	<i>Chair: Luuk Koopal MS Teams session, CTRL+click to join online</i>
13:45 – 14:05	OT11: Walter Schenkeveld, Wageningen University and Research, NL Specificity of metallophores in metal mobilization	OT14: Marcelo Avena, Universidad Nacional del Sur, AR Desorption kinetics of glyphosate by phosphate from goethite. ATR-FTIR experiments and modelling
14:05 – 14:25	OT12: Juan Antelo, University of Santiago de Compostela, ES Trace metal binding to organic reactive (bio)surfaces at the solid/solution interface	OT15: Li Yan, Zhejiang Academy of Agricultural Sciences, CN Enzyme interacting with soil components and its conformational change investigation by spectroscopic techniques
14:25 – 14:45	OT13: Quynh Nguyen-Phuong, University of Reims, FR Geochemical modelling of Cu(II) and Pb(II) adsorption onto humin using NICA-Donnan	OT16: Linchuan Fang, Chinese Academy of Sciences/Ministry of Water Resources, CN Sequestration of heavy metals in soil aggregates induced by glomalin-related soil protein: a five-year phytoremediation field study
14:45 – 15:15	<i>coffee break, first floor s.KS</i>	
15:20	<i>departure of shuttlebus to Steenplein for boat trip</i>	
16:00 – 18:00	<i>boat trip along Scheldt River</i>	
19:00 – 23:00	<i>conference dinner, Felix Pakhuis, Godefriduskaai 30, 2000 Antwerpen</i>	
Wednesday 21 September, s.KS building, Kattenstraat 10, 2000 Antwerpen		
	s.KS.203	s.KS.204
	<i>Chair: Alberto Tiraferrì</i>	
09:00 – 09:45	PN3: Jean-François Dufreche, University of Montpellier/CNRS, FR How molecular simulation can be used to understand interfaces for the environment	
09:45 – 10:15	KN3 (via MS Teams): David Waite, University of New South Wales, AU Integrated suspension anode and ultrafiltration system for defluorination of perfluorooctanoic acid (PFOA) CTRL+click to join online	

10:15 – 10:35	OW1: Silvia Ahualli, University of Granada, ES Capacitive deionization of solutions using functionalized carbon electrodes	
10:35 – 10:55	<i>coffee break, first floor s.KS</i>	
	<i>Chair: Jean-François Dufreche</i>	<i>Chair: Yael Mishael</i>
10:55 – 11:15	OW2: Adi Radian, Technion, IL Superior surface reactivity of montmorillonite decorated with amorphous, nano-sized iron-oxides makes for excellent fenton-like catalyst	OW5: Jose-Paulo Pinheiro, Université de Lorraine/CNRS, FR New insights on the estimation of chemical/electrostatic parameters for humic nanoparticles reactivity from NICA-SPBT-based modelling of proton titration curves: benefits of singular value decomposition and Tikhonov regularization steps in model-independent parameter estimation
11:15 – 11:35	OW3: Sonya Altziter, Hebrew University of Jerusalem, IL. Characterizing organic pollutant oxidation processes on manganese bearing colloids by a geoelectrical method.	OW6: Josep Galceran, Universitat de Lleida, ES Kinetics of the dissolution of In ₂ O ₃ nanoparticles followed with the electroanalytical technique AGNES
11:35 – 11:55	OW4: Yael Zvulunov, Technion, IL Encapsulation of biogenic Mn oxides for improved oxidation of glyphosate	OW7: Elise Rotureau, Université de Lorraine/CNRS, FR Unravelling the electrostatic and chemical components of the stability of indium-nanoparticulate humics complexes
12:00 – 12:15	Closing ceremony	
12:15 – 13:30	<i>lunch, first floor s.KS, and departure</i>	

Abstracts

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Aerosol pH is an overlooked driver of airborne influenza- and coronaviruses inactivation

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The current pandemic has added to the growing evidence that respiratory viruses can be transmitted by the airborne route¹. Non-pharmaceutical interventions, such as mask wearing or ventilation, aim to reduce the public health burden of respiratory diseases by physically preventing airborne virus transmission. Alternatively, a reduction in transmission may be achieved by inactivation viruses in air. This latter approach, however, is hampered by an incomplete understanding of the parameters that modulate airborne virus infectivity.

In this study, we investigate the role of aerosol pH in airborne virus inactivation. Aerosol particles in the natural environment are known to be acidic², and the persistence of some respiratory viruses is known to be reduced by acidic pH³. However, the pH of expiratory aerosol particles and its effect on virus transmission remain unknown. Here, we measured the inactivation kinetics of influenza virus and two coronaviruses (SARS-CoV-2 and hCoV-229E) over a pH range of 2.1 to 7.4 in surrogate lung fluid and in nasal mucus. The physicochemical properties of micron-sized SLF and mucus droplets, such as the water diffusion coefficient, were determined by injecting a fluid droplet into an electrodynamic balance and measuring the relative changes in mass and volume upon changes in relative humidity. Finally, the physicochemical and virological data were integrated into a biophysical aerosol model, to determine virus inactivation times as a function of relative humidity, air composition and aerosol particle size.

We found that influenza virus is readily inactivated at pH < 5, leading to airborne inactivation over the course of hours to minutes, depending on the size of the carrier particles. The inactivation coincides with structural changes in viral proteins, including those involved in host attachment. In contrast, coronaviruses are more stable and can remain infectious within aerosol particles for days. However, acidification of indoor air, and hence of aerosol pH, causes a dramatic decrease in inactivation times for influenza virus and SARS-CoV-2, and to a lesser extent for hCoV-229E. Consequently, pH control of indoor air, e.g., through the addition of nitric acid to the air, is a promising tool for reducing virus transmission. Interestingly, our biophysical aerosol model predicts that air acidification is a more effective tool for reducing the risk of virus transmission than ventilation or filtration.

References

- [1] Wang CC, Prather KA, Sznitman J, Jimenez JL, Lakdawala SS, Tufekci Z, Marr LC. 2021. Airborne transmission of respiratory viruses. *Science* **373**: eabd9149.
- [2] Kakavas S, Patoulias D, Zakoura M, Nenes A, Pandis SN. 2021. Size-resolved aerosol pH over Europe during summer. *Atmospheric Chemistry and Physics* **21**, 799-811.
- [3] Scholtissek C. 1985. Stability of infectious influenza A viruses to treatment at low pH and heating. *Archives of Virology* **85**, 1-11.

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Effect of titanium dioxide nanoparticles on the bioaccumulation of mercury species by crustacean *Daphnia magna*

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Titanium dioxide nanoparticles (nTiO₂) are one of the most widely used nanomaterials. Extensive research has been conducted on the toxicity of nTiO₂ alone and in mixtures with other pollutants. However, studies exploring the influence of nTiO₂ on the accumulation of dissolved pollutants by aquatic organism are rather scarce. The present study aims to explore the role played by nTiO₂ on the uptake and depuration of two major aquatic mercury species (inorganic, IHg and monomethyl mercury, MeHg) by crustacean *Daphnia magna* through waterborne exposure and diets on alga *Chlamydomonas reinhardtii*. To this end, series of experiments were performed to characterize the interactions between IHg/MeHg (10⁻⁸ mol L⁻¹) and nTiO₂ (20 and 200 mg L⁻¹) IHg/MeHg and algae, nTiO₂ and algae. To obtain an insight on the effect of nTiO₂ on the accumulation of IHg/MeHg through water-, particle- and alga-borne exposures, *D. magna* was: (i) treated with mixtures of IHg/MeHg and nTiO₂; (ii) exposed to nTiO₂ pre-treated with IHg/MeHg; (iii) feed on alga pre-treated with IHg/MeHg in the absence and presence of nTiO₂. Experiments were performed in synthetic freshwater. Further details about the experimental conditions can be found in Ref [1].

Results demonstrated the significant aggregation of nTiO₂. nTiO₂ aggregates adsorbed considerable amounts of IHg (80.7% in 200 mg L⁻¹ nTiO₂) and to lower extent MeHg (only 14.6%). A substantial amount of the nTiO₂ (and adsorbed IHg/MeHg) in the suspensions sedimented in particularly at 200 mg L⁻¹. By contrast alga *C. reinhardtii* took up more MeHg than IHg. *D. magna* accumulated significant amount of IHg/MeHg via waterborne exposure. The body burden of mercury (THg,d) in daphnids exposed to MeHg was higher than the one measured for the exposure to comparable IHg concentrations. A decrease in the THg,d was observed after 22h-depuration, showing slow elimination of both Hg species. The addition of the nTiO₂ to the exposure medium resulted in an increase of THg,d in both IHg and MeHg, which was more pronounced for IHg and for higher concentrations of nTiO₂. THg,d of *D. magna* was higher for feeding on nTiO₂ pre-treated with IHg at higher nTiO₂ concentrations, as expected by the higher percentage of IHg adsorbed on nTiO₂ aggregates. Larger values of transfer efficiencies, TEs, from particles to daphnids were obtained at 200 mg L⁻¹ nTiO₂, indicating a key role of nTiO₂ as Hg species carriers. *D. magna* also accumulated significant amount when fed on algae pretreated with IHg/MeHg. The assimilation efficiency of algae pre-treated with MeHg by daphnids were about twice bigger in comparison with those for algae pre-treated with IHg. A considerable amount of THg,d was lost after 22h-depuration. Co-exposure with nTiO₂ significantly reduced the THg,d in daphnids fed on IHg/MeHg pre-treated algae.

Overall, the results of the present study demonstrated the dual role of nTiO₂ played in the accumulation by daphnids and trophic transfer of two major Hg species present in the aquatic environment – IHg and MeHg. The interactions of Hg and nTiO₂, Hg and alga, Hg and daphnids were strongly dependent on the mercury speciation. IHg has higher reactivity to nTiO₂, than MeHg, whereas MeHg has higher reactivity with living organisms, such as alga and daphnids.

References

- [1] Li MT, Slaveykova VI. 2022. Dual role of titanium dioxide nanoparticles in the accumulation of inorganic and methyl mercury by crustacean *Daphnia magna* through waterborne and dietary exposure. *Environmental Pollution* 295, 118619.

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OM1

Deriving nickel (Ni(II)) and chromium (Cr(III)) based environmentally safe olivine guidelines for coastal enhanced silicate weathering

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Mitigating global warming to 1.5 °C requires active atmospheric carbon dioxide (CO₂) removal on a gigaton scale via so called negative emission technologies (NETs). Coastal enhanced silicate weathering is one of the proposed NETs that aims to increase seawater total alkalinity to enhance atmospheric CO₂ removal by deliberately distributing finely ground silicate rock in dynamic coastal waters. The abundant, fast weathering silicate mineral olivine (Mg_{2x}Fe_{2(1-x)}SiO₄) has received most attention for the technique. However, the environmental safety of distributing gigatons of olivine in the coastal seas remains to be investigated. A reason for potential concern is the high nickel (Ni²⁺) and chromium (Cr³⁺) content of olivine. These trace metals are released to the water column and sediment during olivine dissolution and could accumulate to potentially toxic levels. Currently, no marine olivine toxicity data is available. However, a magnitude of Ni²⁺ and Cr³⁺ marine toxicity data is available and summarized in so called environmental quality standards (EQS). These EQS are threshold metal concentrations considered protective for marine biota.

This study aimed to derive the maximum amount of olivine that could be supplied to coastal seas without exceedance of current Ni²⁺ or Cr³⁺ sediment and seawater EQS. This olivine guideline provides a first indication of the environmental safety of coastal enhanced olivine weathering at the gigaton scale. Due to the lack of data on trace metal environmental fate, olivine guidelines were derived under the limiting application scenarios in which all Ni²⁺ and Cr³⁺ released during weathering end up in either the water column or the sediment. Results showed that metal accumulation in the water column is unlikely to exceed existing EQS due to the large seawater dilution effect. However, sedimentary metal concentrations could already exceed EQS, and therefore pose a potential risk to benthic marine biota, if application exceeds 1.4 kg of olivine m⁻² of seabed. On a global scale a maximum of 39 Gt of olivine could be distributed, having the potential to remove an approximately equivalent amount of CO₂ from the atmosphere in the 21st century. This is a low amount in comparison to the 150-1180 Gt of negative CO₂ emissions that are needed to keep global warming below 1.5°C. Hence, we conclude that sedimentary metal accumulation could limit the environmentally safe usage of olivine in gigaton scale coastal enhanced weathering.

Our work provides a first conservative coastal olivine application guideline and highlights the need for research on the *in situ* Ni and Cr release rate, environmental fate, bioavailability, and potential mixture toxicity to derive accurate site-specific olivine application guidelines.

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Stable and deep geological formations are now considered to host disposal or storage facilities of various technological wastes such as high-level radioactive wastes (HLWs) and carbon dioxide capture and storage (CCS). Environmental impacts of such facilities must be assessed beforehand as we do for any similar facilities on the surface, where migration of pollutants plays a central role for proper prediction of the time of their arrival and the magnitude of possible exposure of human being to them. Dissolved organic matters (DOMs) can bind various pollutants and modulate their mobility. DOMs in surface environments have been well studied, and several mechanistic models are developed for their binding with metal ions. Nevertheless, little is known for deep groundwater DOMs due to limited availability of the DOM samples, which hinders our understanding on their origin, physicochemical nature, and ion binding properties [1]. The objective of this study is to clarify the origin and ion binding properties of DOMs in deep sedimentary groundwater, combining fluorescence emission-excitation matrix (EEM) measurement and parallel factor analysis (PARAFAC).

Groundwater samples were collected from boreholes located at various depths in the Horonobe underground research laboratory (URL) operated by Japan Atomic Energy Agency (JAEA). The groundwater samples were filtered through 0.45- μm membranes to remove particulate materials, acidified and neutralized to remove carbonate species, and diluted for EEM measurements. Europium ion (Eu^{3+}) was added to the groundwater samples at different concentration. EEM were measured by a fluorescent spectrometer, and a series of EEM data was simultaneously decomposed into EEMs of independent components and their loadings by PARAFAC. The loading of each component for a given groundwater sample as a function of Eu^{3+} concentration was fit to the Stern-Volmer (SV) model to quantify the magnitude of the binding. The results of the PARAFAC decomposition and the SV fitting were further processed by partial least squares (PLS) regression with various biogeochemical parameters of the sampled groundwater as explanatory variables.

Four independent components were obtained from the PARAFAC decomposition of the series of EEM data, covering a wide region of the URL and the Eu^{3+} concentrations. Two of them were categorized as humic-like organic matters originated from a surface environment and its alteration product; one as cysteine or similar biomolecule; one as a unique EEM without similarity to EEM of DOMs in surface environments. Based on the SV fitting, the humic-like components exhibited the largest magnitude of Eu^{3+} binding. PLS analyses further revealed the possible origin of the components and how their Eu^{3+} binding was affected.

References

- [1] Saito, T., Terashima, M., Aoyagi, N., Nagao, S., Fujitake, N., Ohnuki, T. 2015. Physicochemical and ion-binding properties of highly aliphatic humic substances extracted from deep sedimentary groundwater. *Environ. Sci.: Process. Impacts* **17** 1386-1395.

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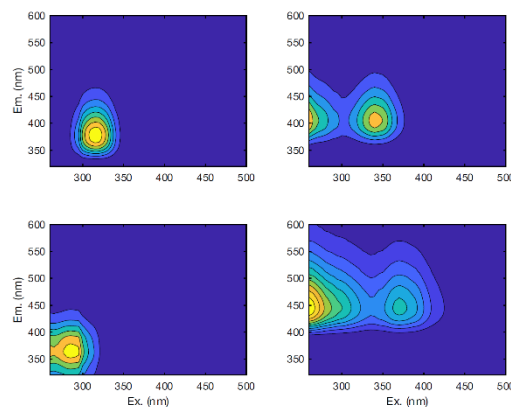


Fig. 1: EEM of the four components obtained by PARAFAC decomposition

Effect of land use pattern on the bioavailability of heavy metals: a case study with a multi-surface model

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In modern agricultural practice, the land use pattern has been changing due to economic reasons and related policies, which significantly affects the basic physical and chemical properties of soils, thereby influencing the speciation and distribution of heavy metals (HMs) in soils. We selected three typical types of land use patterns (vegetable field, paddy field and forest field) in Shaoguan City, Guangdong Province, China, to analyze the content and distribution of HMs, screen the sensitive physicochemical properties, and predict the phytoavailability of HMs under different land use patterns with the multi-surface model (MSM). The forest field had relatively lower levels of labile and free HM ions than both paddy and vegetable fields, which may be attributed to the lower HM content in forest field.

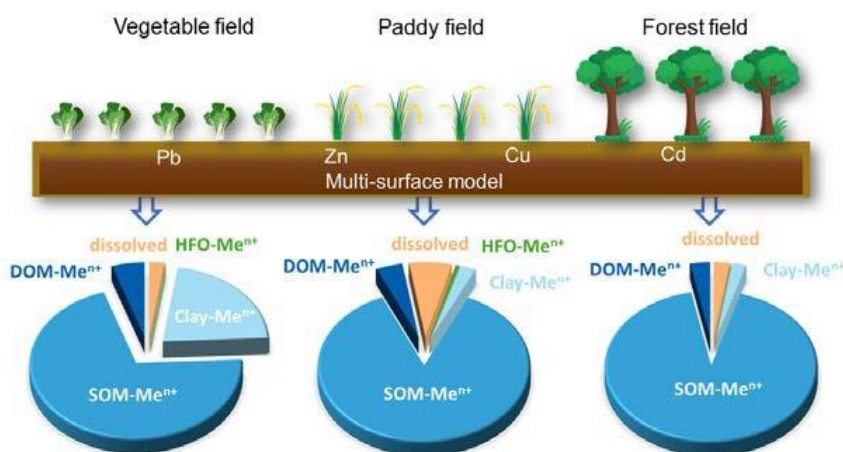


Fig. 1: Distribution of HMs on the surface of soil active components

The modeling results revealed that organic matter (OM) is the primary carrier of HMs, accounting for 0.19%–97.92% of labile HMs. The sensitivity of soil physicochemical properties to free HM ions followed the order of pH > SOM > goethite > clay. Besides, the conversion of paddy field into vegetable or forest field increased the environmental risk of HMs.

Our results may help better decision making in agricultural restructuring to reduce the risk of HM- contaminated soils, as well as give a demonstration for the application of the MSM in predicting the phytoavailability of HMs as a powerful technique.

References

- [1] Zhu B, Liao Q, Zhao X, Gu X, Gu C. 2018. A multi-surface model to predict Cd phytoavailability to wheat (*Triticum aestivum* L.). *Sci. Total Environ.* **630**, 1374-1380.
- [2] Weng L, Temminghoff EJM, van Riemsdijk WH. 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ. Sci. Technol.* **35**, 4436-4443.

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OM4 Retention and abrasion of microplastic fibers in sandy soil

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The fate of microplastics in terrestrial environments has recently attracted great attention due to their high occurrence and potential risk. The reuse of sludge in agriculture practices introduces high amounts of microplastic fibers originating from synthetic textiles; however, little information is available on their fate in soils. In this study, we established a novel protocol enabling precise slicing of common textile fibers, polyester and nylon, to relevant environmental sizes and characterized their transport in sand columns. The fibers were highly retained (>94%) and mostly accumulated in the upper layer, even under unfavorable retardation conditions such as high concentration of dissolved organic matter. Smaller fibers were slightly more mobile, and nylon showed marginally higher mobility than polyester fibers (Fig. 1). Some fibers peeled and split as they flowed through the soil pores, forming thinner, shorter and more mobile fibers (Fig. 2).

Overall, this suggests that in agricultural settings, the mobility of microplastic fibers is negligible and will lead to their continuous accumulation in the upper part of the soil. However, it can be expected that MP impacts on the soil environment will change with time due to MP fragmentation into smaller pieces, which will increase their mobility and may lead to ground water pollution.

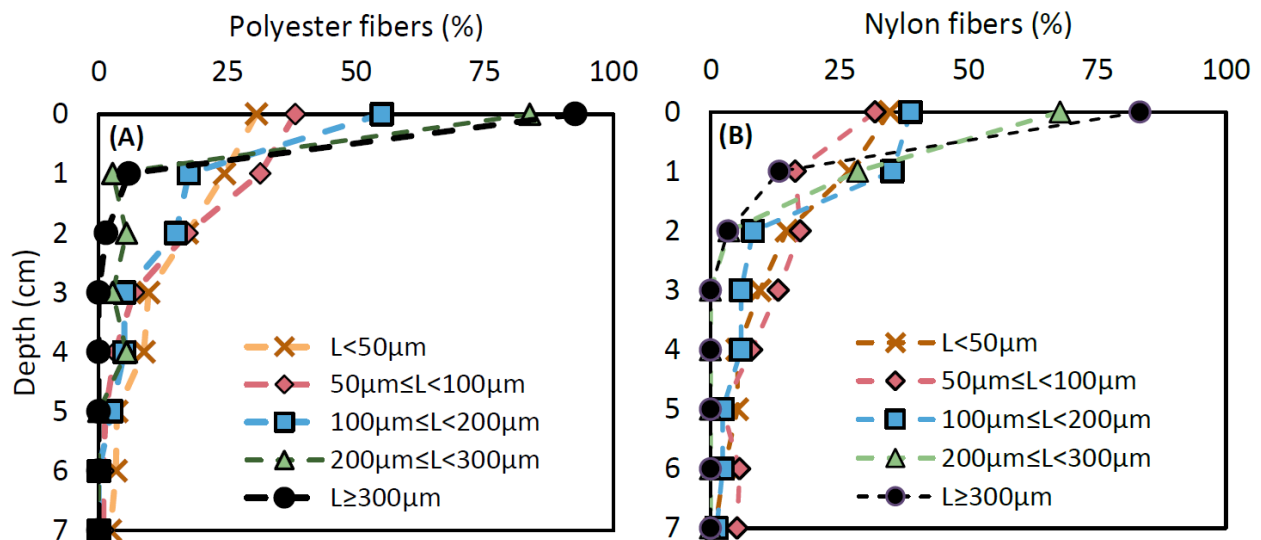


Fig. 1: Depth profile of retained (A) polyester fibers and (B) nylon fibers

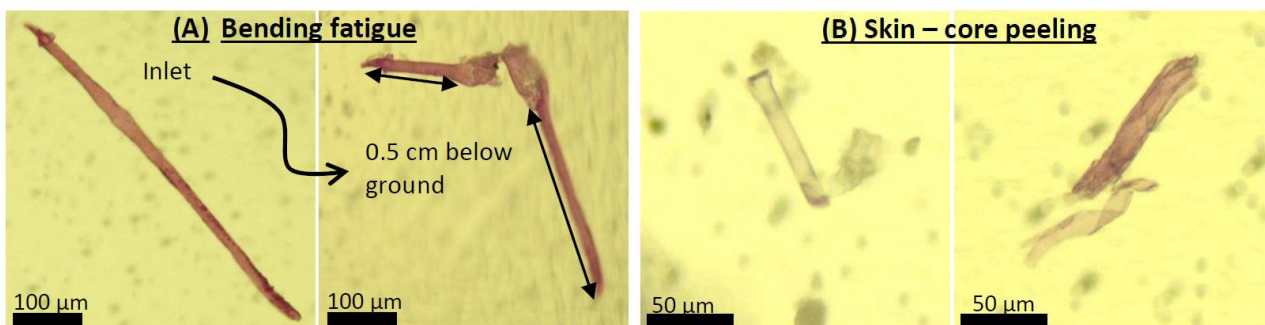


Fig. 2: Microscope images of (A) polyester fiber before and after flowing through sandy soil, exhibiting a bending fatigue, and (B) skin-core peeling of polyester fiber after flowing through sandy soil

OM5

Enzymatic hydrolysis of biodegradable polyesters as assessed by co-hydrolysis of an embedded fluorogenic probe

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A viable strategy to help overcome the circularity gap as well as plastic pollution of the environment is to replace conventional plastics composed of stable polymers with biodegradable alternatives in specific applications. Most biodegradable plastics of commercial interest contain polyesters which undergo hydrolysis of the ester bonds to form low molecular weight products that can be metabolically utilized by microorganisms. For most polyesters, hydrolysis is catalyzed by extracellular esterases and is considered the rate determining step in overall biodegradation in diverse receiving environments. As a consequence, there is great interest in characterising polyester enzymatic hydrolysis in order to predict polyester biodegradation, to identify competent esterases and the microorganisms secreting these enzymes, and to design hydrolysable polyesters for the future.

In this contribution, we present a novel high-throughput assay that we developed to readily quantify enzymatic polyester hydrolysis. This assay is based on monitoring of the co-hydrolysis of a polyester-embedded fluorogenic ester probe which, upon hydrolysis, releases a fluorescent reporter molecule that can be quantified by fluorescence reading. This assay is implemented on a microwell platform to allow for simultaneous analysis of various enzyme concentrations. We show that the rate of fluorescence release from the probe indeed is controlled by the rate at which the polyester surrounding the probe is enzymatically hydrolyzed. We present data for the hydrolysis rate of a total of six cutinases and lipases on eight polyester films containing the embedded probe. The polyesters include a series of poly(butylene adipate-co-terephthalate) with varying terephthalate contents, polycaprolactone, polylactic acid and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). We show that the hydrolysis rates can be accurately described by the inverse Michaelis Menten equation, allowing us to extract kinetic parameters from the experimental data for the respective esterase-polyester pairs. The obtained kinetic parameters for the enzymes and polyesters are consistent with previous published information, supporting that the assay provides reliable information on enzymatic polyester hydrolyzability.

The anticipated application domain of this assay is wide, including the characterisation of enzymatic hydrolyzabilities of polyester, comparisons of the enzymatic activities of different esterases, quantification of esterase activities in samples from polyester-containing natural environments (e.g., compost and soils) and identification of microbial strains secreting extracellular esterases capable of hydrolysing polyesters.

Hydrophobic dyes removal from effluent wastewater using selective cavity of hybrid imogolite

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Contamination of surface water by organic dye pollutants, discharged from many industries, is considered a serious problem leaving harmful impacts on both environment and humans. Among the different treatment methods used, adsorption-based techniques have been proven to be effective, simple, and of a low cost. In the current work, hybrid Imogolite nanotubes were chosen as adsorbents to evaluate their adsorption efficiency toward dyes. This versatile material is considered highly dispersible in water due to its gibbsite-like external surface. The internal surface is covered with Si-OCH₃ groups providing a hydrophobic microporous cavity which is suitable for encapsulation of hydrophobic molecules [1].

To evaluate the hydrophilic / hydrophobic character of both surfaces present in Imogolite, an original characterization study was carried out using immersion calorimetry (Setaram C80 equipment) which allows the determination of the wettability enthalpy.

The dried form of Imogolite nanotubes exhibit specific assembly, and tends to assemble in intertwined bundles where three kinds of porosity appear (Fig. 1). Thus textural analysis was conducted using N₂ adsorption to evaluate the specific surface area and the porosity, in order to establish correlation with the wettability in water. This investigation included different dried systems (freeze, spray, and ambient drying), and samples with different degrees of purity as well as varied temperatures of degassing.

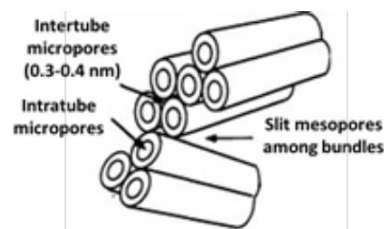


Fig. 1: Different types of porosity present in dried Imogolite [2]

An optimized adsorption isotherm of dye molecules into hybrid imogolite from water was also developed. The dyes utilized were mostly with a solvatochromatic character allowing their tracking from the water medium into the nanotubes using UV-Vis spectroscopic methods. They were either ionic and well dissolved in water or non-ionic with low water solubility. Concerning the latter, aggregation of dyes in water was observed and different aggregates were identified. The adsorption capacity of imogolite towards the different dyes was determined.

Finally, the encapsulation of these dyes inside hybrid imogolite was explored using a multi-scale approach. Macro-scale approach is followed by isothermal titration calorimetry (ITC) allowing the estimation of adsorption enthalpy, thus, the interaction between both the host molecule and the material. Local approaches generally include methods such as second harmonic scattering to study the organization of dyes when confined [3].

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OM7

Unique sorption of Cs and Sr onto mesoporous silicas

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In the deep underground, groundwater flows through very small rock pores, which sometimes measure in the nm order. It is necessary to consider sorption of radionuclides in these pores when evaluating their migration in deep underground environments. It has been reported that water properties and chemical reactions in mesoscale (2-50 nm) and microscale (<2 nm) pores differ from those in larger pores [1]. However, it is not clear how the sorption of ions changes in confinement. In this study, we examine the sorption of ions (cesium (Cs) and strontium (Sr)) under different chemical conditions, using two types of mesoporous silicas (MCM-41 (M) and SBA-15 (S)) with three different mesopore diameters (Table 1) as analogues of natural rocks in order to acquire an understanding of ion sorption in small pores. Moreover, the sorption results were used for fitting of surface complexation modeling to find potential factors affecting the unique sorption in confinement.

Table 1: Pore size distribution of the silicas determined by nitrogen gas adsorption.

	M3.4	M6.8	M12.4	S7.1	S7.9	S8.2
Mesopore diameter (nm)	3.4	6.8	12.4	7.1	7.9	8.2
Specific surface area <2nm (m ² /g)	32	414	94	232	246	252
Specific surface area >2nm (m ² /g)	589	214	337	224	236	284

The silicas were immersed in aqueous solutions with different pH and ionic strength. After measuring pH, a CsNO₃ or Sr(NO₃)₂ solution was added, and after a certain period of time the concentration of Cs or Sr in the liquid phase was measured by ICP-MS to determine the sorption amount. The absolute values of the surface charge densities of M12.4 were larger than those of the other silicas. By contrast, M6.8 and all of the SBA-15 silicas had a particularly large sorption amount of Cs per unit surface area compared with M3.4 and M12.4, suggesting that the sorption amount of Cs per unit surface area is larger in pores with diameters of less than 2-3 nm than in larger pores. Moreover, the sorption of Sr did not equilibrate even after 15 days under high ionic strength conditions. This indicated the existence of a slow reaction such as the diffusion of ions into small pores. Thus, it is suggested that the sorption characteristics in micropores vary depending on the pore diameter and the cation types.

Surface complexation modeling based on the Stern representation of charge distribution of the solid/water interface and the cylindrical Poisson-Boltzmann equation was fitted to the surface charge densities, optimizing the Stern layer capacitances of a micropore with a common diameter that was set as 1.36 nm for all the silicas, and mesopores with diameters as shown in Table 1. The optimized capacitances of the micropore and the 3.4 nm mesopore were smaller than those of the other mesopores. Considering that the thickness of the Stern layer is related to the size of the water layer and the hydrated ions sorbed on the surface, the decrease of the capacitance in small pores could be interpreted as a decrease of the dielectric constant of water near the surface, which could lead to unique deprotonation and sorption reactions in confinement. The fitting results of the surface complexation modeling to the experimental results of the sorption tests will be reported in the presentation.

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Thallium adsorption onto phyllosilicate minerals in soils and sedimentsVoegelin A^{1*}, Wick S¹, Baeyens B², Marques Fernandes M²¹ Eawag, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland.² Paul Scherrer Institute, Forschungsstrasse 111, CH-5232 Villigen PSI, Switzerland.

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Thallium (Tl) is a potentially toxic trace element. In the environment, Tl mainly occurs as monovalent Tl(I). From contaminated soils and sediments, Tl may be taken up by plants or leach into groundwater, and thereby enter the (human) food chain. The bioavailability and mobility of Tl in soils and sediments are largely controlled by adsorption processes on clay minerals. Owing to its similar ionic radius and similarly low hydration enthalpy, the Tl⁺ cation shows a similar geochemical reactivity as the alkali metal cations K⁺, Rb⁺, and Cs⁺ and can substitute K in a range of minerals including K-feldspar and mica. Consequently, micaceous clay minerals have long been assumed to play a key role as sorbents of Tl in soils and sediments.

In an earlier laboratory study on the adsorption of Tl(I) onto the micaceous clay mineral illite [1], we confirmed that Tl⁺ exhibits a very high adsorption affinity and that its uptake in the presence of competing major cations (Ca²⁺, Na⁺, K⁺, NH₄⁺) can be quantified using a 3-site cation exchange model that has previously been developed to quantify the highly specific adsorption of Cs⁺ and Rb⁺ at the frayed particle edges of illite. Cation selectivity coefficients derived for Tl⁺ in comparison to reported coefficients for Cs⁺ and Rb⁺ showed that the adsorption selectivity followed the sequence Cs⁺ > Tl⁺ > Rb⁺, and that K⁺ and NH₄⁺ effectively compete for adsorption onto high affinity sites. In subsequent work, the calibrated 3-site model was successfully used to describe the solubility of exchangeable Tl in soils [2].

In this work, we studied the adsorption of Tl onto a wider range of phyllosilicate minerals: Na- and K- saturated illite and Na-saturated smectite, muscovite, vermiculite and a complex soil clay mineral assemblage [3]. To assess the link between the affinity of Tl adsorption onto the different phyllosilicate minerals and the mode of Tl adsorption, macroscopic Tl adsorption data was combined with Tl L_{III}-edge X-ray absorption spectroscopy for the characterization of the adsorbed Tl. The results show that the complexation of dehydrated Tl⁺ between two siloxane cavities at the frayed edges of illite particles or around collapsed zones in the interlayer of vermiculite results in very strong Tl retention. Strong Tl⁺ adsorption can also result from the complexation of Tl onto siloxane cavities on the planar surfaces of illite and muscovite. In the expanded interlayers of smectite (and vermiculite), on the other hand, Tl⁺ remained hydrated and adsorbed comparatively weakly. The result of this study confirm that the adsorption of Tl⁺ onto micaceous clay minerals follows the same trends as the adsorption of Cs⁺, which has been extensively studied over the last few decades with regard to the retention of radiocesium in contaminated soils, sediments and in host rocks of nuclear waste repositories. Consequently, mechanistic insights on Cs uptake onto micaceous clay minerals and established model concepts for the quantification of the adsorption and retention of Cs in soils and sediments are transferable to the assessment of the fate and impact of Tl(I) in the environment.

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Introduction : Geopolymers are defined as chains or networks of inorganic molecules linked with covalent bonds where their physicochemical properties received great attention in case of nuclear waste management [1]. Among those properties, ion sorption is significantly important for environmental applications such as retention of heavy metals or radionuclides [2]. However, apart from the sorption capacities, there is no significant studies in literatures regarding the sorption mechanisms of radionuclides to sodium activated metakaolin based geopolymers (Na-MKGP). In this study, the sorption mechanisms of Na-MKGP are investigated as a function of pH and background salt concentrations for Cs^+ , Sr^{2+} and Eu^{3+} . Obtained results were evaluated together with the 2SPNE/CE model to clarify Na-MKGP's radionuclide sorption mechanisms.

Experimental Procedures: About 50 grams of Na-MKGP were used in powder form by crushing and grounding until $\leq 1 \mu\text{m}$. The sorption samples were prepared with a fixed 1g/L concentration of Na-MKGP as a function of pH (pH 4 to 10) at 0.1 or 1 mM Cs^+ , Sr^{2+} and Eu^{3+} and 0.1 or 0.01 M NaClO_4 . The concentration of these ions remaining in the solution after sorption were measured with an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500cx). The obtained quantitative results were applied to the 2SPNE/CE model by Phreeqc (Version 3) and Phreeplot for fitting the sorption results to the model.

Results : The Cs^+ , Sr^{2+} and Eu^{3+} sorption amounts as a function of pH to the washed GP, namely sorption edges, are presented in Figure 1. According to the sorption edges, it was revealed that the sorption of Eu^{3+} on the material was dependent on pH, increasing from pH 4 and reaching to 100% sorption around pH 6. Meanwhile, the sorption of Cs^+ hardly depended on pH, but on the salt concentration. This situation can be explained by the inner-sphere (I.S.) surface complexation of Eu^{3+} and ion exchange or outer-sphere (O.S.) complexation of Cs^+ with Na-MKGP. The sorption of Sr^{2+} was dependent on both ionic strength and pH where ion exchange and surface complexation reactions were suggested to occur simultaneously.

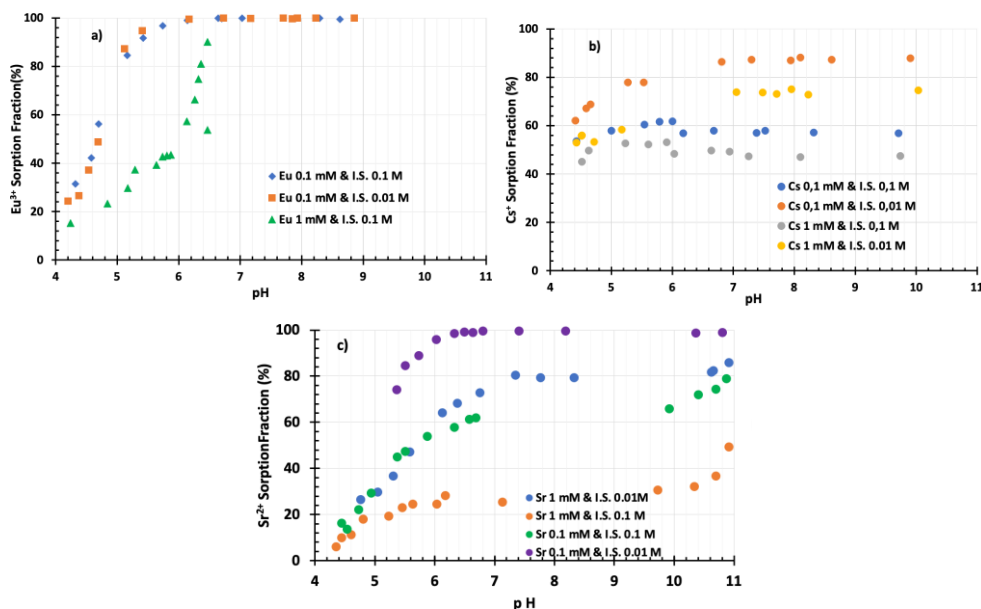


Fig. 1: Sorption edges of a) Eu^{3+} b) Cs^+ c) Sr^{2+} on the washed Na-MKGP at different aqueous conditions.

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OM10

Electrokinetics and stability of silica/clay mixtures at high copper concentration. Environmental and technical implicationsValenzuela-Elgueta J¹, Jiménez YP², Delgado AV³, Ahualli SA³¹ *Departamento de Ingeniería Química y Procesos de Minerales, Facultad de Ingeniería, Universidad de Antofagasta, Av. Angamos 601, Antofagasta, Chile*² *Department of Chemical Engineering, Universidad Católica del Norte, Av. Angamos 0610, Antofagasta, Chile*³ *Department of Applied Physics, School of Sciences, University of Granada, 18071 Granada, Spain***Presenting author e-mail contact: adelgado@ugr.es*

The processes of mineral benefit are designed according to the mineralogical characteristics of the material containing the element of interest and the geological unit to which they belong. For the case of copper ores, sulfuric acid is used as solvent in the leaching process. In this operation, a copper-rich solution is generated, from which Cu must be selectively separated by solvent extraction operation (SX) [1]. The high cost and the soil contamination potential of the solvents used for solvent extraction is one of the major concerns of this industry. This unwanted process is favored by the fact that the feeding solution in the SX process contains impurities such as silica and clays (mainly kaolinite). Hence, it can be understood that its behavior is intimately related to the colloidal nature and characteristics of kaolinite-silica systems under the operational conditions: low pH, and high ionic strength and particle concentration. A systematic study of their cooperative effects on the stability and electrokinetic behavior when both colloids are present has been recently carried out [2]. In this work, we analyze the electrokinetic properties of the individual and mixed systems in conditions that mimic the actual mining process. We determine the surface (electrokinetic, or zeta) potential by electroacoustic methods, which have been demonstrated to be compatible with the extreme working conditions [3]. We also analyze the correlation of these data with the stability and electron microscope observations.

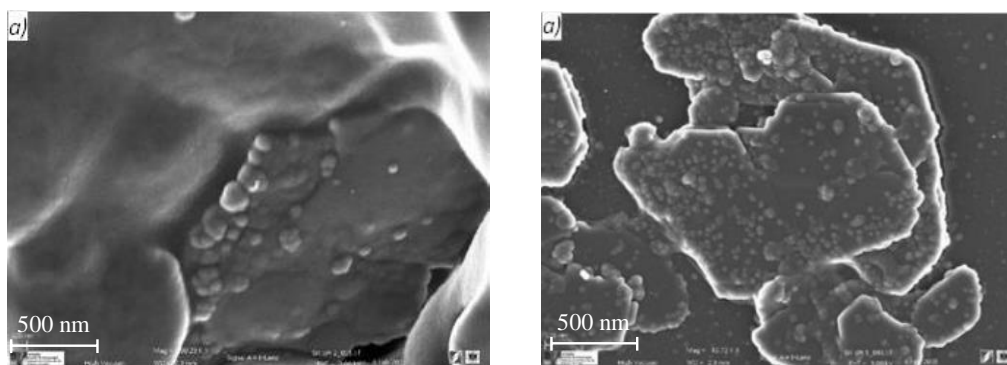


Fig. 1: SEM Image for mixed suspensions at pH 2 (left) and pH 5 (right).

As an example, Fig. 1 shows the heterostructures promoted by the conditions of the suspensions under study. It demonstrates that at low pH, attractions between silica and alumina edges are dominant. In contrast, at higher pH, the silica particles do not show any preference with respect to the facets for the agglomeration, although we can expect that attraction between negative silica and positive alumina will favor the adhesion of the nanoparticles on the faces of the latter, as observed.

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OM11

Amorphous iron-oxide montmorillonite composite for phosphate adsorption and reuse

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As the human population increases, the demand for food increases as well. As a result, demand for fertilizers rich in phosphate (P) has increased dramatically in recent years, and the natural sources for P are continuously decreasing. In parallel, environmental hazards due to P overuse such as habitat loss and eutrophication of water bodies are a growing problem. Thus, removal of P from contaminated water sources and finding eco-friendly P resources are both necessary.

Herein, we propose a novel sorbent that is based on montmorillonite (MMT) clay decorated with amorphous iron oxide nanoparticles (FeO_x-MMT) for the removal of P from water and as a potential fertilizer after use. The nano-sized iron-oxides deposited on the MMT show high adsorption affinity towards P due to the increase in reactivity and surface area. Results show high capacity and rapid uptake of the phosphate ions that adheres to the pseudo-second-order kinetic model. The adsorption of P was found to be specific and unaffected by competing anions such as carbonates and sulfates, or by dissolved organic matter, and also increases with increasing ionic strength of the wastewater. Adsorption was also pH-dependent and was found to be highest in acidic pHs. Desorption experiments showed high recovery of P in neutral to high pH ranges which suggests that the sorbent could be used once it is spent as a slow-releasing P fertilizer in neutral and basic soils. Initial column and funnel experiments strengthen our hypothesis that this material can be highly advantageous in removing P from secondary effluent and then releasing it back into the soil. Overall, this recover-and-apply technology can help close the P-cycle in a sustainable and cost-effective way.

OM12

Glyphosate adsorption to ferrihydrite: batch experiments and interpretation with CD-Music modellingGeysels B^{1,2*}, Groenenberg JE¹, Comans RNJ¹

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While pesticides generally feature hydrophobic properties and a corresponding association with soil organic matter, glyphosate shows a particularly strong interaction with metal (hydr)oxide surfaces due to its phosphonate group [1]. It has been suggested that glyphosate mobility and bioavailability in soils is thus controlled by metal (hydr)oxides rather than by soil organic matter [2]. Additionally, colloidal iron oxides in surface waters are likely to be important factors in controlling the bioavailability of glyphosate. In this study, we investigated the binding of glyphosate to ferrihydrite (Fh), a nano-sized iron (hydr)oxide that is abundant in natural soils. Due to its very small particle size, Fh has a high specific surface area and a corresponding high binding capacity. Ferrihydrite has been identified as an important proxy for the natural metal (hydr)oxides in soils [3].

Glyphosate adsorption was studied using batch experiments with freshly prepared Fh. Results are scaled to the specific surface area of Fh which was determined for each batch by anion probing with phosphate [4]. The experiments included a range of environmental conditions including pH and ionic strength. Orthophosphate (PO₄) concentration was varied since it has a strong interaction with iron oxides and is an important competitor for glyphosate adsorption in soils [5]. Likewise, calcium (Ca²⁺) concentrations were varied as this commonly occurring cation has been shown to form ternary complexes with PO₄ which enhances its overall adsorption on Fh [6] and glyphosate is expected to show similar adsorption behaviour. The adsorption data was interpreted with the charge distribution-multisite complexation (CD-MUSIC) model, which revealed strong inner-sphere interactions between the phosphonate group of glyphosate and Fh. These results provide mechanistic support that the soil metal (hydr)oxide fraction is an important parameter that determines the environmental fate of glyphosate and should be considered in speciation modelling and risk assessment of glyphosate in soils and surface waters.

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The concept of gate-sorption site coupling for understanding time-independent desorption hysteresis observed in solution experiments

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Mechanistic understanding of the behavior and fate of pollutants in environmental and engineered systems is closely related to our ability to describe sorption-desorption processes at interfaces between solutions and diverse natural or artificial materials (e.g., soils, sediments, sludge, coagulated organic matter, natural and modified clays and carbons). When examining sorption from solutions on such sorbents, desorption hysteresis often occurs, a poorly understood phenomenon compared to that commonly investigated for vapor sorption. The liquid-phase sorption-desorption hysteresis (SDH) may also be claimed to lack time-dependence, thus suggesting that the mechanisms responsible for SDH are not associated with poorly accounted or overlooked sorption-desorption kinetics. These mechanisms could involve the physical entrapment of sorbed molecules in a sorbent matrix, thus preventing them from an exchange with an external phase. The presence of irreversibly binding/reacting sorption sites might also lead to SDH, if the accessibility of such sites would be sorbate concentration-dependent. Following both above-mentioned mechanisms, fixing pollutants might result in meaningful (and opposite) environmental consequences, i.e., postponing dangerous biological effects or serving as a decontamination method by burying chemicals into the environmental matrices [1]. There is a limited understanding of how to model the time-independent liquid-phase SDH associated with the formation of entrapped or irreversibly bound chemicals. This contribution proposes a novel concept [2] that can quantitatively explain and model time-independent SDH in these two major scenarios, i.e., when sorbed pollutant molecules are physically blocked from their exchange with the molecules present in solution, or they are irreversibly bound to sorbent matrix. In addition, the attempt is made to examine whether this concept could be extended to explain SDH associated with forming a non-relaxed sorbent state where nevertheless the free exchange of sorbate molecules with the environment occurs [3,4]. The major idea behind this concept is that accessibility of sorption sites in a matrix may be governed by moieties acting mostly as "gates" and undergoing cooperative opening or closure, depending on solute concentration. "Gates" become open, and sorption sites accessible at increased solute concentrations such that these sites may be involved in reversible or irreversible interactions with sorbing molecules. Upon desorption, the gates capable of a "turning-off" control the opportunity for sorbed molecules to be released into the environment. Coupling between varieties of gates and sorption sites is accounted by introducing their statistical distributions. Therefore, three different mechanisms are examined: 1) a *Blocked Exchange* model considering that the exchange with the environment is prevented due to the closure of the gates upon desorption; 2) a *Lack of Exchange* model clarifying how the sorption sites capable of irreversible binding may not be fully occupied in the presence of non-zero solute concentrations; 3) a *Free Exchange* model allowing the gates remain in their open non-relaxed state during desorption. The models have the potential to explain, represent and even predict desorption data using a minimal number of adjustable parameters determined by model application to sorption isotherm and the first desorption step. Finally, the examples of data analysis, model assumptions and the ways to further verify the concept are discussed.

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Chemical speciation changes in the environmental cycles of metal contaminants. Inputs from field studies

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The chemical speciation of metal contaminants is widely recognized to control their natural cycles and the efficiency of remediation strategies. However, the directions and time-scales of speciation changes are particularly difficult to predict in low-temperature natural systems, where various chemical ligands and competitors influence redox, sorption and precipitation reactions, and where kinetics are largely influenced by biological processes. It is then particularly challenging to identify key reactions at the water-mineral-microorganisms interfaces and to integrate them over time and space, up to the field scale.

In this talk, we will present recent studies that we have conducted on field sites impacted by metal, metalloid or actinide contamination and subjected to remediation or management issues. The studies presented will emphasize the input from bulk X-ray absorption spectroscopy (XAS) for solving trace elements speciation at the atomic scale, in complex natural materials such as soils, sediments and biofilms. Particular focus will be put on natural analogues of contaminated media, in which the evolution of toxic element speciation can be observed over thousands of years. This speciation information, when rescaled to the field dimensions and in a temporal perspective thanks to isotopic and dating approaches, helps identify the physicochemical factors to consider for improving water treatment processes and waste management strategies.

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KN2

Ligand facilitates electron extraction from solid Fe(II) for hydroxyl radical production and contaminant attenuation

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We recently demonstrated the potential of oxygenating Fe(II)-bearing sediments for hydroxyl radicals ($\bullet\text{OH}$) production and contaminants degradation, and the electron utilization efficiency for $\bullet\text{OH}$ production depends on the speciation of Fe(II) [1,2]. Here we further show that specific ligands can largely enhance $\bullet\text{OH}$ production and contaminant degradation during sediment oxygenation due to increased utilization efficiency of sediment electrons [3]. With the addition of 0-2 mM sodium ethylene diamine tetraacetate (EDTA) or sodium tripolyphosphate (TPP) in sediment suspension (50 g/L, pH 7.0), trichloroethylene (TCE, 15 μM) degradation increased from 13% without ligand to a maximum of 80% with 2 mM TPP, and was much higher with TPP than EDTA because EDTA competes for $\bullet\text{OH}$. Electron utilization efficiency for $\bullet\text{OH}$ production increased with increased ligand concentration and was enhanced by up to 6-7 times with 2 mM EDTA or TPP. The formation of dissolved Fe-ligand complex facilitates the electron extraction from sediment matrix to dissolved Fe(III)-ligand due to the increased Fe cycling in aqueous phase. The shift of electron transfer channel from sediment- O_2 to sediment-Fe-ligand complex- O_2 is mainly accountable for the enhanced electron utilization efficiency by the ligands. We further show the feasibility of enhancing TCE degradation by ligand injection in a simulated 2-D tank. Our results implicate the importance of manipulating electron transfer in solid-water interface for enhancing contaminant degradation during sediment oxygenation.

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OT1

The use of composted sewage sludge in brownfield soil remediation

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Sewage sludge (SS), the by-product of the waste water treatment process, is primarily regarded as waste. About 10 million tons of dry SS is produced in Europe annually, with increasing amount over time, leading to issues related to SS management including storage and disposal [1]. Alternatives for SS disposal include its use (i) in agriculture for improving soil fertility [2]; (ii) at degraded lands for land reclamation [3]; and (iii) in contaminated soils for stabilizing risk elements such as metal(loid)s [4]. However, SS may contain pollutants and pathogens that hinder its direct use in soil and calls for SS treatment before its application in soil.

To close the gap between SS quality and application in degraded/contaminated soil, we set up a pilot field experiment with the main goal of assessing the impact of composted SS application in soil on soil characteristics and leachability of risk elements from the SS-amended soil under field conditions. Preliminary analyses of the basic characteristics and leachability of the (composted) SS showed that composting generally led to decreased total concentration and leachability of risk elements contained in SS.

The site with composted SS application is being monitored regularly (once/month), including collection of soil, soil solution, and plant (during vegetation period) samples. The samples collected for the first six months and after one year of application were analyzed for (risk) element concentrations using various experimental and analytical methods. The first results of risk element leaching from the amended soils determined by the TCLP soil extraction method show that release of risk elements decreases in the following order: Zn > Cu > Ni > Cr > Co > As > Pb > Sb > Cd, and this trend is similar for the field amended with SS and compost (control field). Long-term monitoring of the site is key in understanding the long-term effects of composted SS application in soil on the mobility of risk elements.

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Sorption of metformin and lamotrigine in a digestate-amended soil in the presence of metal contamination

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Digestate is the end-product of anaerobic digestion (AD), being an organic matter - nutrient rich matrix that can be used as soil amendment depending on waste origin and compliance to national legislations. Most of the globally produced digestate does not meet the quality standards imposed by legislations, thus it is treated as waste discarded in landfills. New uses for digestate are needed in the frame of a circular bioeconomy approach. One possible application is its use as soil amendment for marginal land restoration coupled with sustainable energy crop cultivation. For this reason, the fate of contaminants, potentially contained in the digestate, must be monitored and thoroughly studied. Contaminants of emerging concern, such as many recalcitrant pharmaceutical compounds, were shown not to be removed completely by AD process, accumulating in the solid phase of the digestate [1]. It is important to understand the behaviour of these compounds and their interaction with other contaminants, such as trace metals, to evaluate their mobility and fate in the soil/water system. Two poorly studied recalcitrant pharmaceuticals, classified as contaminants of emerging concern, namely metformin (MET) an antidiabetic drug and lamotrigine (LMT) an anticonvulsant drug, were selected for the study. Their sorption behaviour in a loamy sand soil amended with a solid digestate originating from a non-source-separated Organic Fraction of Municipal Solid Waste (OFMSW) was assessed, considering the influence of trace metals. For both pharmaceuticals, the adsorbed amounts were compared when added singularly and when simultaneously added with a metallic cation (Zn, Ni, Cu, Pb, Cr, Co) at different pharmaceutical/metal ratios. The adsorbed amounts were also measured for the corresponding non-amended soil to assess the effect of digestate application. This presentation will highlight the different observed trends dependent on the experimental conditions (contaminant ratio, pharmaceutical and metal nature), which in turn will determine if the metals increase, decrease or do not significantly affect the pharmaceutical sorption behaviour.

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OT3

Effects of dissolved organic compounds on the structure, colloidal stability and phosphate uptake of Fe(III)-precipitates formed by Fe(II) oxidation in oxygenated anoxic groundwater

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Excessive phosphorus (P) inputs into surface waters lead to the eutrophication and deterioration of aquatic ecosystems. The oxidation of dissolved Fe(II) at environmental redox boundaries such as anoxic groundwater exfiltration sites induces the precipitation of amorphous to poorly crystalline Fe(III)-solids that can retain phosphate (PO₄)¹. Dissolved organic matter (DOM) may affect the structure and colloidal stability of Fe(III)-precipitates and the co-precipitation of PO₄, adding to the coupled effects of inorganic solutes such as Ca, PO₄, and SiO₄ that interfere with Fe(III)-polymerization². To date, mechanistic studies on the coupled effects of different types of DOM, Ca, and PO₄ on the formation, composition, and PO₄ uptake of Fe(III) precipitates formed by Fe(II) oxidation at environmentally relevant concentrations are still scarce.

The aim of this work was to assess how different organic ligands (citrate, 2,4-dihydroxybenzoic acid, galacturonic acid, humic acid) affect the structure and colloidal stability of Fe(III)-precipitates and PO₄ co-precipitation. Laboratory experiments were performed in bicarbonate-buffered aqueous solutions at pH 7.0, with Na or Ca as electrolyte cation, at two molar PO₄/Fe ratios (0.25, 0.05), and at multiple levels of the organic ligands (molar C/Fe from 0.1 to 9.6). After adding 0.5 mM Fe(II) to the aerated solutions, Fe was left to oxidize and precipitate over 18 h. Solutions were analyzed for Fe, Ca, Na, and P (ICP-MS) and organic C (TOC-L). The suspended solids were analyzed by dynamic and electrophoretic light scattering (DLS, ELS; hydrodynamic diameter and zeta potential). The dried solids were characterized by Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy (local Fe coordination), Fourier-transform infrared spectroscopy (FTIR; molecular vibrations) and transmission electron microscopy with energy-dispersive X-ray detection (TEM-EDX; particle morphology and elemental composition).

Fe(III)-precipitates formed without DOM were mixtures of amorphous Fe(III)-phosphate and poorly-crystalline lepidocrocite². For the studied organic ligands, our data indicated that higher C/Fe ratios did not reduce P uptake through competitive sorption, but instead resulted in lower residual dissolved PO₄ levels by inducing the formation more amorphous Fe(III) precipitates with a higher PO₄ sorption capacity. At the same time, increasing C/Fe ratios also resulted in lower aggregate sizes and more negative zeta potentials. The tested organic ligands may thus enhance both the PO₄ binding and colloidal mobility of Fe(III)-DOM co-precipitates, the size of this effect depending on the type of ligand.

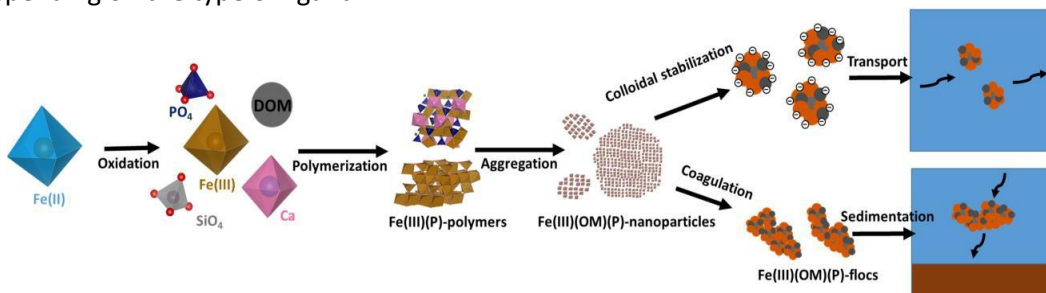


Fig. 1: A schematic of Fe(III)-phosphate co-precipitate formation in the presence of interfering solutes.

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The role of competing cations in ligand-induced U mobilization: comparisons from biogenic non-crystalline U(IV) and a bioreduced field sediment

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Organic ligands have been shown to be able to mobilize uranium (U) from various reduced phases even under anoxic conditions, especially from labile tetravalent uranium (U(IV)) phases such as non-crystalline U(IV). Yet, the ability of organic ligands to mobilize U in the environment is predicated on each ligands' affinity for both U and other cations present in the subsurface which are able to form complexes.

So as to gain insights into the relative effects of competing cations on ligand-induced U mobilization, batch experiments were carried out with both biogenic non-crystalline U(IV) as well as with a bioreduced field sediment (containing a mixture of non-crystalline U(VI), non-crystalline U(IV), and uraninite (UO₂)) under anoxic conditions. In the current study two organic ligands were chosen to assess the differing effects of competing cations. These include 2,6-pyridinedicarboxylic acid (DPA), a tridentate low-molecular-weight organic acid, and N,N'-di(2-hydroxybenzyl)ethylene-diamine-N,N'-diacetic acid (HBED), a hexadentate synthetic chelator. Competition effects were probed in non-crystalline U(IV) experiments by pre-complexation of cations to each respective ligand including Ca²⁺, Fe³⁺, and Zn²⁺ with comparisons drawn to cation-free treatments. In the bioreduced field sediments, which natively contain an abundance of competing cations including Fe, Mn, Al, and Ca, competitive effects were additionally assessed across a wide range of ligand concentrations.

The results of this work highlight the vastly differing extents of U mobility when competing cations are present, varying per ligand based on the respective ligand's affinity towards each cation. These effects ranged from no discernible difference compared to cation-free treatments to near-complete inhibition of U mobility. Within such, the findings of this work aim to provide a deepened level of understanding of the effects of competing cations in the environment on organic ligand-induced U mobilization including two structurally diverse organic ligands and two reduced U(IV) phases targeting differing levels of environmental complexity. These findings provide meaningful insights regarding the stability of U(IV) phases in the environment under anoxic conditions in the presence of organic ligands.

Kinetic model development for coupled processes: a study of phosphate release during sulfidation of iron (hydr)oxides

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Biogeochemical models, such as sediment diagenetic models, require empirical rate laws. Typically, such rate laws are formulated and parameterized based on experimental data performed under controlled conditions. However, building up a kinetic model for complex processes could be challenging when several reactions are coupled and can act in parallel. Here, the release of phosphate(P) during sulfidation of lepidocrocite(γ -FeOOH) was investigated. This process is important for the P dynamics in lakes and oceans as it can contribute to the recycling of P from aquatic sediments, when iron (hydr)oxides with sorbed P become exposed with sediment burial.

Sulfidation experiments of P-containing lepidocrocite were performed at pH values of 7.3 and 8.3 using flow-through reactors, which contain filters at the outflow to retain the solids inside the reactor. The concentration of S(-II) and P in the outflow were monitored throughout the whole process (~7 hours). In general, P release corresponded to the progress of sulfidation of lepidocrocite, but was most pronounced at the early and last stage of the reaction. To better understand the reactions coupling, we developed a dynamic zero-dimensional model in R that allowed us to interactively assess the suitability of different generic forms of rate expressions for the processes involved and, subsequently estimate the related rate constants. The release of P is expected to be driven by loss of sorption sites due to the transformation of lepidocrocite into FeS, which is expected to have a lower affinity to P than lepidocrocite. This implies that the kinetics of sulfidation have to be included in the model, too. Additionally, the direct competition between P and sulfide for sorption sites can contribute to P release. After testing different generic forms of rate laws we were able to find a model, which can reproduce our experimental data for both S(-II) and P. This model for the rate law of sulfide consumption included: the proportion of un-reacted lepidocrocite, the concentration of S(-II) as well as the decrease in reactivity of lepidocrocite due to shrinking interfacial area and the heterogeneity of particle size. The mass balance for P release included desorption and (re)-adsorption of P and ligand exchange with sulfide. After obtaining the proper generic rate law, the parameters were fine-tuned by using differential equation solver, finally the sensitivity analysis and model justification were achieved by applying Markov Chain Monte Carlo (MCMC) simulations.

We will present the challenges on the quest of finding suitable rate expression based on the available data and discuss the limitations of our approach. We believe that our study provides a good example for the identification and parameterisation of kinetic models based on laboratory experiments for complicated, coupled biogeochemical reactions.

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Poorly-crystalline ferrihydrite is ubiquitous in the terrestrial environment that has important contributions to controlling the fate of arsenic in sediments and soils. Although there is clear evidence that ferrihydrite has a higher affinity towards As(III) relative to As(V), little is known about how and why As(III) is readily immobilized by ferrihydrite. In this study, ferrihydrite was employed to evaluate the As(III) and As(V) adsorption capacities. The characteristics of ferrihydrite such as morphology, pore size distribution, arsenic adsorption species, and adsorption energies of arsenic at different sites were carefully examined using the experimental characterizations of TEM-EDS mapping, positron annihilation lifetime (PAL) spectroscopy, X-ray absorption spectroscopy (XAS), and N₂ adsorption isotherms and theoretical calculations of density function theory (DFT). Batch adsorption experiments revealed that adsorption of As(III) on ferrihydrite was larger than that of As(V). The results of PAL characterization and pore size distribution analysis confirmed that ferrihydrite had abundance of vacancy clusters-like micropores, which consisted of 10-20 atom deficiencies (V10-20). The greater As(III) adsorption of ferrihydrite was attributed to its surface adsorption sites as well as its abundant micropore adsorption sites, available only to As(III), due to its size matching well with ferrihydrite micropores, thus significantly contributing to great As(III) immobilization.

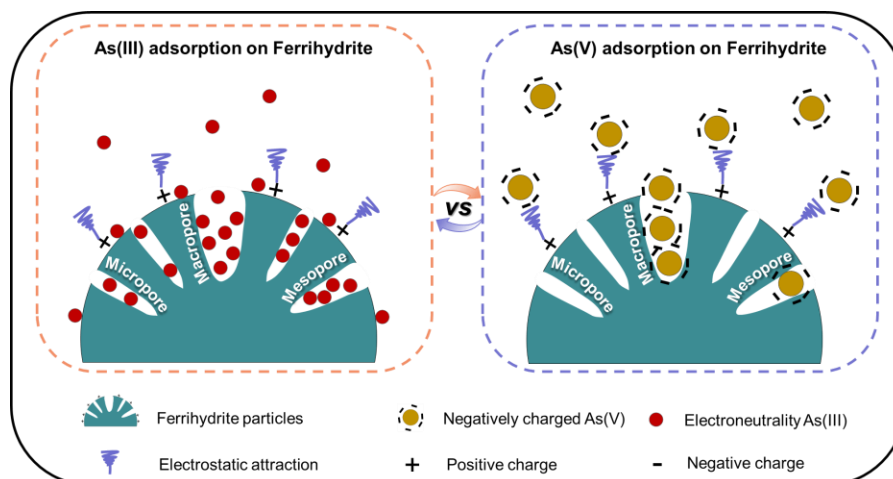


Fig. 1: Schematic illustrations of difference adsorption behaviors of As(III) and As(V) on ferrihydrite.

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Quantitative characterization of the site density and charged state of functional groups on biochar

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Charge density and proton dissociation state of surface groups play a crucial role in understanding biochar's sustainable applications in environment. Such knowledge is still limited due to the complexity of biochar. Biochar RWB and RPB and their base/acid treated equivalents (TWB, TPB) are characterized to testify the graphitization degree, specific surface area, porosity, zeta potential, "Boehm" acidic functional group contents and surface charge vs. pH curves. A trimodal NICA model with strong and weak acid-type groups and a basic-type group, each with continuous proton affinity distribution (PAD), is applied to describe the functional group protonation and charge density of TWB and TPB. Acidic group densities are roughly matched with the Boehm titration results. The $\log K_H$ and $m_{j,H}$ values shows a linear dependence with $\log c_{KCl}$ caused by electrostatic interaction. The trimodal PAD which is a material-specific 'finger print' of biochar and charged state of functional groups were calculated. The model also describes successfully the charge curves of three series of biochar reported by Li *et al.* [1] and Mia *et al.* [2]. NICA modelling allows a quantitative comparison between biochar and humic substances, although the latter have no basic-type group. Quantifying the relation between the surface groups and the charge density of biochar with the NICA model analysis provides crucial information for assessing and improving the targeted applications of biochar in nature.

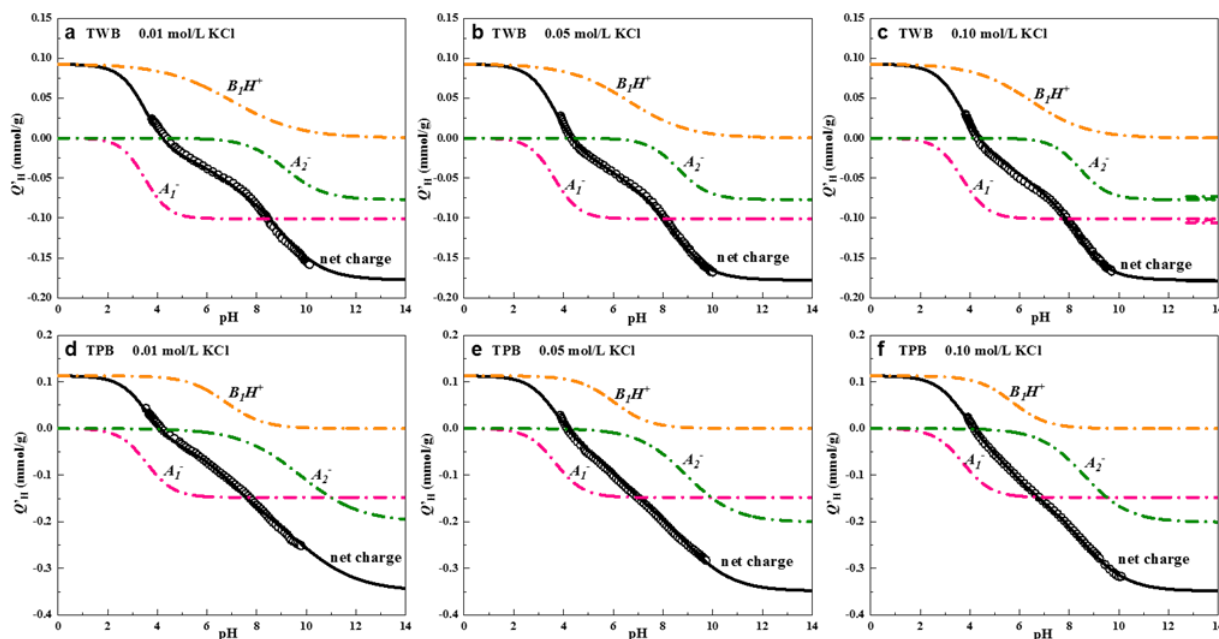


Fig. 1: The calculated and experimental charge density Q'_H ($\mu\text{H}/\text{F}$) vs. pH curves and the contributions of the three functional group types to the charge density development as a function of pH for TWB (a-c) and TPB (d-f). Symbols: experimental data; black solid lines: charge density predicted by the NICA model; pink dashed lines: deprotonated low-affinity acidic groups; green dashed lines: deprotonated high-affinity acidic groups; orange dash lines: protonated basic groups.

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Assessment of cadmium bioavailability and stabilization strategies guidance in rice-soil system based on multi-surface speciation model

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Bioavailable cadmium (Cd) has been regarded as a more reasonable indicator of rice Cd bioaccumulation risk than total Cd content in paddy soil. Given the heterogeneity and complexity of paddy soil, it was difficult to build an accurate model to predict rice Cd bioaccumulation or bioavailable Cd at large scale space. This study firstly tried to apply multi-surface speciation model (MSM) predicting bioavailable Cd at large scale space based on soil- rice samples from Yangxin county. There was a significant relationship between MSM predicting free ion of Cd and Cd accumulation in rice grains ($R=0.51$, $P<0.001$). Besides, MSM could well estimate CaCl_2 extracted Cd with an extremely strong correlation between them ($R=0.93$, $P<0.001$). In addition, pH was found the most critical sensitivity factor at county scale based on RDA hierarchical partitioning, traditional regression model and MSM-based sensitivity analysis. Based on scenarios-simulated sensitivity analysis of MSM, the study demonstrates the stabilization of free ion of Cd could attend over 50% and 75% under raising 0.5 and 1 pH unit regulation. These results showed that MSM was useful for predicting Cd bioavailability and the effectivity of Cd stabilization strategies, thus this model can be applied for rice Cd bioaccumulation risk assessment and Cd stabilization strategies guidance.

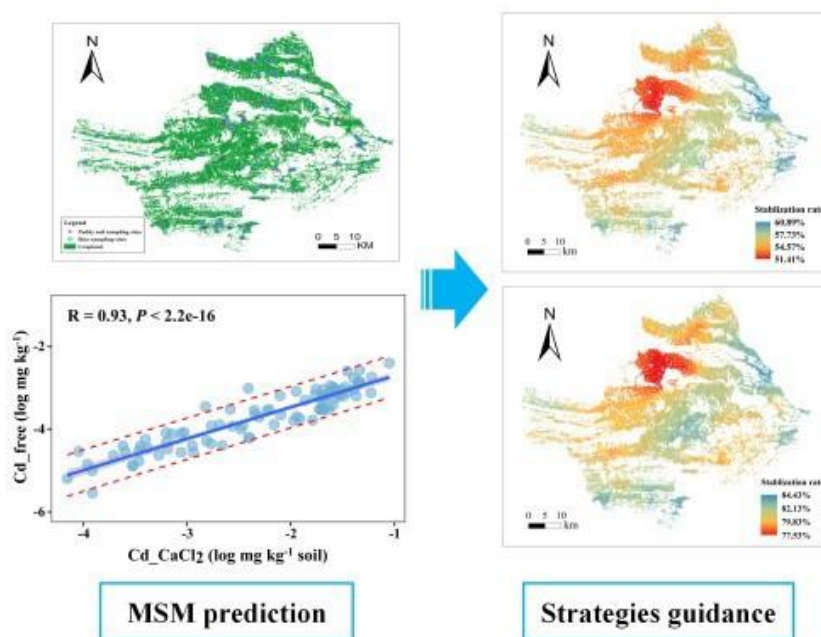


Fig. 1: The application of MSM for bioavailable Cd prediction and remediation strategies guidance in paddy soil at large scale space

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Generic CD-MUSIC-eSGC model parameters for proton binding by iron (hydr)oxides

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Surface reactivity of iron (hydr)oxides plays a crucial role in controlling their interfacial reactions, for which various surface complexation models have been developed. The diversity of mineralogical properties of iron (hydr)oxides has resulted in a redundancy of model parameters, which is hindering modeling of iron (hydr)oxides in environment. Goethite, hematite and ferrihydrite dominate the iron (hydr)oxide mass fraction in soils. To capture their combined surface reactivity, generic protonation parameters of the Charge Distribution-Multisite Complexation (CD-MUSIC) model were derived by reanalyzing literature datasets and characterizing newly synthesized iron (hydr)oxides. It was observed that the proton and monovalent ion-pair affinity constants of different iron (hydr)oxides located in a relative narrow range. The unified affinity constants were ~ 8.3 and 11.7 for protonation of singly- and triply-coordinated hydroxyl sites and -0.5 for ion pairs. Fixed site densities of singly-/triply-coordinated hydroxyl sites of $3.45/2.70$, $5.00/2.50$, and $5.80/1.40$ sites/nm² for, respectively, goethite, hematite, and ferrihydrite provided good results. The generic model parameters can simplify model calculations when the variable reactivity is interpreted with a different specific surface area (SSA). The Stern layers capacitance can be easily acquired through a simple correlation with SSA. The generic model parameters enable good quality modeling predictions of the overall surface reactivity of iron (hydr)oxides.

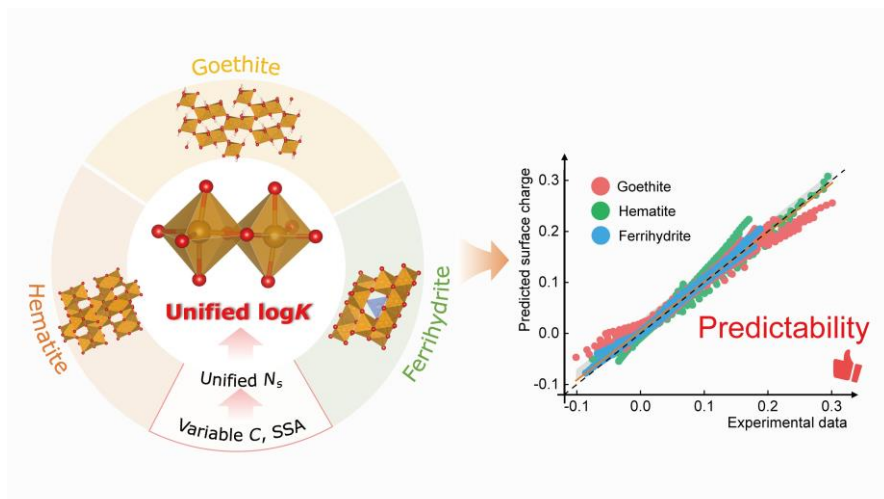


Fig. 1: Generic CD-MUSIC-eSGC model parameters for proton binding by iron (hydr)oxides.

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OT10

Impact of soil active components on heavy metal speciation and an advanced model through soil-plant continuum

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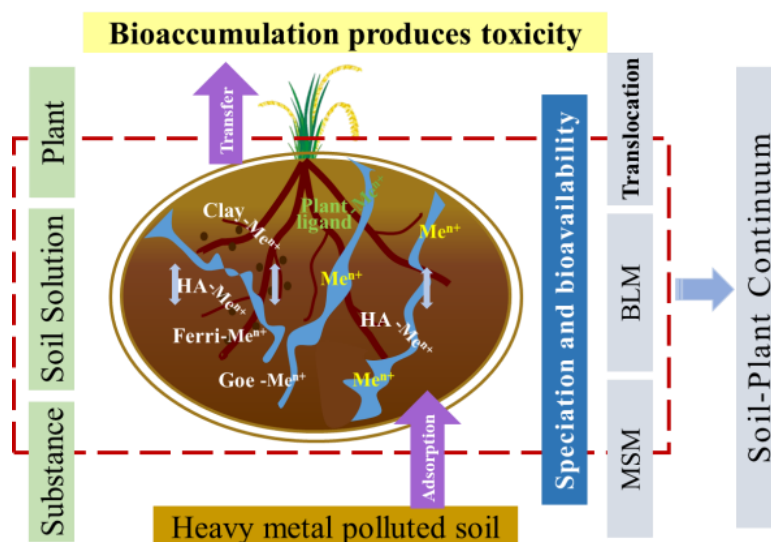
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Soil interfacial interactions have profound effects on the sequestration, degradation and biological metabolism of the pollutants. Therefore, focusing on the chemical behaviors of external pollutants in soil and developing soil remediation technologies to meet the social and public needs were of prime importance. To date, our understanding of the impacts of soil mineral–organic matter–microbe interactions on the behaviors of heavy metals in soils, and of an advanced model through soil-plant continuum is still relatively limited. The application of in-situ measurement, micro-examination and element tracing technologies significantly accelerated the development of studies with related to heavy metal interactions with soil active components. It is necessary to make accurate assessments of heavy metal species and speciation distribution. Geochemical models are widely used to predict the speciation and transport of heavy metals that will be important in the control of the solubility, bioavailability and the fate of heavy metals. In addition, an advanced model through soil-plant continuum is also crucial to screen the trace elements from soil particle, to soil solution and plant rhizosphere. Fundamental understanding of these reactions and processes at the atomic, molecular, and microscopic levels is essential for remediation of heavy metal pollution in soils, and enhancing soil health as well as sustain the ecosystem integrity.



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Plants and microorganisms exude chelating ligands called metallophores for the purpose of nutrient acquisition, particularly under conditions of low nutrient availability. Through mineral surface reactions such as ligand-controlled dissolution or by metal-exchange reactions, these metallophores form soluble complexes with metal ions in the external environment, thereby mediating the transport and uptake of metal nutrients. However, metallophores also have affinity for metals other than the target nutrient, including toxic heavy metals such as Ni, Co, U, etc. Complexation of toxic metals may lead to undesirable mobilization, leaching and uptake by biota, and compromises the efficiency of the nutrient acquisition strategy. This raises the question to what extent metallophores specifically mobilize the target nutrient and how this depends on the speciation of other metals.

The specificity of metallophores was examined through multi-surface equilibrium modelling and kinetic soil interaction experiments. The ligands considered were the siderophores desferrioxamine B (DFOB) and 2'-deoxymugineic acid (DMA), which are exuded for acquiring Fe. Multi-surface models predict metal speciation in soils by combining surface complexation models that describe metal ion binding to individual reactive soil constituents (soil organic matter, metal(hydr)oxide minerals, clay minerals). The siderophores were included into these models and soil-specific equilibrium speciation was predicted. Model predictions were compared with results from kinetic batch experiments in which DFOB and DMA were applied to soil suspensions and mobilized metal concentrations were monitored over time.

In most treatments, equilibrium was not reached during the 1-week kinetic experiments and competitive metal exchange reactions were still ongoing. For DFOB, the predicted equilibrium speciation and experimental results were still largely in agreement: DFOB speciation was dominated by Fe and Al complexes. Fe mobilization by DFOB was overpredicted, but experimental Fe concentrations continued to increase towards equilibrium at the expense of Al. In contrast, for DMA, no Fe complexation was predicted; Cu-, Ni- and ZnDMA complexes dominated the ligand's equilibrium speciation. However, the kinetic experiments did show a fast initial Fe mobilization, before Fe became increasingly displaced by other metals (Cu, Ni and Co) competing for complexation by DMA. This implies that, although thermodynamic specificity was lacking, a temporary increase in Fe concentrations could still be induced through kinetic specificity. This kinetic specificity of DMA for Fe can induce a time window during which organisms can benefit from enhanced Fe bioavailability. Our results demonstrate that the required specificity of metallophores can be effectuated either by thermodynamic or kinetic factors.

Trace metal binding to organic reactive (bio)surfaces at the solid/solution interface

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The environmental risk associated with trace metals in aqueous and soil systems is strongly influenced by the metal ion binding to reactive organic phases at the solid/solution interface. Thus, the presence of organic colloidal particles control the partitioning, bioavailability and bioaccumulation of metal ions in natural systems. The reactive organic (bio)surfaces commonly found in the environment show a high affinity for trace metals at variable environmental conditions. These organic (bio)surfaces possess a high concentration of acidic functional sites, i.e. carboxylic, phenolic or phosphoryl groups, which provide a high reactivity against metal ions.

In the present work we have assessed the physico-chemical properties of different reactive organic (bio)surfaces, including metal ion binding properties. Among the reactive organic (bio)surfaces studied we have considered humic substances (extracted from soil and compost), organo-mineral composites (FeOx-citric acid; FeOx-HA), biochar (derived from plant and animal waste), and natural or cloned mosses (terrestrial and aquatic species). Special attention was given to moss biosurfaces since they are considered potential biomonitors of atmospheric pollution in rural, urban and industrial areas and can be used to control metal pollution in aquatic systems. The fundamental physico-chemical mechanisms that underlie the charging behaviour and trace metal binding processes were addressed for aquatic and terrestrial mosses (*F. antipyretica*, *S. denticulatum*, *S. palustre* and *P. purum*). The heterogenous nature of the functional groups in the organic (bio)surfaces was ascribed to the presence of different acidic groups, carboxylic and phenolic, and the total site abundance and $\log K_H$ of these groups were obtained with a bimodal distribution model. Adsorption or complexation experiments of trace metals were conducted at constant or variable pH conditions with the different (bio)surfaces. Also, adsorption data for three metal cations, i.e. Cu, Cd and Pb, were obtained at constant or variable pH. From the metal adsorption isotherms (Figure 1) we can conclude that the soil humic substances showed a higher copper affinity than the aquatic and terrestrial mosses (*F. antipyretica* and *S. denticulatum*), while biochars (*Z. mays* and *A. melanoxylon*) showed the lowest copper affinity.

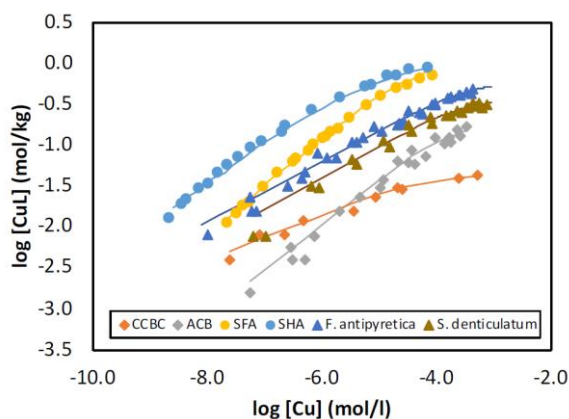


Fig. 1: Copper binding isotherms obtained for different organic (bio)surfaces: soil humic substances, biochars and aquatic and terrestrial mosses.

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OT13

Geochemical modelling of Cu(II) and Pb(II) adsorption onto humin using NICA-Donnan

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Humin, which is the insoluble part of humic substances, plays an important role in regulating the behaviour and fate of metallic trace elements (MTE) at the soil/water interface [1,2]. However, compared to the two other fractions of humic substances, humic acid and fulvic acid, humin has been the least studied due to its insolubility and intractable properties [1,2]. To our knowledge, there is no research studying on the modelling of metal ions on soil humin. In this study, humin was extracted from a peat soil sampled in Marne (Northeast France) after removing soluble fractions following the International Humic Substances Society (IHSS) protocol. The adsorption behaviour of copper(II) and lead(II) onto humin as a function of pH was studied using the batch technique at different solid charges and metallic cation concentrations. This study, with an assumption of similar adsorption properties of humin and humic acid [1], is the first research to apply NICA-Donnan model to account for the binding of copper and lead, onto humin. The proportion of the two types of functional group considered in this model, carboxylic and phenolic groups was determined by Cross Polarization/Magic Angle Spinning solid-state ¹³C Nuclear Magnetic Resonance spectroscopy (¹³C CP/MAS NMR). The NICA-Donnan model allows a good description of the experimental adsorption data at the different tested conditions.

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OT14

Desorption kinetics of glyphosate by phosphate from goethite. ATR-FTIR experiments and modelling

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The study of the adsorption-desorption kinetics of ions and molecules at the mineral-water interface is fundamental to understand the dynamics of pollutants and nutrients in the environment. This work reports the desorption kinetics of the herbicide glyphosate from goethite, as studied in a flow cell using ATR-FTIR spectroscopy and employing phosphate as the desorbing agent. The flow cell allowed to study the adsorption-desorption kinetics under well controlled transport conditions. The ATR-FTIR spectroscopy, on the other hand, allowed to identify and monitor simultaneously the desorbing glyphosate and the adsorbing phosphate species as a function of time. Experiments were performed using a synthetic goethite sample, at pH 7.0 and in 0.1 M NaCl as supporting electrolyte. A 2.95×10^{-4} M glyphosate solution was added first, and its adsorption kinetics was monitored for 60 min. Afterwards, the glyphosate desorption was induced by flowing a phosphate solution (concentration range 1×10^{-5} M – 1×10^{-3} M), and thus the desorption of glyphosate and the adsorption of phosphate were continuously monitored for another 60 min. A kinetic model was developed taking into account glyphosate and phosphate transport, and glyphosate and phosphate attachment-detachment reactions. A good fitting of data could be obtained for glyphosate desorption kinetics, phosphate adsorption kinetics and the individual adsorption isotherms, using the same set of model parameters. The results clearly show that the desorption of glyphosate by phosphate is simply a competition process, where both substances compete for the same adsorption sites.

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Enzyme interacting with soil components and its conformational change investigation by spectroscopic techniques

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Enzyme has a strong affinity to soil minerals and humic acids (HAs). Binary system for enzyme-HA is relatively well studied [1,2]. However, the conformational changes for different charged enzyme interacting with HA are not clear, the investigations of ternary systems including enzyme, mineral and HA are lacking. Here, we investigated the protein structure and microenvironment of amino residues for lysozyme (LSZ) and urease with spectroscopic techniques. And the effect of HA on the interaction of lysozyme (LSZ) with kaolinite (Kao) and montmorillonite (Mont) was also investigated at (initial) pH_i 5 and 8. Our results showed that the binding of enzyme with HA and conformational change of enzyme were largely determined by the enzyme surface charge. For conditions at which both urease and HA are negatively charged, the enzyme conformational and microenvironment changes were insignificant due to the electrostatic repulsion especially at higher pH values. While for positively charged LSZ in natural environment, the binding of LSZ with HA was strong. Circular dichroism and attenuated total reflectance Fourier transform infrared spectroscopy showed that the helix content reached a minimum at the mass ratio of its iso electric point (IEP), f_{IEP} . The minimum of helix content at f_{IEP} corresponded with the minimum LSZ activity and maximum aggregate size of HA/LSZ-complex/aggregate (HA/LSZ-c/a) [3]. UV- vis spectra and fluorescence measurements indicated that the amino acid residues in LSZ were in a more hydrophobic microenvironment before f_{IEP} , while were gradually exposed to a more polar microenvironment beyond f_{IEP} with the disaggregation of HA/LSZ-c/a. At $f < f_{IEP}$ the HA/LSZ complexes were positively charged and adsorbed well to the negatively charged Mont and Kao surface fractions. The adsorption levels on Mont are considerably larger than on Kao, which is mainly due to the much larger area fraction of modestly hydrophobic basal plates of Mont. The presence of HA increased the plateau adsorption of LSZ on Kao and Mont for both pH_i values and the increase in LSZ adsorption increased with increasing HA content and pH_i. At pH_i 8 complications arised for low initial LSZ concentrations, for $f < f_{IEP}$ the HA/LSZ complexes were only weakly positive and formed dispersed aggregates and for $f > f_{IEP}$ the HA/LSZ complexes were negative, both conditions caused relatively high equilibrium concentrations of LSZ in solution that decreased with increasing initial LSZ concentration. The present results are helpful for understanding the function and transportation of enzyme in complicated and multi-component environment.

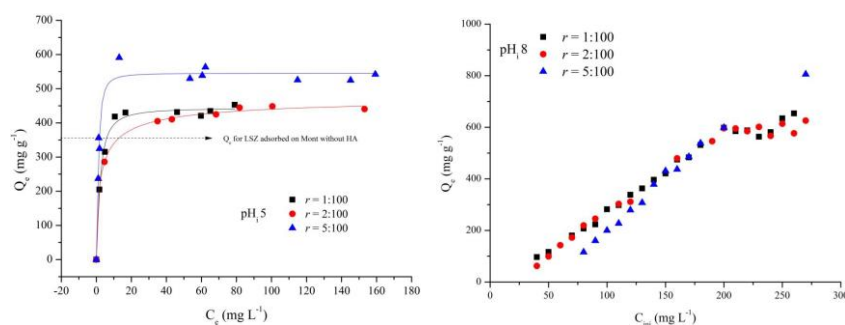


Fig. 1: LSZ adsorption on Mont at pH_i 5 and pH_i 8 with three HA/Mont mass ratios r

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OT16

Sequestration of heavy metals in soil aggregates induced by glomalin-related soil protein: A five-year phytoremediation field study

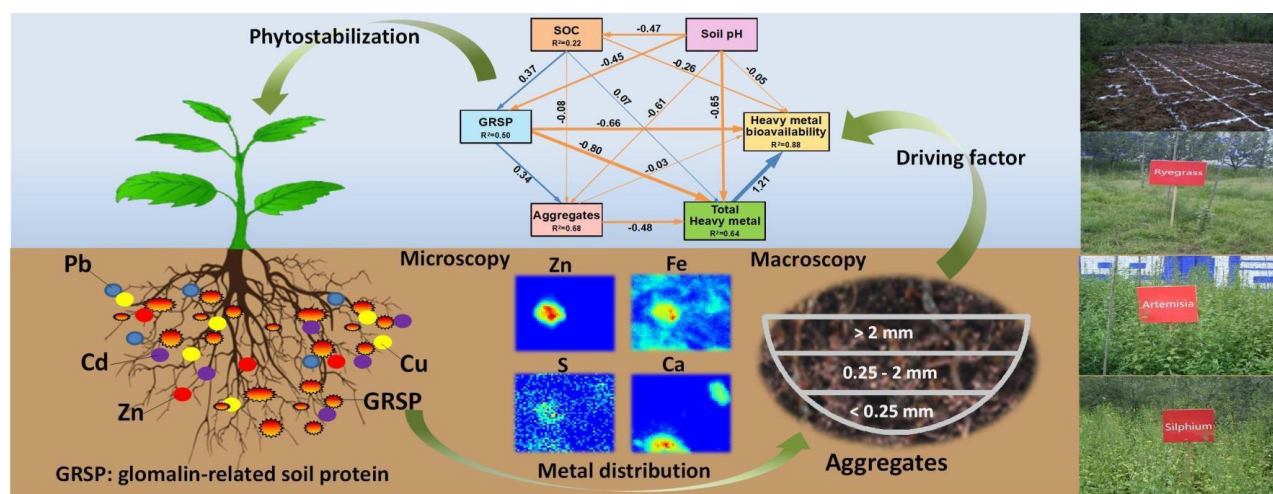
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Glomalin-related soil protein (GRSP) is an essential bioactive component that may respond to heavy metal stress; however, its exact influence on metal bioavailability and the associated mechanism remains poorly understood. This study investigated the speciation and distribution of heavy metals in soil aggregates associated with GRSP through macroscopic and microscopic approaches. A field study showed that the metal ions were distributed to the macro-aggregate fraction by partitioning the particle size classes during phytoremediation. Partial least squares path modeling (PLS-PM) demonstrated that the heavy metal bioavailability was negatively affected by aggregate stability (61.5%) and GRSP content (52.8%), suggesting that the soil aggregate properties regarding GRSP were vital drivers in mitigating environmental risk closely associated with toxic metal migration in soil-plant systems. The nonideal competitive adsorption (NICA)-Donnan model fitting suggested that GRSP were rich in acid site density, and the complexation with deprotonated groups dominated the speciation of heavy metals in soil. Further, the microfocuss X-ray absorption/fluorescence spectroscopy analysis indicated that GRSP might promote the formation of stable metal species by binding with sulfur-containing sites. This study highlights the role of GRSP in heavy metal sequestration in contaminated soils, providing new guidance on the GRSP intervention for phytoremediation strategies.



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PN3

How molecular simulation can be used to understand interfaces for the environment

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Understanding and predicting the behaviors of aqueous interfaces are of permanent interests to describe numerous environmental processes. Molecular modelling can achieve this goal by providing an accurate picture, at the atomic level, of the matter involved. In recent years, it has been possible to use such simulations to predict many systems of environmental interest, in conjunction with experiments. We will present here recent work mainly in two complementary fields:

- The domain of oxide/solution interfaces [1-3]. A multiscale approach makes it possible to describe many complex materials (porous glasses, geological media) on large time and space scales.
- The domain of fluid/fluid interfaces [4-8], such as the water/air interface, where the transport of organic molecules can be studied, for example for communication between insects by pheromone.

The role of molecular modelling thus appears to be multiple, since it allows us to obtain a great deal of information that is not directly accessible, for example on speciation. It also makes it possible to ask new questions, *e.g.* about the role of curvature. It completes or corrects macroscopic models to take account of relevant effects. Even if much progress remains to be made before it is truly and reliably predictive, particularly in terms of force fields, molecular modelling has thus become the method of choice for validating hypotheses and interpreting experiments at small scales.

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KN3

Integrated suspension anode and ultrafiltration system for defluorination of perfluorooctanoic acid (PFOA)

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While suspension anode systems can efficiently generate hydroxyl radicals ($\cdot\text{OH}$) and significantly enhance direct electron transfer (DET) processes that result in the oxidation of target contaminants via a charge percolating network of anode particles, challenges remain in constructing suspension anodic oxidation systems that can be operated continuously with stable performance. Here we incorporate an ultrafiltration (UF) membrane module into a suspension anodic oxidation system and achieve the continuous defluorination of perfluorooctanoic acid (PFOA) for 12 days with over 94% efficiency and reasonable energy consumption (around 38 Wh mg^{-1}) compared to other advanced oxidation processes by using a mixture of conducting $\text{Ti}_x\text{O}_{2x-1}$ and Pd/CNT particles as the flow anode [1]. The results indicate that DET, $\cdot\text{OH}$ mediated oxidation and adsorption processes play critical roles in the degradation of PFOA during the suspension anodic oxidation process. The synergistic effect of the $\text{Ti}_x\text{O}_{2x-1}$ and Pd/CNT particles enhances the defluorination efficiency by 3.2 times at 4.5 V vs Ag/AgCl compared to the control experiment (no suspension anode particles present) and promotes the release of F^- into solution while other intermediate products remain adsorbed to the surface of the Pd/CNT particles. Although the Pd/CNT particles were oxidized after long-term operation, no obvious Pd ion leakage into solution was observed. Results of this study support the feasibility of continuous operation of a suspension anode/UF system and pave the way for the translation of this advanced oxidation technology to practical application [2].

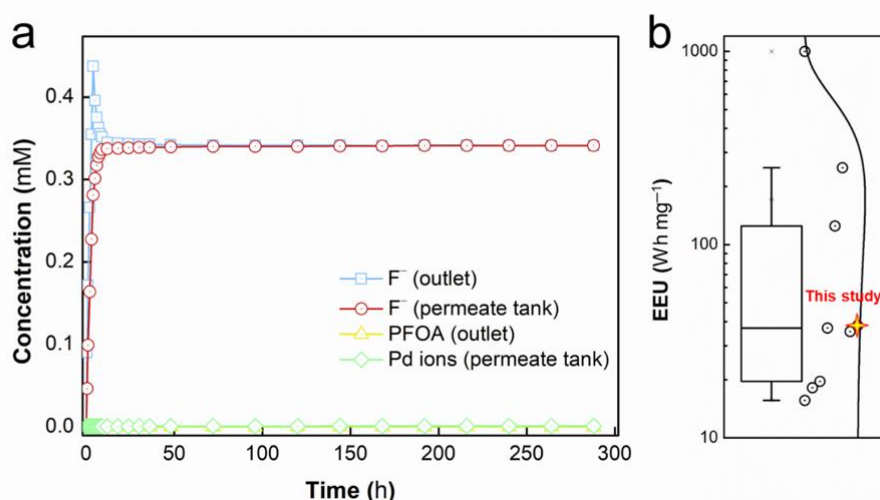


Fig. 1: (a) Variations of F^- , PFOA and Pd ions concentration in a continuously operated flow anode system for 12 days. (b) Comparison of electric energy consumption per unit mass of F^- of the flow anode/UF system with other technologies treating PFOA (from Xie et al. [1]).

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OW1

Capacitive deionization of solutions using functionalized carbon electrodes

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Investigation of the properties and applications of capacitive interfaces has grown dramatically in recent years. This is not surprising due to the huge capacitance associated to the Electrical Double Layer formed when these interfaces are in contact with an ionic solution. The capacitance allows the adsorption of ions (Capacitive Deionization, CDI) or, the reciprocal process, the generation of energy by exchanging solutions with different salinities (Capacitive Donnan Potential, CDP). With respect to CDI, an electric potential difference is established between electrodes immersed in an aqueous solution bringing about the migration of ions to their respective counter-electrodes and then a reduction of the ionic content of the bathing solution. In CDI as well as in CDP, the use of ionic exchange membranes adjacent to the electrodes plays a very important role. In the first case, it improves the efficiency of desalination and, in CDP, is the responsible of Donnan potential generation by exchanging solutions of different salinities.

We analyze the use of modified electrodes, in which the activated carbon layer, ultimately responsible for the ion transport processes, is just directly coated with a polyelectrolyte shell. This sort of “soft” electrodes have shown a good performance for both desalination and energy harvesting (Fig. 1), while not requiring the use of additional membranes [1,2]. In this work, we propose a significantly improvement of the method by chemically grafting the polyelectrolytes onto the electrode surfaces (cationic or anionic, respectively one each electrode). In such way, the polymer brushes coating the whole surfaces of macropores resulting in a more efficient capacitive process and encouraging the ionic selectivity adsorption.

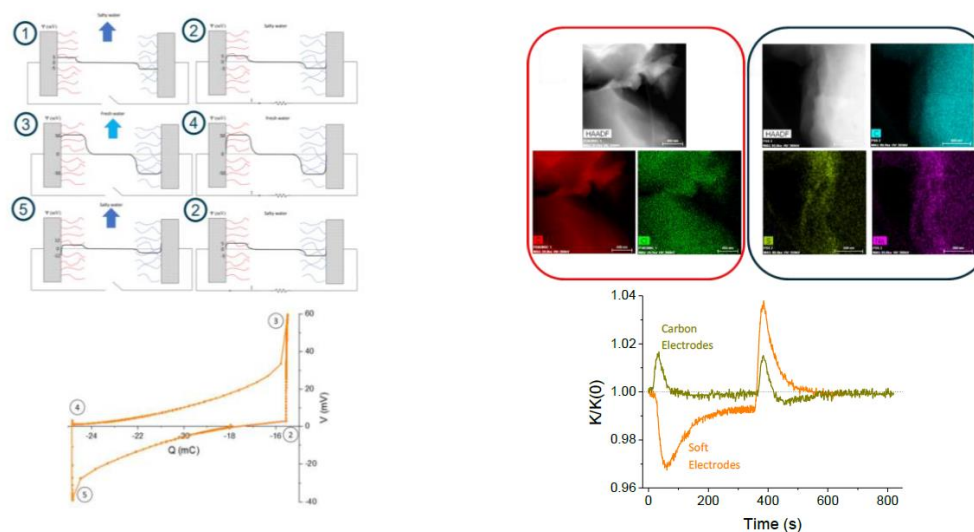


Fig. 1: Left: Time evolution of the potential and potential vs. charge (the enclosed area is the extracted energy) in a cycle of salinity exchange in soft electrodes Right: Relative conductivity using bare and soft carbon electrodes for adsorption and desorption steps in desalination of 20 mM NaCl solution. The cationic/anionic polyelectrolyte is indicated by chloride/sodium ions in EDX analyses.

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OW2

Superior surface reactivity of montmorillonite decorated with amorphous, nano-sized iron-oxides makes for excellent Fenton-like catalyst.Radian A^{1*}, Ioffe M¹, Sampti Kundu S¹, Levy L¹¹ Faculty of Civil and Environmental Engineering, Technion, Haifa, Israel

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Advanced oxidation processes are the leading technology for the removal and destruction of highly recalcitrant organic pollutants such as toxic polyphenols, high MW PAHs and per-fluorinated (PFAS) compounds. In the following work, montmorillonite was decorated with nano-sized iron oxides through a simple wet deposition method. The resulting surface (FeOx-MMT) was characterized in terms of size, charge, morphology, and chemical composition using electrochemical methods such as cyclic voltammetry and spectral induced polarization; electron microscopy (SEM-EDS and HRTEM), zeta potential, XRD, XPS and TGA measurements [1-3]. The nano-sized oxides on the clay were highly amorphous and the resulting material exhibited high redox surface reactivity compared to bare clay. The reactivity of the material was further tested in terms of peroxide and persulfate activation, pollutant degradation, and was compared to magnetite, hematite, and their nano-iron-clay composites.

The FeOx-MMT particles showed very high reactivity in all systems (persulfate, peroxide and mixed oxidant systems) and outperformed the other widely used iron-oxide as Fenton-like catalyst. The difference in reactivities was most pronounced in the hydrogen peroxide system, where the model pollutant phenanthrene was completely mineralized within 90 min of reaction [3]. The amorphous iron-clay was also tested in other systems with other pollutants - reaching exceptional mineralization of PFAS and PFOS and several small polyphenols [4,5]. The underlying degradation mechanisms were studied using chemical probes and EPR measurements. The results revealed a high complexity regarding the type and concentration of radicals formed – for aromatic compounds, hydroxyl radicals were formed along side singlet oxygen and superoxide species, whereas for the aliphatic PFAS systems, only hydroxyl radicals were identified. Furthermore, surface complexation of the oxidation and pollutant was found to be key in successful mineralization.

Overall, the synthesis of this reactive material is simple and could occur naturally in soils and sediments. As such, we maintain that this in-depth study is important both from an engineering and a geochemical perspective, and can advance remediation strategies as well as help identify pathways of recalcitrant pollutants in soils and sediments.

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OW3

Characterizing organic pollutant oxidation processes on manganese bearing colloids by a geoelectrical method

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Soil and groundwater pollution by various organic pollutants, such as ethers or phenols, is a widespread and severe environmental problem that requires remediation and monitoring, which may be complex due to the mobility of the pollutants and the heterogeneous nature of the subsurfaces. To address this problem, we studied manganese-bearing colloids such as MnO₂, for adsorption and oxidation of ethers and phenols. To monitor soil pollution remediation, we tracked the changes in the Spectral Induced Polarization (SIP) signatures of soil containing manganese-bearing colloids, with and without pollutants. We measured the adsorption and oxidation of methyl-tert-butyl-ether (MTBE) by MnO₂ and by engineered zeolite using GC/MS and monitored the progress with SIP. MTBE adsorption was measured, but no oxidation was observed by the analytical (GC-MS) or geoelectrical (SIP) methods, on MnO₂ or even on an engineered zeolite, carrying a stronger Mn oxidizer, MnO₄⁻. Hydroquinone oxidation by MnO₂ was rapid and followed by the formation of benzoquinone. Untreated zeolite adsorbed hydroquinone effectively, but obviously did not oxidize it, while oxidation was observed by the engineered zeolite. SIP measurements demonstrate that upon the addition of MnO₂ to control quartz columns, a change in the in-phase conductivity was obtained with no change in polarization. The change in the in-phase conductivity can be explained by the increase in conducting surfaces in the soil column. Considering the oxidation of hydroquinone by MnO₂, we suggest that the SIP signature will change, due to oxidation, the in-phase and quadrature conductivity may be reduced due to fewer conducting surfaces. We aim to further demonstrate that SIP may provide a means for in-situ monitoring of phenol oxidation in contaminated soils.

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Microbially produced manganese oxides (BioMnOx) are potent oxidants and adsorbents for a wide variety of environmental pollutants. BioMnOx are often more reactive than their abiotic counterparts [1-4]. In addition, reduced metal ions released in the oxidation reaction can be re-assimilated by the bacteria to regenerate the oxide, whereas abiotic oxides are destined to be consumed. In this study, BioMnOx were applied for the first time for the oxidation of the herbicide glyphosate and its degradation product AMPA, using the Mn-oxidizer *Pseudomonas putida* MnB1. The effect of Mn dose on BioMnOx formation and reactivity was studied, revealing that *P. putida* MnB1 could assimilate up to 1 mM Mn without significant passivation of the surface by Mn(II). The relationship between pH, BioMnOx levels, pollutant concentrations and oxidation kinetics was investigated. Our results show that increasing oxide concentration significantly increased oxidation rates of both glyphosate and AMPA. By localizing the BioMnOx in liquid-core capsules, removal kinetics as well as BioMnOx reusability were greatly improved compared to suspended oxides (Fig. 1). Capsule composition was further optimized for durability over continuous use and solute transport into the capsule core. Overall, we show that the smart design of encapsulation matrices, tailored to the desired remediation process, can be used to develop efficient treatment strategies for a variety of environmental contaminants.

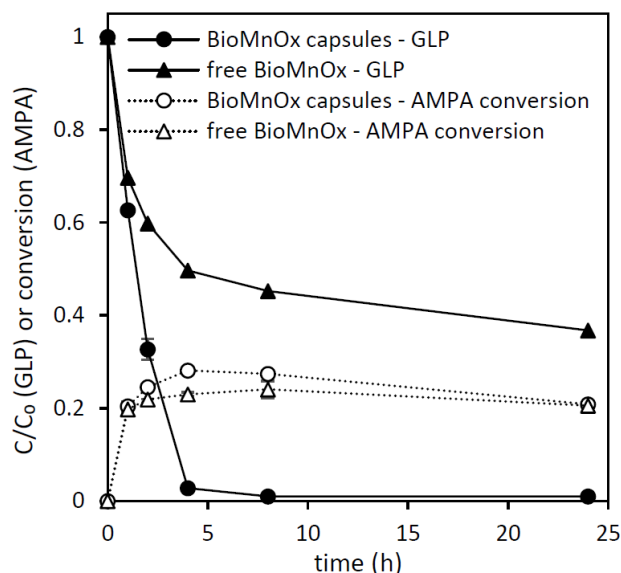


Fig. 1: Glyphosate (GLP) oxidation and conversion to AMPA by suspended and encapsulated BioMnOx.

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New insights on the estimation of chemical/electrostatic parameters for humic nanoparticles reactivity from NICA-SPBT-based modelling of proton titration curves: benefits of singular value decomposition and Tikhonov regularization steps in model-independent parameter estimation

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We recently proposed a physically sound Poisson-Boltzmann electrostatic theory to unravel the coupled electrostatic and chemical contributions to the binding of protons to soft (ion-permeable) humic nanoparticles (HNPs) [1]. In that work, we further reported a methodology to estimate the relevant HNPs reactivity parameters (of chemical and electrostatic origins) from the theoretical reconstruction of raw proton titration curves and of their corresponding proton affinity spectra as measured at various solution ionic strengths. The method is based on the optimization of these parameters upon coupling a home-made Fortran program SPBT (for Soft Poisson Boltzmann-based Titration) with PEST module (Model-Independent Parameter Estimation and Uncertainty Analysis) [2]. As a follow-up of this work, we then elaborated a new method for a proper absolute positioning of proton titration curves collected at different solution ionic strengths, with the estimation of the particle charge Q_0 at the first collected titration point [3]. In all these studies, parameters estimation proceeds according to an iterative procedure inspired by Lenoir and Manceau [4] and the impossibility they argued for estimating simultaneously more than six parameters from potentiometric titration data on humic nanoparticles [5]. The objective of the current work presented in this contribution is to modify the parameter optimisation methodology we reported earlier by introducing a singular value decomposition (SVD) step and by using Tikhonov regularisation [6], therewith allowing for simultaneous optimisation of the ensemble of eight parameters involved in the inverse problem to be solved (two electrostatic parameters and six chemical parameters). The excellent results obtained with this new optimisation approach will be illustrated with measured titration data on HNPs of diverse origins and original datasets published by Milne et al. [7], along with their respective full reparametrizations using so- updated SPBT-PEST.

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OW6

Kinetics of the dissolution of In_2O_3 nanoparticles followed with the electroanalytical technique AGNESGalceran J^{1*}, Rosales-Segovia K¹, Companys E¹, Puy J¹¹ Dep. Química, Universitat de Lleida, and AGROTECNIO-CERCA, Rovira Roure 191, 25198, Lleida, Catalonia, Spain

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Indium is a Technology Critical Element widely employed in electronic devices. In some applications (such as sensors for detecting volatile organic compounds), indium appears as In_2O_3 nanoparticles. So, the dynamics of the dissolution of such nanoparticles should be studied in order to assess for derived potential environmental impacts. Due to its high amalgamation capacity and moderately negative redox potential, indium (III) is a suitable analyte for AGNES (Absence of Gradients and Nernstian Equilibrium Stripping) [1-4]. Thus, AGNES can determine free indium concentrations, $[\text{In}^{3+}]$, in dispersions of nanoparticles (without the need of any previous separation).

An excess of In_2O_3 nanoparticles were dispersed either in KNO_3 0.1 mol L^{-1} (pH 2, 3, 4, 5, 6, 7 and 8) or in synthetic seawater (pH 8). Dispersions were continuously stirred with temperature carefully controlled at 25°C . Aliquots from the dispersion were taken during a period up to 6 months, and $[\text{In}^{3+}]$ was obtained with AGNES using a Thin Mercury Film Rotating Disc Electrode.

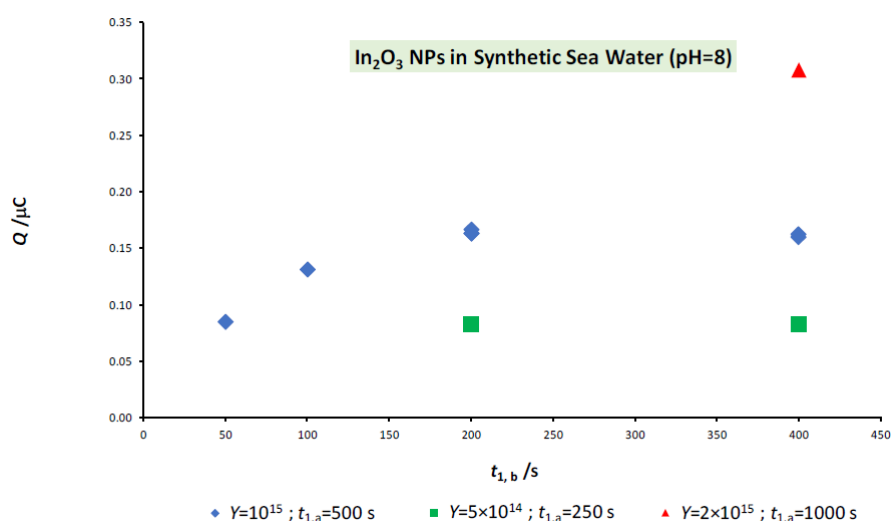


Fig. 1: Trajectories (time-course experiments) at three different gains or pre-concentration factors (Y), showing the typical plateaus which also hold Nernstian proportion. Dispersion: synthetic seawater where In_2O_3 -NP have been dissolving for 148 days.

The presentation will discuss the $[\text{In}^{3+}]$ found in the dispersions at several contact days, from trajectories as those shown in Fig. 1 (from which a free concentration of $1.17 \text{ attomol L}^{-1}$ was determined). At pH below 6, dissolution kinetics last around 90 days, while in seawater less than 18 days. Labile complexes in seawater critically help to reach huge gains in short times with AGNES. The solubility products of $\text{In}(\text{OH})_3$ and In_2O_3 will be compared.

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OW7

Unravelling the electrostatic and chemical components of the stability of indium-nanoparticulate humics complexes

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The fundamental role played by electrostatics on the binding of trivalent metal ions (Indium) to humic nanoparticles (HNPs, ≈ 5 nm radius) was here investigated so as to evaluate the intrinsic (chemical) stability of In-HNPs complexes [1]. To that end, a set of apparent stability constants was experimentally obtained at various metal-to-ligand ratios and ionic strengths using the electroanalytical technique AGNES (Absence of Gradient and Nernstian equilibrium stripping) well-adapted to measure free indium concentrations at the nanomolar level [2,3]. Following the strategy developed by Town *et al.* [4], the Boltzmann factors which quantify the electrostatically-driven partitioning of free indium ions and its cationic hydrolysis products between HNP body and bulk solution, were computed by solving the nonlinear Poisson Boltzmann (PB) equation for soft nanoparticles [5]. The PB-based modelling captures the magnitude and structure of particle electric field operating in the extra- and/or intra-particulate regions with or without considering the neutralization of the structural HNP charges due to accumulation of counterions from electrolyte solution. By taking into account HNP charge neutralization effects on the particle electric field distribution, we found a consistent agreement between theory and experiments over the whole range of tested electrolyte concentrations. Our results reveal a significant metal ions accumulation in the intraparticulate body of HNP particles. The intrinsic stability constants of In-HNP complexes were then recovered from their apparent counterparts and reported for several metal-to-site coverages. Finally, we demonstrated that the Donnan electrostatic representation implemented within popular NICA-Donnan speciation code, were unable to recover the here-reported experimental results, mainly due to its incapability to properly capture the bell-shaped potential profiles operational within and outside HNP nanoparticles.

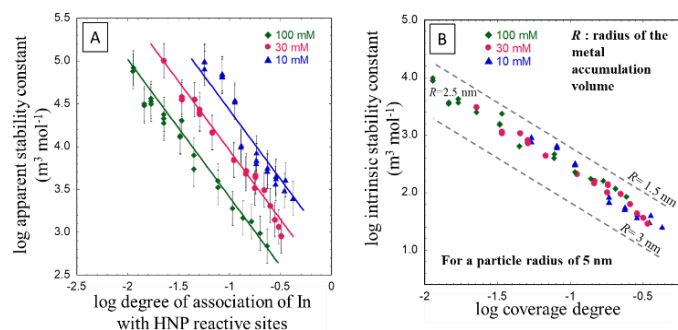


Fig. 1: Apparent stability constants for the indium complexes formed with nanoparticulate humics as a function of the degree of association of In with HNP reactive sites (**Panel A**), obtained at 10 mM, 30 mM, 100 mM NaClO₄ concentration and pH = 4.0. Intrinsic stability constant of indium-HNP complexes (**Panel B**) as a function of the degree of association of In with HNP reactive sites, at different radii R (indicated) for the sphere of metal accumulation within HNP.

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POSTERS

P1

Characterization of the accumulation kinetics of psychoactive drugs in agarose-based and Affinisep™ HLB and MCX sorbent gels

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Wastewater analysis of drugs and their metabolites can provide information on drug use and abuse in general populations. Conventionally, 24 h composite samples are analyzed and the chemical reactivity of the compounds within the wastewater matrix is ignored. In practice, these compounds are likely to associate with the diverse particles present in the wastewater matrix. Negligence of such interactions will lead to erroneous estimations of analyte concentrations. To address this issue, innovative active- passive sampling (APS) strategies are optimized to quantify psychoactive compounds in wastewater, taking into account their chemodynamic behaviour. The APS device incorporates a controlled hydrodynamic flow of the sample matrix across selective sorbents which accumulate the target compounds. After exposure, the analyte concentration adsorbed depends on its concentration in the bulk medium, sorbent/water partitioning coefficient (K_{SW}), and accumulation rate constant (k_x). In this study, polymeric sorbents HLB (Hydrophilic-Lipophilic-Balanced) and MCX (Mixed-mode Cation Exchange) as sorbent gels were assessed for their affinity for psychoactive drug metabolites (amphetamine, benzoylecgonine, morphine, norcitalopram, O-desmethylvenlafaxine, sertraline, and tramadol). Agarose-based and commercially-available (Affinisep™) sorbent gels were characterized for their suitability in APS. The sorption kinetics were evaluated by exposing the sorbent gels in spiked tap water at different exposure times (1 – 168 h). Quantification of target compounds was done using LC- MS/MS.

P2**Efficiency of different Fe-based treatments for metal(loid) stabilisation in a contaminated soil**Mitzia A^{1*}, Vítková M¹¹ Czech University of Life Science Prague, Faculty of Environmental Sciences, Department of Environmental Geosciences, Kamýcká 129, Praha-Suchdol, 16500, Czech Republic

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The use of Fe-based amendments for the remediation of metal(loid) contaminated media is increasingly popular. Nano zero-valent iron (nZVI), for instance, is considered the most often used nanomaterial for water and soil remediation in EU and the US [1]. Modifications of nZVI such as sulphidised nZVI (nZVI-S) and composites of nZVI and biochar (BC) have been used to increase the efficiency of nZVI and/or mitigate its tendency to create agglomerates [2]. On the other hand, local and low-cost sources of potential remediation agents need to be considered. The objective of our study was to compare the efficiency of various Fe-based amendments in a specific timeline to properly assess their further environmental use.

In this study, we used contaminated soil from a post-mining area in the Czech Republic. The soil was incubated for 1, 3 and 6 months in individual pots with 2 wt.% of different Fe amendments. The following treatments were used: i) control (without any amendments), ii) nZVI, iii) nZVI-S, iv) a composite of Fe/sulphidised Fe-biochar (Fe/FeS-BC) and v) Fe scrap (waste product resulting from industrial processing of Fe materials). At the end of each incubation period, aliquots ($n=3$) from each treatment were subjected to single-step extractions in H₂O and CaCl₂[3]. The physico-chemical properties of the extractants were also recorded. According to our results, significant stabilisation of the target metal(loid)s (i.e., Zn, Pb, Cd and As) was noticed in all the amended soil samples to some extent. The pH, which is a crucial parameter strongly associated with the metal retention, was also significantly increased by most of the amendments (except for Fe/FeS-BC). The stabilisation efficiency of the amendments varied in time, implying that long-term studies are crucial in order to assess the amendment efficiency.

Another implication of this study is the financial/environmental sustainability of soil amendment application: the potential of using waste materials (such as Fe scrap) for remediation might be a promising and cost-effective solution but close attention needs to be put in the behaviour of these materials before field applications.

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P3

Analysis of small microplastics and nanoplastics in complex matrices

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Plastic pollution is ubiquitous and persistent in the aquatic environment. Its distribution is heterogeneous in terms of both physical (e.g. size, shape, density, porosity, colour) and chemical properties (e.g. polymer type, surface charge, polarity, presence of additives or persistent organic pollutants). A strong international research effort has been made over the past 15 years, notably on methods development, to collect, prepare, and thus analyse plastic items with dimensions between 10 µm and 5 mm denoted as microplastics (MPs). However, MPs will eventually degrade in the environment - with a concomitant modification of their initial characteristics - to successively smaller entities, eventually reaching the nano- size range: they are then denoted as nanoplastics (< 1 µm; NPs). Nanoplastics are expected to be widely present in the environment and to represent a hazard for the ecosystem and ultimately for humans, but there is a paucity of reliable data on the concentration and distribution of small MPs (< 10 µm ; sMPs) and NPs in environmental matrices. Furthermore, there is currently a knowledge gap on these particles notably because of sampling and analytical challenges with methods that need to diverge from the ones developed at present for MPs. The current lack of relevant and standardized methods for sampling, preparing, and then quantifying and characterizing sMPs and NPs precludes the development of robust environmental risk assessment strategies. Indeed, by knowing their realistic distribution in the environment, it will be possible to set ecotoxicological studies with notably relevant concentration and particles types of plastics.

The end goal of the present work is to identify reliable and relevant methods applicable for sampling, preparing, and determining the concentration and distribution of sMPs and NPs in complex environmental matrices (water, sediment and fauna) including information on their physical and/or chemical characteristics. The developed analytical toolbox will provide the means to establish realistic input values for further ecotoxicological studies and risk assessment regarding plastic particles with size smaller than 10 µm.

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P4

Automated quantification of apoptosis signals in bivalve hemocytes as a proxy for micro- and nanoplastic risk assessment

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Plastic particles are prevalent in the environment, and the risks they pose especially to aquatic organisms are of growing concern. A range of responses attributed to micro-and-nanoplastic particle (MPs/NPs) exposure has been documented across various levels of biological organization, extending from cellular to population-level endpoints. However, systematic analyses of effect endpoints at the cellular level, which are considered a sensitive response variable to plastic particle exposure, are still lacking. It has been established that plastic particles can be internally distributed in organisms through various ways, such as translocation and penetration of biological barriers. In particular, particles with dimensions in the order of nanometers (i.e. nanoplastics, NPs, <1000 nm) are able to enter cells via endocytotic pathways, i.e. phagocytosis. These cellular processes have been highlighted as integral factors that influence key physiological functions including cellular immunity. Hemocytes are responsible for cell-mediated immunity in bivalve mollusks such as the mussel *Mytilus edulis*, which is highly susceptible to NP exposure due to its sedentary and filter-feeding lifestyle. The hemocytes circulate within the hemolymph and can cross all epithelial boundaries, acting as phagocytes against foreign particles, including plastic particles. Assessing the different physicochemical properties of MPs/NPs, such as polymer type, size, shape, and surface charge, is crucial as these parameters may directly affect the cellular uptake mechanisms as well as cytotoxicity. Hence, this study aims to validate and apply a microscopy-based method for determining whether MPs/NPs exposure induces apoptosis/necrosis (cellular death) in the hemocyte of mussels *M. edulis* as a proxy for micro-and-nanoplastic risk assessment. An in-vitro approach will be applied to characterize and interpret the response profiles under environmentally relevant exposure conditions and in assessing differential effects linked to characteristics of the plastic particles (type, size, shape). The apoptosis and necrosis signal quantification will be carried out through dual staining approach using an apoptosis detection kit (Biovision) and by the complementary application of fluorescence microscopy and ImageJ, an open-source image processing program. The results will provide insights into the underlying mechanisms associated with different physicochemical characteristics of MPs/NPs at a cellular level which is crucial for fate and toxicity assessment in aquatic organisms.

P5

Plastic pellet flux in the harbor of Antwerp

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The harbor of Antwerp is the leading polymer hub in Europe for production, handling and distribution of preproduction plastic pellets. In the marine environment, microplastics, including plastic pellets, are a big source of plastic pollution.

The Port of Antwerp and the companies of the entire production chain (polymer industry, transport, logistics) are taking measures to reduce pellet losses to the surrounding environment, however little is known about the efficacy of the measures. So the question is: How many pellets are still being released into the environment and where is this occurring? The answers to these questions can give industry an opportunity to focus on the problematic issues. In addition, despite the increasing awareness of the impact of plastic pollution, there is still not much known about the effect of plastic pellet pollution on biota in the surrounding area, i.e. the dock water and the Scheldt estuary.

In this first part of the study we take a deeper look at the most recent losses of the plastic pellets on the public road, during one year, 2022. A total of 57 critical points were monitored using manual sampling with a quadrant of 50 by 50 cm.

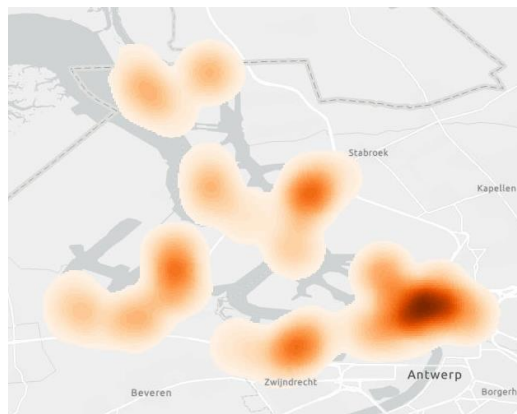


Fig. 1: Heatmap showing total amount of pellets sampled, spring 2022

The first results from the monitoring campaign in spring 2022 show considerable ongoing plastic pellet loss. In a period of 15 days, 8000 pellets were sampled, or 182 g (Fig. 2).

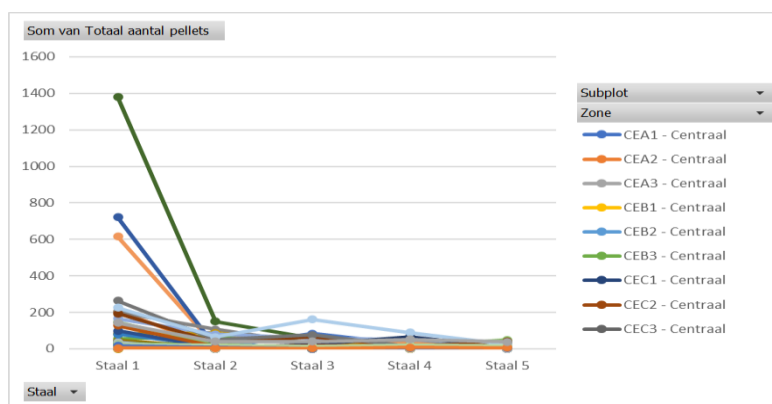


Fig. 2: Trendlines sample 1-5 on each subplot, spring 2022

Although the sampling started right after the road was swept, on most of the sampling points, the first sample contained the most pellets. Thus sweeping the road might not be sufficient to clean up the pellets.

P6

Adsorption of fluoroquinolones and metallic trace elements onto soils and amended-soilsMortada G^{1*}, Guillon E¹, Sayen S¹

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Fluoroquinolones are synthetic antibiotics which are detected in biosolids, manure and wastewater treatment plant effluents, and thus widely encountered in the environment especially in soils and waters *via* amendments and/or irrigation [1,2]. Their environmental consequences imply complex processes which threaten the human and environmental health, and thus need to be studied. One of the first steps needed to assess the transfer risk of these antibiotics and predict their fate is to understand their retention/release behavior at the soil/water interface which is governed by their sorption. Metallic trace elements (MTE) which are naturally present in soils or originate from industrial wastes and various agricultural treatments, can significantly modify the antibiotics sorption properties since they are likely to interact together by complexation [3]. It is thus important to bring knowledge in this sense in a context of multi-contamination as it is the case in the real environment.

In this study we focused on two fluoroquinolones, ciprofloxacin and enrofloxacin, widely used in human and veterinary medicine, respectively, and three MTE, Cu(II), Ni(II) and Zn(II), present in soils and biosolids. Their adsorption was studied on several soils of different composition and physico-chemical properties (texture, organic carbon and carbonate contents, pH and CEC) using the batch technique. The same experiments were carried out onto amended-soils (prepared by mixing different biosolids with the selected soils) in order to study the impact of the amendment on contaminant behaviors. Finally, similar experiments were conducted for bi-adsorbate systems (one antibiotic and one MTE) in order to study the influence of antibiotic and MTE co-presence on their respective retention/mobility in soils and amended-soils.

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P7**Influence of humic acid to structure of matrices in cementitious materials**Toda K^{1*}, Saito T¹¹ School of Engineering, The University of Tokyo, 2-22 Shirakata Shirane, Naka, Tokai, Ibaraki 319-1188, Japan

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Dissolved organic matters (DOM) in groundwater may interact with the construction materials used at radioactive waste disposal sites. The long term alteration of calcium silicate hydrates (C-S-H), matrix material of cement, is well studied to simulate the radionuclide transport through the material [1]. In addition to cement, low pH cement and geopolymers which composes of magnesium silicate hydrate (M-S-H) and sodium silicate aluminate hydrate (N-A-S-H) respectively, are alternative cementitious materials used at the sites. However, the influence of DOM to the structure of metal silicate hydrates are not well understood, which may affect the radionuclide transport within those materials. In previous studies, synthetic organic polymers with carboxylic functional groups are reported to affect the polymerization state of C-S-H silicate chains [2], where difference in polymerization state of C-S-H is known to affect its Cs retention capacity [3].

As a starting point to evaluate the interaction of DOM with cementitious matrices, this study focused on the interaction of model DOM, Aldrich humic acid (AHA) 's effect to C-S-H, M-S-H and N-A-S-H. The interactions were evaluated with multiscale analysis from nano to micro meter scale, to elucidate the effect of AHA on chemical bondings and aggregation structures of metal silicate hydrates. Synthesis of C-S-H, M-S-H and N-A-S-H in coexistence of variable AHA concentration (between 0 to 20wt% addition against total weight of reactants) were carried out to understand the effect of coexisting AHA at their formation. Cylindrical molds of C-S-H, M-S-H and N-A-S-H were also reacted with AHA solutions for 1,3 and 6 months. To evaluate the interaction of metal silicate hydrates with AHA, the mineralogical characteristics, chemical bonding properties, nm-scale aggregation structures of metal silicate hydrates and AHA, alteration mapping of cylindrical specimens, were evaluated using XRD, FT-IR, SAXS and SANS, and SEM, respectively. With SAXS evaluating the metal silicate hydrate aggregation structures and SANS evaluating that of AHA, the nm-scale interactions of DOM and metal silicate hydrates were interpreted.

Addition of AHA at the synthesis of metal silicate hydrates within the experimental condition did not influence the mineralogical structure of metal silicate hydrates, except C-S-H, where basal spacing was broadened by addition of AHA. Also, C-S-H formation was inhibited at higher dosage of AHA, with reactants remaining in the synthesis products, indicating the AHA inhibition to the precipitation of C-S-H. With further characterization of the synthesis products and the solidified molds after alteration experiments, the changes in the metal silicate hydrates structures by AHA both in terms of chemical bondings and aggregation, and the cause of the different AHA effects among three metal silicate hydrates will be discussed at the presentation.

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P8

Time-response of whole-cell biosensors for metal detection: mechanistic connections between cell signal and bioavailabilities of both metals *and* nutrients.

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The signal produced by aqueous dispersions of bioluminescent, metal-responsive whole-cell bacterial sensors is indicative of the concentration of bioavailable metal ions in solution. The conventional calibration-based strategy followed for measuring this concentration is however inadequate to provide quantitative prediction of the cell response over time as a function of, e.g., cell growth features, defining metal bioaccumulation properties, or physicochemical medium composition. Such an evaluation is still critically needed for assessing on a mechanistic level the performance of biosensors in terms of metal bioavailability and toxicity monitoring. In this contribution, we report a comprehensive formalism unraveling how the dependence of bioluminescence on time is governed by the dynamics of metal biouptake tackled beyond the restrictive Biotic Ligand Model (BLM) framework, by the activation kinetics of *lux*-based reporter gene, and by the ensuing rate of luciferase production and light emission kinetics. The foundations of the theory are supported by quantitative confrontation with experimental measurements on whole-cell Cd-inducible *PzntA-luxCDABE* and constitutive *rrnB P1-luxCDABE*-based *Escherichia coli* biosensors incubated in media differing with respect to sources of amino acids (tryptone or Lysogeny Broth) and carbon (glucose, xylose and mixtures thereof). We demonstrate that the resulting coupling between cell stringence response and glucose/xylose-mediated catabolite repressions leads to well-defined multi-modalities and shapes of bioluminescence signal over time in line with theory. Biosensor performance, position, shape and magnitude of detected peaks are discussed in relation with the metabolic pathways operative during the successive light emission modes identified here over time. In agreement with theory, we further highlight the cell photoactivity patterns shared by Cd-specific and constitutive biosensors despite their very distinct time-dependent bioluminescence response. All in all, beyond specifying the intimate connection between cell response, metal bioaccumulation and passive metal biosorption, the theory clarifies contributions of metal/nutrient bioavailabilities and food quality to cell signal typology.

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Electrostatics of soft (bio)interfaces: corrections of Mean-Field Poisson-Boltzmann theory (MFPB) for molecular effects

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The evaluation of electrostatic interactions operational between particles (of biological origin or not) is required to understand *e.g.* particle aggregation [1], (bio)adhesion [2], or cell-virus recognition [3], with help of the historical DLVO theory. For that purpose, the electrostatic potential distribution at charged particle/solution interfaces is classically derived from Poisson-Boltzmann (PB) theory for hard particles (*i.e.* ion-impermeable, particles with a defining surface charge density) [4]. However, the electrostatics of biological particles like microorganisms cannot be described within the framework of hard particle-based representation. Indeed, biosurfaces generally display a 3D charge distribution due to the presence of soft (*i.e.* ion-permeable) structures in their peripheral region [5]. In turn, soft (porous or core/shell) particles exhibit *e.g.* peculiar electrophoretic response that cannot be captured on the basis of standard hard-particle electrokinetic models [6]. In addition, the corrections of standard mean field PB (MFPB) theory for molecular effects (due to finite ions size, ion-ion correlations and dielectric-decrement) have been mainly reported so far for the only case of hard particles [7-9] and not for soft particles that better represent biological interfaces, as briefly argued above. Following these contextual elements, we propose here a correction of the MFPB formalism for charged soft interfaces with account of molecular effects associated with finite ion size, dielectric decrement and ion-ion correlations in aqueous electrolyte (monovalent and multivalent ionic systems can be both tackled). Accordingly, we develop a numerical tool for the computation of the electrostatic potential distribution in the vicinity of an isolated soft interface from so-corrected MFPB model. In this poster, we shall report the strategy we adopted to elaborate this new electrostatic model for soft interfaces and we illustrate the outcome for a number of selected and illustrative computational examples highlighting the aforementioned effects taken separately or in a combined manner.

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P10

Complexation mechanism of Pb^{2+} at the ferrihydrite-water interface: the role of Al-substitutionLiang Y^{1,2*}, Wang M¹, Tan W¹¹ State Environmental Protection Key Laboratory of Soil Health and Green Remediation, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China² Tropical Crops Genetic Resources Institute, Chinese Academy of Tropical Agricultural Sciences, Haikou, 571101, China

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Ferrihydrite is a poorly crystalline iron (hydr)oxide and highly efficient adsorbent for heavy metals. Al-substitution in ferrihydrite is ubiquitous in nature. However, the effect of Al-substitution on the surface reactivity of ferrihydrite remains unclear due to its low crystallinity. The present study aims to clarify the microstructure and interfacial reaction of Al-substituted ferrihydrite. Al-substitution had little effect on the morphology and surface site density of ferrihydrite, while the presence of $\equiv AlOH^{0.5}$ sites resulted in higher proton affinity and surface positive charge of ferrihydrite. Besides, the affinity constant of Pb^{2+} adsorption on the surface of ferrihydrite decreased at higher Al content, which further decreased the adsorption performance of ferrihydrite for Pb^{2+} . The modeling results revealed that bidentate complex was the dominant Pb complexation species on the surface of ferrihydrite, which was less affected by Al-substitution. The present study provides important insights into the effect of Al-substitution on the interfacial reaction at the ferrihydrite-water interface. The obtained parameters may facilitate the future advance of surface complexation model.

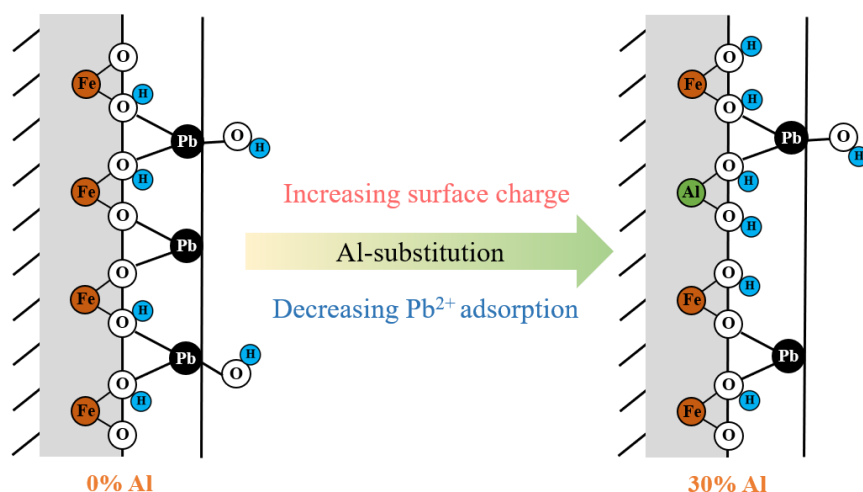


Fig. 1: Effects of Al-substitution on the surface charge and Pb^{2+} adsorption performance of Ferrihydrite

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The adsorption of selenium(Se) by iron oxides is of great importance but the interaction mechanism between them remains largely elusive, thus limiting our understanding of the release, immobilization and bioavailability of Se in nature. The current study aimed at investigating the speciation of adsorbed Se(IV) on goethite surface using macroscopic sorption-desorption experiment as well as microscopic attenuated total reflection-Fourier transform infrared (ATR-FTIR) and X-ray photoelectron (XPS) spectroscopic techniques. The pH-dependent adsorption edge and corresponding chemical extraction results show that the surface-adsorbed Se(IV) was mainly (> 90%) ligand exchangeable at pH 5.0, however, higher or lower pH promoted the transformation of exchangeable Se(IV) into residual fractions. ATR-FTIR and XPS measurements reveal that Se(IV) formed simultaneously inner- and outer-sphere complexes on goethite, and hydrogen-bonded Se(IV) was an important species of surface-adsorbed Se(IV). In addition, high-resolution O 1s XPS demonstrates that the mechanism for the increase in residual Se under more acidic and basic pH conditions is due to the effect of incorporation or coating of newly formed hydrous iron oxides generated with the dissolution-recrystallization of goethite. Overall, our research may facilitate mechanistically understanding the environmental behavior and bioavailability of Se.

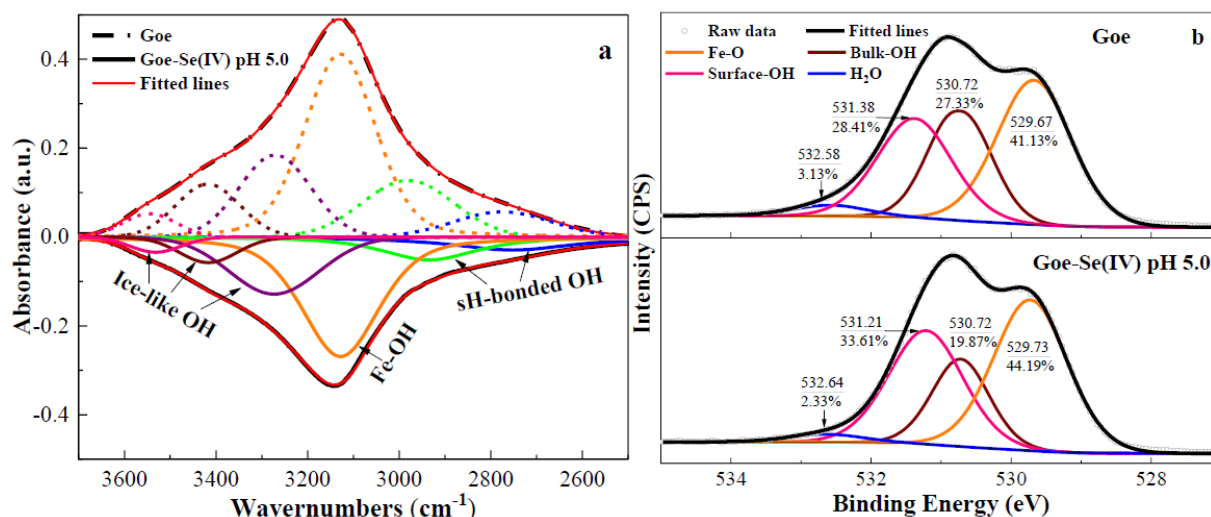


Fig. 1: ATR-FTIR spectra (3800 - 2500 cm^{-1}) (a) and high-resolution O 1s XPS (b) of pure goethite and solid sample after reaction with Se(IV) at pH 5.0.

After reaction with Se(IV), intensities of OH stretching bands including structure hydroxyl (Fe-OH) decreased significantly (Fig. 1a) and the ratio of Fe-O and Surface-OH increased by 3.06% and 5.20% (Fig.1b), respectively, indicating that three types of surface OH were all involved in the Se(IV) adsorption process and Se(IV) formed simultaneously outer- and inner-sphere complexes on goethite with a ratio of 0.59^[1,2]. The observed redshift and broadening of strongly hydrogen-bonded OH vibration demonstrate that new hydrogen bonds are formed between surface-adsorbed Se(IV) and water molecules.

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Alginate promotes soil phosphorus solubilization synergistically with redox-active antibiotics through Fe(III) reduction

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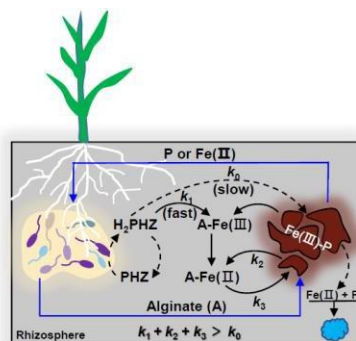


Fig. 1: The work reveals alginate can enhance the beneficial physiological effect of redox- active antibiotics, and their synergistic effect can further promote the bioavailability of Fe/P.

Redox-active antibiotics have been recently found to enhance phosphorus (P) bioavailability through reductive dissolution of Fe(III) oxides and solubilization of adsorbed P. However, there has been a lack of quantitative insights into their effect on Fe(III)-P minerals in natural environments with extracellular polymeric substances (EPS). Here, by taking phenazine (PHZ) antibiotics for a case study, we quantified the Fe(II) production and P solubilization with batch reduction experiments and *in situ* reductive dissolution kinetics of Fe(III)-P (amorphous and crystalline phases) by liquid-cell atomic force microscopy (AFM) technique. Firstly, we captured the differences in the amount of Fe(II) production and P solubilization after exposure to different reduced PHZ-bearing buffer solutions under simulated environmental conditions, which were further confirmed by the nanoscale surface dissolution as indicated by the formation of etch pits. In addition, Fe speciation analysis and content measurement clearly showed enhanced Fe(III) reduction in the presence of a binary combination of alginate and H₂PHZ, independent of the types of H₂PHZ and Fe(III)-P. Similarly, an increase in the concentration or polymerization degree of alginate promoted the dissolution rate of Fe(III)-P compared with the controls. By providing Fe(III) in a soluble organic form, the alginate-Fe(III)/H₂PHZ in solution could significantly facilitate the redox reaction process relative to solid-phase Fe(III)/H₂PHZ and/or free Fe(III)/H₂PHZ, resulting in alginate-promoted reduction of solid-phase Fe(III) and solubilization of co-precipitated P. These results indicate a widespread but previously ignored role of EPS coupled with redox- active antibiotics in expanding the bioavailable pools of Fe(II) and P. We also suggest that similar studies of ligand-enhanced microbial redox of Fe-bearing minerals may reveal how ligands and microbes collectively control the redox process to affect the biogeochemistry cycling of Fe and P, and thus the eventual nutrient management for agronomical and environmental sustainability.

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