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Organic Aerosol Composition: Effects on Health and Climate

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Organic material is the main fraction in atmospheric aerosol particles and strongly determines their effects on climate but also on human health. Due to the highly complex and poorly known composition of the organic material in aerosols there is only limited understanding of their effects in the atmosphere. Since decades, epidemiological studies have linked exposure to increased concentrations of atmospheric aerosol to mortality and hospital admissions but it remains unclear which particle properties are causing these health effects. It is often hypothesised that these negative health effects are due to redox active compound such as reactive oxygen species (ROS, defined here as inorganic and organic peroxides and radicals), which are present in aerosol particles or generated upon deposition in the lung. Established methods to quantify ROS in aerosol particles mostly rely on particles being collected on filters, followed by subsequent extraction steps and chemical analysis. Many ROS components, however, are short-lived and thus filter-based techniques risk to underestimate ROS concentrations in ambient particles.

To overcome these limitations and to understand the atmospheric variability of ROS components, we developed a range of online optical spectroscopy [1, 2, 3] and mass spectrometry [4, 5, 6, 7] methods and instruments to characterise the complexity of organic aerosol composition and the nature and concentration of the short-lived but reactive and potentially health-relevant compounds with high time resolution and without delay between particle collection and analysis. We will discuss ROS concentrations in particles generated in laboratory experiments under a range of typical air pollution conditions and from field experiments at urban locations in Asia and Europe, which indicate that a wide range of particle sources contribute to ambient ROS levels but also that photochemical processes in the atmosphere play a dominant role. Further laboratory studies will be presented, which focus on the elucidation of the molecular structure of organic radicals such as Criegee Intermediates and peroxides, an abundant but poorly characterised oxidising class of components in the gas and particle phase.

[1] F.P.H. Wragg, S.J. Fuller, R. Freshwater, D.C. Green, F.J. Kelly, M. Kalberer,*Atmos. Meas. Tech.*, **2016**, 9, 4891–4900.
[2] S. Campbell, B. Utinger, D. Lienhard, S.E. Paulson, J. Shen, P.T. Griffiths, A.C. Stell, M. Kalberer, *Anal. Chem*., **2019**, 20, 13088-13095.
[3] S.E. Paulson, P.J. Gallimore, X.M. Kuang, J.R. Chen, M. Kalberer, D.H. Gonzalez, *Sci. Adv.,* **2019**, 5, eaav7689.
[4] P.J. Gallimore, M. Kalberer, *Environ. Sci. Technol*., **2013**, 47, 7324−7331.
[5] C. Giorio, S. J. Campbell, M. Bruschi, F. Tampieri, A. Barbon, A. Toffoletti, A. Tapparo, C. Paijens, A. J. Wedlake, P. Grice, D J. Howe, M. Kalberer, *J. Am. Chem. Soc*., **2017**, 139, 3999−4008.
[6] S.S. Steimer, A. Delvaux, S.J. Campbell, P.J. Gallimore, P. Grice, D.J. Howe, D. Pitton, M. Claeys, T. Hoffmann, M. Kalberer,*Atmos. Chem. Phys*., **2018,** 18, 10973-10983.
[7] I. Kourtchev, C. Giorio, A. Manninen, E. Wilson, B. Mahon, J. Aalto, M. Kajos, D. Venables, T. Ruuskanen, J. Levula, M. Loponen, S. Connors, N. Harris, D. Zhao, A. Kiendler-Scharr, T. Mentel, Y. Rudich, M. Hallquist, J.-F. Doussin, W. Maenhaut, J. Bäck, T. Petäjä, J. Wenger, M. Kulmala, M. Kalberer, **,** *Scientific Reports*, **2016**, 6, DOI: 10.1038/srep35038.

Photochemical degradation of iron(III)-citrate/citric acid aerosol quantified with the combination of three complementary experimental techniques and a kinetic process model

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Iron(III) carboxylate photochemistry plays an important role in aerosol aging, especially in the lower troposphere. These complexes can absorb light over a broad wavelength range, inducing the reduction of iron(III) and the oxidation of carboxylate ligands [1]. In the presence of O_2, ensuing radical chemistry leads to further decarboxylation, and the production of OH, HO_2, peroxides, and oxygenated volatile organic compounds, contributing to particle mass loss. The oxidants, in turn, re-oxidize iron(II) back to iron(III), closing a photocatalytic cycle [2]. In a cold and/or dry atmosphere, organic aerosol particles tend to attain highly viscous states. While the impact of reduced mobility of aerosol constituents on dark chemical reactions has received substantial attention, studies on the effect of high viscosity on photochemical cycles and processes are scarce. Here, we choose iron(III)-citrate (Fe^{III}(Cit)) as a model light absorbing iron carboxylate complex that induces citric acid (CA) degradation to investigate how transport limitations influence photochemical processes. Three complementary experimental approaches were used to investigate kinetic transport limitations. The mass loss of single, levitated particles was measured with an electrodynamic balance, the oxidation state of deposited particles was measured with X-ray spectromicroscopy, and HO_2 radical production and release into the gas phase was observed in coated wall flow tube experiments. We developed a numerical multi-layered photochemical reaction and diffusion (PRAD) model that treats chemical reactions and transport of various species to quantitatively compare with our experiments and determine important physical and chemical parameters for our system. We observed significant photochemical degradation, with up to 80 % mass loss within 24 hours of light exposure. When we decreased relative humidity our particles were exposed to, the observed mass loss rate also decreased. This is consistent with strong kinetic transport limitations for highly viscous particles. The PRAD model reproduced all experimental results and captured the essential chemistry and molecular transport during irradiation. In particular, the photolysis rate of Fe^{III}, the re-oxidation rate of Fe^{II}, HO_2 production, and the diffusion coefficients of species in aqueous Fe^{III}(Cit)/CA system as function of relative humidity and Fe^{III}(Cit)/CA molar ratio could be constrained. Photochemical degradation under atmospheric conditions predicted by the PRAD model shows that release of CO_2 and re-partitioning of organic compounds to the gas phase may be very significant to accurately predict organic aerosol aging processes.

[1] Jing Dou, Beiping Luo, Thomas Peter, Peter A. Alpert, Pablo Corral Arroyo, Markus Ammann, Ulrich K. Krieger, *The Journal of Physical Chemistry Letters*, **2019,** 10, 4484–4489.
[2] Christian Weller, Andreas Tilgner, Peter Bräuer, Hartmut Herrmann, *Environmental Science & Technology*, **2014,** 48, 5652–5659.

A decade of atmospheric CO_2 mole fraction and stable isotope ratios at Jungfraujoch measured by QCLAS, GC-FID and IRMS

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Long-term monitoring of the atmospheric carbon dioxide mole fractions (CO_2) in pristine environments provides representative information on its long-term variability and rate of change. Such records are essential to understand the natural carbon cycle and the impact of anthropogenic activities. Stable isotope ratios ($\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2) provide additional constraints in models describing the source-sink processes in the carbon cycle, such as partitioning of CO_2 between the different environmental reservoirs through physical, chemical and biochemical reactions: atmosphere, biosphere and ocean systems. Furthermore, evaluating atmospheric transport simulations against highly time-resolved observations helps refining bottom-up estimates of anthropogenic greenhouse gas fluxes and identifying gaps in our understanding of regional and category-specific contributions. This insight is critical in the efforts to monitor and mitigate anthropogenic impact on the environment. Key pre-requisites of long-term atmospheric observations are, however, high analytical precision, reliable operation resulting in adequate data coverage, and consistency among various monitoring sites and measurement techniques.

Here, we present a unique observational data set of atmospheric CO_2, $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 for a nine year period (2009-2017) obtained at the high altitude research station Jungfraujoch, located in the Swiss Alps at 3580 m above sea level. The station contributes to Swiss, European and global monitoring programs and was labelled as a class 1 station within the European Integrated Carbon Observing System (ICOS) in 2018. The atmospheric CO_2, $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 measurements are performed with two different analytical techniques and independent sampling strategies. High-resolution in-situ data are obtained continuously using a quantum cascade laser absorption spectrometer (QCLAS) [1-4]. Further, discrete air samples are collected as snapshots bi-weekly in form of triplicates in 1L glass flasks. The samples are subsequently analyzed off-line with gas chromatography and flame ionization detection (GC-FID) and isotope ratio mass spectrometry (IRMS) [5-6]. For interpretation and evaluation, we use receptor-oriented transport model simulations for CO_2 mole fraction and $\delta^{13}C$-CO_2 as described in [7] and references therein.

The comparison of the two independent sampling and measurement systems yielded good agreement and allowed determining decadal trends and seasonal profiles at Jungfraujoch under unpolluted free troposphere conditions. The high-resolution in-situ observations by QCLAS enhance our understanding of European CO_2 sources and sinks by capturing hourly and diurnal variations and the shorter term dynamics of atmospheric CO_2. Together with the transport simulations they allow to interpret the observed mole fractions when Jungfraujoch is influenced by air masses from the planetary boundary layer.

[1] Tuzson B, et al, **2008**, APB, 92, 451;
[2] Nelson, DD, et al, **2008**, APB, 90, 301;
[3] Tuzson B, et al, **2011**, ACP, 11, 1685;
[4] Sturm P, et al, **2013**, AMT, 6, 1659;
[5] Van Der Laan-Luijkx, IT, et al., **2013**, AMT, 6, 1805;
[6] Ghosh, P, et al, **2005**, RCMS, 19, 1097;
[7] Pieber SM, et al, **2020**,
online at: https://presentations.copernicus.org/EGU2020/EGU2020-10588_presentation.pdf

Plant and microbiota-dependent effects on arsenic behavior in the soil-plant system

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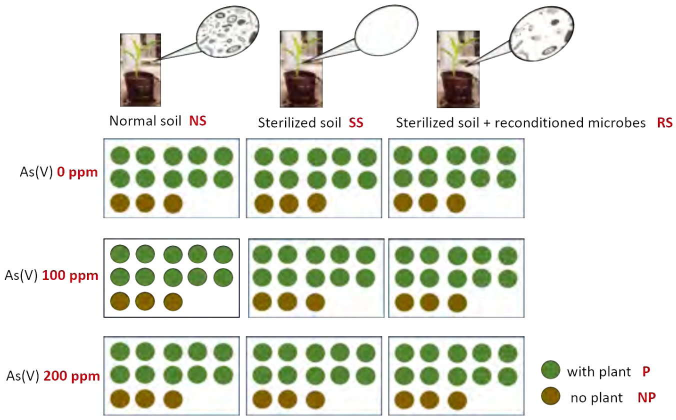
Arsenic (As) is a trace metalloid known as “the king of poisons”. As is also a class one carcinogen and its high toxicity correlates with a host of human diseases e.g. skin cancer. The speciation of As largely regulates its mobility, bioavailability and toxicity in the environment. As speciation is not only driven by abiotic parameters (pH, DOC), but also controlled by biotic interactions with plants and microbes. Soil microbiota can enzymatically transform As from inorganic to less-toxic organic forms. We performed an experiment to investigate the effects of plant and soil microbiota on As behavior in the soil-plant system as well as the physiological responses of maize plants to As exposure.

In the experiment, we set up nine experimental groups: three soil treatments (normal soil (NS), sterilized soil (SS) and first-sterilized soil reconditioned with microbes (RS)) intersecting with three As concentration groups (0, 100 and 200 ppm). In each treatment group, 10 pots with maize plants and three pots without maize were cultivated (Figure 1). For the As treatments we spiked soils with different levels of As. After soil incubation for two months allowing for the equilibration of As with soils, we grew 99 maize plants and regularly determined multi-element concentrations in soil water with ICPMS as well as As speciation by means of HPLC-ICPMS.

First, the sum of organic As species showed positive correlations with DOC in soil water but negative relations with the pH values, which indicates that pH and DOC are two controlling abiotic factors regarding As methylation in the soil environment. Second, the maize phenotyping data revealed the hazardous physiological effects of As on plant health. With the increasing of As concentrations, plants experienced smaller plant height, lower chlorophyll content, and greater scale of spot disease on leaves. Third, microbes do play a key role in As speciation and its effects on plant health. Plants from NS acquired the best health conditions even at high As levels due to the presence of native microbes; on the contrary, the health conditions of plants in SS were the worst. Thanks to the recondition of native microbes in RS, the health condition level of plants from RS was between NS and SS. Overall, As behavior in soil-plant system is not only controlled by abiotic parameters including DOC content and pH values in soil water, but also strongly influenced by the biotic factor – soil microbiota. Until SCS Fall Meeting 2020, we will furthermore analyze various plant tissues (root, stem, leaf and kernel) by means of ICP-MS and HPLC-ICPMS to fulfill information regarding the concentrations and speciation of As, which gains us a better understanding of As behavior in the soil-plant system as well as As transformation and toxicity along the food chain.



Species-specific isotope tracking of mercury bioaccumulation and biotic transformations by natural pico-nanoplankton communities in a eutrophic lake

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Phytoplankton could influence the aquatic cycle of mercury directly through uptake and biotic transformations, and indirectly through the excretion of bioligands influencing different abiotic and biotic transformations. Opposite to the substantial work performed with bacteria, the role of phytoplankton in Hg transformations is poorly understood.

The goal of the study is to get insights on the role of phytoplankton natural community in biotic transformations in the freshwater system of an eutrophic lake, Soppensee (Switzerland). Since the biotic transformations are essentially intracellular, the accumulation of inorganic (iHg) and monomethylmercury (MeHg, CH_3Hg^+), their subcellular distribution, and transformations by the natural community of the lake were studied. Phytoplankton communities were harvested in-situ at 2 different depths with Niskin bottle and concentrated by centrifugation. Then, the re-suspended community is exposed to 1nM of ^{199}iHg and 100pM of ^{201}MeHg for exposure of 24h. The cellular accumulation of Hg species was determined following isolation from the exposure medium by gentle centrifugation. To get information about cellular compartments involved in the possible transformations, the cells were further separated into membranes/organelles and cytosol fractions. Hg analyses were carried out by isotopic dilution analysis gas chromatography coupled to inductively plasma mass spectrometry. The changes in the ratio between the difference of control isotopes concentrations before and after exposure and the measured isotopes concentrations before exposure in the whole cells and the cellular fractions were used to quantify the Hg biotransformations.

Results showed that chemical parameters are similar to the 2 depths and, the phytoplanktonic community is heterogeneous at the first depth and dominated by diatoms at the second depth. Both communities accumulated a significant amount of iHg and MeHg but, the cellular distribution was species- and community-dependant. Under comparable incubation conditions, Hg species were more accumulated in membranes and, results showed that community dominated by diatoms accumulated more Hg in the cytosol and less in membranes than the heterogeneous community. The Hg uptake is almost equal without dependence on Hg species or community. The calculation of biotic transformations did not allow the detection of Hg methylation. The demethylation process was found, higher in cytosol fraction and at the second depth. Statistical analysis showed a dependence on the community with a positive correlation between the demethylation and diatoms group.

Identity of the Cu(II) Active Site on Alumina for the Stepwise Selective Conversion of Methane to Methanol

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The direct conversion of methane into methanol is one of the major challenges of modern catalysis, since it has the potential for a transition from a fossil fuel-based economy to more renewable energies. However, this direct transformation is challenging due to the increased reactivity of the desired product compared to methane, leading to the formation of overoxidized products.[1] Among recent materials explored, Cu-exchange zeolites have shown the greatest potential for the selective oxidation of methane to methanol under stepwise reaction conditions.[2] Recent economic studies have shown the economic limitation of these materials, among them the high price of zeolite and long cycling times.[3] In that context, cheap and readily available supports such as oxides, must be further explored.

Surface organometallic chemistry (SOMC)[4] combined with thermolytic molecular precursors (TMP)[5] has emerged as a powerful approach to generate isolated metal sites with controlled nuclearity and oxidation state on oxide supports, allowing to derive structure – reactivity relationships for a wide range of reactions.[6] Employing this methodology, we generated well-dispersed monomeric Cu(II) sites on a series of transitional aluminas (γ-,η-, θ- and α-Al_2O_3) and were able to rationalize reactivity observed (Figure 1a) to specific properties of the support. The identity of the reactive monomeric Cu(II) site could be unambiguously determined by its EPR spectroscopic signature (Figure 1b). Combination of advanced spectroscopic techniques (EPR, IR, XAS) with DFT calculation allowed the assignment of the reactive Cu(II) site to a tricoordinated Cu(II) present on the (110) facet of alumina.

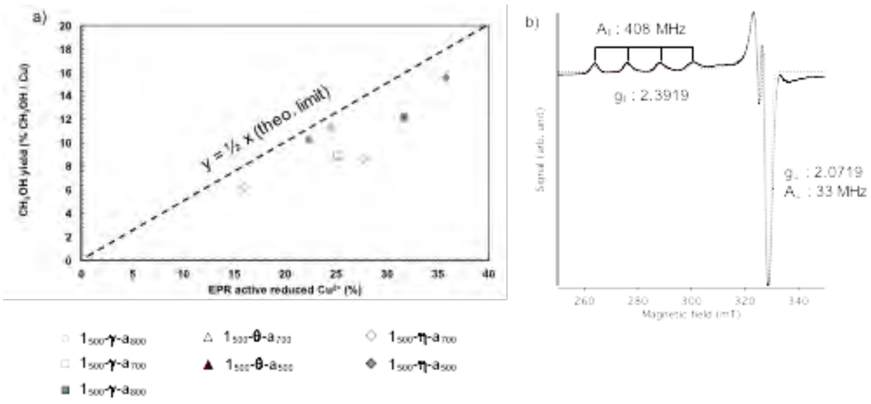

Figure 1. a) methanol yield vs. Cu(II) reduction for the alumina series b) EPR signature of the reactive monomeric Cu(II) species.

[1] a) Crabtree *et al. Chem. Rev.* **1995**, *95, 987-1007* b) Labinger *et al. Nature* **2002**, *417*, 507-514 c) Schwarz *et al. Angew. Chemie Int. Ed.* **2011**, *50*, 10096-10115 c) Ravi *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 16464-16483 d) Meyet *et al. Angew. Chemie Int. Ed.* **2019**, *58*, 9841-9845

[2] Groothaert *et al. J. Am. Chem. Soc.* **2005**, *127*, 1394-1395

[3] Lange *et al. Ind. Eng. Chem. Res.* **2019**, *58*, 8674-8680

[4] Copéret et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 6398-6440

[5] Fujdala et al. *Topics Organometal. Chem.* **2005**, *16*, 69–11

[6] Copéret et al. *Acc. Chem. Res.* **2019** *52*, 1697-1708

Crop protection in a changing climate

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Agriculture and farmers are facing environmental, societal and economic challenges. Our innovation landscape in crop protection is integrating these concerns to support a sustainable agriculture and the food supply.

For example, water is a limited resource essential to agriculture and food production. Climate change and an increasing population will increase further the pressure on its access. In this context, we have developed a program in crop protection research to address climate change resilience exploring phytohormones and their analogues to reduce the impact of an unfavorable environment to corn. In this presentation, we will illustrate how chemistry can play a key role in mitigating drought stress or cold stress in an essential crop.

[1] Cutler S.; Lachia, M. & all*, ACS Chem. Biol.* **2019**, *14*, 332−336
[2] De Mesmaeker, A. & all *Chimia*, **2019**, *73*(7), 549-560

Exploring extracellular wastewater peptidases to inform the design of sustainable peptide-based antibiotics

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One promising way to reduce anthropogenic pollution of natural environments is to replace persistent chemicals with alternatives that are biodegraded at the point-of-entry. Motivated by the negative effects caused by the presence of antibiotics in municipal and industrial wastewater (e.g., the increasing emergence and spread of antibiotic resistance), we pursued such a benign-by-design framework for antibiotics. We focused on peptide-based antibiotics because of their potential to be rapidly hydrolyzed and inactivated by extracellular wastewater peptidases, which we expect to limit the emergence and spread of antibiotic resistance in wastewater and wastewater-receiving environments. The major impediment for the assessment and the (re-)design of more sustainable peptide-based antibiotics is our limited understanding of the specificity of wastewater peptidases. To address this knowledge gap, we used a set of peptides to assess the specificity of extracellular wastewater peptidases. Our results suggest that peptidase-catalyzed hydrolysis occurs at specific bonds and that there is substantial overlap in specificity across enzyme pools derived from independent wastewater treatment plants. Complementary to assessing the specificity of extracellular wastewater peptidases, we assessed the stability of the set of peptides in human blood plasma, which mimics the system in which peptide-based antibiotics used for the treatment of systemic infections need to be stable. By comparing the results from wastewater and blood plasma experiments, we identified amino-acid motifs that are hydrolyzed by extracellular wastewater peptidases but not by peptidases in human blood plasma. These motifs might be promising candidates for the (re-)design of peptide-based antibiotics. This contribution offers a significant step towards a better understanding of the fate of peptide-based antibiotics and the presented framework will create opportunities for the design of biodegradable chemicals in general.

The relevance and role of “long-lived” photooxidants in aquatic organic photochemistry

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Sunlight irradiation of dissolved organic matter (DOM) leads to the formation of photochemically produced reactive intermediates, which can induce the indirect phototransformation of a variety of organic contaminants. A previously observed enhancement effect in the indirect phototransformation of electron-rich phenols at submicromolar concentration was ascribed to so far unexplored “long-lived” photooxidants (LLPO). Such LLPO, having estimated lifetimes $\tau>100$ µs, are hypothesized to occur concomitantly with the shorter-lived excited triplet states of DOM, ^{3}DOM* ($\tau\sim2$ µs). We studied the relevance and role of LLPO by steady-state irradiations, chemical model systems and kinetic modelling. By comparing the transformation rate constant at a high (5.0 µM) and a low (0.1 µM) initial concentration of target compounds, LLPO were observed to enhance the transformation of electron-rich compounds out of various chemical classes, namely phenols, anilines, phenylureas and sulfonamides. Chemical model systems consisting of a photosensitizer and an electron-poor phenol produced an analogous enhancement effect on transformation rates of electron-rich compounds, supporting the hypothesis that electron-poor phenolic moieties of the DOM are plausible LLPO prescursors.

Natural toxin mobility in soils – Mechanistic insights into multifunctional, ionizable organic compound sorption

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Natural toxins are a diverse group of rather polar, multifunctional and often ionizable organic compounds.[1,2] While generally understudied, some exemplary compound classes can be found both in the soil and aqueous environment. Concentrations, e.g., for pyrrolizidine alkaloids, vary from a few ng/L to several hundred µg/L in surface waters[3,4] or can reach up to more than 1000 µg/kg in clayey soils.[4]

By systematically quantifying sorption coefficients to major geosorbents, the compounds' mobility in soils can be assessed to allow for reliable environmental exposure/risk assessment. For the purpose of systematic high-throughput analysis of sorption coefficients, we optimized a column chromatography setup[5,6] to investigate natural toxin sorption to organic carbon and clay mineral sorbents (kaolinite, montmorillonite). A set comprising over 100 natural toxins from 30 different subclasses was studied under changing environmental conditions with regards to pH as well as the type of inorganic ion and ionic strength (IS) in the aqueous solution.

Soil organic carbon (SOC) sorption of analytes which are neutral under experimental conditions is largely governed by hydrophobic partitioning and H-donor/-acceptor interactions. In contrast, strong effects of variable pH and IS suggest that electrostatic interactions majorly contribute to the sorption affinity of multifunctional, ionizable compounds. Cation exchange (CE) is the major sorption mechanism for cationic natural toxins stressed by the significant decrease in sorption in presence of competing inorganic cations in solution. Enhanced sorption is additionally striking for (partially) cationic N-heterocyclic natural toxins with aromatic moieties. Those compounds undergo cation-/π-interactions that significantly increase their affinity to SOC. For analytes with complexing ligands on neighboring C-atoms, pH and IS effects point to ternary complex formation involving Ca^{2+}. When comparing cation exchange capacity normalized sorption coefficients for SOC and clay minerals, both cationic N-heterocyclic aromatic and complexing analytes sorb less or equally strong to clays, while those compounds merely dominated by CE show up to ten times larger sorption coefficients. Overall, varying sorption affinities of natural toxins highlight that the sorption of multifunctional, ionizable organic compounds is the result of a complex interplay of various interaction mechanisms. These are not only dependent on the compounds' properties, but also the sorbent characteristics and composition of the aqueous medium. Our results allow to disentangle those complex mechanisms to pinpoint key structural moieties dominating natural toxin mobility and provide valuable insights for understanding and modelling environmental transport and fate processes. The large dataset additionally allows to test existing modeling approaches for their applicability for multifunctional, ionizable compounds in general.

[1] Schönsee and Bucheli; **2020**. *J. Chem. Eng. Data* 65, 1946−1953
[2] Günthardt, et al; **2018**. *J. Agric. Food. Chem.* 66, 7577-7588
[3] Günthardt, et a.; **2020**. *CHIMIA* 74, 129–135
[4] Hama and Strobel; **2019**. RSC Advances 9, 30350-30357
[5] Schenzel, et al; **2012**. *Environ. Sci. Technol.* 46, 6118-6126
[6] Metzelder and Schmidt; **2017**. *En*viron. Sci. Technol. 51, 4928-4935

Occurrence of pesticide residues in agricultural soils and their impact on indicators for soil life

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Pesticides are applied in large quantities to agroecosystems worldwide, leading to accumulation and dispersion of potentially persistent and toxic residues in the environment. Despite their benefits for crop yield, the intensive and widespread use of pesticides increasingly raises environmental concerns due to contamination of natural resources [1] and their negative impact on bird, insect and pollinator populations [2-4]. While the occurrence and effect of pesticides in aquatic environments received considerable attention, only few reports are available on multi-residual analysis of pesticides in soils and it is still unclear whether pesticides are a potential threat to soil microorganisms, which drive pivotal soil processes such as plant nutrient uptake, carbon and nutrient cycling.

Here we provide a comprehensive overview of the presence and abundance of 45 widely applied pesticides (22 herbicides, 17 fungicides, and six insecticides) in soils of 100 agricultural fields, including 40 fields under organic management. Fields from arable and vegetable farming systems were compared and it was assessed whether the occurrence of pesticides depends on management types (conventional, conventional without soil tillage, and organic management). Moreover, we tested whether the duration of organic management affects the occurrence of pesticides. Additionally, it was assessed whether important indicators of soil life were linked to the number of pesticide residues present in the soil.

Pesticide residues were found in all of the investigated fields and up to 16 different pesticides were present in the soil 20 years after conversion to organic management. This indicates that a range of pesticides is much more persistent than previously thought. The number of pesticides in the soil was negatively linked to the abundance of an important group of beneficial soil fungi (mycorrhizal fungi). Our results indicate that the ubiquitous and continuous pollution of agricultural soils with a variety of different pesticides can have a long-term negative effect on soil life.

[1] Arias-Estévez, M., et al., Agriculture, Ecosystems & Environment, 2008, **123**(4), p. 247-260.
[2] Hallmann, C. A., et al., Nature, 2014, **511**(7509), p. 341-343.
[3] Sánchez-Bayo, F. and Wyckhuys, K. A. G., Biological Conservation, 2019, **232**, p. 8-27.
[4] Gill, R. J., et al., Nature, 2012, **491**, p.105-108.

Environmentally conscious use of surfactant TPGS-750-M in water-based synthesis

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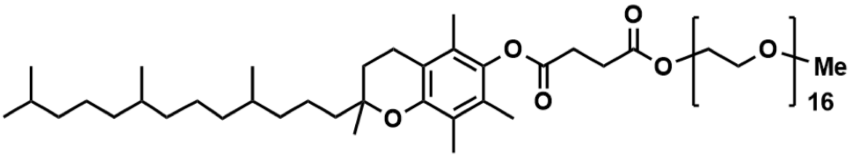
In recent years, surfactant TPGS-750-M has emerged as a powerful tool for performing organic chemistry in aqueous media [1,2]. E.g., catalytic C-C bond formations such as the Sonogashira reaction can be performed in water under mild conditions [3]. Replacing an organic reaction solvent by water results in strongly reduced CO_2 emission from waste incineration and is, therefore, highly desirable. In addition, the possibility to replace teratogenic solvents such as DMF, DMA or NMP by aqueous solutions of TPGS-750-M represents a major step towards safer chemical manufacturing [4].



TPGS-750-M

So far, available TPGS-750-M data were mostly related to the synthetic use and were limited. The presentation will provide insight into biodegradability, hydrolytic stability and other properties of TPGS-750-M and their implications for the assessment of related process waste waters. The current status of reaction work-up options with data on the fate of the surfactant will be presented.

[1] B. H. Lipshutz, S. Ghorai, *Aldrichimica Acta,* **2008**, 41, 59-72.
[2] M. Cortes-Clerget, N. Akporji, J. Zhou, F. Gao, P. Guo, M. Parmentier, F. Gallou, J.-Y. Berthon, B. H. Lipshutz, *Nature Comm.*, **2019**,10, 2169.
[3] M. Jakobi, F. Gallou, C. Sparr, M. Parmentier, *Helv. Chim. Acta*, **2019**, e1900024.
[4] N. A. Isley, R. T. H. Linstadt, S. M. Kelley, F. Gallou, B. H. Lipshutz, *Org. Lett.,* **2015**, 17, 4734-4737.

On the Real Aging of Diesel Oxidation Catalyst

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Air pollution from emissions of fossil fuel powered vehicles is currently a great concern due to the adverse effects on the environment and health. Catalytic converters are a widely applied technology to abate these emissions and in case of diesel engines, diesel oxidation catalysts (DOC) are used to oxidize CO and unburned hydrocarbons (HC); these consists of monolith honeycombs coated with a noble metal based catalyst [1]. In addition, DOC oxidizes NO to NO_2 to assist the downstream selective catalytic reduction process converting NO_x into N_2. In order to develop durable catalysts, it is necessary to gain detailed understanding on the deactivation caused by the mileage. Thermal deactivation and chemical poisoning (due to accumulation of S and P compounds present in fuel and lube oils) are known to contribute to the aging of DOC [1]. While thermal events cause the sintering of metal nanoparticles, several effects have been attributed to chemical poisoning; these include prevention of Pt particle growth, changes in support acidity/surface area as well as changes in the redox properties of [1, 2, 3].

Due to the large number of overlapping effects, it is often difficult to discriminate between the impact of each aging phenomena. This research aims at gaining further insight into the DOC deactivation; hence, in-depth characterisation of a commercial DOC monolith was performed in its fresh and aged state (aged for 288 kkm). To account for inhomogeneities along the monolith, the field aged DOC was divided into several segments, which were evaluated individually. The characterisation performed includes inductively coupled plasma-optical emission spectrometry (ICP-OES), scanning transmission electron microscopy (STEM), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The catalytic activity was evaluated under simulated diesel exhaust gas. The results suggest a particularly detrimental effect of P on NO oxidation performance.

The insights obtained on the commercial DOC were used to design combined P poisoning and thermal aging studies on a model DOC. A set of P containing 1 wt% Pt/Al_2O_3 catalysts were synthesised via consecutive impregnation using platinum nitrate and ammonium phosphate. In one case, Pt was added to alumina followed by P treatment ($(Pt\text{-}Al_2O_3)\text{-}P$), in a second case the support was treated with P prior Pt addition ($Pt\text{-}(Al_2O_3\text{-}P)$). A fraction of the samples were then hydrothermaly (HT) aged (10 vol% H_2O in air, 750 °C, 16 h) while NO oxidation was measured under continuous flow of 1000 ppm NO, 7 vol% H_2O, 10 vol% O_2 in N_2 during temperature ramps to 500 ^oC. The fresh Pt/Al_2O_3 exhibited small Pt nanoparticles of 1.1 nm. Hydrothermal aging resulted in a significant NO conversion improvement due to sintering of Pt nanoparticles up to 30 nm. Unlike for $Pt\text{-}(Al_2O_3\text{-}P)$, the presence of P strongly influenced the Pt particle morphology on $(Pt\text{-}Al_2O_3)\text{-}P$ while NO conversion decreased. DRIFT and X-ray absorption measurements suggest that while P induces changes in Pt redox properties, the deactivation in $(Pt\text{-}Al_2O_3)\text{-}P$ is largely due to the blockage of active surface.

[1] A. Russell, W.S. Epling. *Catal. Rev.*, **2011**, 53, 337; [2] M.S. Kumar, E. Kondratenko, M.H. Aguirre, P. Hug, D. Rentsch, A. Winkler, A. Weidenkaff, D. Ferri. *Appl. Catal. B,* **2013,** 129, 214; [3] M. S. Wilburn, W. S. Epling. *Emiss. Control Sci. Technol.*, **2018**, 4, 78.

Product Generation and Imaging of Photoactive and Viscous Organic Aerosol Particles

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Heavy aerosol loading threatens human health across the globe and is typically related to photochemical processing associated with emission of organic, inorganic and trace metal compounds [1]. Aerosol particles dominated by organic solutes may attain a high or ultra-high viscosity (>10^{12} Pa s) becoming solid-like in cold and dry air, limiting diffusion of organic and reactive molecules through the particle volume, and thus slowing chemistry. In contrast, illumination and thus photochemistry, to produce radicals may occur through the bulk of light absorbing particles irrespective of diffusion limitations. We investigated iron oxidation state changes in particles containing various concentrations of citric acid and iron(III)-citrate using environmental X-ray spectromicroscopy and coated wall flow tube experiments. Chemical images of aerosol particles with resolution currently as low as 35x35nm were acquired in a humidified microreactor revealing spatial gradients in the concentration of iron(II) and iron(III) compounds [2]. We have also quantified the release of volatile products, such as acetic acid, acetaldehyde and acetone, due to radical reactions and decarboxylation subsequent to ligand to metal charge transfer [3] using proton transfer reaction mass spectrometry. Condensed phase products, such as compounds with 6-11 carbon atoms were determined from HPLC-MS analysis implying functionalization, oligomerization and possibly radical-radical recombination reactions occurred during photochemical cycling. We have found striking evidence that particles and films quickly became anoxic due to reactions with organic radical species, despite being in an O_2 atmosphere, which may explain our vast molecular product distribution in terms of carbon number. Our results are highly important for the accurate prediction of aerosol phase radical generation and chemical loss of oxygenated organic aerosol dominated by carboxyl functionalities [4]. These findings are important for other photochemically active species commonly found in the atmosphere, implying a ubiquity of persistent radicals in airborne particles.

[1] H. Tong et al. *Faraday Discuss.* **200**, 251-270 (2017).
[2] P. A. Alpert et al. *Phys. Chem. Chem. Phys.* **21**, 20613-20627 (2019).
[3] J. Dou et al. *J. Phys. Chem. Lett.* **10**, 4484-4489 (2019).
[4] A. Laskin et al. *Annu. Rev. Anal. Chem.* **9**, 117-143 (2017).

Plant protection products in soils: Determination of bioavailability by means of passive samples

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The current risk assessment and legislation of organic contaminants, such as plant protection products, in soils is mainly based on the determination of the total concentration (C_{total}) of these contaminants in dry bulk soil. However, C_{total} does not properly express the exposure of soil organisms, plants and humans. Instead, the so-called bioavailable concentration would constitute a more realistic proxy [1]. The recent development of passive sampling (PS) methods (e.g., low density polyethylene or silicone sheet materials) allows the measurement of this bioavailable concentration, such as the freely dissolved concentration of the contaminants (C_{free}) in the pore water [2]. The C_{free} can be obtained by equilibrating PS methods with the study soil under *ex situ* conditions. Then, the absorbed concentration of the compounds in the well-characterized PS together with the laboratory measured polymer-water partition coefficient ($K_{polymer,water}$) allows the calculation of the C_{free}. This far, PS has been mainly used for non-polar plant protection products in soils. However, information about whether these techniques can be used for more polar or semi-polar plant protection products has been scarcely reported.

For this study, we used J-Flex silicone sheet PS to investigate seven plant protection products within an octanol-water partition coefficient range between log 2.5 to 3.7. The study was divided into three parts (Figure 1) [3]: (1) a kinetic experiment to estimate the equilibrium time for each compound between the polymer and the water phase, (2) an equilibrium experiment to calculate their $K_{polymer,water}$, and (3) a pilot study to assess their C_{free} in eleven agricultural soils (eight field aged soils and three spiked soils) under *ex situ* soil suspension conditions.

We will present the results of $K_{polymer,water}$ values and the C_{free} concentrations in the agricultural soils. Preliminary results in specific compounds show variability in C_{free} in soils with the same C_{total}. Data will be compared to previous literature and discussed in terms of risk assessment and legislation.

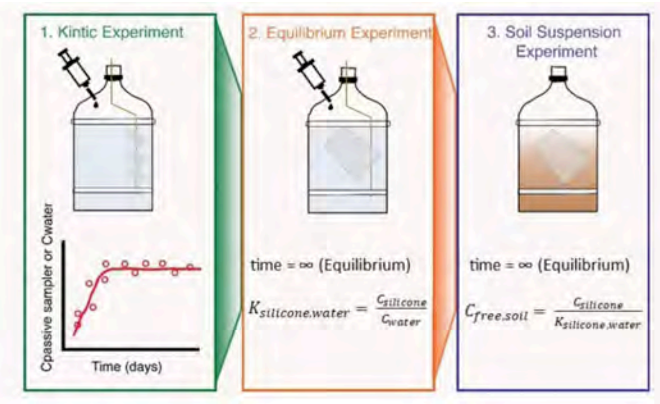

Figure 1: Graphical summary of the three experiments where (1) represents the kinetic experiment, (2) shows the equilibrium experiment, and (3) exemplifies the pilot study with soil suspensions under ex situ conditions.

Acknowledgment: Funding by the Federal Agency of Environment (FOEN) in Berne is gratefully acknowledged. This project is part of the Action Plan for Risk Reduction and Sustainable Use of Pesticides.

[1] Ortega-Calvo, J.-J., et al.,. Environmental Science & Technology, 2015. **49**(17): p. 10255-10264.
[2] Reichenberg, F. and P. Mayer,. Environmental Toxicology and Chemistry, 2006. **25**(5): p. 1239-1245.
[3] Rusina, T.P., et al., Science of The Total Environment, 2019. **696**: p. 133935.

Unraveling Enzyme Kinetics of Organic Contaminant Oxygenations with the use of Kinetic Isotope Effects

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Oxygenases are among the most important enzymes that initiate biodegradation of persistent organic pollutants in contaminated environments. Even though many biochemical aspects of this diverse group are well-known, quantifying rates of contaminant removal by enzymatic oxygenations remains a challenge for two major reasons. First, enzymes use different strategies to activate molecular oxygen but both experimental and computational studies on the contribution of oxygen activation to the rate of oxidative biodegradation are scarce and contradictive. Secondly, nonproductive reaction pathways lead to an uncoupling of oxygen activation from substrate metabolism but only few quantitative and systematic studies have considered this phenomenon.

To understand these key aspects of the enzymatic cycle, we conducted systematic kinetic analyses of a series of nitroaromatic compounds in laboratory model systems of two Rieske non-heme iron dioxygenases, a subfamily of mononuclear non-heme iron oxygenases, that hydroxylate unactivated aromatic structures. We analyzed the reaction kinetics, ^{13}C-, and ^{2}H-apparent kinetic isotope effects of organic substrates and products, quantified the stoichiometries of dissolved O_2 consumption, and derived ^{18}O-KIEs. For all substrates, we observed similar oxygen isotope fractionations suggesting that O_2 activation was rate-limiting regardless of substrate. However, the efficiency of oxygenation was substrate-specific and varied between 0% and 70% of the available O_2. The extent of this uncoupling reaction is correlated with the extent of isotope fractionation measured in the organic substrate. We hypothesize that oxygen uncoupling allows the detection of substrate KIEs after the rate-determining O_2 activation by the release of unreacted substrate from the activated enzyme-substrate complex. Our findings provide new insights into the catalytic mechanism of aromatic dioxygenations.

Photochemistry of organic matter in the atmosphere and its effect on mixed-phase cloud formation

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Aerosol-cloud interactions play a key role in the earth's energy budget, yet contribute to the largest uncertainty in radiative forcing in climate model estimates.[1] Aerosols are impacted by photochemistry during their lifetime of days to weeks in the atmosphere, altering their chemical and physical compositions. Indeed, in the time interval between where organic aerosols are emitted and/or formed and where they act as CCN and INP, they will undoubtedly be exposed to sunlight and thus undergo atmospheric processing through photochemistry.[2,3] Yet, the effect of photochemistry on the propensity of organic matter to participate in the initial cloud-forming steps is difficult to predict.

To explore the effect of photochemistry on organic matter in cloud water conditions, we explored three different types of samples: (1) field-collected dissolved organic matter from lakes and rivers relevant for lake spray aerosols,[4] (2) humic substance standards,[4] (3) lignin, as a subcomponent of organic matter, (4) firewood smoke, (5) ammonium sulfate methyl glyoxal brown carbon solutions, and (6) lab-generated secondary organic aerosols[5].

Our group's research aims to better understand how direct and indirect photochemistry impact the hygroscopicity and ice nucleating ability of atmospheric organic matter. Experimentally, our organic matter samples were dissolved in water and subjected to photochemical reactions in a photoreactor. Subsequently, the samples were (1) aerosolized and analyzed using a cloud condensation nuclei counter and (2) measured using our home-built drop freezing ice nuclei counter, for their ability to activate clouds. We correlate changes in hygroscopicity, using the kappa parameter, with changes in chemical composition including, total organic carbon (TOC), pH, UV/Vis absorbance, and CO, CO_2, acetic acid, pyruvic acid and formic acid production. Importantly, we find that the kappa of organic matter of all six samples tested increase substantially upon photo-oxidation, up to a factor of 2.5. This result is consistent with a photomineralization mechanism where the organic carbon is mineralized to CO_2, and where carbon mass is lost. On the other hand, the ice nucleation ability changes upon photoirradiation of the six samples does not follow a consistent trend and remains difficult to predict. Our running hypothesis is that the size of the macromolecules may be playing a role in their ability to template ice. In all, photomineralization can alter the aerosol-cloud radiative effects of organic matter by modifying the supercooled liquid water-to-ice crystal ratio in mixed-phase clouds with implications for cloud lifetime, precipitation patterns and the hydrological cycle.

[1] O. Boucher et al., 'Clouds and Aerosols. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the IPCC', Cambridge University Press, United Kingdom and New York, NY, USA, **2013**.
[2] C. George, M. Ammann, B. D'Anna, D. J. Donaldson, S. A. Nizkorodov, *Chem. Rev.* **2015**, *115*, 4218.
[3] A. Laskin, J. Laskin, S. A. Nizkorodov, *Chem. Rev.* **2015**, *115*, 4335.
[4] N. Borduas-Dedekind, R. Ossola, R. O. David, L. S. Boynton, V. Weichlinger, Z. A. Kanji, K. McNeill, *Atmos. Chem. Phys.* **2019**, *19*, 12397.
[5] N. Borduas-Dedekind, S. Nizkorodov, K. McNeill, *Chim. Int. J. Chem.* **2020**, *74*, 142.

Monitoring of priority substances in sediments of Switzerland

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In Switzerland, surface waters are protected by the Swiss Water Protection Ordinance (OEaux), which stipulates that the water quality shall be such that: "the water, suspended matter and sediments contain no persistent synthetic substances to ensure the protection of aquatic life". Current sediment quality assessment in Switzerland mainly consists of physico-chemical analyses, primarily of metals and to a lesser extent polycyclic aromatic hydrocarbons and polychlorinated biphenyls. Sediments, however, may accumulate a large number of substances including, e.g. pesticides, pharmaceuticals and industrial chemicals. For the preparation of recommendations for sediment quality assessment in Switzerland, a screening system was implemented in 2017 for the identification and ranking of substances relevant for sediment monitoring. The screening approach was largely based on the NORMAN (network of reference laboratories, research centers and related organizations for monitoring emerging environmental substances) system. Based on the available quantity of exposure and effect data, sediment-relevant substances were classified into five action categories: 1) substances with enough monitoring data on Swiss sediments and identified environmental risks; 2) substances with limited monitoring data; 3) substances with no or limited ecotoxicological data; 4) substances with no environmental data for Swiss sediments; 5) substances with enough monitoring data and no identified risks. This classification was useful in setting monitoring recommendations and priorities while it could be updated as new data emerged. A set of 20 substances was prioritized for sediment monitoring, according to several exposure, hazard and risk scores. This set of substances included the traditional sediment contaminants (metals, PAHs, PCBs), several pesticides (e.g. chlorpyrifos), one antibiotic and the hormones (EE2, E2 and E1), several sewage effluent markers (e.g. triclosan, tonalide), one phthalate, one PFAS and BDEs among others. In 2017 and 2018 two monitoring campaigns were carried out that targeted these 20 substances and other substances that could be simultaneously measured using the same analytical methods. We will present the results of these monitoring campaigns in terms of measured environmental concentrations and distribution in Swiss sediments. We will also discuss recommendations for improving sediment quality monitoring in Switzerland.

The role of surface states on reduced TiO_2@$BiVO_4$ photoanodes: Enhanced water oxidation performance through improved electron transfer

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The efficient transfer of photogenerated carriers and stability against corrosion are essential prerequisites for the design of photoelectrodes to boost photoelectrochemical performance.[1-3] Here, a reduced TiO_2 protected $BiVO_4$ ($HTiO_2$@$BiVO_4$) photoanode has been prepared to meet both criteria. Electrochemical impedance spectroscopy was employed to investigate the behavior of surface states during water oxidation. Two localized surface states were found on the $HTiO_2$@$BiVO_4$ photoanode: the first one located near the onset potential; the second one located slightly lower than the water oxidation potential. The first surface state is suggested to be strongly correlated with the oxygen vacancies in the TiO_2 layer to trap electrons and initiate an earlier onset photocurrent, which was confirmed by x-ray photoelectron spectroscopy and cyclic voltammetry results. The second surface state is proposed to be a reaction center, arising from the formation of unoccupied oxygen vacancies with adjacent V^{5+} sites. Additionally, surface recombination centers, derived from irreversible surface reduction reaction of VO_2^+ to VO^{2+} in $BiVO_4$, was greatly passivated through this strategy. In conclusion, the reduction process can tune the electron trapping process between the two surface states to achieve a high photocurrent of 2.0 mA cm^{-2} at 1.23 V_{RHE} and a more negative onset potential of around 265 mV_{RHE}. These observations provide further understanding on controversies over the role of surface states and function of oxygen vacancies in $BiVO_4$ photoanodes, offering some insights into their impact upon photoelectrochemical performance.

[1] Park, Y.; McDonald, K. J.; Choi, K.-S., *Chem. Soc. Rev.* **2013**, *42*, 2321–2337.
[2] Tian, Z.; Zhang, P.; Qin, P.; Du Sun; Zhang, S.; Guo, X.; Zhao, W.; Zhao, D.; Huang, F., *Adv. Energy Mater.* **2019**, *9*, 1901287.
[3] Li, J.; Wan, W.; Triana, C. A.; Novotny, Z.; Osterwalder, J.; Erni, R.; Patzke, G. R., *J. Am. Chem. Soc.* **2019**, *141*, 12839–12848.

Bioaccumulation and transformation of mercury compounds by model phytoplankton: focus on green algae and cyanobacteria

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Phytoplankton could influence the aquatic biogeochemical cycle of mercury (Hg) directly through uptake and biotic transformations, and indirectly through the excretion of ligands influencing both abiotic and biotic transformations. Opposite to the substantial work performed with bacteria, the role of phytoplankton, such as green algae and cyanobacteria, in Hg transformation is poorly understood.

The goal of the study is to get insights on the role of model phytoplankton in biotic transformations in freshwater systems. Since biotic transformations are essentially intracellular, the accumulation of inorganic (iHg) and monomethylmercury (MeHg), their subcellular distribution, and transformation in green algae *Chlamydomonas reinhardtii*, and cyanobacterium *Synechocystis* PCC 6803 were studied. Model organisms were harvested at mid-exponential and stationary growth phases and exposed to 3nM of ^{199}iHg and 0.3nM of ^{201}MeHg during 96h. The cellular uptake of both Hg species was determined following isolation from the exposure medium by gentle centrifugation. To get information about cellular compartments involved in the possible transformations, the cells were further separated into membranes and cytosol fractions. Hg content determination was carried out by isotopic dilution analysis gas chromatography coupled to inductively coupled plasma mass spectrometry. The changes in the ratio between the difference of spiked isotopes concentration before and after the exposure and the concentration of the transformed isotopes during exposure in the whole-cell and the subcellular fractions were used to determine the Hg transformations.

The results demonstrated a rapid accumulation of iHg and MeHg by green alga and cyanobacterium. However, the cellular concentrations were species- and growth-dependant. Under comparable conditions, *Synehocystis* accumulated about twice more iHg than *C. reinhardtii*. No significant Hg transformations have been found in cyanobacteria cells in our studies conditions while green alga cells are able to demethylate MeHg mainly in the cytosolic fraction and more specifically in the stationary phase of growth. The results have important implications for the improved understanding of the role of phytoplankton in the aquatic environment as well as for the accumulation of Hg species in the aquatic food webs.

Transgenerational Fate of Polychlorinated Biphenyls from Cow to Calf during Gestation and Lactation

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Consumption of food of animal origin accounts for 90% of the total human exposure to polychlorinated biphenyls (PCBs), which are listed as persistent organic pollutants (POPs). In the case of bovine meat, former Swiss monitoring plans focusing on suckling cow production systems recorded 5% missing conformity. Understand, assess and manage the risk of entry of POPs into suckling cow and calf meat is therefore mandatory to ensure human health and the sustainability of these production systems. This study aims to better understand the fate of PCBs from grass and soil oral intake to cows and their calves over the end of gestation as well as full lactation and assess depuration kinetics as a counter-measure.

Twelve Simmental cows and their calves were monitored, starting 113 days before calving and ending after 255 days in milk (DIM). Cows were allocated into two groups based on body weight and parity (6 primi- and 6 multiparous) and received one of two *ad libitum* treatments: control (only grass silage, n = 4) and exposed (grass silage mix with 2.5% POP-loaded soil on dry matter (DM) basis, n = 8). The latter was further divided into 4 exposed and 4 depurating pairs after 164 DIM, continuing for 91 days. Calves were fed with milk from their respective mother, completed by non-contaminated hay offered *ad libitum* and concentrate. To study the fate of PCBs, milk and cow/calf serum samples were taken on DIM 1, 29, 60 (not for cow serum), 89, 164, 199, 227 and 255, with additional milk samples on DIM 7, 14, 21, 128, 167, 171, 178 and 185 for GC-MS analyses.

Considering its 2.5% soil content, the grass silage mix contained 7.2 µg indicator PCBs (iPCBs) and 0.7 ng TEQ dioxin-like PCBs (dlPCBs)/kg DM, compared to 1.2 µg and 0.07 ng TEQ/kg DM, respectively for the control diet. This resulted in 35.8 µg iPCBs and 6.1 ng TEQ dlPCBs/kg colostrum fat at DIM 1 for the exposed cows. After 7 days, a drop in milk concentration by 52% for iPCBs and 60% for dlPCBs was reported, after which the concentration slowly increased by 25% and 9% respectively until DIM 164, being 23.3 µg and 4.0 ng/kg fat. For control animals a similar pattern was seen along the lactation, with 4-8 fold lower iPCB and dlPCB concentrations compared to the exposed cows. Within serum, exposed cows show a concentration of 16.3 µg iPCBs and 0.6 ng TEQ dlPCB/kg fat at DIM 1, which drops over time by 40-70% in cow and calf. The calf serum is along the lactation 2-3 fold higher in PCB concentration compared to the cow serum. Switching exposed cows to the control diet after 164 DIM results in a 2-phased depuration, with shorter half-lives in multiparous than in primiparous cows (6 & 200 in primi- vs. 4 & 155 days in multiparous for iPCBs; 7 & 412 and 6 & 175 days for dlPCBs respectively). In serum, the concentration of iPCBs halved during 91 days of decontamination in cow and calf, demonstrating that the dilution of iPCBs due to growth of the calf could be as efficient as elimination via milk. These results will be useful for assessing the predictive capabilities of physiological based toxicokinetic (PBTK) models, in order to ensure their efficient use for risk assessment and management.

Exposure assessment of pyrrolizidine alkaloids in Swiss surface water combining retrospective data analysis and particular invasive *Senecio* monitoring

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Pyrrolizidine alkaloids (PAs) are toxic plant secondary metabolites produced by approximately 3% of all flowering plants for defense against insects and herbivores. Lately, Hama et al. detected some of these toxins leaching from plant hotspots and we demonstrated their occurrence in a Swiss creek with invasive, PA producing, *Senecio inaequidens* growing in the proximity.[1,2] Therefore, the questions arise, if PAs are regularly present in surface water or if plant hotspots or invasive species are the main cause of their occurrence. To answer these questions we 1) performed a retrospective data analysis to assess the general occurrence of PAs, and 2) conducted a specific monitoring study to measure the impact of the invasive *S. inaequidens* on the occurrence of PAs in two small creeks.

The retrospective data analysis was performed on two complementary surface water monitoring campaigns each covering in total eight sites from different biogeographical regions measured with liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS).[3,4] For full confirmation of the PAs some samples were remeasured with the same method. The two additionally monitored creeks receive highway storm water, which is important since the invasive Senecio species grows in Switzerland along highways. These two sites were monitored from Mai until December and the samples measured with a newly developed LC-MS/MS method targeting PAs.

The results of the retrospective analysis show that PAs occurred at all investigated sites. However, the detected concentrations strongly varied with maximal, total PA concentrations between below 10 ngL^{-1} and up to 98 ngL^{-1}. The highest concentrations were only detected over short periods that coincide with rain events. Therefore, a washout effect is assumed as most probable contamination path. Also, the toxin pattern varied between the different sites and in time. Whereas Senecio spp. dominating toxins were detected at all sites, echimidine-type PAs were only detected at 80% and intermedine-type PAs at 30% of the sites. Intermedine-type PAs had a general tendency to appear later in the season, which can possibly be explained with the later start of the flowering period of Eupatorium cannabinum, the main plant producing PAs of this type.

Only preliminary results of the second study are available this far. One site with invasive Senecio in the catchment area showed higher concentrations and even a constant contamination whereas the other site is not remarkably high. The measurement of toxin patterns in the biomass of the Senecio species in proximity will identify the most contributing species.

[1] Hama, J. R.; Strobel, B. W., *RSC Advances*, **2019**, 9, 30350-30357.
[2] Günthardt, B. F.; Schönsee, C. D.; Hollender, J.; Hungerbühler, K.; Scheringer, M.; Bucheli, T. D., *CHIMIA*, **2020**, 74, 129-135.
[3] Doppler, T.; Mangold, S.; Wittmer, I.; Spycher, S.; Comte, R.; Stamm, C.; Singer, H.; Junghans, M.; Kunz, M., *Aqua und Gas,* **2017,** *4*, 46-56.
[4] Spycher, S.; Mangold, S.; Doppler, T.; Junghans, M.; Wittmer, I.; Stamm, C.; Singer, H, *Environ. Sci. Technol.,* **2018,** *52*, 4526-4535.

Application of *in vitro – in vivo* extrapolation to predict the bioaccumulation potential of fragrance chemicals

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In the regulatory assessment of chemicals, bioaccumulation in aquatic species is a critical endpoint. Usually, the bioconcentration factor (BCF) is determined in fish according to the OECD Test Guideline (TG) 305. *In vitro* systems measuring biotransformation rates of chemicals have been established as alternative methods, to refine *in silico* BCF models which are based on hydrophobicity (i.e. log Kow), and were recently adopted as new OECD TGs (319A,B) [1, 2]. *In vitro - in vivo* extrapolation (IVIVE) models can then be applied to estimate liver clearance and a “whole body” biotransformation.

In this study, *in vitro* biotransformation rates were measured for 23 fragrance chemicals and 7 chemicals from other use categories in rainbow trout liver S9 fractions (RT-S9) following the OECD TG 319B. Substrate depletion assays were performed using RT-S9 in potassium phosphate buffer (pH 7.8) in presence of cofactors at 12°C with initial concentrations of 1 µM. The concentrations of the parent chemicals were analysed by GC-MS or LC-MS. The majority of fragrance chemicals (log Kow values ranging from 3.9 to 6.1) were moderately to rapidly biotransformed with *in vitro* intrinsic clearance rates ranging from 0.12 to 33.69 mL/h/mg protein. No significant biotransformation was observed with Musk Xylene, pentachlorobenzene, chlornitrofen, 1,3,5-tribromobenzene and 2,5-dichloro-1,1'-biphenyl.

BCF values were predicted using extrapolated whole-body biotransformation rate constants from a commonly used IVIVE model [3] and compared with available *in vivo* measured BCFs. Predicted BCFs were within 0.5 log units (factor of 3.16) for 44 % of the chemicals compared to *in vivo* BCFs, whereas predicted BCFs were more than half a log unit greater than the empirical values for 56 % of the chemicals (i.e. predicted BCFs were >3.16-fold greater than empirical BCFs). None of the chemicals were underpredicted by more than 0.5 log units (i.e. predicted BCF smaller than the empirical BCF). Possible biological reasons for the tendency to underpredict BCFs may be the impact of extrahepatic metabolism, protein binding and species differences, but there is also the possibility, that the IVIVE model has fundamental flaws requiring reassessment of key model parameters.

In conclusion, the IVIVE-BCF estimation approach provides a significant improvement over methods that ignore biotransformation (“K_{OW} driven”) for bioaccumulation assessment. Thus, the RT-S9 assay is a powerful tool to determine the *in vitro* intrinsic clearance of fragrance chemicals and demonstrate their potential to be biotransformed. However, further refinements of the IVIVE models and understanding the potential role of extrahepatic biotransformation and protein binding should be a key goal for future research to reduce the uncertainties involved.

[1] OECD (2018): Determination of *in vitro* intrinsic clearance using cryopreserved rainbow trout hepatocytes (RT-HEP). OECD Guideline for the Testing of Chemicals, No. 319A.
[2] OECD (2018): Determination of *in vitro* intrinsic clearance using rainbow trout liver sub-cellular fraction (RT-S9). OECD Guideline for the Testing of Chemicals, No. 319B.
[3] Nichols, J., Huggett, D. B., Arnot, J. A. et al. (2013). Environ Tox Chem 32, 1611-1622.

Quantification of Oxidant-Reactive Carbonous Sites in Dissolved Organic Matter

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The application of ozone for disinfection or abatement of micropollutants during treatment of drinking water and wastewater is accompanied by ozone reactions with matrix components such as dissolved organic matter (DOM). Besides the influence of DOM on the efficiency of the process, its reaction with ozone leads to the formation of undesired oxidation by-products (OBPs) such as low molecular weight aldehydes, ketones or quinones. Ozone applications to impaired waters as for enhanced wastewater treatment or water reuse may lead to an increase in OBPs. Consequently, there is a need to quantify and characterize reactive functional moieties in DOM for a better prediction of the oxidation efficiency and OBP formation. The purpose of this study is the quantification of oxidant-reactive phenolic precursors in DOM, because phenolic moieties have been identified as major contributors to the consumption of oxidants by DOM. We propose to quantify phenolic moieties with chlorine dioxide (ClO_2) by oxidative titration and by applying a novel derivatization method for phenols in DOM to block their reactivity with chemical oxidants. The oxidative titration is based on the pH dependence of apparent second-order rate constants for the reactions of model compounds representing functional moieties in DOM with chlorine dioxide. From this data it can be concluded, that chlorine dioxide reacts considerably faster with phenolic compounds compared to amines or olefins. The experimental approach first modeled with the simulation software Kintecus was subsequently tested with phenolic model compounds before applying it to DOM from various sources. Changes due to oxidation were characterized by optical methods, the electron donating capacity (EDC) and the measurement of inorganic by-products. The principle of oxidative titration worked for the model compound phenol and the results were in line with kinetic simulations. The majority of phenolic model compounds was efficiently derivatized and quantified by means of the loss of electron-donating capacity. As expected, derivatized phenol solutions were masked during oxidative titration and thus served as control. The application of oxidative titration to various DOM sources was successful, however, remaining phenol concentrations after derivatization of DOM warrants further investigations. The oxidatively titrated phenol concentrations of IHSS DOM isolates were compared to their estimated phenol content and all tested DOM samples were correlated to the EDC of the respective sources. To conclude, oxidative titrations provide a novel and promising tool to quantify oxidant-reactive moieties in complex mixtures such as DOM. Furthermore, derivatization of phenolic moieties in DOM is a potentially useful tool to better understand the characteristics of DOM and aids in quantifying the phenolic and other oxidant-reactive moieties in DOM by oxidative titration.

Automated method to analyse cyanobacterial toxins and secondary metabolites in Swiss surface waters by online SPE-LC-HRMS/MS

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Cyanobacterial bloom events pose significant risks to human & animal health and to the security and safety of drinking water supplies. The release of potentially toxic cyanobacterial secondary metabolites in to the water column during bloom development and decay is of particular concern. To-date, over 2000 cyanobacterial secondary metabolites are reported [1], yet only a fraction have ever been assessed in terms of their concentrations in surface waters and toxicological risks. Analytical techniques capable of analysing the full spectrum of these metabolites are needed to enable effective time-resolved monitoring and comprehensive risk assessment.

We validated a high-throughput, online solid phase extraction-liquid chromatography-high resolution tandem mass spectrometry (online-SPE-LC-HRMS/MS) method for emerging cyanobacterial metabolites in surface waters. Using a completely automated procedure, analytes present in 10 mL of sample are enriched on to an SPE cartridge, from which they are subsequently back-flushed onto a solid-core analytical LC column for analyte separation, followed by data-dependent HRMS/MS analysis. Validation parameters demonstrate that our online-method is competitive with offline enrichments procedures, yet excels in terms of required sample volumes, sample throughput and overall reproducibility. We demonstrate application of this method in analysing surface water samples collected during a 2019 lake monitoring campaign of Swiss lakes. The low sample volume required and automated enrichment facilitates monitoring of lakes prone to harmful cyanobacterial blooms. Such surveillance capabilities are needed given the increasing frequency and intensity of harmful cyanobacterial bloom events, globally.

[1] Jones, M. R., Pinto, E., Torres, M. A., Dörr, F., Mazur-Marzec, H., Szubert, K., Tartaglione, L., Dell'Aversano, C., Miles, C., Beach, D. G., McCarron, P., Sivonen, K., Fewer, D., Jokela, J. and Janssen, E.M.-L. (pre-print, 2020) Comprehensive database of secondary metabolites from cyanobacteria. *BioRxiv*, https://doi.org/10.1101/2020.04.16.038703.

Mineral respiration of Geobacter sulfurreducens

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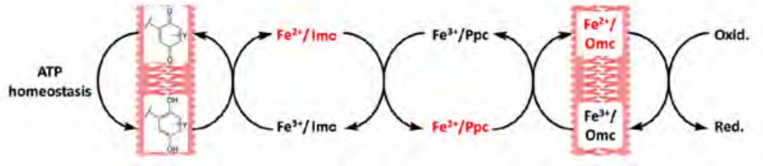
Geobacter sulfurreducens is an anaerobic microorganism that utilizes extracellular metal salts as acceptors for electrons that are generated during respiration. Key for this process is a mechanism called extracellular electron transfer (EET) in which electrons migrate from the inner membrane through the periplasm and the outer membrane to the metal ions. EET relies mainly on *c*-type cytochromes, which contain one to several iron heme cofactors as electron carriers. In this work, EET rates were determined *in vivo* by addition of silver (Ag^+) or chromate ions (CrO_4^{2-}) to *G. sulfurreducens*. The time dependence of the chromate and iron heme concentrations were measured by UV/Vis spectroscopy. We measured electron production and electron flux rates to about $5 \bullet 10^5$ e^-/s per *G. sulfurreducens*. Remarkably, these rates are independent of the oxidants, and follow a zero order kinetic.



A vital requirement for life is the maintenance of a constant ATP concentration (ATP homeostasis) during respiration under different environmental conditions. It now turned out that anaerobic bacteria that require extracellular metal salts for respiration are independent of the concentration and of the redox potential of the oxidants. This zero order kinetic is achieved by a high concentration of iron/hemes that buffer extracellular electron transfer rates.

[1] Chabert, V., Babel, L., Füeg, M. P., Karamash, M., Madivoli, E., Herault, N., Dantas, J. M., Salgueiro, C. A., Giese, B., and Fromm, K. M., *Angew. Chem.* **2020**. doi.org.10.1002/anie.201914873

Transformation of chlorinated paraffins by the bacterial dehalogenase LinB –Identification of hydroxylated metabolites

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Chlorinated paraffins (CPs) and hexachlorocyclohexanes (HCHs) are or have been produced via radical chlorination of alkanes or benzene. Since 2009, major HCH isomers (α, β, γ) and since 2017 short chain CPs (SCCPs, C_{10-13}) are classified as persistent organic pollutants (POPs) under the Stockholm Convention [1,2]. POPs are bio-accumulating, persistent and toxic. They hardly degrade in the environment and show high long-range transport potential. Eventually, these compounds will be ingested and metabolized by biota. Therefore, it is of interest to study and identify possible metabolites of such compounds.

In dumpsites which were heavily contaminated with HCH, bacteria of the *Sphingomonadacea* family were isolated which can transform HCHs[3]. These bacteria express the dehalohydrogenase LinB, which catalyzes the transformation of HCHs to hydroxylated metabolites [3]. Herein, it was hypothesized that LinB might converts CPs as well. Hence, a mixture of chlorinated tridecanes were exposed to LinB. Analysis of CPs and respective transformation products was achieved with liquid chromatography and high-resolution mass spectrometry. Several hydroxylated metabolites of CPs are detected and reported for the first time. The remaining starting material shows a higher chlorination degree after LinB-exposure, suggesting that higher chlorinated CPs are more persistent than lower chlorinated CPs.

This study shows that LinB transforms hexa- to undeca-chlorinated tridecanes into dehalohydroxylated metabolites. However, toxicity and environmental impact of these newly identified transformation products are yet unknown and need further investigations.

[1] UNEP, 2009. In: Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants (Fourth Meeting), UNEP/POPS/COP.4/38, 8 May, 2009.
[2] UNEP, 2017. In: Report of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants (eighth meeting), UNEP/POPS/COP.8/32, 13. July, 2017.
[3] Lal, R., Pandey, G., Sharma, P., Kumari, K., Malhotra, S., Pandey, R., Raina, V., Kohler, H.-P.E., Holliger, C., Jackson, C., Oakeshott, J.G., 2010. Biochemistry of Microbial Degradation of Hexachlorocyclohexane and Prospects for Bioremediation. Microbiol. Mol. Biol. Rev. 74, 58–80

Current Trends and Future Challenges of Rechargeable Aluminum-Graphite and Other Dual-Ion Batteries

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Rechargeable aluminum-graphite dual-ion batteries (AGDIBs) have attracted the attention of electrochemists and material scientists in recent years due to their low cost and high-performance metrics, such as high power density (up to 175 kW kg^{-1}), energy efficiency (≈ 80–90%), long cycling life, and high energy density (up to 70 Wh kg^{-1}), suited for grid-level stationary storage of electricity.[1, 2] The key feature of AGDIBs is the exploitation of the reversible oxidation of the graphite network with concomitant and highly efficient intercalation/de-intercalation of $AlCl_4^-$ anionic species between graphene layers. In this talk, we discuss the utility of AGDIBs as a highly promising post-Li-ion technology for low-cost and/or large-scale storage of electricity.[3, 4] In particular, we provide a balanced analysis of the overall cell-level energy density of AGDIBs. In view of its non-rocking chair operation mechanism, we show the achievable energy densities as a function of the composition of chloroaluminate ionic liquid ($AlCl_3$ content) and compare it with other battery electrochemistries suited for stationary storage of electricity (such as lead-acid or vanadium redox flow). Specific emphasis is given to the unbiased and correct reporting of their theoretical cell-level energy densities. Furthermore, we discuss also other issues associated with this technology, one being the incompatibility of most metallic current collectors with the corrosive $AlCl_3$-based ionic liquids. We then demonstrate a novel concept of flexible AGDIB using current collectors from earth-abundant elements and point to key challenges in the development and practical deployment of AGDIBs.[5] Finally, we also discuss an alternative dual-ion battery utilizing a highly concentrated electrolyte solution of 5 M potassium bis(fluorosulfonyl)imide in alkyl carbonates.[6] The resultant battery offers an energy density of 207 Wh kg^{-1}, owing to the high weight content of the electroactive species (65 wt%) in the electrolyte and a high operation voltage of 4.7 V.

[1] Kostiantyn V. Kravchyk, Maksym V. Kovalenko, *Advanced Energy Materials*, **2019,** 1901749.
[2] Kostiantyn V. Kravchyk, Carlotta Seno, Maksym V. Kovalenko, *ACS Energy Letters,* **2020,** 545-549.
[3] Kostiantyn V. Kravchyk, Shutao Wang, Laura Piveteau, and Maksym V. Kovalenko, *Chemistry of Materials*, **2017,** 29, 4484-4492.
[4] Shutao Wang, Kostiantyn V. Kravchyk, Frank Krumeich, and M.V. Kovalenko, *ACS Applied Materials & Interfaces*, **2017,** 9, 28478-28485.
[5] Shutao Wang, Kostiantyn V. Kravchyk, Alejandro N. Filippin, Ulrich Müller, Ayodhya N. Tiwari, Stephan Buecheler, Maryna I. Bodnarchuk, and Maksym V. Kovalenko, *Advanced Science*, **2017,** 1700712.
[6] Kostiantyn V. Kravchyk, Preeti Bhauriyal, Laura Piveteau, Christoph P. Guntlin, Biswarup Pathak, Maksym V. Kovalenko, *Nature Communications*, **2018,** 9, 4469.

Reactions of nitrogen-containing compounds with ozone: kinetics and mechanisms

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Nitrogen-containing compounds are widespread in natural waters as natural (dissolved organic nitrogen) and anthropogenic (micropollutants) substances. Because of the electron-rich nature of nitrogen in its neutral form, nitrogen-containing compounds are often reactive towards electrophilic agents such as ozone. Therefore, reactions of nitrogen-containing compounds with ozone inevitably occur in water and wastewater treatment where ozonation is applied for disinfection or oxidation purposes. Despite the great relevance of nitrogen-containing compounds for ozone chemistry, understanding of their reactions with ozone is still limited to certain functional groups.[1] This study aimed to broaden the understanding of nitrogen-ozone reactions by selecting simple model compounds for common nitrogen-containing functional groups (aliphatic amines and azoles) and identifying their transformation products by various analytical methods such as LC-HRMS/MS and NMR. Ethylamine, diethylamine, and triethylamine, the model compounds of aliphatic amines, reacted with ozone predominantly via oxygen-transfer on the nitrogen to form *N*-oxides or nitro compounds as major products.[2] Pyrrole, imidazole, and pyrazole, the azole model compounds, reacted with ozone via an initial ozone attack on a C=C double bond of the ring to form ring products (maleimide) as well as ring-opened products (cyanate, formamide).[3] Most nitrogenous transformation products identified in this study are expected to be abated by biological post-treatment after ozonation and do not appear to pose a direct threat to the aquatic environment. However, if present as substructures of more complex compounds, e.g., micropollutants, they might be persistent during the post-treatment and may lead to unknown ecotoxicological consequences.

[1] C. von Sonntag and U. von Gunten, *Chemistry of Ozone in Water and Wastewater Treatment*; IWA Publishing: London, **2012,** pp 131-159.
[2] S. Lim, C.S. McArdell, U. von Gunten, *Water Research*, **2019**, 157, 514–528.
[3] A. Tekle-Röttering, S. Lim, E. Reisz, H.V. Lutze, M.S. Abdighahroudi, S. Willach, W. Schmidt, P.R. Tentscher, D. Rentsch, C.S. McArdell, T.C. Schmidt, U. von Gunten, *Environ. Sci.: Water Res. Technol.*, **2020**, 6, 976-992.

Development of a Unified UHPLC-QTOF-MS Method for Benzoxazinoids Analysis

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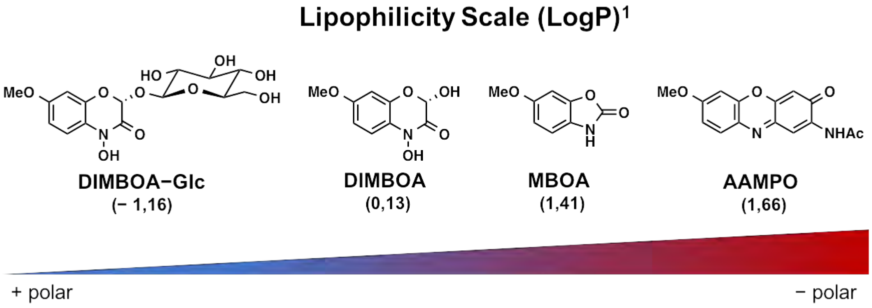
Benzoxazinoids represent a wide family of plant secondary metabolites found in grasses like maize and wheat. By consuming these plants, humans are chronically exposed to these bioactive compounds, which may thus affect health directly[1] but also indirectly by changing the composition of the gut microbiota. As plant secondary metabolites are important for plant health, for instance by shaping the soil microbiome,[2] they may also determine the dietary quality of the plant and thereby have cascading effects along the food chain. In this context, the IRC One Health aims at studying how benzoxazinoids, and their degradation products, structure the microbiomes at the interface between soil, cereals, cattle, and mice (as a human model). To reach this aim, an analytical method needs to be available to quantify benzoxazinoids across different biological matrices.[3] We addressed this challenge by synthesizing a set of deuterated benzoxazinoids to complement currently available internal standards. We then established and optimized a solid-phase extraction procedure in combination with UHPLC-QTOF-MS (Ultra-High Performance Liquid Chromatography-Quadrupole Time-of-Flight-Mass Spectrometry) analysis. The method was validated by evaluating matrix effects, recovery, accuracy and precision.[4] This method now allows us to quantify 11 different benzoxazinoids in lake sediments, soil, maize and mouse related samples with optimal accuracy and precision, and a limit of quantification below 2 ng/mL.


Lipophilicity Scale (LogP)[1]

[1] Adhikari et al. *Mol. Nutr. Food Res.*, **2015**, 59, 1324-1338.
[2] Hu et al. *Nat. Commun.* **2018**, 9, 1-13.
[3] Tetko et al. *J. Comput. Aid. Mol. Des.*, **2005**, 19, 453-463.
[4] Matuszewski et al. *Anal. Chem.*, **2003**, 75, 3019–3030.

Non-destructive method based on infrared spectroscopy and partial least square regression for the quantification of the ionic component of atmospheric particulate matter

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Atmospheric aerosols influence radiative forcing through interaction with solar radiation and indirectly by acting as cloud condensation nuclei and have a negative impact on air quality especially in urban scenarios. With socio-economic models suggesting that in a growing global population, 70% of the humans will live in urban areas by 2050, the adverse impact on urban air quality is a prominent societal and health issue, expected to become more and more severe in the future. In order to introduce effective mitigation strategies and monitor their effect, the state and characteristics of pollution need to be characterized and main sources identified. Offline-analysis of particulate matter (PM) collected on filter samples offers such insight. However, PM chemical composition is highly complex, and its comprehensive characterization and quantification requires advanced instrumentation and data analysis techniques and strategies.

Here, we present the development and application of a novel analytical non-destructive method. We acquired Fourier-transform infrared spectroscopy (FTIR) spectra of ambient PM collected on Teflon filters at various locations in Italy. FTIR allows to obtain high-resolution spectral data non-destructively and therefore to detect and quantify functional groups of organic and inorganic species present in the aerosol PM. The spectral dataset was analyzed by applying partial least squares regression (PLS regression) methods in order to allow quantification of ammonium, sulphate and nitrate ionic PM components. This statistical method allowed to disentangle the inner complexity of the PM sample and to train a statistical model for each of the three ionic species. In our conference contribution, the so developed models are discussed and compared with the more traditional analytical method, ionic chromatography (IC).

Further information:

Cuccia, et al., **2011,** Atmospheric Environment, 45(35), 6481–6487.
https://doi.org/10.1016/j.atmosenv.2011.08.004

Piazzalunga, A., et al., **2013**, Analytical and Bioanalytical Chemistry, 405(2–3), 1123–1132.
https://doi.org/10.1007/s00216-012-6433-5

Russell, L. M., et al., **2009**, Atmospheric Environment, 43(38), 6100–6105.
https://doi.org/10.1016/j.atmosenv.2009.09.036

Towards Incorporation of Minor Elements in synthetic C-S-H

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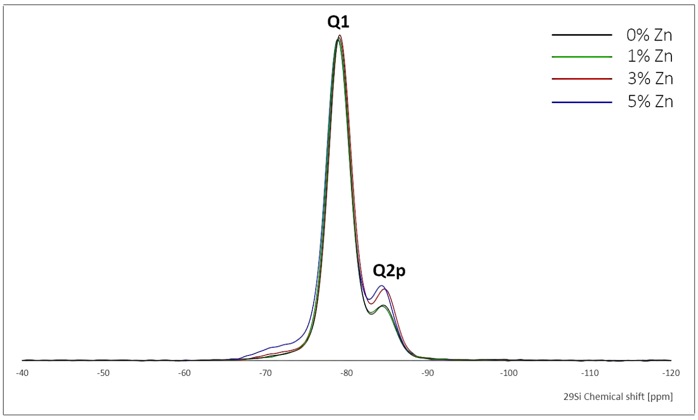
Cementitious materials are the most widely used man-made materials in the world, making up to 30-50% of all materials we produce. The main reasons why cementitious materials are so popular and widely spread are their low cost of only 0.12USD/kg, their versatility, and their low carbon footprint of 0.13kgCO_2/kg. However, despite being one of the materials with the lowest environmental impact per kg, the cement industry is responsible for 5-10% of CO_2 emissions worldwide due to the increase of infrastructure and construction development. The demand for cementitious materials is expected to increase in the next decades and with it, the cement-related CO_2 emissions. In order to mitigate the CO_2 emissions produced by the cement industry, there is a need for novel construction solutions which are equally abundant, easy to implement, economically viable and which are also more environmentally friendly.

The aim of this project is to study the impact of minor elements (particularly zinc) on the hydration of cement by determining its role during the precipitation of Calcium Silicate Hydrate (C-S-H) which is the most important hydration product of cement acting as the main binder between anhydrous grains. It is known that low concentrations of minor elements such as zinc in the reactive cement phases can drastically increase the amount of reaction in the first day (main hydration peak). This indicates a potential to increase the reactivity of cement and so allow higher amounts of CO_2 intensive clinker to be substituted by more environmentally friendly materials with lower reactivity, such as granulated blast furnace slag, coal fly ash or calcined clay.

In order to be able to add minor elements such as Zn during the production of cement it is crucial to understand the growth mechanisms, thermodynamics and kinetics of C-S-H precipitation in a controlled environment with and without minor elements. By precipitating C-S-H in presence of different concentrations of Zn and characterizing the resulting samples with different techniques (XRD, TEM and STEM imaging, EDX, TGA and DNP enhanced Si^{29} MAS NMR) we show for the first time evidence that Zn is incorporated in the C-S-H structure. Understanding the role of Zn in the C-S-H structure framework will help us elucidate how to implement this minor element in the cement production in order to be able to allow a higher substitution of CO_2 reactive clinker, and therefore help mitigate the CO_2 emissions of this industry.



[1] Kumar, Abhishek, et al. *The Journal of Physical Chemistry,* 2017, 17188-17196.

[2] L’Hôpital, E., et al. *Cement and Concrete Research* 75, 2015, 91-103.
[3] Andalibi, M. Reza, et al. *Journal of Materials Chemistry,* 2018, 363-373.

Singlet oxygen quantum yields in environmental waters: critical evaluation of measurement techniques

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Singlet oxygen is a photochemically produced reactive intermediate ubiquitous in sunlit aquatic environments and atmospheric aqueous phases. In the past years, there has been a steady increase in the number of publications reporting apparent singlet oxygen quantum yields (Φ_Δ) of natural organic matter samples. Singlet oxygen quantum yields are defined as the ratio of the amount of singlet oxygen molecules produced per photon absorbed by the sensitizer. This parameter is an important piece of information required to model singlet oxygen steady-state concentrations (thus, to model the environmental fate of contaminants and biomolecules), and can also be used to gain insights into fundamental photophysical properties of dissolved organic matter.

Despite this general interest in measuring Φ_Δ, some major technical problems still need to be addressed. The most striking one is the lack of reproducibility in singlet oxygen quantum yields across research groups and publications. This problem stems from a combination of factors, including the overall low values of Φ_Δ (typically, 0.5 – 5 %), the complex chemical nature of the sensitizer, and the considerable variability in experimental conditions.

In this work, we review 58 publications from 1977 to March 2020, and we critically evaluate the techniques that have been used to measure singlet oxygen quantum yields of natural organic matter. We provide an overview of the approaches, and we analyze one by one the various variables that are involved in the calculations. For each variable, we describe what has been done by past authors, and we highlight possible sources of errors based on qualitative and quantitative considerations. Based on this analysis, we identify the rate of light absorption as the most sensitive parameter in Φ_Δ determinations. This work highlights the need for shared general guidelines and validation protocols for quantum yield measurements in the environmental photochemistry community.

Wavelength dependence of singlet oxygen quantum yields from dissolved organic matter

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Singlet oxygen is a reactive species produced photochemically from the chromophoric fraction of dissolved organic matter (CDOM) in sunlit surface waters. As it is involved in pollutant photodegradation reactions and pathogen inactivation, its concentration in natural waters contributes to controlling pollutant lifetime and microorganism fate in the environment. The efficiency by which a given type and source of CDOM produces singlet oxygen is termed the singlet oxygen quantum yield (Φ_Δ), and over the past four decades, the wavelength dependence of this parameter has been investigated. In general, Φ_Δ has been found to decrease with increasing excitation wavelength (lower energy light), however few studies have measured CDOM Φ_Δ far into the visible range. Additionally, typical steady-state experimental methods are limited to measuring Φ_Δ at only a few wavelengths.

In this work, Φ_Δ from CDOM was measured using singlet oxygen phosphorescence, a more direct way of measuring the singlet oxygen produced by a dissolved organic matter sample. This technique takes advantage of tuneable laser output to measure Φ_Δ at a wide range of excitation wavelengths with greater resolution than has previously been measured. We found an approximate linear decrease in Φ_Δ with longer excitation wavelength for two representative organic matter isolates and two unamended natural waters. This work underscores the importance of incorporating the wavelength-dependent behavior of Φ_Δ when investigating pollutant degradation by photochemical processes in the natural environment or in laboratory experiments where a polychromatic light source is used.

Occurrence of natural estrogens in surface waters of a catchment with intensive livestock farming in Switzerland

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Estrogens in surface waters might have negative effects on reproduction and development of aquatic organisms. Agriculture may be a significant source for natural estrogens in surface waters. Several studies in different countries have demonstrated that the application of manure from husbandry animals to soil causes the release of natural estrogens to surface waters. Whereas in the UK agriculturally derived estrogens were found in surface waters, no estrogens were detected in Austrian surface waters and only low estrogenicity was observed upstream of a wastewater treatment plant in Switzerland. Therefore, we aimed to investigate systematically the prevalence of agriculturally derived estrogens in Swiss surface waters to understand better the exposition of aquatic organisms to estrogens. Our surface water monitoring campaign took place in the catchment of Lake Baldegg, which sustains the highest husbandry animal densities in Switzerland. At the beginning of the vegetation period 2019, we collected daily time-proportional composite water samples for 30 days of five Lake Baldegg tributaries. None of the sampling sites contained effluents of wastewater treatment plants. Thereby, we ensured that we measured only agriculturally derived estrogens. We conducted a liquid-liquid extraction, quantified estrone (E1), 17α-estradiol (E2α), 17β-estradiol (E2β) and estriol (E3) chemically with LC-MS/MS. Furthermore, the water samples were analysed with ERα-CALUX. Estrone (max. mean concentration in a tributary: 0.54 ng/L) and E3 (max. mean concentration in a tributary: 0.27 ng/L) were most abundant in time-proportional water samples from Lake Baldegg tributaries. During our sampling campaign, threshold concentrations of natural estrogens in surface waters were never exceeded for longer than a day.

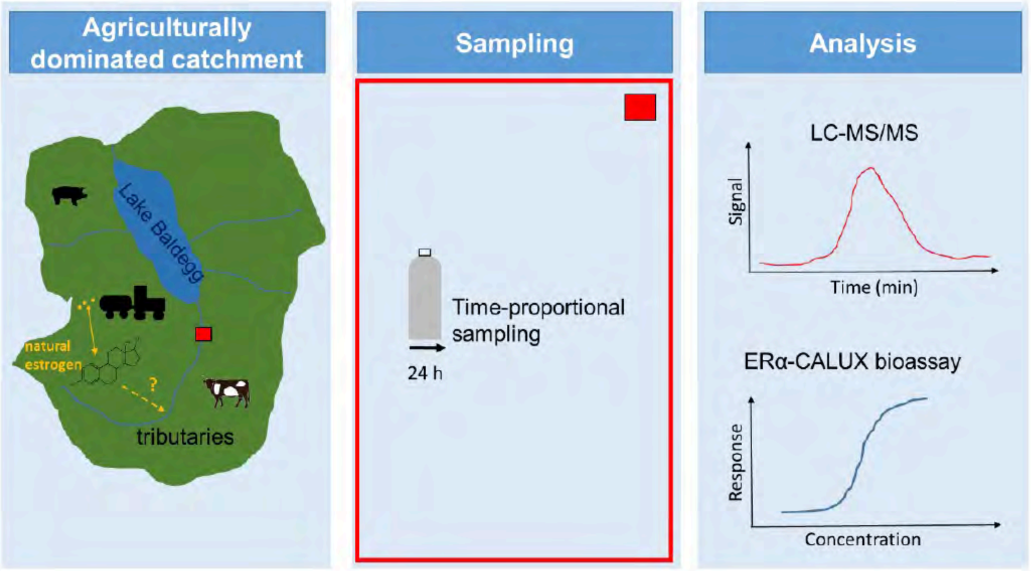

Fig. 1: Study design to assess the occurrence of agriculturally derived natural estrogens in surface waters in the Lake Baldegg catchment.

First Halogenated Greenhouse Gas Measurements at the Beromünster Tall Tower in Switzerland

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Synthetic halocarbons reach the atmosphere as a result of a wide range of anthropogenic activities. Once in the atmosphere, these substances act as strong greenhouse gases and – when containing chlorine and bromine – contribute to the depletion of the stratospheric ozone layer. Therefore, most of the halocarbons are regulated under the Montreal and Kyoto Protocols and country-specific, usually bottom-up derived emission estimates have to be reported via national inventories. In order to monitor the long-term atmospheric abundance and trends of halocarbons, global large-scale measurement networks, such as the Advanced Global Atmospheric Gases Experiment (AGAGE), are in place. However, to better derive regional abundances, characterize and allocate local pollution sources, and to improve top-down validation of country-specific bottom-up emission estimates, additional, less remote observations, focusing on smaller scales, are required. For this purpose, devoted field campaigns at selected tall tower sites combined with top-down modelling offer the possibility to widen the spatial domain in which top-down emissions can be assessed. In Europe, multi-month measurement campaigns were already carried out in the Eastern Mediterranean and Eastern Europe. However, halocarbon emissions from many European regions remain largely unexplored in terms of atmospheric observations.

The present study provides the first continuous halocarbon measurements covering the most industrialized and densely populated area of Switzerland, the Swiss Plateau. The data obtained during a one-year measurement campaign at the Beromünster tall tower in the canton of Lucerne, complement the long-term measurements at the high altitude research station at Jungfraujoch. Measurements were performed via an analytical setup used globally within the AGAGE network[1,2]: Air samples are pre-concentrated in a two-trap process at low temperatures within the specially developed Medusa pre-concentration unit, before the analytes are separated by gas chromatography (GC) and detected by quadrupole mass spectrometry (MS). The acquired atmospheric mixing ratios provide the basis for an improved picture of halocarbon abundance and source allocation in Switzerland, and allow for a quantification of Swiss halocarbon emissions.

[1] Benjamin R. Miller, Ray F. Weiss, Peter K. Salameh, Toste Tanhua, Brian R. Greally, Jens Muhle, Peter G. Simmonds, *Analytical Chemistry*, **2008**, 80, 1536-1545.
[2] Tim Arnold, Jens Muhle, Peter K. Salameh, Christina M. Harth, Diane J. Ivy, Ray F. Weiss, *Analytical Chemistry*, **2012**, 84, 4798-4804.

The role of diatom *Cyclotella meneghiniana* in aquatic Hg species transformations

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Mercury is a persistent contaminant that can cause serious damage to human and environmental health. Despite the low concentration levels, mercury can bioaccumulate in the aquatic organisms, and in the case of organic mercury organic, it can be biomagnified through the aquatic food web posing serious health issues to fish consumers. Primary producers such as phytoplankton species are at the base of the food web, therefore playing a crucial role in the Hg transfer. The aim of the present study is to explore mercury species bioaccumulation and biotransformation capability of diatoms, as representative phytoplankton species. Species-specific isotope tracers technique was used to quantify the uptake, methylation and demethylation by diatom *Cyclotella meneghiniana*. The changes in the ^{199}Hg(II) and/or $^{201}CH_3Hg$ concentrations over exposure time were followed by gas chromatography coupled with inductively coupled plasma mass spectrometry (GC-ICP MS). To account for the contribution of the abiotic transformation, a comparison was made with the system in the absence of diatoms. Results demonstrated a significant accumulation of both Hg(II) and CH_3Hg by *C. meneghiniana,* and CH_3Hg demethylation. Additionally, ^{199}Hg(II) loss due to Hg(II) reduction to Hg0, ultimately released into the atmosphere (via volatilization process) was detected. The implications of the results are discussed with respect to the mercury incorporation at the base of the food-webs and possible contribution of diatoms in Hg cycling.

Keywords: diatom, *Cyclotella meneghiniana*, species-specific isotope mercury, methylation, demethylation, Hg volatilization.

Biotransformation of chemicals in water-sediment suspensions – Influencing factors and implications for persistence assessment

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To date, it remains impossible to fully prevent bioactive and therefore potentially harmful substances (i.e. pharmaceuticals and pesticides) from entering the aquatic environment. Therefore, the EU has regulatory frameworks in place that require the assessment of a substance's environmental persistence in tiered biotransformation studies prior to its market authorization. For the evaluation of chemicals that may enter surface water systems, two testing guidelines are relevant: The OECD 308 guideline, which targets transformation at the water-sediment interface, and the OECD 309 guideline, which assesses transformation in a pelagic water body. Since their introduction, several shortcomings of the OECD 308/ 309 studies have been discussed; in general, study outcomes are often highly variable and in many cases not reproducible. A thorough understanding of relevant transformation processes and system-specific differences is still missing.

This work targets the connection between persistence measured in different regulatory water-sediment test systems and for different types of sediment. Various OECD 308 and 309-type experiments were set up and the fate of 43 substances, mostly pharmaceuticals and pesticides, was followed. Transformation-influencing factors such as the amount and composition of degrader biomass, sorption/ desorption processes, or substance concentration were investigated to gain a better understanding of biotransformation at the water-sediment interface. Investigating influencing biological factors is currently not required from the regulatory side. However, we show that it is crucial to further study those parameters to increase experimental reproducibility of biotransformation data in order to derive robust substance half-lives for regulatory persistence assessment.

The concentration-time series that were observed for the test substances over the time course of the individual experiments varied significantly based on experimental setup and time point of environmental matrix sampling. Greatest variabilities were observed when substances were spiked in water-sediment suspensions (OECD 309-type experiment). Here, biotransformation kinetics of several compounds differed even for experimental replicates. Comparing suspension tests conducted in different environmental matrices showed that the composition and metabolic activity of the microbial community, and its behaviour over time strongly influences biotransformation of trace contaminants to the point that it changes risk assessment outcomes.

While the microbial community in the water phase undergoes dynamic changes over time, its composition appears much more stable in the sediment compartment. Consistently, biotransformation increases while variabilities decrease in test systems with higher amounts of sediment-born biomass. An experimental setup, in which a stagnant sediment layer is covered by an aerated water column (OECD 308-type experiment), showed to be very robust and consistent for biotransformation studies. Extraction of sediment and abiotic controls allowed distinguishing between biotransformation, phase transfer, and abiotic transformation processes in those water-sediment systems.

The measured concentration-time series of the OECD 308-type experiments and transformation-influencing parameters were used to feed an inverse modelling framework to estimate actual biotransformation rate constants. With that, we aim to find a data evaluation system that will allow for comparing different OECD 308 studies to identify persistent chemicals in a consistent manner.

Dissolved organic matter as a modifier of Hg bioavailability to phytoplankton

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Dissolved organic matter (DOM) is recognized to play utmost role in aquatic ecosystems by binding toxic trace metals and thus influencing their speciation, bioavailability and biological effects. According to the current paradigm the organic matter protects aquatic phytoplankton from metal stress. However, in the specific case of mercury, the effect of DOM on Hg bioavailability to phytoplankton in freshwaters is not well understood.

The present study aimed at better understanding the dynamics of the DOM under winter conditions i.e. lake is ice-covered and its role in Hg bioavailability. Water from Lake Onega (Russia) was sampled at three depths and five sites at the River Shuya - open lake intersect under ice-covered and ice-free conditions. Bulk characteristics, the composition and the molar mass of the DOM were determined, as well as the amount of the SH- reactive groups. The role of the DOM as a modifier of mercury bioavailability to phytoplankton were addressed for the first time. Hg bioavailability to green alga *Chlamydomonas reinhardtii*, as a representative phytoplankton specie, was characterized by determining whole cell and intracellular Hg concentrations during the exposure to Lake Onega waters enriched with 1 and 10nM of $Hg(NO_3)_2$ to mimic a strong pollution input.

The results showed a quite high DOC concentrations, typical for humic-rich waters of the boreal areas, following a gradual decrease from River Shuya to open lake both under ice-cover and ice-free lake. Refractory humic like component of fulvic type (FA), represented about 80% of the organic matter pool in the size range from 300Da to 0.45mm, independently of the sampling site location, depth, presence or not of ice-cover. Flow field-flow fractionation coupled to fluorescence detector and ICP-MS revealed a prevailing association of Hg to FA fraction, however a Hg was also found in high-size Al, Fe and Mn containing colloids. The whole cell and intracellular Hg concentrations were lower in alga exposed in water sampled from ice-free than from ice-covered lake. However no specific trends in the Hg uptake by *C. reinhardtii* were observed over DOC concentration gradients, showing that the DOC is not a good predictor of Hg buffering capacity of natural waters. A negative correlataion between whole cell and intracellular Hg and –SH concentrations, fluorescence and humification indexes was found. Such relationships evidenced possible negative feedbacks with these DOM characteristics and Hg bioavailability. The significance and implications of the results are discussed with respect to the narrowing the gap in lab-to-field extrapolation.

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Dating the recent past. chronometirc potential of Si-32 | Part 1: Chemical separation and preparation in a pure state

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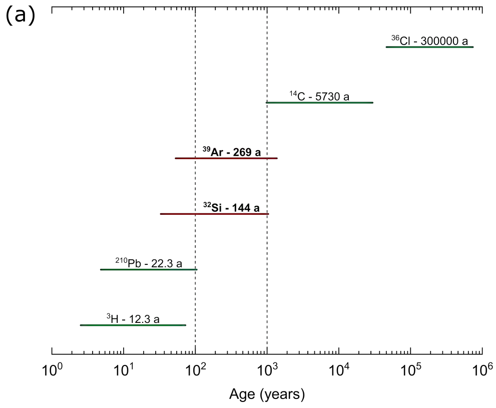
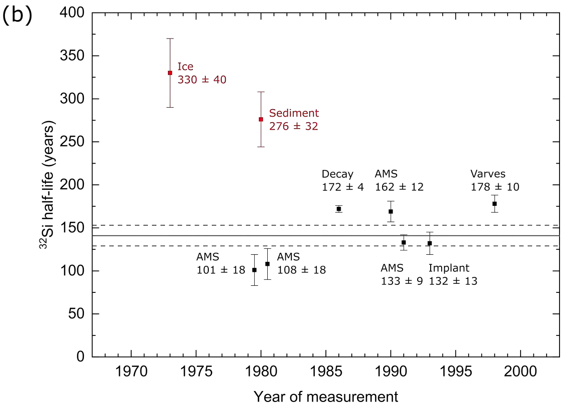
Cosmic-ray-induced spallation of ^{40}Ar in the atmosphere leads to a continuous production of ^{32}Si, which is transferred to Earth's surface by precipitation, and subsequently deposited in terrestrial sediments, snow, and ice.[1] As a result, ^{32}Si is of primary interest concerning the application in environmental sciences, as it has the potential to fill the current dating gap (**Fig. 1a**) that lies between those chronologies based on the isotopes of ^{210}Pb ($T_{1/2}$ = 22.3 a) and ^{14}C ($T_{1/2}$ = 5730 a). The prerequisite to finding an application as a geochronometer is thus a precisely determined half-life. However, several attempts to determine the half-life of ^{32}Si led to notable discrepancies, including large uncertainties in the actual half-life determination (**Fig. 1b**). Accordingly, as the very imprecisely determined half-life is an actual deal-breaker for the application as a geochronometer,[1,2] a more precise and accurate determination remains necessary.

Generally, the annual atmospheric production of ^{32}Si is severely low, resulting in a rare natural abundance. Therefore, an alternative way was chosen by the artificial production of the radionuclide at the Paul Scherrer Institute (PSI) by a two-year proton-irradiation of metallic vanadium using PSI's 590 MeV ring cyclotron. As a result, around 20 MBq of ^{32}Si are available, exceeding previously reported activities by several orders of magnitude. Here, the authors present a radiochemical separation procedure that allows the preparation of ^{32}Si samples with high purity. Applying cation- and anion-exchange chromatography combined with extraction chromatography, it was possible to separate silicon from the vanadium matrix and various spallation products. Finally, ^{32}Si-fractions of high activity concentrations could be obtained.

Concerning the re-determination of the ^{32}Si half-life, complementary measurements with different techniques such as Liquid Scintillation Counting (LSC), Accelerator Mass Spectrometry (AMS), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) will be utilized. For this, a collaboration with different partners has been established, e.g., with leading experts in radionuclide metrology.





[1] Keith Fifield, Uwe Morgenstern, *Quaternary Geochronology*, **2009**, 4(5), 400-405.
[2] Dinkar Kharkar, Karl Turekian, Martha Scott, *Earth and Planetary Science Letters*, **1969**, 6(1), 61-68.