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Oxidation processes for micropollutant abatement: An Eldorado for environmental chemists

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The field of oxidative water treatment has evolved significantly in the last decades. Initially, disinfection was the main focus, but more recently oxidation processes such as ozonation are widely applied for micropollutant abatement. Initially research and application focused on the disappearance of target compounds, however, nowadays the formation of transformation products is an important issue, because they can be detected thanks to improved analytical tools. Furthermore, the question about the toxicological relevance of transformation products for water quality has to be considered. Based on these concerns, it is obvious, that (eco)toxicological test procedures of such processes needed to be included in the overall assessment. Furthermore, the biodegradability of transformation products emerged as an important topic for the assessment of the relevance and fate of these compounds. The strong focus on the feasibility of micropollutant abatement during ozonation should not distract from the fact, that most of the oxidation power is lost to the organic matrix (dissolved organic matter, DOM). To this end, knowledge from the reactions of individual compounds can be applied to assess the reactivity of DOM with ozone and allows to potentially predict the formation of oxidation byproducts. In the future, the broad knowledge gained in the last decades should be compiled for the development of prediction models for kinetics, transformation product formation and (eco)toxicity, to improve the assessment of oxidation processes in general beyond a case by case evaluation of individual organic micropollutants.

Combination of advanced analytical tools with toxicological assays promote the understanding of transformation reactions occurring during wastewater ozonation

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Ozonation is increasingly integrated into wastewater treatment trains to abate micropollutants, which are known to induce adverse effects to aquatic organisms in receiving water bodies. While ozonation has been found to enhance the biological quality of wastewater as reflected by the reduced toxicity in a range of bioassays, concerns remain with regard to the potential formation of toxic (mutagenic/genotoxic) ozonation byproducts (OBPs) and ozonation transformation products (OTPs) from ozone reactions with the matrix components and with micropollutants, respectively. While most of the toxicity is thought to originate from OBPs as they are typically formed at orders of magnitude higher levels than OTPs, the latter can be used as a tracer to elucidate unknown reaction mechanisms. Except for some specific byproducts such as bromate and nitrosamines, little is so far known about the identity of toxic OBPs/OTPs and their formation pathways. Such an understanding is essential to ensure the optimization of wastewater treatment processes and for the potential implementation of source control measures limiting the introduction of problematic precursors into wastewaters. However, the complexity of wastewater samples along with the typical occurrence of OBPs and OTPs at trace concentration levels constitute main challenges when the identification of unknown reaction pathways is sought. Non-target analysis based on high-resolution mass spectrometry (HRMS) applied synergistically with toxicological assays can constitute a powerful tool to address these challenges and discover unknown toxicologically relevant byproducts. The present study aimed at the identification of unknown reactions that might be relevant with regard to the induction of mutagenicity in ozonated wastewaters. Samples were collected at different wastewater treatment steps: secondary treatment, ozonation, and biological filtration. Solid-phase extraction was performed for enrichment followed by liquid chromatography HRMS/MS and toxicological assays. Prioritization of signals was achieved by comparing their occurrence and intensity in the categorized samples (secondary treatment vs. ozonation vs. biological filtration). Compound identification efforts focused on prioritized compounds classified as OTPs/OBPs and were based on isotope patterns, retention time, and fragmentation spectra. The applied workflow revealed the formation of nitration products during ozonation. Considering the potential toxicity of nitro compounds in general and the recently discovered role of nitrite in the formation of mutagenic compounds during ozonation, this nitration pathway is considered toxicologically relevant. This study highlights how a synergistic approach involving the application of robust non-target screening and toxicological assays can contribute to enhancing our understanding of oxidative wastewater treatment.

Laboratory validation of a laser absorption spectrometer for balloon-borne measurements of upper air water vapor

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Water vapor (H_2O) in the upper troposphere-lower stratosphere (UTLS) is of great importance to the Earth's radiative balance. However, accurate measurements of H_2O in this region are notoriously difficult, and significant discrepancies were found in the past between different techniques. Currently, cryogenic frostpoint hygrometry is considered as the reference method for balloon-borne measurements of UTLS H_2O [1]. However, these devices are currently undergoing a fundamental reconception due their use of fluoroform (HFC-23) as cooling agent, which must be phased out due of its high global warming potential. Here, we present a new mid-IR quantum-cascade laser absorption spectrometer for balloon-borne measurements of UTLS H_2O (ALBATROSS). The spectrometer incorporates a specially designed segmented circular multipass cell that allows an optical path length of 6 m [3], while meeting stringent requirements in terms of mass (< 3.5 kg), size, and temperature resilience. Two successful test flights demonstrated the instrument's outstanding capabilities under real atmospheric conditions up to 28 km altitude [2].

The accuracy and precision of ALBATROSS at UTLS-relevant conditions were validated by a laboratory campaign at the Swiss Federal Institute of Metrology (METAS). Using a dynamic-gravimetric permeation method [4], we generated SI-traceable reference mixtures with H_2O amount fractions as low as 2.5 ppmv in synthetic air. The results show that ALBATROSS achieves an accuracy better than ± 1.5 % at all investigated pressures (30-250 mbar) and H_2O amount fractions (2.5-35 ppmv), and a precision of 0.3 % at 2.5 ppmv H_2O and 1 s resolution. Precision can be further improved until 2 ppbv by integrating the measurements in time over approximately 100 s. ALBATROSS also achieves a linear response within ± 2 ppmv up to 180 ppmv H_2O. Overall, this represents an unprecedented level of accuracy and precision for a balloon-borne hygrometer. ALBATROSS recently participated to the AquaVIT-4 international intercomparison of atmospheric hygrometers (Karlsruhe, Germany) [5], and further in-flight validation campaigns are planned in 2022.

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In situ quantification of Cobalt and Nickel in natural waters using innovative chemical sensors

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Assessing the impact of trace metals on aquatic ecosystems and ultimately human health is challenging. Trace metals are distributed in a variety of redox states and chemical species that may vary continuously in space and time [1,2]. Only some trace metal species are bioavailable. The development of robust and adaptive submersible sensitive trace metal bioavailability-assessment tools is therefore required to support the establishment of environmental quality standards and guidelines based on realistic risk assessment to protect aquatic life and biodiversity, and ultimately human health.

Toward this aim, we developed on-chip chemical sensors consisting of an array of interconnected iridium-based microdiscs that are electroplated with appropriate sensing elements and covered with a hydrogel as efficient antifouling membrane [2,3]. Incorporated in in-house submersible probes and interrogated by Square Wave Anodic Stripping Voltammetry (SWASV), these gel-integrated microelectrode arrays (GIME) allow for the direct *in situ* quantification of the dissolved metal species that are available for uptake by phytoplankton (first chain of the food-web) [2.3]. To date, only trace metals that can be electrochemically reduced and pre-concentrated at the surface of the electrode could be measured. A wider range of trace metals may become accessible by adsorptive cathodic stripping voltammetry (AdCSV) as this approach allows for preconcentration by electrochemical adsorption of trace metal complexes upon adding a selective complexing agent to the sample. This technique has been mainly applied with renewable mercury or bismuth film electrodes. However, the renewal of the sensing element after each measurement is difficult to adapt for *in situ*measurements.

We report here on the optimization and evaluation of AdCSV on GIME for the direct quantification of the sufficiently labile Co and Ni dissolved species in aquatic systems mediated by a ligand on a time scale of less than 10 minutes. The methodology was first characterized and validated in laboratory. The optimized protocol was then applied on a GIME incorporated in a submersible probe to *in situ* determine the sufficiently labile Co and Ni dissolved species in both fresh and sea waters. In addition, samples were collected to analyze the total acid-leachable (unfiltered samples), the total dissolved (0.2 µm filtered samples) and the “truly” dissolved (0.02 µm filtered samples) fractions. The combination of these four fractions allowed to better assess the Co and Ni speciation in the environment, something never achieved before. Selected examples of analytical optimization results in the laboratory and of field outcome will be presented.

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Acidity of expiratory aerosols controls the infectivity of airborne influenza virus and SARS-CoV-2

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The current pandemic has added to the growing evidence that respiratory viruses can be transmitted by the airborne route, yet the parameters modulating the infectivity of viruses in aerosol particles are poorly understood. Aerosol particles in the natural environment can by highly acidic, and acidic pH is known to reduce the persistence of some respiratory viruses. Yet, the pH of expiratory aerosol particles in indoor air and its effect on virus transmission remains unknown.

In this work, we assessed the role of aerosol pH in virus inactivation, and we evaluated if pH control of indoor air can reduce airborne virus transmission. The inactivation of influenza A virus (A/WSN/33) and two coronaviruses (hCoV-229E and SARS-CoV-2) was monitored in surrogate lung fluid (SLF) over a pH range of 2.1 to 7.4. The physicochemical properties of micron-sized SLF droplets, such as the water diffusion coefficient, were determined by injecting a fluid droplet into an electrodynamic balance (EDB) and measuring the relative changes in mass and volume upon changes in relative humidity. The physicochemical and virological data were then integrated into a biophysical aerosol model, to determine inactivation as a function of relative humidity, air composition and aerosol particle size.

Influenza virus was found to be readily inactivated at pH < 5, leading to airborne inactivation over the course of hours to minutes, depending on the size of the carrier particles. In contrast, coronaviruses are much more stable and can remain infectious within aerosol particles for days. The model results suggest that the addition of 50 ppm nitric acid to indoor air lowers the aerosol pH below 2 and thereby causes a dramatic decrease in inactivation times for influenza virus and SARS-CoV-2, and to a lesser extend for hCoV-229E. Alternatively, air acidification can be achieved by scrubbing of gaseous ammonia, though the resulting reduction in aerosol pH is insufficient to reduce coronavirus persistence. Finally, the model also suggests that the enrichment of air with nitric acid is more effective than ventilation or air filtration to limit the relative risk of virus transmission in indoor environments. Consequently, pH control may be an effective strategy to limit the transmission of a disease in indoor environments such as hospitals and schools.

Adsorption and transport of water-soluble, biodegradable polymers in soils: Process elucidation using experimental model systems

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Synthetic structural polymers in plastics are used ubiquitously and are indispensable for our daily lives. However, most of these polymers are highly persistent and accumulate in the environment if improperly disposed of after use. This accumulation of plastic has triggered a scientific discussion about potential associated risks for humans and the environment. In contrast to structural polymers, the environmental fate and potential persistence of water-soluble polymers have received much less attention and remain poorly studied and understood. Yet, water-soluble polymers are used in many applications, which result in a direct release of these polymers into the environment (e.g., water-soluble polymers in agricultural spray formulations). Akin to structural polymers, such emissions are problematic if the water-soluble polymers are persistent and accumulate over time. One promising solution to overcome accumulation and potentially associated ecological risks is to replace conventional with biodegradable, water-soluble polymers. Our research focuses on the fate of water-soluble polymers in soils and the elucidation of adsorption and transport processes affecting biodegradation. In this contribution, we report on systematic analyses of the forces driving adsorption of six different water-soluble polymers (Dextran, Diethylaminoethyl-dextran. Carboxymethyl-dextran, Poly(ethylene glycol), Poly-L-Lysine, Poly(acrylic acid)) to silica and iron-oxide surfaces, two minerals common to most soils. The polymers were fluorescently labelled to follow adsorption and transport in packed columns at low, environmentally relevant polymer concentrations. The effects of solution pH and ionic strength (IS) on adsorption to silica were studied using batch solution depletion experiments and surface adsorption techniques, including quartz crystal microbalance with dissipation monitoring and optical waveguide lightmode spectroscopy. Transport of these polymers in porous media was determined in water-saturated sand- and iron oxide-coated sand (IOCS) -columns, followed by fitting the polymer breakthrough curves using the advection-dispersion equation with a Langmuir adsorption term. Besides electrostatic interactions between the polymers and the mineral surfaces, polymer conformations in the adsorbed states and hydrogen bonding appear to determine adsorption capacities and, therefore, the extent of polymer transport through columns. The implications of the findings for the fate of water-soluble polymers in soils will be highlighted.

Investigating the Applicability of Laboratory derived Toxicokinetics to the Field

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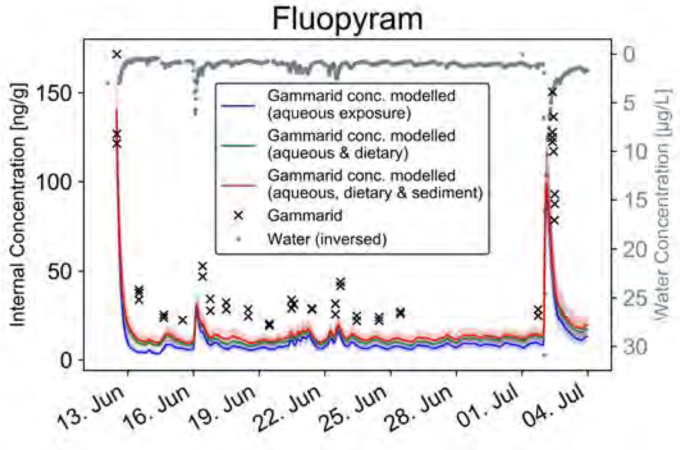
Knowledge on bioaccumulation and biotransformation of organic micropollutants are essential to link exposure to effect and to designate appropriate environmental quality standards. Bioaccumulation and biotransformation of organic micropollutants in aquatic organisms have been investigated in laboratory experiments extensively. For several micropollutants, especially pesticides, however, the measured internal concentrations in gammarids in field trials exceeded the predictions based on the laboratory data, sometimes by multiple orders of magnitude.

In this work, we tested the applicability of laboratory derived toxicokinetic rate constants for caged gammarids deployed in a small Swiss stream known for high pesticide loads. Using an automated mobile LC-ESI-HRMS/MS system, the aqueous concentrations of 49 pesticides were measured at high temporal resolution throughout several rain events during the application season (every 20 min for 1 month). The water concentrations from this study were then employed to model the whole body concentration of gammarids using a one-compartment toxicokinetic model with toxicokinetic rate constants derived in an accompaning lab study. This data was then compared to the measured whole body concentration of the caged gammarids. Furthermore, the pesticide concentrations in the stream sediment, dietary source (leaves) as well as in suspended particles during rain events were measured and used to model their effect on the bioaccumulation of the pesticides.

Our results show that the internal pesticide burden of gammarids is highly dynamic, with the aqueous exposure as the main influencing factor. While the laboratory derived toxicokinetic rate constants predicted the temporal trends in whole body concentrations reasonably well, the values were systematically underestimated over the whole time period. The highest underestimation occurred shortly after rain events with the model underestimating the pesticide concentrations by a factor of up to 31 ± 3.0. Finally, we demonstrated that while uptake from sediment does not contribute significantly to the total body burden even under worst case uptake assumptions, the suspended solids had considerably higher pesticide concentrations than the sediment and could explain the observed underestimation after rain events partially. Further possible reasons such as decreased biotransformation under field conditions or concentration dependence of the toxicokinetics are currently explored.



Organ-specific biotransformation in salmonids: insight into enzyme kinetics and micro-pollutant clearance

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The bioaccumulation potential of environmental pollutants is significantly influenced by the organism's ability to biotransform chemicals. For aquatic animals, like fish, bioaccumulation evaluations have largely focused on the biotransformation capacity of the liver as the organ responsible for a large proportion of biotransformation activity. However, there is limited knowledge regarding extrahepatic biotransformation and the ability of different organs to support biotransformation processes. In the present study, we provide insight into organ-specific biotransformation through evaluation of *in vitro* phase I and II biotransformation enzyme kinetics, estimation of intrinsic clearance, and the formation of biotransformation products of selected micro-pollutants (e.g. pharmaceuticals and pesticides). Comparative studies using the liver, intestine, gills, and brain of two salmonid species, rainbow trout (*Oncorhynchus mykiss*) and brown trout (*Salmo trutta*), suggest that, while the liver displays the highest activity of specific Cytochrome P450 (phase I) and conjugation (phase II) enzymes, significant activity is also observed in other organs, with certain enzymes, such as CYP2B, displaying similar activity as in the liver. Moreover, based on preliminary chemical analysis, it is likely that the organ-specific clearance and biotransformation product formation of pharmaceuticals and pesticides is proportional to the specific activity of enzymes responsible for their biotransformation. These observations have significant implications for environmental hazard and risk assessments, where the consideration of different biotransformation pathways in different organs would be beneficial for predicting the bioaccumulation potential of chemical pollutants.

enviRule: An End-to-end System for Automatic Extraction of Reaction Patterns from Environmental Contaminant Biotransformation Pathways

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Pesticides are widely used all over the world in large quantities and are now taken as major environmental pollutants. Pesticide transformation products (TPs), formed in the environment, can have similar or even more serious adverse environmental effects than parent pesticides. However, the experimental characterization of TPs is time-consuming and labor-intense. Several tools for the *in silico* prediction of TPs have therefore been developed over the past few decades (e.g., envipath.org). One key challenge in developing *in silico* prediction tools is the extraction of reaction rules from biotransformation reaction databases. So far, in the majority of existing tools, rule extraction has been done non- or half-automated, requiring manual interference at several points in the rule extraction procedure. Typically, the degree of specificity of the thus extracted rules is arbitrary and non-validated, meaning that resulting rules are likely to produce too many false positives or too few true positives. Additionally, databases on biotransformation reactions are constantly growing, but adapting existing rules to cover new reactions becomes quickly intractable for manually extracted and curated rules. In our project, we developed an end-to-end automatic rule generation tool called enviRule, which does not require any manual interference for rule generation or adaption. enviRule consists of three main functional modules, namely, reaction clusterer, reaction adder, and rule generator. It is capable of clustering biotransformation reactions into different groups based on the similarities of reaction fingerprints, and of then extracting and generalizing reaction patterns for each reaction group as SMIRKS. The specificity of each rule can be automatically adjusted through a feedback loop until the rule achieves a decent ratio of true positive over false positives. When new reactions are added, they are distributed into existing reaction groups with similar reaction fingerprints, and the corresponding rules of these groups are then automatically self-updated. Using the enviRule tool drastically decreases the time required for rule extraction compared with manual design. Additionally, high recall and precision were achieved when using the automatically extracted rules in combination with machine learning models. Most importantly, to the best of our knowledge, enviRule is the first tool that implements automatic rule adaption to deal with the growing number of reported biotransformation reactions.

Development and scale-up of bio-based solvents by carbohydrate functionalization

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Nowadays solvent use in industry is facing increasing regulatory and commercial pressure due to tightening legislation and an evolving awareness of health and safety issues. In parallel, growing environmental concerns over the source and life cycle of common solvents encourage the development of bio-based alternatives that can compete with petroleum-derived counterparts.

Lignocellulosic biomass is a promising feedstock for the production of renewable solvents since it is available in large quantities and does not compete with food crops. Several biomass-derived solvents have been developed and commercialized so far. However, their use in industry is still considered problematic due to various reasons such as high production cost (GVL, Dimethyl isosorbide), high flammability (2-Me-THF), instability in harsh conditions (Cyrene, cyclic carbonates). Newly emerging candidates that aim to replace hazardous analogs are also facing challenges. In this regard, acetal-stabilized xylose derivatives that can be inexpensively produced directly from biomass at over 90% yield (on a xylan basis) by aldehyde-assisted fractionation technology developed in our lab could be interesting candidates for use as solvents[1].

In this work, we explored diformylxylose (DFX) and its derivatives as potential solvents by assessing their performance in model reactions, as well as measuring their physical and solvatochromic parameters. DFX was found to have similar solvation properties to conventional polar aprotic solvents such as NMP, DMF, DMAc, while DFX’s derivatives were closer to medium-polarity solvents such as acetone and THF, according to a comparison of Kamlet-Abboud-Taft parameters. The specific properties of DFX made it a promising component of deep eutectic solvents, which were also prepared in this work. Hansen Solubility Parameters indicated that DFX has high similarity to Dimethyl Isosorbide while being potentially much less expensive. At the same time, DFX's derivatives can complement the list of conventional ethers and ketones, while bringing new physical properties and, possibly, a safer profile.

Notably, we demonstrated that performance of the developed solvents in alkylation, cross-coupling, and hydrogenation reactions was comparable with conventional problematic analogs and in some cases outperforming existing green alternatives[2]. DFX was also found to have potential in many other applications including polymer synthesis, solid-phase peptide synthesis, biomass processing, liquid exfoliations, etc.

A preliminary toxicological assessment (bacterial Ames test) performed on DFX showed that this molecule is unable to cause mutations both directly and indirectly and cannot be considered a mutagenic compound.

Finally, we demonstrated that DFX and its derivatives can be produced sustainably from biomass, specifically corn cobs in a kg-scale. This shows an excellent example of how waste biomass can be valorized into valuable chemicals with relatively low cost and high efficacy. A life cycle assessment has been performed, which demonstrated high competitiveness of this new class of solvents against conventional analogs.

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Decentralized solar ammonia: performance targets for environmental and economic benefits

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Decoupling the synthesis of ammonia from the use of fossil fuels is critical to sustainably meet the projected increase in the demand for fertilizers due to the growing population. In contrast to intense efforts devoted to developing a green Haber-Bosch (HB) process, the feasibility of decentralized sustainable ammonia production has yet to be assessed. In fact, a distributed approach could facilitate the establishment of an ammonia economy, where this compound plays the double role of precursor for other chemicals and of energy vector.[1] Herein we assess the question of where and to what extent solar ammonia may be a valuable strategy. Small-scale reactors performing electrocatalytic reduction of nitrogen powered by photovoltaic energy (NH_3-leaves) are studied, assuming water as a direct co-reactant. We included scenarios where the water electrolysis reaction yields hydrogen as a by-product, later converted on-site with a fuel cell, to account for the imperfect selectivity of the best state-of-the-art electrolyzers. The environmental and economic impacts of the selected processes were assessed, employing the global warming impact (GWI) and the levelized cost of ammonia. We found that environmental benefits are maximized for GWI. Several technical parameters were varied in the analysis, leading to an atlas of breakeven electricity-to-NH_3 efficiencies required to outperform industrial and green HB (GHB) on the assessed metrics worldwide. Modest values of less than 19% (HB) and 22% (GHB) are sufficient for the average irradiation in the case of GWI, values already comparable to the current state-of-the-art efficiency.[2] Production costs are estimated between ca. 1.5 and 25.7 USD kg_{NH3}^{-1}. These performance requirements can guide the development of NH_3-leaves and suggest that they may become a strong ally of GHB to develop a sustainable ammonia production scheme.

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Significant Enhancement in Performance of Sb_2Se_3 Photocathode via Sequential Etching and $CuCl_2$ Treatment

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In an effort to further improve the auspicious Sb_2Se_3 thin films for photoelectrochemical water-splitting in a low-cost manner, simple and low temperature treatments were explored. The FTO/Ti/Au/Sb_2Se_3 semiconductor is treated with $(NH_4)_2S$ as an etching solution followed by $CuCl_2$ treatment which collectively increased the onset potential from 0.15 V to 0.28 V vs reversible hydrogen electrode (RHE) and the photocurrent from 17 mA cm^{-2} to 22.5 mA cm^{-2} at 0 vs RHE as compared to the untreated Sb_2Se_3 films. From SEM and XPS studies it is clear that the etching treatment induces a morphological change as well as removes the surface Sb_2O_3 layer. $CuCl_2$ then further enhances the performance due to the passivation of the surface defects, improving charge separation at the interface. The simple and low-cost semiconductor synthesis method combined with these facile, low-temperature treatments further increase the practical potential of Sb_2Se_3 for large scale water splitting.

Biodegradation of mulch films in Swiss agricultural soils assessed in laboratory, mesocosm and field incubations

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Non-biodegradable polyethylene mulch films are widely used in agriculture to allow for an earlier harvest and improved crop yields. These mulch films are, however, difficult to completely recollect from the field after use. Residual mulch film pieces can accumulate in soils over time, thereby negatively impacting soil productivity and turning agricultural soils into sources of plastics to surrounding environments. Mulch films certified as biodegradable in soils promise to be a solution to these problems. Yet, a thorough assessment of the biodegradation dynamics of biodegradable mulch film products in soils in the field is lacking. So far, certification relies exclusively on laboratory soil incubations coupled to respirometric analysis of CO2 formed from the mulch films during biodegradation. Respirometric analyses are, however, very challenging to implement in field incubation studies. To overcome the lack of appropriate analytical techniques for residual mulch film quantification in soils, our group has developed a methodology to extract and quantify the main synthetic polymeric components of mulch films, poly(butylene adipate-co-terephthalate) (PBAT) and polylactic acid (PLA), from soil. The methodology is based on exhaustive Soxhlet extraction coupled to quantitative 1H-NMR of extracted PBAT and PLA. Here, we use this approach to assess the biodegradation of two biodegradable mulch films commercially available in Switzerland in three Swiss agricultural soils in a multiyear incubation study. These incubations are conducted in three experimental incubation scales: flasks in the laboratory, mesocosms in a greenhouse and the actual field. We statistically compare biodegradation rates and extents between three soils and two tested films across the three incubation scales. Thereby, we assess the transferability of biodegradation results from laboratory incubations to field incubations. Our results highlight variations in biodegradation between soils and polyesters and call for caution when using laboratory incubation studies to predict biodegradation in the field.

The Bioaccumulation of Anionic and Cationic Organic Compounds in Rainbow Trout Cell

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Keywords: in-vitro systems, bioaccumulation, alternatives to animal experimentation, ionizable organic compounds

The assessment of chemicals for their bioaccumulative potential requires *in vivo* testing with fish, which is resource intense, costly, time consuming and of ethical concern due to the sacrifice of animals. Therefore, alternative *in vitro*models are being sought to replace these tests with fish.

In this work, we explore how well rainbow trout (*Oncorhynchus mykiss*) cell lines, in particular RTL–W1 (liver) can predict the bioaccumulation and biotransformation potential of ionizable organic compounds (IOC) in fish. IOC comprise a large proportion of the chemicals in commerce and are ubiquitously detected in the environment and biota. Based on the availability of high quality *in vivo* data and the substances' charge state at physiological pH, four anionic and three cationic compounds were selected: Pentachlorophenol (PCP, CAS 87-86-5), Diclofenac (DCF, CAS 15307-79-6), Tecloftalam (TT,CAS 76280-91-6) and Benzotriazol-t-butyl-hydroxyl-phenyl propanoic acid (BHPP, CAS 84268-36-0); and N,N,N-trimethyltetradecylamine (Q14, CAS 4574-04-3), N,N-dimethyldecylamine (T10, CAS 1120-24-7) and N-methyldodecylamine (S12, CAS 7311-30-0). First, non-toxic chemical concentrations were determined for each compound following the acute cell toxicity assay (OECD TG249), resulting in exposure concentrations that ranged from 5 µg/L to 200 µg/L for further assessment. The kinetic experiments were performed over 48h and 72h for anions and cations, respectively, with a total of 6 sampling time points. Cell, medium and plastic fraction were sampled separately at each time point and measured using high resolution tandem mass spectrometry after online solid phase extraction (for anions) or with direct injection of extracts (for cations). The anionic compounds, given as a fraction of the total compound mass in the test system, accumulated at steady state in the following order in RTL-W1 cells: BHPP (7%) > TT (5%) > PCP and DCF (below limit of quantification, 0.5 to 0.1% respectively). In contrast, the tested cations were associated with cells to a much larger extent. Measured as fractions of total compound mass in the test system, the RTL-W1 cells contained at steady state 30 % for T10, 75 % for S12 and 87 % for Q14. Finally, the compound's predicted bioconcentration factors based on their octanol affinity (K_{ow} or D_{ow}) or their membrane lipid affinity (D_{mlw}) were compared with the *in vitro* derived steady-state bioconcentration factors. From these comparisons it could be concluded that the tested compound's accumulation in the cells is strongly driven by the compound's interactions with the cell membrane of the RTL-W1 cells, represented through D_{mlw} ($R^2 = 0.93$).

Solution and gel-phase quantification of lignin structural features with improved 2D-HSQC$_0$ NMR processes

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Lignin upcycling towards renewable aromatic monomers can be performed by depolymerization. Most strategies rely on ß-O-4 ether cleavage because they are the most abundant and the easiest to cleave. However, the issue of quantifying lignin's initial structural features has made assessing the efficiency of lignin extraction and its upgradability difficult, especially in whole cell walls where gel phase are typically used. We previously demonstrated promising results to quantify lignin ether functionalities with the use of 2D-HSQC$_0$ NMR. Here, we developed an improved and rapid high-temperature HSQC$_0$ sequence with automatized peak fitting that avoids past errors related to user bias, relaxation and magnetization transfer, notably using polystyrene as a standard. Structural features of synthetic polymer model compounds were successfully quantified, with less than 5% error. This approach also allows quantification of features on gel-phase NMRs, which could allow precise quantification of lignin features in whole cell wall samples. We are using this analytical method on a wide range of lignin streams to predict relationships between lignin structure and reactivity. In particular, current efforts to use this method on both whole plant cell walls and extracted lignins are being used to elucidate longstanding questions regarding lignin extraction mechanisms.

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Non-target screening reveals the identity of carbonous and nitrogenous carbonyl-containing oxidation byproducts formed during ozonation of various water types

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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 and hydroxyl ($^{\bullet}OH$) reactions with matrix components such as dissolved organic matter (DOM). This leads to the formation of undesired oxidation byproducts (OBPs) such as low molecular weight aldehydes and ketones. By applying a recently developed non-target workflow, 180 carbonous and nitrogenous carbonyl compounds were detected during bench-scale ozonation of two lake waters and three wastewater effluent samples. A core of carbonyl compounds was detected in all water types. Wastewater effluents showed a significantly higher share of *N*-containing carbonyl compounds (30%) compared to lake water (17%). Formation trends upon ozonation and comparison of the results to conditions in the presence and absence of the $^{\bullet}OH$ radical scavenger DMSO in combination with kinetic and mechanistic information allowed to draw conclusions on potential carbonyl structures. A link between the detected carbonyl compounds and their precursors was established by ozonating six model compounds (phenol, ethylphenol, methoxyphenol, sorbic acid, 3-buten-2-ol and acetylacetone) which formed around one third of the detected carbonous carbonyl compounds detected in real waters. Several carbonyl compounds were identified, including hydroxylated aldehydes and ketones (e.g. hydroxyacetone, confidence level (confidence level (CL) = 1), unsaturated dicarbonyls (e.g. acrolein, CL = 1; 2-butene-1,4-dial, CL = 2; 4-oxobut-3-enoic acid, CL = 2) and also a nitrogen-containing carbonyl compound (2-oxo-propanamide, CL =1).

Insights on the carbonation mechanism of alkali metal nitrate promoted MgO by ^{18}O isotope labeling

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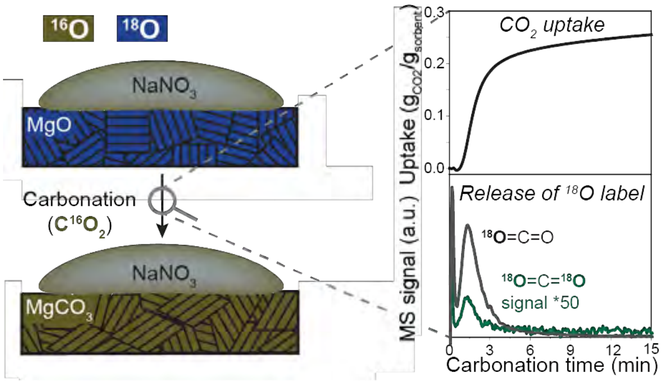
MgO-based CO_2 sorbents promoted with alkali metal nitrates (e.g. $NaNO_3$) are promising materials for CO_2 capture and storage technologies due to their low cost and high theoretical uptake capacities. However, the exact mechanism by which molten alkali metal nitrates promote the carbonation of MgO is highly debated. Here, we provide insights into the carbonation mechanism of alkali metal nitrate promoted MgO with the help of ^{18}O isotope labeling experiments. We developed facile synthesis methods to yield MgO and $NaNO_3$ with high ^{18}O-content. ^{18}O labeling experiments complemented by Raman spectroscopy, in situ thermogravimetrical analysis in combination with mass spectrometry on model MgO-based CO_2 sorbents allowed for the tracking of the ^{18}O label in both the solid ($NaNO_3$ and $MgCO_3$) and gas phase (CO_2). Our experimental work provides evidence for a rapid oxygen exchange between CO_2 and MgO that is taking place at the surface of MgO. Based on these findings in combination with density functional theory calculations, we discuss potential promotion mechanisms.



Schematic of a carbonation experiment in which $NaNO_3$–promoted $Mg^{18}O$ is reacted with CO_2 at 315 °C. In situ thermogravimetrical analysis in combination with mass spectrometry shed light on the oxygen exchange reaction occuring during carbonation.

The Impact of Temperature on Biodegradation of Poly-3-hydroxybutyrate-3-hexanoate (PHBH) in Soil

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Biodegradable polymers have gained attention as an important conventional polymer material substitute in applications where plastics enter the organic waste stream or where plastics entering the environment is probable. Current certification of soil biodegradability relies on laboratory soil incubations at constant temperature coupled to respirometric analyses of polymer conversion to CO_2. However, the transferability of biodegradation results from laboratory experiments at elevated temperatures (25 ºC) to the field with variable and lower temperatures has been called into question. Primarily, we do not understand how temperature impacts the rate of polymer biodegradation. In this work, we have determined the effect of temperature on biodegradation using a readily biodegradable polymer, poly-3-hydroxybutyrate-3-hydroxyhexanoate (PHBH), by tracking the decrease in the amount extractable from soil using extraction and ^{1}H-NMR as well as by imaging methods of PHBH films to understand microbial colonization dynamics on the polymer surface. To this end, we incubated PHBH in three different types of standard LUFA soils (6S, 2.4, and 2.2) at four different temperature (5, 15, 25, and 35 ºC). We observed soil-dependent variability in the rates of PHBH biodegradation, but all soils showed increasing biodegradation rates with increasing temperature. The temperature dependence of biodegradation was poorly described by the Arrhenius rate law. Also, at lower temperatures, a lag period was observed prior to the onset of biodegradation. Visible light and scanning electron microscopy imaging revealed that growth of fungal hyphae onto the PHBH films plays an important role in the initial colonization and biodegradation of PHBH and will be discussed further. The results suggest that using the Arrhenius equation to extrapolate environmental biodegradation rates based on laboratory testing is not viable.

Development of an Automated Total Nitrosamines (TONO) Analyzer

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Formation of *N*-nitrosamines in water and wastewater treatment is of concern due to their high carcinogenic potency, e.g., *N*-nitrosodimethylamine (NDMA) is estimated to be several hundred times more potent than the regulated trihalomethanes in drinking water. Rather than a direct release from specific sources, *N*-nitrosamines are known to be mainly formed *in situ* during disinfection processes such as chlorination, ozonation, etc. They are categorized as disinfection byproducts (DBPs). In principle, nitrosation can take place with any nitrogen-containing organic precursor present in water with a potential formation of a variety of *N*-nitrosamines. However, robust analytical tools available to date are somewhat limited to the commonly known individual *N*-nitrosamines, e.g., NDMA. In 2017, Breider and von Gunten developed an analytical platform which, based on UV photolysis and chemiluminescence, determines the total content of *N*-nitrosamines in water samples.[1] This system had many shortcomings and therefore, the TONO analyzer is currently upgraded, aiming for a complete automation of the analytical procedure from sampling to detection including data analysis without human intervention. All the hardware modules such as autosampling platform, syringe pumps, valves, photoreactor, etc. were 3D-designed, 3D-printed and assembled in-house. Open-source microcontrollers (i.e., Arduino) were used to control individual hardware modules with firmwares written in C++ and the user interface written in Python for serial communication with microcontrollers.

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Antibiotic uptake by spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) - distribution between above- and belowground plant fractions, soil, and soil pore-water

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Antibiotics are extensively used in animal husbandry for disease treatment, illness prevention and growth promotion. The major route for excreted antibiotics and their metabolites to croplands is via the application of animal manure fertilizers. Once in the agricultural soils, the antibiotics can be taken up by plants and accumulate into edible tissues. The extent to which this process takes place depends on the physiochemical properties of the antibiotic compounds, soil sorption potential, crop species and environmental conditions. The objectives of this study were to evaluate the uptake of five antibiotics to spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) and their distribution between roots, leaves, soil and soil pore-water. A mixture of five antibiotics from different antibiotic classes; clarithromycin (macrolide), sulfamethoxazole (sulfonamide) and the co-applied trimethoprim, chlortetracycline (tetracycline) and enrofloxacin (fluoroquinolone), were applied to the soil in four concentrations ranging from 0 mg/kg to 10 mg/kg (dry weight). Following antibiotic addition, the crops were grown for 6 weeks under controlled environmental and climatic conditions, after which they were harvested. Soil and soil pore-water samples were collected over the course of the cultivation, at 2 days, 1, 3, and 6 weeks. Delayed sprouting and reduced biomass production were observed for radishes exposed to the highest antibiotic treatment. The antibiotic analysis, to be performed, will demonstrate the distribution of antibiotics between the plant, soil and soil pore-water.

Mineralizing Wood using Clock Reactions

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Controlling the formation of inorganic particles in time using clock reactions is a promising approach for the design and functionalisation of materials with novel properties. Here we demonstrate the calcification of wood by exploiting alkali-generating reactions with nonlinear kinetics. First, we investigate the time-controlled precipitation of calcium carbonate using two different pH-clocks, namely the methylene glycol-sulfite (MGS) and the urease-urea systems. Our results demonstrate that it is possible to generate carbonate ions in situ with temporal control, and that in presence of calcium ions this results in the precipitation of calcium carbonate particles. We then apply periodate oxidation to bulk wood to generate immobilized aldehyde groups enabling the precipitation of calcium carbonate in conditions similar to that of the MGS system. In a parallel investigation we apply urease-rich protein bodies extracted from watermelon seeds (watermelon seed particles, WMSP), as *in situ* generators of carbonate ions. After confirming that the urease-urea system is able to precipitate calcium carbonate, we investigate different wood surface modifications to enhance the adhesion of the urease-containing particles, and as a means to direct the formation of calcium carbonate polymorphs. Our results demonstrate the feasibility of using pH-clock inspired systems for the precipitation of calcium carbonate in wood.

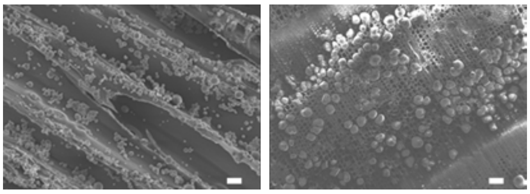

Figure 1. Scanning electron micrographs of Norway spruce mineralized using urease-rich WMSP: (a) radial section (scale bar: 10 µm), (b) cross-section (scale bar: 100 µm).

Bioinspired Polymetallic Sulfido Clusters for Nitrate and Nitrite Reduction to Ammonia

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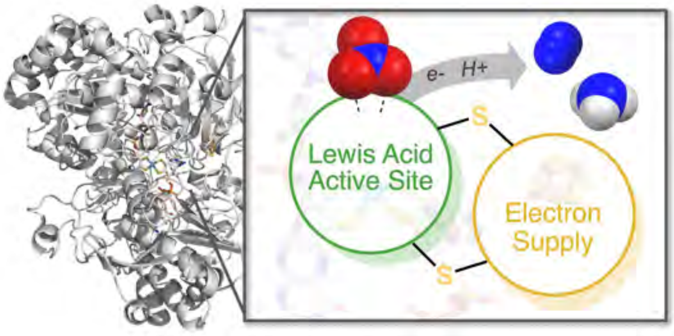
Nitrate pollution of soils and water bodies caused by intensive agriculture has become a pervasive global problem. While the input of fertilizers increased by 800 % during the last 50 years, eutrophication of lakes, ponds and coastal water bodies is now a serious biodiversity threat and a primary water quality issue. The development of new processes to remove nitrate from polluted water is crucial to address this environmental crisis, and a unique source of inspiration for the design of artificial catalysts can be found in enzymes. Dissimilatory nitrate reductase catalyzes the two-electron reduction of nitrate to nitrite and consists of a molybdopterin active site and a chain of [Fe_4S_4] clusters. The efficiency of the enzymes lies in the powerful combination of a binding site and an electron supply chain in close vicinity. Although this is achieved through the protein environment, it can be translated in synthetic chemistry by a metal-sulfur linkage. Metal-sulfur bonds are ubiquitous in biological systems and confer to the active site the possibilities of ligand redox and internal electron transfer.[1] Combining such electron relays with a potent Lewis acidic site would uncover a system capable of pre-activating the substrate while providing the electrons necessary for reduction. Trivalent lanthanide ions are hard Lewis acids and are therefore candidates of choice for the reduction of substrates such as NO_3^- and NO_2^-. Contrary to other Lewis acids such as early transition metals, they are stable towards hydrolysis and therefore suitable for applications in water. Due to their large coordination sphere, they can accommodate multiple ligands to store electrons. On the other hand, tetrathiometallates can act as convenient electron storage and relay sites by accepting electron density in low-lying, empty *d* orbitals. As tetrahedral species with d^0 configuration, $[MS_4]^{2-}$ (M= Mo,W) can coordinate to other metal centers via the potentially bridging sulphide ions.[2]



Consequently, we developed an original synthetic route towards the formation of polymetallic sulfido clusters combining lanthanide ions and biorelevant tetrathiomolybdate and tetrathiotungstate.[3] These assemblies can readily bind nitrate and can further be electrodeposited onto Gas Diffusion Electrodes (GDE) to provide a homogenous deposit $Ln_xM_yS_z$@GDL (M = Mo, W). Electrocatalytic nitrate and nitrite reduction were then performed in aqueous media and show high selectivity towards ammonia.

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Bio-oil Deoxygenation: A Contribution Towards a Sustainable Society

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Climate change, the inevitable depletion of crude oil and the related geopolitical circumstances have led to a necessity of alternative energy sources and base materials for fine chemicals. For countries like Switzerland with plenty of agriculture and forestry, one promising candidate is bio-oil, which is a waste product in biomass pyrolysis. Depending on its origin, bio-oil is composed of a mixture of organic molecules containing various functional groups (e.g. alcohols, ethers, acids, esters, sugars ...), many of which contain oxygen. In order to increase the value of bio-oil with hindsight towards fuel, complete deoxygenation without hydrogenation of unsaturated bonds would be ideal, due to the optimized energy density. Furthermore, catalytic deoxygenation targeted to specific compounds or functional groups could enable alternative synthesis routes for fine chemicals allowing their production on an industrial scale from sustainable precursors.

The endeavor to transition from crude oil to sustainable products can be successful if chemical processes can be improved (in terms of activity, selectivity, and stability), among other ways, using heterogeneous catalysis. In this study, Ir, Rh, and Ni promoted by Mo were supported on SiO_2 and tested in the deoxygenation of substrates containing ether, alcohol, and other functional groups. Bimetallic materials have shown enhanced performance compared to their monometallic counterparts. The synergistic effects between the noble metals and the promoter can allow optimizing the catalytic performance but also strongly increase the structural complexity of the catalytic materials. Therefore, a combination of analytic techniques is necessary to uncover the structure-performance relationships. Our methodology is based on the preparation of well-defined catalysts by Surface Organometallic Chemistry (SOMC), model substrates consisting of representatives for bio-oil compounds, combination of high-throughput methods, and systematic structural characterization of initial and used catalysts. This approach allows not only an extensive but also a detailed investigation of these complex systems with a focus on the catalysts' evolution and the structure-activity relationships. Catalytic tests are performed with a high throughput setup allowing eight reactions simultaneously. Analysis of the particles is done with a combined approach of XAFS spectroscopy and Transmission Electron Microscopy (TEM) to elucidate particle size, oxidation state and degree of alloying. Nuclear Magnetic Resonance Spectroscopy (NMR) allows quantification of surface hydroxyl groups, whose mechanistic role in this catalytic process is controversial. Special care is taken to avoid contact of catalysts to air during preparation, catalytic tests, and structural characterization before and after reaction.

Characterization of reactive nitrogen moieties in natural organic matter with different methodologies: oxidative and stable isotopic approach

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Natural organic matter (NOM), ubiquitous in all water types, is a major precursor of toxic nitrogenous disinfection byproducts (N-DBPs), especially during disinfection/oxidation process in water treatment. Nitrogenous moieties in NOM have been reported previously as amino acids, peptides, and humic substances, but still only a small fraction of them has been identified. To better understand the nature of reactive nitrogenous moieties in NOM, in this study novel methodologies including oxidative probing and stable isotope analysis were developed, which were demonstrated with the mixture of model-N compounds first, and followed by screening of natural organic matter isolates. Chlorination was conducted with chlorine stock solutions, and organic chloramines were quantified with DPD/KI. A continous ozone system was set up as batch reactor equipped with real-time UV probe (Avantes) to quantify O_3 and measure alteration of the water matrix. Ozonation experiments were performed in excess of tertiary butanol (100 mM) to exclude reactions with OH radical. The concentration of formed nitrate was determined by IC or HPLC/UV (λ= 210 nm). Stable isotope analysis of nitrate was performed by nitrate conversion by biological or metal catalytic process, followed by instrumental analysis with an isotope ratio mass spectrometer (IR-MS) or laser spectrometer. Chlorination led to the formation of chloramines in the reaction with reactive amine moieties, which can be further distinguished as primary or secondary amines, and amino acids, respectively. Ozonation led to the conversion of organic nitrogen to nitrate, which has a biphasic chemistry in terms of the kinetics of nitrate formation according to the structural differences of nitrogenous moieties. A derivatization of reactive amine moieties, led to a further distinction between amino acids and oximes. Overall, these techniques made it possible to qualitatively and quantitatively estimate the presence of the different oxidant-reactive nitrogenous moieties in NOM isolates. Stable isotope analysis of $^{15}N/^{15}N$ and $^{18}O/^{16}O$ in nitrate was preliminarily performed with the two ozonated representative model-N compounds, glycine and ethylamine, as representative nitrogenous moieties in NOM. The findings from this study will be discussed with regard to the basis for the understanding of N-DBPs formation potential by the reaction between oxidants and NOM in water treatment process. Based on these findings, mitigation processes can be derived.

Simulation of Realistic Aqueous Ozonation Conditions: Use of Small Scavenger Molecules as Surrogate for Dissolved Organic Matter

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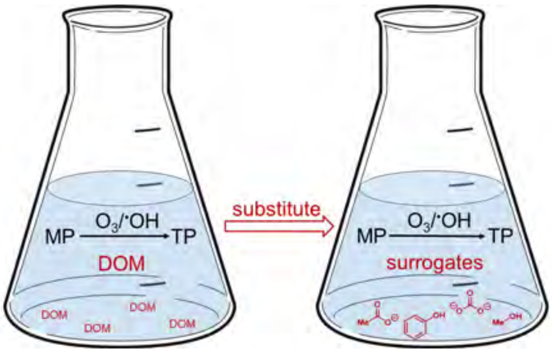
To investigate kinetics and mechanisms of micropollutant (MP) abatement and the formation of ensuing transformation products (TP) during ozonation both the reactions with ozone and hydroxyl radicals, and the interplay between the two oxidants needs to be known. Due to the constraints of using real waters on high-end analytical instruments, a tool is needed to accomplish realistic ozonation conditions without using dissolved organic matter (DOM).

Herein, the development of a standardized system to simulate realistic ozonation conditions is reported using the concept of initiators, promoters and inhibitors to control the ozone decay. Small molecules are used as model scavengers to act as surrogate for (DOM). Phenol substitutes fast-reacting moieties of the DOM, causing an initial phase of fast ozone decay. The interaction of DOM with hydroxyl radicals is mimicked by the addition of methanol and acetate, acting as promoter and inhibitor of ozone decay, respectively. The ratio between methanol and acetate defines the ozone stability and hydroxyl radical exposure of the second phase of slower ozone decay. Additionally, carbonate is added to mimic the alkalinity of real waters and its influence on ozone stability. With these surrogates, the ozonation conditions can be varied and adjusted for different types of waters such as surface waters or wastewaters.

Using this system, different water matrix surrogates have been constructed mimicking different types of water such as Lake Zürich water and secondary wastewater effluents. The initial ozone demand and the ratio of the concentrations of hydroxyl radical to ozone were in good agreement with the real water systems. As a consequence, the degradation of MPs and the formation of TPs, e.g. for bezafibrate, matched really well for the synthetic and real water matrix . Moreover, the formation of bromate has been investigated as a complex model reaction which is a good indicator, if the ozonation conditions are matched. Similar kinetics and extents of bromate formation were observed in the real and the artificial water matrix. Concluding, realistic ozonation conditions for surface waters and wastewaters can be accomplished using this model system to mimic real waters.



Speed it up: How temperature drives toxicokinetic processes in aquatic invertebrates

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Studies for the environmentally risk assessment of chemicals are generally conducted under highly standardised laboratory conditions. However, environmental parameters and external stressors are known to exert a strong influence on organism fitness. The ongoing climate change draws a lot of attention towards the parameter temperature. Many studies found a higher sensitivity of aquatic invertebrates towards contaminants with increasing or dynamic exposure temperature. However, the exact mechanisms do remain unraveled [1]. Few studies have been carried out to achieve a more structured and in depth understanding of this link [2]. This study aimed to investigate the influence of temperature on toxicokinetic parameters in *Gammarus pulex* and *Hyalella azteca*.

Bioconcentration experiments at four different temperatures (6, 11, 16 and 21°C) with a mix of 12 compounds were carried out using the two amphipod species. Tissue and medium samples were taken in regular intervals and analysed by online-SPE LC-HRMS/MS. From these data toxicokinetic rate constants were modelled and analysed in dependence of the exposure temperature using the Arrhenius equation [3].

A positive, exponential relationship between uptake, elimination and biotransformation rates versus temperature was observed. Nevertheless, the kinetic bioconcentration factors (BCFs) of the compounds were generally similar between the different temperatures due to a similar Arrhenius temperature of the uptake and elimination rate constants. The calculated Arrhenius temperatures were in the range of the ones determined for physiological processes [4]. However, in some cases the BCFs were decreasing towards higher temperatures. The later observation could potentially be explained by the influence of temperature on biotransformation rates, which was supported by high biotransformation product (BTP) concentrations.

The present study demonstrated that temperature can be an important driver of toxicokinetic processes and provides data and methods for risk assessment implications. The obtained results help understanding the mechanisms of temperature on chemical uptake, biotransformation and elimination and their interaction resulting in different sensitivity towards chemicals. Further, generated toxicokinetic rate constants can support modelling of environmental exposure as well as toxicodynamic laboratory studies under different temperature conditions.

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Ferrate(VI) oxidation of primary amines in water: kinetics, reaction products and implication for N-containing byproduct formation

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Ferrate (Fe(VI)) is a novel water treatment oxidant that can efficiently be used for micropollutant or disinfection byproduct abatement [1,2]. Considering the diversity of micropollutant structures or the complexicity of disinfection byproduct precursors, fundamental knowledge of Fe(VI) interaction with organic moieties is needed. The fate of nitrogenous moieties have gained great interest due to the generally high potency observed for nitrogenous disinfection byproducts such as halonitromethanes or haloacetonitriles [3]. More specifically, primary amines are moieties that can be found in contaminants (e.g., oseltamivir, cephalexin, gabapentin) or in dissolved organic matter, notably in amino acids. However, knowledge on the impact of Fe(VI) on primary amines is still largely lacking. Therefore, the kinetics and products of various primary amines (including amino acids) were investigated. Second-order apparent rate constants ranged from 2-50 M^{-1} s^{-1} in the pH range 6-10. An unusual pH effect on rate constants was observed for all studied primary amines, which could only be explained by the reversible formation of ionisable intermediates from the reaction between $HFeO_4^-$ and the amine (both in neutral and protonated form). Using borate as buffer led to higher rate constants compared to phosphate buffer, demonstrating the involvement of intermediate iron species (Fe(IV)/Fe(V)). A mixture of nitrile, nitrite/nitrate, ammonia, amide, and/or nitroalkane was recovered after primary amine oxidation, explaining > 80% of the amine decrease. The pH, buffer type and amine structure (e.g., the presence of a carboxylate on the Cα) greatly affected the product speciation. A general pathway was proposed to explain the product speciation as well as its dependence on pH, buffer type and carboxylate presence. The implications of primary amine oxidation products will be discussed, notably in comparison to other oxidants such as ozone.

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Porous Polyisothiocyanurates for Selective Palladium Recovery and Heterogeneous Catalysis

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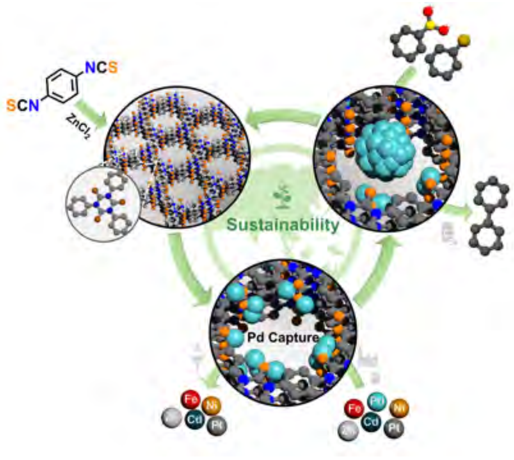
Palladium (Pd) is an indispensable metal due to its wide range of industrial applications. Pd refining, however, is an extremely energy intensive process with a serious environmental impact (e.g. 3.88 tons CO_2 emission per 1 kg of Pd production). Thus, the selective recovery of Pd from secondary sources is rather important. Heterogeneous sorbents are promising candidates owing to their reusability. Here, we present the synthesis of porous polyisothiocyanurates through the trimerization of 1,4-phenyldiisothiocyanate under ionothermal conditions, named Covalent Isothiocyanurate Frameworks (CITCFs), bearing *in-situ* generated thiourea moieties as binding sites for Pd. High surface area of CITCFs, 1589 m^2 g^{-1}, along with the presence of abundant sulfur atoms within a hierarchically porous network enabled an exceptional Pd(II) uptake capacity of 909.1 mg g^{-1}, fast adsorption kinetics, stable uptake over a wide pH range and selective Pd(II) recovery from waste water conditions. Moreover, the reduction of recovered Pd(II) within the polymer networks led to highly efficient heterogeneous catalysts for the Suzuki-Miyaura cross-coupling reaction.



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Heavy metals in agricultural urban and semi-urban soils and vegetables in Havana, Cuba.

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Heavy metals (HMs) can affect urban and semi-urban agricultural soils and food safety implying a risk to human health. Cuba has been practicing urban agriculture for decades and Havana has a developed system on that. Heavy metals are not yet regulated in Cuban soils. However, Cuba has a regulation for HMs in vegetables for lead (Pb) and cadmium (Cd). The main objective of this study was to determine HMs concentrations in soils and there growing vegetable in the Havana province area. Soil sampling criteria were potential pollution sources and farming types, such as agricultural and organoponic cultivation. Samples were taken from 12 agricultural soils and eight organoponics. Soil sampling followed the Swiss soil monitoring network (NABO) protocol (Desaules et al. 2008; Gubler et al. 2015), while the vegetables were sampled by randomly taking a 1 kg of sample (CIBA-GEIGY, 1992) from organoponics, exclusively. All HMs in the extract were measured with inductively coupled plasma-optical emission spectrometry (ICP-OES) except Hg. Mercury was measured by cold vapor-atomic fluorescence spectroscopy (Agroscope, 2020). Mean HM concentrations in all studied soils were 0.87, 54, 130, 48, 118, 137, and 0.07 mg/kg for Cd, Cr, Cu, Ni, Pb, Zn,and Hg, respectively (Figure 1). Twenty to 60% of individual metal concentrations exceeded the quality reference values (QRV), that represent non-legally binding benchmarks for HM concentrations of little anthropogenic influence (Rodriguez et al. 2015). The QRV (black line in Fig. 1 in mg/kg Cd 0.6, Cu 83, Pb 50, Zn 86, Hg 0.1) represent benchmark values of quality standards, hence soils with HM concentrations of little anthropogenic influence, but are not legally binding (Rodríguez et al., 2015) in Cuba. Swiss guide values in soils (VBBo, 1998) are in mg/kgdw Cd 0.8, Cr 50, Cu 40, Pb 50, Zn 150 and between seven to 18 of the soil samples from the capital exceeded individual metal concentrations in comparison with this guideline. Thus, these sites can be used without limitations, according to the Swiss law but need be monitored. Figure 1 represent the values of HMs in agriculture and organoponic soil and exceed the Cuban QRV for Cd, Cu, Pb and Zn and according with the Swiss guide values, all of the previously mentioned HMs as well as Cr and Ni. The mean concentration of HMs in spinach (Figure 2, n=4) in mg/kg were: Cr (nd), Pb (0.3), Cu (1.5), Zn (0.0003), Hg (0.005) and in chard (Figure 2, n=3): Cr (nd), Pb (nd), Cu (0.4), Zn (0.0002), Hg (0.005). Lead in spinach represent a risk to humans because concentrations in all samples exceeded the maximum residual limit (MLR) established in Cuba (0.1 mg/kg) (NC:493-2015) and the European Union (0.3 mg/kg) regulation (Commission Regulation (EU), 2021/1317). The pathway of impact of this study is to assess urban contaminant's concentrations in soil and vegetables, which serves as a basis for the Cuban government to establish regulatory guidance values for HMs in soils and to know the possible risk to human health trough vegetable consumption.

Figure 1. Heavy metals in agricultural and organoponic soils of Havana, Cuba. The bold black line in the box represents the median of the respective concentrations in the soil use. The lines in the boxplots indicate soil quality reference values in Cuba (black) and Swiss trigger values (pink). Equal letters indicate no significant difference (p≤0.05).

Figure 2. Heavy metals in the spinach and chard from organoponics of Havana, Cuba. The bold black line in the box represents the media of the respective concentration in the soil use. The lines in the boxplots indicate maximum residual limits (MRL) established in Cuba (black) and the European Union (pink). For Cu, Zn and Hg no MRL are available. Equal letters indicate no significant difference (p≤0.05).

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First steps toward sustainable circular uses of chemicals: advancing the assessment and management paradigm

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Environmental and human health impacts associated with chemical production and losses from value chains make the current linear produce-use-dispose model no longer an option for chemicals. Based on our analysis herein, we propose steps on how to embed the concept of “circularity” into practice (including the design phase) to foster systemic transition toward sustainable circular uses of chemicals. We first analyze major causes of chemical losses throughout their life cycles. Then, we propose to advance the current chemicals assessment and management paradigm by (1) introducing the consideration of multiple use cycles in the hazard and risk assessment stage and (2) introducing an additional “sustainable circularity” assessment stage, as a critical first step to guide systematic decision-making at all levels toward sustainable circular use of chemicals. We further look into how to enable the proposed changes and a larger systemic transition, both on the technical and socioeconomic sides.

Permanganate reduction by hydrogen peroxide: formation of reactive manganese species and superoxide and enhanced micropollutant abatement

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Permanganate (MnO_4^-, Mn(VII)) is mostly used at the initial water treatment step to remove sulfur-derived taste and odor compounds, Mn(II) and Fe(II) and the color of dissolved organic matter (DOM). It can also mitigate the formation of disinfection byproducts (DBPs) by the oxidative and adsorptive removal of precursors, or a reduction on the chlorine demand. Mn(VII) has a strong selectivity and therefore a limited applicability for the abatement of a broad range of micropollutants. Hydrogen peroxide (H_2O_2) is another commonly applied oxidant in advanced oxidation processes of water treatment. In this study, it was found that Mn(VII) reacts quickly with H_2O_2 in the practical pH range of 6.0–8.5, and a complete depletion of Mn(VII) was observed within 50 s. As the pH increases from 6.0 to 8.5, the lag-phase in the seconds range was significantly shortened, which strongly indicates an involvement of reactive species that undergo acid-base speciation. Mn(VII) underwent a one-electron reduction by H_2O_2 to potentially form Mn(VI) and superoxide radical ($O_2^{\bullet-}$) at molar ratios $[H_2O_2]_o$:$[Mn(VII)]_o \leq 1$ and pH 7.5, with a yield of 100% for $O_2^{\bullet-}$ based on the consumed Mn(VII). The Mn(VI) produced by Mn(VII)-H_2O_2 induced a significant enhancement on Mn(VII) oxidation of micropollutants with certain functional groups, such as ciprofloxacin, unsubstituted aniline, 4-chloroaniline, 4-cyano-*N*,*N*-dimethylaniline, acethydrazide and *p*-toluenesulfonyl hydrazide. The precipitation of Mn(VI) by Ba^{2+} scavenged the enhancement effect, which indicates that the Mn(VI) produced from the Mn(VII)-H_2O_2 process may be beneficial for abating specific moieties in organic compounds. When H_2O_2 was in excess of Mn(VII) (molar ratios $[H_2O_2]_o$:$[Mn(VII)]_o$ = 2–10), $O_2^{\bullet-}$ yields of 145–245% were observed. This indicates that other H_2O_2-reactive manganese species might also be formed and react with H_2O_2 to produce more $O_2^{\bullet-}$.

Significant Enhancement in Performance of Sb_2Se_3 Photocathode via Sequential Etching and $CuCl_2$ Treatment

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In an effort to further improve the auspicious Sb_2Se_3 thin films for photoelectrochemical water-splitting in a low-cost manner, simple and low temperature treatments were explored. The FTO/Ti/Au/Sb_2Se_3 semiconductor is treated with $(NH_4)_2S$ as an etching solution followed by $CuCl_2$ treatment which collectively increased the onset potential from 0.15 V to 0.28 V vs reversible hydrogen electrode (RHE) and the photocurrent from 17 mA cm^{-2} to 22.5 mA cm^{-2} at 0 vs RHE as compared to the untreated Sb_2Se_3 films. From SEM and XPS studies it is clear that the etching treatment induces a morphological change as well as removes the surface Sb_2O_3 layer. $CuCl_2$ then further enhances the performance due to the passivation of the surface defects, improving charge separation at the interface. The simple and low-cost semiconductor synthesis method combined with these facile, low-temperature treatments further increase the practical potential of Sb_2Se_3 for large scale water splitting.

Biodegradation of mulch films in Swiss agricultural soils assessed in laboratory, mesocosm and field incubations

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Non-biodegradable polyethylene mulch films are widely used in agriculture to allow for an earlier harvest and improved crop yields. These mulch films are, however, difficult to completely recollect from the field after use. Residual mulch film pieces can accumulate in soils over time, thereby negatively impacting soil productivity and turning agricultural soils into sources of plastics to surrounding environments. Mulch films certified as biodegradable in soils promise to be a solution to these problems. Yet, a thorough assessment of the biodegradation dynamics of biodegradable mulch film products in soils in the field is lacking. So far, certification relies exclusively on laboratory soil incubations coupled to respirometric analysis of CO2 formed from the mulch films during biodegradation. Respirometric analyses are, however, very challenging to implement in field incubation studies. To overcome the lack of appropriate analytical techniques for residual mulch film quantification in soils, our group has developed a methodology to extract and quantify the main synthetic polymeric components of mulch films, poly(butylene adipate-co-terephthalate) (PBAT) and polylactic acid (PLA), from soil. The methodology is based on exhaustive Soxhlet extraction coupled to quantitative 1H-NMR of extracted PBAT and PLA. Here, we use this approach to assess the biodegradation of two biodegradable mulch films commercially available in Switzerland in three Swiss agricultural soils in a multiyear incubation study. These incubations are conducted in three experimental incubation scales: flasks in the laboratory, mesocosms in a greenhouse and the actual field. We statistically compare biodegradation rates and extents between three soils and two tested films across the three incubation scales. Thereby, we assess the transferability of biodegradation results from laboratory incubations to field incubations. Our results highlight variations in biodegradation between soils and polyesters and call for caution when using laboratory incubation studies to predict biodegradation in the field.

The Bioaccumulation of Anionic and Cationic Organic Compounds in Rainbow Trout Cell

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Keywords: in-vitro systems, bioaccumulation, alternatives to animal experimentation, ionizable organic compounds

The assessment of chemicals for their bioaccumulative potential requires *in vivo* testing with fish, which is resource intense, costly, time consuming and of ethical concern due to the sacrifice of animals. Therefore, alternative *in vitro*models are being sought to replace these tests with fish.

In this work, we explore how well rainbow trout (*Oncorhynchus mykiss*) cell lines, in particular RTL–W1 (liver) can predict the bioaccumulation and biotransformation potential of ionizable organic compounds (IOC) in fish. IOC comprise a large proportion of the chemicals in commerce and are ubiquitously detected in the environment and biota. Based on the availability of high quality *in vivo* data and the substances' charge state at physiological pH, four anionic and three cationic compounds were selected: Pentachlorophenol (PCP, CAS 87-86-5), Diclofenac (DCF, CAS 15307-79-6), Tecloftalam (TT,CAS 76280-91-6) and Benzotriazol-t-butyl-hydroxyl-phenyl propanoic acid (BHPP, CAS 84268-36-0); and N,N,N-trimethyltetradecylamine (Q14, CAS 4574-04-3), N,N-dimethyldecylamine (T10, CAS 1120-24-7) and N-methyldodecylamine (S12, CAS 7311-30-0). First, non-toxic chemical concentrations were determined for each compound following the acute cell toxicity assay (OECD TG249), resulting in exposure concentrations that ranged from 5 µg/L to 200 µg/L for further assessment. The kinetic experiments were performed over 48h and 72h for anions and cations, respectively, with a total of 6 sampling time points. Cell, medium and plastic fraction were sampled separately at each time point and measured using high resolution tandem mass spectrometry after online solid phase extraction (for anions) or with direct injection of extracts (for cations). The anionic compounds, given as a fraction of the total compound mass in the test system, accumulated at steady state in the following order in RTL-W1 cells: BHPP (7%) > TT (5%) > PCP and DCF (below limit of quantification, 0.5 to 0.1% respectively). In contrast, the tested cations were associated with cells to a much larger extent. Measured as fractions of total compound mass in the test system, the RTL-W1 cells contained at steady state 30 % for T10, 75 % for S12 and 87 % for Q14. Finally, the compound's predicted bioconcentration factors based on their octanol affinity (K_{ow} or D_{ow}) or their membrane lipid affinity (D_{mlw}) were compared with the *in vitro* derived steady-state bioconcentration factors. From these comparisons it could be concluded that the tested compound's accumulation in the cells is strongly driven by the compound's interactions with the cell membrane of the RTL-W1 cells, represented through D_{mlw} ($R^2 = 0.93$).

Solution and gel-phase quantification of lignin structural features with improved 2D-HSQC$_0$ NMR processes

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Lignin upcycling towards renewable aromatic monomers can be performed by depolymerization. Most strategies rely on ß-O-4 ether cleavage because they are the most abundant and the easiest to cleave. However, the issue of quantifying lignin's initial structural features has made assessing the efficiency of lignin extraction and its upgradability difficult, especially in whole cell walls where gel phase are typically used. We previously demonstrated promising results to quantify lignin ether functionalities with the use of 2D-HSQC$_0$ NMR. Here, we developed an improved and rapid high-temperature HSQC$_0$ sequence with automatized peak fitting that avoids past errors related to user bias, relaxation and magnetization transfer, notably using polystyrene as a standard. Structural features of synthetic polymer model compounds were successfully quantified, with less than 5% error. This approach also allows quantification of features on gel-phase NMRs, which could allow precise quantification of lignin features in whole cell wall samples. We are using this analytical method on a wide range of lignin streams to predict relationships between lignin structure and reactivity. In particular, current efforts to use this method on both whole plant cell walls and extracted lignins are being used to elucidate longstanding questions regarding lignin extraction mechanisms.

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Efficacy of environmental friendly iron-based metal-organic framework/polymer composites to reduce silver ion toxicity to Zebrafish embryos (*Danio rerio*)

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Metal-organic framework (MOF) / polymer composites have been used for rapid and selective removal of heavy metals from water samples. Given their intended use for water purification, we studied the toxicity of these MOF to developing zebrafish (*Danio rerio*) embryos and then explored the capacity of these MOF to protect the embryos from silver ion toxicity. Structural integrity of the MOF in terms of crystallinity and no detectable leaching of iron to the medium were maintained in different embryo exposure media, which varied in salt composition and absence/presence of albumin as organic component. None of the MOF exhibited toxicity to zebrafish embryo up to the concentration of 100 mg/L. The Fe-BTC/PDA polymer composite (Fe-BTC = Fe, 1, 3, 5 benzenetricaboxy and PDA = Polydopamine) yielded the best results with regard to the removal of silver ions from exposure medium. Without the application of Fe-BTC/PDA, 0.1 mg/L silver ion exposure concentration resulted in 100 % mortality in the first day of observation of the Fish Embryo Toxicity (FET) test, but with 20 mg/L of Fe-BTC/PDA application, no mortality, delay of hatching or sublethal endpoints was observed for the embryos exposed up to 4 mg/L of initial silver ion concentration, during 120 hpf FET test. For 7 and 8 mg/L initial Ag ion concentrations, no mortality at 72 hpf was observed but delayed mortality of 42 and 94 %, respectively was observed at the end of 120 hpf FET test. The essential metal concentrations in embryos did not significantly decrease with the exposure of 20 mg/L of Fe-BTC/PDA composite.

Biotransformation capacity for trace contaminants - from wastewater to natural surface water

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Complex mixtures of trace organic contaminants (TrOCs) resulting from human activity and released into the environment are a major threat for ecosystems. Microbial biotransformation has the potential to remove them from the environment, but there is limited mechanistic understanding of the drivers of contaminant biotransformation. Activated sludge treatment in wastewater treatment plants (WWTPs), for instance, acts as partial barrier to prevent trace organic contaminants from entering the environment, but treatment efficiency varies among compounds and treatment facilities. Furthermore, treated effluents have been shown to affect the ecological functioning of downstream river biofilm communities, including their potential to biotransform TrOCs. In this project, the overall goal is to better understand and ultimately predict the level of TrOCs biotransformation during wastewater treatment and in downstream natural environments at the level of microbial communities and to evaluate the relevance and practical implications of these findings for contaminant transformation in wastewater-impacted freshwater microbiomes. We are, in a first step, exploring the biotransformation capacity of river biofilm communities grown up- and downstream of six WWTP, as well as of the associated activated sludge, for a diverse selection of 200 test substances covering different classes of TrOCs. We aim to deepen our knowledge on the previously shown increased biotransformation capacity in downstream microbiomes, particularly with respect to whether it is indeed a result of concentration-dependent adaptation in the WWTP, and, if so, how it depends on the WWTP treatment technology employed (i.e., carbon eliminating, de-/nitrifying, de-/nitrifying with moving bed). The biotransformation kinetic data, which we will gather for the altogether 36 microbial communities, will further allow us to answer to what extent increased downstream biotransformation of certain substances is related to their specific molecular structure , and how consistent patterns of variability among substances with similar potentially enzymatically transformed moieties, as predicted by enviPath (envipath.org), are.

The Impact of Temperature on Biodegradation of Poly-3-hydroxybutyrate-3-hexanoate (PHBH) in Soil

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Biodegradable polymers have gained attention as an important conventional polymer material substitute in applications where plastics enter the organic waste stream or where plastics entering the environment is probable. Current certification of soil biodegradability relies on laboratory soil incubations at constant temperature coupled to respirometric analyses of polymer conversion to CO_2. However, the transferability of biodegradation results from laboratory experiments at elevated temperatures (25 ºC) to the field with variable and lower temperatures has been called into question. Primarily, we do not understand how temperature impacts the rate of polymer biodegradation. In this work, we have determined the effect of temperature on biodegradation using a readily biodegradable polymer, poly-3-hydroxybutyrate-3-hydroxyhexanoate (PHBH), by tracking the decrease in the amount extractable from soil using extraction and ^{1}H-NMR as well as by imaging methods of PHBH films to understand microbial colonization dynamics on the polymer surface. To this end, we incubated PHBH in three different types of standard LUFA soils (6S, 2.4, and 2.2) at four different temperature (5, 15, 25, and 35 ºC). We observed soil-dependent variability in the rates of PHBH biodegradation, but all soils showed increasing biodegradation rates with increasing temperature. The temperature dependence of biodegradation was poorly described by the Arrhenius rate law. Also, at lower temperatures, a lag period was observed prior to the onset of biodegradation. Visible light and scanning electron microscopy imaging revealed that growth of fungal hyphae onto the PHBH films plays an important role in the initial colonization and biodegradation of PHBH and will be discussed further. The results suggest that using the Arrhenius equation to extrapolate environmental biodegradation rates based on laboratory testing is not viable.

Development of an Automated Total Nitrosamines (TONO) Analyzer

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Formation of *N*-nitrosamines in water and wastewater treatment is of concern due to their high carcinogenic potency, e.g., *N*-nitrosodimethylamine (NDMA) is estimated to be several hundred times more potent than the regulated trihalomethanes in drinking water. Rather than a direct release from specific sources, *N*-nitrosamines are known to be mainly formed *in situ* during disinfection processes such as chlorination, ozonation, etc. They are categorized as disinfection byproducts (DBPs). In principle, nitrosation can take place with any nitrogen-containing organic precursor present in water with a potential formation of a variety of *N*-nitrosamines. However, robust analytical tools available to date are somewhat limited to the commonly known individual *N*-nitrosamines, e.g., NDMA. In 2017, Breider and von Gunten developed an analytical platform which, based on UV photolysis and chemiluminescence, determines the total content of *N*-nitrosamines in water samples.[1] This system had many shortcomings and therefore, the TONO analyzer is currently upgraded, aiming for a complete automation of the analytical procedure from sampling to detection including data analysis without human intervention. All the hardware modules such as autosampling platform, syringe pumps, valves, photoreactor, etc. were 3D-designed, 3D-printed and assembled in-house. Open-source microcontrollers (i.e., Arduino) were used to control individual hardware modules with firmwares written in C++ and the user interface written in Python for serial communication with microcontrollers.

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Antibiotic uptake by spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) - distribution between above- and belowground plant fractions, soil, and soil pore-water

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Antibiotics are extensively used in animal husbandry for disease treatment, illness prevention and growth promotion. The major route for excreted antibiotics and their metabolites to croplands is via the application of animal manure fertilizers. Once in the agricultural soils, the antibiotics can be taken up by plants and accumulate into edible tissues. The extent to which this process takes place depends on the physiochemical properties of the antibiotic compounds, soil sorption potential, crop species and environmental conditions. The objectives of this study were to evaluate the uptake of five antibiotics to spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) and their distribution between roots, leaves, soil and soil pore-water. A mixture of five antibiotics from different antibiotic classes; clarithromycin (macrolide), sulfamethoxazole (sulfonamide) and the co-applied trimethoprim, chlortetracycline (tetracycline) and enrofloxacin (fluoroquinolone), were applied to the soil in four concentrations ranging from 0 mg/kg to 10 mg/kg (dry weight). Following antibiotic addition, the crops were grown for 6 weeks under controlled environmental and climatic conditions, after which they were harvested. Soil and soil pore-water samples were collected over the course of the cultivation, at 2 days, 1, 3, and 6 weeks. Delayed sprouting and reduced biomass production were observed for radishes exposed to the highest antibiotic treatment. The antibiotic analysis, to be performed, will demonstrate the distribution of antibiotics between the plant, soil and soil pore-water.

Mineralizing Wood using Clock Reactions

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Controlling the formation of inorganic particles in time using clock reactions is a promising approach for the design and functionalisation of materials with novel properties. Here we demonstrate the calcification of wood by exploiting alkali-generating reactions with nonlinear kinetics. First, we investigate the time-controlled precipitation of calcium carbonate using two different pH-clocks, namely the methylene glycol-sulfite (MGS) and the urease-urea systems. Our results demonstrate that it is possible to generate carbonate ions in situ with temporal control, and that in presence of calcium ions this results in the precipitation of calcium carbonate particles. We then apply periodate oxidation to bulk wood to generate immobilized aldehyde groups enabling the precipitation of calcium carbonate in conditions similar to that of the MGS system. In a parallel investigation we apply urease-rich protein bodies extracted from watermelon seeds (watermelon seed particles, WMSP), as *in situ* generators of carbonate ions. After confirming that the urease-urea system is able to precipitate calcium carbonate, we investigate different wood surface modifications to enhance the adhesion of the urease-containing particles, and as a means to direct the formation of calcium carbonate polymorphs. Our results demonstrate the feasibility of using pH-clock inspired systems for the precipitation of calcium carbonate in wood.

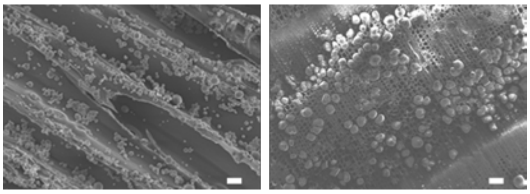

Figure 1. Scanning electron micrographs of Norway spruce mineralized using urease-rich WMSP: (a) radial section (scale bar: 10 µm), (b) cross-section (scale bar: 100 µm).

Bio-oil Deoxygenation: A Contribution Towards a Sustainable Society

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Climate change, the inevitable depletion of crude oil and the related geopolitical circumstances have led to a necessity of alternative energy sources and base materials for fine chemicals. For countries like Switzerland with plenty of agriculture and forestry, one promising candidate is bio-oil, which is a waste product in biomass pyrolysis. Depending on its origin, bio-oil is composed of a mixture of organic molecules containing various functional groups (e.g. alcohols, ethers, acids, esters, sugars …), many of which contain oxygen. In order to increase the value of bio-oil with hindsight towards fuel, complete deoxygenation without hydrogenation of unsaturated bonds would be ideal, due to the optimized energy density. Furthermore, catalytic deoxygenation targeted to specific compounds or functional groups could enable alternative synthesis routes for fine chemicals allowing their production on an industrial scale from sustainable precursors.

The endeavor to transition from crude oil to sustainable products can be successful if chemical processes can be improved (in terms of activity, selectivity, and stability), among other ways, using heterogeneous catalysis. In this study, Ir, Rh, and Ni promoted by Mo were supported on SiO_2 and tested in the deoxygenation of substrates containing ether, alcohol, and other functional groups. Bimetallic materials have shown enhanced performance compared to their monometallic counterparts. The synergistic effects between the noble metals and the promoter can allow optimizing the catalytic performance but also strongly increase the structural complexity of the catalytic materials. Therefore, a combination of analytic techniques is necessary to uncover the structure-performance relationships. Our methodology is based on the preparation of well-defined catalysts by Surface Organometallic Chemistry (SOMC), model substrates consisting of representatives for bio-oil compounds, combination of high-throughput methods, and systematic structural characterization of initial and used catalysts. This approach allows not only an extensive but also a detailed investigation of these complex systems with a focus on the catalysts' evolution and the structure-activity relationships. Catalytic tests are performed with a high throughput setup allowing eight reactions simultaneously. Analysis of the particles is done with a combined approach of XAFS spectroscopy and Transmission Electron Microscopy (TEM) to elucidate particle size, oxidation state and degree of alloying. Nuclear Magnetic Resonance Spectroscopy (NMR) allows quantification of surface hydroxyl groups, whose mechanistic role in this catalytic process is controversial. Special care is taken to avoid contact of catalysts to air during preparation, catalytic tests, and structural characterization before and after reaction.

Characterization of reactive nitrogen moieties in natural organic matter with different methodologies: oxidative and stable isotopic approach

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Natural organic matter (NOM), ubiquitous in all water types, is a major precursor of toxic nitrogenous disinfection byproducts (N-DBPs), especially during disinfection/oxidation process in water treatment. Nitrogenous moieties in NOM have been reported previously as amino acids, peptides, and humic substances, but still only a small fraction of them has been identified. To better understand the nature of reactive nitrogenous moieties in NOM, in this study novel methodologies including oxidative probing and stable isotope analysis were developed, which were demonstrated with the mixture of model-N compounds first, and followed by screening of natural organic matter isolates. Chlorination was conducted with chlorine stock solutions, and organic chloramines were quantified with DPD/KI. A continous ozone system was set up as batch reactor equipped with real-time UV probe (Avantes) to quantify O_3 and measure alteration of the water matrix. Ozonation experiments were performed in excess of tertiary butanol (100 mM) to exclude reactions with OH radical. The concentration of formed nitrate was determined by IC or HPLC/UV (λ= 210 nm). Stable isotope analysis of nitrate was performed by nitrate conversion by biological or metal catalytic process, followed by instrumental analysis with an isotope ratio mass spectrometer (IR-MS) or laser spectrometer. Chlorination led to the formation of chloramines in the reaction with reactive amine moieties, which can be further distinguished as primary or secondary amines, and amino acids, respectively. Ozonation led to the conversion of organic nitrogen to nitrate, which has a biphasic chemistry in terms of the kinetics of nitrate formation according to the structural differences of nitrogenous moieties. A derivatization of reactive amine moieties, led to a further distinction between amino acids and oximes. Overall, these techniques made it possible to qualitatively and quantitatively estimate the presence of the different oxidant-reactive nitrogenous moieties in NOM isolates. Stable isotope analysis of $^{15}N/^{15}N$ and $^{18}O/^{16}O$ in nitrate was preliminarily performed with the two ozonated representative model-N compounds, glycine and ethylamine, as representative nitrogenous moieties in NOM. The findings from this study will be discussed with regard to the basis for the understanding of N-DBPs formation potential by the reaction between oxidants and NOM in water treatment process. Based on these findings, mitigation processes can be derived.

Simulation of Realistic Aqueous Ozonation Conditions: Use of Small Scavenger Molecules as Surrogate for Dissolved Organic Matter

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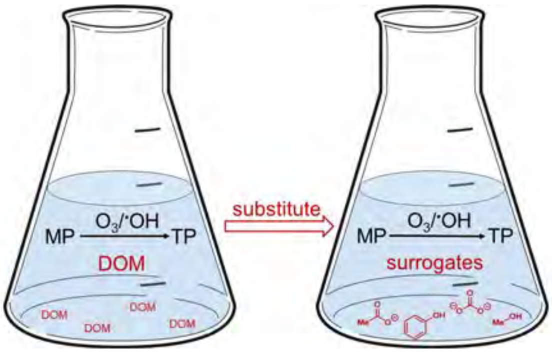
To investigate kinetics and mechanisms of micropollutant (MP) abatement and the formation of ensuing transformation products (TP) during ozonation both the reactions with ozone and hydroxyl radicals, and the interplay between the two oxidants needs to be known. Due to the constraints of using real waters on high-end analytical instruments, a tool is needed to accomplish realistic ozonation conditions without using dissolved organic matter (DOM).

Herein, the development of a standardized system to simulate realistic ozonation conditions is reported using the concept of initiators, promoters and inhibitors to control the ozone decay. Small molecules are used as model scavengers to act as surrogate for (DOM). Phenol substitutes fast-reacting moieties of the DOM, causing an initial phase of fast ozone decay. The interaction of DOM with hydroxyl radicals is mimicked by the addition of methanol and acetate, acting as promoter and inhibitor of ozone decay, respectively. The ratio between methanol and acetate defines the ozone stability and hydroxyl radical exposure of the second phase of slower ozone decay. Additionally, carbonate is added to mimic the alkalinity of real waters and its influence on ozone stability. With these surrogates, the ozonation conditions can be varied and adjusted for different types of waters such as surface waters or wastewaters.

Using this system, different water matrix surrogates have been constructed mimicking different types of water such as Lake Zürich water and secondary wastewater effluents. The initial ozone demand and the ratio of the concentrations of hydroxyl radical to ozone were in good agreement with the real water systems. As a consequence, the degradation of MPs and the formation of TPs, e.g. for bezafibrate, matched really well for the synthetic and real water matrix . Moreover, the formation of bromate has been investigated as a complex model reaction which is a good indicator, if the ozonation conditions are matched. Similar kinetics and extents of bromate formation were observed in the real and the artificial water matrix. Concluding, realistic ozonation conditions for surface waters and wastewaters can be accomplished using this model system to mimic real waters.



Speed it up: How temperature drives toxicokinetic processes in aquatic invertebrates

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Studies for the environmentally risk assessment of chemicals are generally conducted under highly standardised laboratory conditions. However, environmental parameters and external stressors are known to exert a strong influence on organism fitness. The ongoing climate change draws a lot of attention towards the parameter temperature. Many studies found a higher sensitivity of aquatic invertebrates towards contaminants with increasing or dynamic exposure temperature. However, the exact mechanisms do remain unraveled [1]. Few studies have been carried out to achieve a more structured and in depth understanding of this link [2]. This study aimed to investigate the influence of temperature on toxicokinetic parameters in *Gammarus pulex* and *Hyalella azteca*.

Bioconcentration experiments at four different temperatures (6, 11, 16 and 21°C) with a mix of 12 compounds were carried out using the two amphipod species. Tissue and medium samples were taken in regular intervals and analysed by online-SPE LC-HRMS/MS. From these data toxicokinetic rate constants were modelled and analysed in dependence of the exposure temperature using the Arrhenius equation [3].

A positive, exponential relationship between uptake, elimination and biotransformation rates versus temperature was observed. Nevertheless, the kinetic bioconcentration factors (BCFs) of the compounds were generally similar between the different temperatures due to a similar Arrhenius temperature of the uptake and elimination rate constants. The calculated Arrhenius temperatures were in the range of the ones determined for physiological processes [4]. However, in some cases the BCFs were decreasing towards higher temperatures. The later observation could potentially be explained by the influence of temperature on biotransformation rates, which was supported by high biotransformation product (BTP) concentrations.

The present study demonstrated that temperature can be an important driver of toxicokinetic processes and provides data and methods for risk assessment implications. The obtained results help understanding the mechanisms of temperature on chemical uptake, biotransformation and elimination and their interaction resulting in different sensitivity towards chemicals. Further, generated toxicokinetic rate constants can support modelling of environmental exposure as well as toxicodynamic laboratory studies under different temperature conditions.

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Ferrate(VI) oxidation of primary amines in water: kinetics, reaction products and implication for N-containing byproduct formation

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Ferrate (Fe(VI)) is a novel water treatment oxidant that can efficiently be used for micropollutant or disinfection byproduct abatement [1,2]. Considering the diversity of micropollutant structures or the complexicity of disinfection byproduct precursors, fundamental knowledge of Fe(VI) interaction with organic moieties is needed. The fate of nitrogenous moieties have gained great interest due to the generally high potency observed for nitrogenous disinfection byproducts such as halonitromethanes or haloacetonitriles [3]. More specifically, primary amines are moieties that can be found in contaminants (e.g., oseltamivir, cephalexin, gabapentin) or in dissolved organic matter, notably in amino acids. However, knowledge on the impact of Fe(VI) on primary amines is still largely lacking. Therefore, the kinetics and products of various primary amines (including amino acids) were investigated. Second-order apparent rate constants ranged from 2-50 M^{-1} s^{-1} in the pH range 6-10. An unusual pH effect on rate constants was observed for all studied primary amines, which could only be explained by the reversible formation of ionisable intermediates from the reaction between $HFeO_4^-$ and the amine (both in neutral and protonated form). Using borate as buffer led to higher rate constants compared to phosphate buffer, demonstrating the involvement of intermediate iron species (Fe(IV)/Fe(V)). A mixture of nitrile, nitrite/nitrate, ammonia, amide, and/or nitroalkane was recovered after primary amine oxidation, explaining > 80% of the amine decrease. The pH, buffer type and amine structure (e.g., the presence of a carboxylate on the Cα) greatly affected the product speciation. A general pathway was proposed to explain the product speciation as well as its dependence on pH, buffer type and carboxylate presence. The implications of primary amine oxidation products will be discussed, notably in comparison to other oxidants such as ozone.

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Porous Polyisothiocyanurates for Selective Palladium Recovery and Heterogeneous Catalysis

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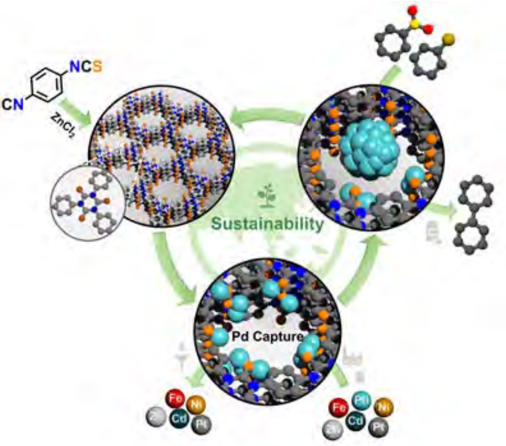
Palladium (Pd) is an indispensable metal due to its wide range of industrial applications. Pd refining, however, is an extremely energy intensive process with a serious environmental impact (e.g. 3.88 tons CO_2 emission per 1 kg of Pd production). Thus, the selective recovery of Pd from secondary sources is rather important. Heterogeneous sorbents are promising candidates owing to their reusability. Here, we present the synthesis of porous polyisothiocyanurates through the trimerization of 1,4-phenyldiisothiocyanate under ionothermal conditions, named Covalent Isothiocyanurate Frameworks (CITCFs), bearing *in-situ* generated thiourea moieties as binding sites for Pd. High surface area of CITCFs, 1589 $m^2\ g^{-1}$, along with the presence of abundant sulfur atoms within a hierarchically porous network enabled an exceptional Pd(II) uptake capacity of 909.1 mg g^{-1}, fast adsorption kinetics, stable uptake over a wide pH range and selective Pd(II) recovery from waste water conditions. Moreover, the reduction of recovered Pd(II) within the polymer networks led to highly efficient heterogeneous catalysts for the Suzuki-Miyaura cross-coupling reaction.



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Heavy metals in agricultural urban and semi-urban soils and vegetables in Havana, Cuba.

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Heavy metals (HMs) can affect urban and semi-urban agricultural soils and food safety implying a risk to human health. Cuba has been practicing urban agriculture for decades and Havana has a developed system on that. Heavy metals are not yet regulated in Cuban soils. However, Cuba has a regulation for HMs in vegetables for lead (Pb) and cadmium (Cd). The main objective of this study was to determine HMs concentrations in soils and there growing vegetable in the Havana province area. Soil sampling criteria were potential pollution sources and farming types, such as agricultural and organoponic cultivation. Samples were taken from 12 agricultural soils and eight organoponics. Soil sampling followed the Swiss soil monitoring network (NABO) protocol (Desaules et al. 2008; Gubler et al. 2015), while the vegetables were sampled by randomly taking a 1 kg of sample (CIBA-GEIGY, 1992) from organoponics, exclusively. All HMs in the extract were measured with inductively coupled plasma-optical emission spectrometry (ICP-OES) except Hg. Mercury was measured by cold vapor-atomic fluorescence spectroscopy (Agroscope, 2020). Mean HM concentrations in all studied soils were 0.87, 54, 130, 48, 118, 137, and 0.07 mg/kg for Cd, Cr, Cu, Ni, Pb, Zn,and Hg, respectively (Figure 1). Twenty to 60% of individual metal concentrations exceeded the quality reference values (QRV), that represent non-legally binding benchmarks for HM concentrations of little anthropogenic influence (Rodriguez et al. 2015). The QRV (black line in Fig. 1 in mg/kg Cd 0.6, Cu 83, Pb 50, Zn 86, Hg 0.1) represent benchmark values of quality standards, hence soils with HM concentrations of little anthropogenic influence, but are not legally binding (Rodríguez et al., 2015) in Cuba. Swiss guide values in soils (VBBo, 1998) are in mg/kgdw Cd 0.8, Cr 50, Cu 40, Pb 50, Zn 150 and between seven to 18 of the soil samples from the capital exceeded individual metal concentrations in comparison with this guideline. Thus, these sites can be used without limitations, according to the Swiss law but need be monitored. Figure 1 represent the values of HMs in agriculture and organoponic soil and exceed the Cuban QRV for Cd, Cu, Pb and Zn and according with the Swiss guide values, all of the previously mentioned HMs as well as Cr and Ni. The mean concentration of HMs in spinach (Figure 2, n=4) in mg/kg were: Cr (nd), Pb (0.3), Cu (1.5), Zn (0.0003), Hg (0.005) and in chard (Figure 2, n=3): Cr (nd), Pb (nd), Cu (0.4), Zn (0.0002), Hg (0.005). Lead in spinach represent a risk to humans because concentrations in all samples exceeded the maximum residual limit (MLR) established in Cuba (0.1 mg/kg) (NC:493-2015) and the European Union (0.3 mg/kg) regulation (Commission Regulation (EU), 2021/1317). The pathway of impact of this study is to assess urban contaminant's concentrations in soil and vegetables, which serves as a basis for the Cuban government to establish regulatory guidance values for HMs in soils and to know the possible risk to human health trough vegetable consumption.

Figure 1. Heavy metals in agricultural and organoponic soils of Havana, Cuba. The bold black line in the box represents the median of the respective concentrations in the soil use. The lines in the boxplots indicate soil quality reference values in Cuba (black) and Swiss trigger values (pink). Equal letters indicate no significant difference (p≤0.05)

Figure 2. Heavy metals in the spinach and chard from organoponics of Havana, Cuba. The bold black line in the box represents the media of the respective concentrations in the soil use. The lines in the boxplots indicate maximum residual limits (MRL) established in Cuba (black) and the European Union (pink). For Cu, Zn and Hg no MRL are available. Equal letters indicate no significant difference (p≤0.05)

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First steps toward sustainable circular uses of chemicals: advancing the assessment and management paradigm

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Environmental and human health impacts associated with chemical production and losses from value chains make the current linear produce-use-dispose model no longer an option for chemicals. Based on our analysis herein, we propose steps on how to embed the concept of "circularity" into practice (including the design phase) to foster systemic transition toward sustainable circular uses of chemicals. We first analyze major causes of chemical losses throughout their life cycles. Then, we propose to advance the current chemicals assessment and management paradigm by (1) introducing the consideration of multiple use cycles in the hazard and risk assessment stage and (2) introducing an additional "sustainable circularity" assessment stage, as a critical first step to guide systematic decision-making at all levels toward sustainable circular use of chemicals. We further look into how to enable the proposed changes and a larger systemic transition, both on the technical and socioeconomic sides.

Permanganate reduction by hydrogen peroxide: formation of reactive manganese species and superoxide and enhanced micropollutant abatement

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Permanganate (MnO_4^-, Mn(VII)) is mostly used at the initial water treatment step to remove sulfur-derived taste and odor compounds, Mn(II) and Fe(II) and the color of dissolved organic matter (DOM). It can also mitigate the formation of disinfection byproducts (DBPs) by the oxidative and adsorptive removal of precursors, or a reduction on the chlorine demand. Mn(VII) has a strong selectivity and therefore a limited applicability for the abatement of a broad range of micropollutants. Hydrogen peroxide (H_2O_2) is another commonly applied oxidant in advanced oxidation processes of water treatment. In this study, it was found that Mn(VII) reacts quickly with H_2O_2 in the practical pH range of 6.0–8.5, and a complete depletion of Mn(VII) was observed within 50 s. As the pH increases from 6.0 to 8.5, the lag-phase in the seconds range was significantly shortened, which strongly indicates an involvement of reactive species that undergo acid-base speciation. Mn(VII) underwent a one-electron reduction by H_2O_2 to potentially form Mn(VI) and superoxide radical ($O_2^{\bullet -}$) at molar ratios $[H_2O_2]_o$:$[Mn(VII)]_o \leq 1$ and pH 7.5, with a yield of 100% for $O_2^{\bullet -}$ based on the consumed Mn(VII). The Mn(VI) produced by Mn(VII)-H_2O_2 induced a significant enhancement on Mn(VII) oxidation of micropollutants with certain functional groups, such as ciprofloxacin, unsubstituted aniline, 4-chloroaniline, 4-cyano-*N*,*N*-dimethylaniline, acethydrazide and *p*-toluenesulfonyl hydrazide. The precipitation of Mn(VI) by Ba^{2+} scavenged the enhancement effect, which indicates that the Mn(VI) produced from the Mn(VII)-H_2O_2 process may be beneficial for abating specific moieties in organic compounds. When H_2O_2 was in excess of Mn(VII) (molar ratios $[H_2O_2]_o$:$[Mn(VII)]_o$ = 2–10), $O_2^{\bullet -}$ yields of 145–245% were observed. This indicates that other H_2O_2-reactive manganese species might also be formed and react with H_2O_2 to produce more $O_2^{\bullet -}$.

Assessment of chlorine stability in recycled handwashing water: Role of amide-type compounds from soaps

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In low- and middle-income countries where healthcare facilities and schools are not connected to functional water supply systems, stand-alone handwashing systems provide a solution to safely recycle and reuse handwashing water. In handwashing water reuse possibly a chemical disinfectant (e.g., chlorine, chloramine, peracetic acid) needs to be added and its stability in handwashing water needs to be tested. Based on a survey, the compounds with amide structures abundantly present in handwashing waters from the use of soaps could control the decay of chlorine on a long-term scale. In this study, we selected six different amides as surrogates (acetamide, benzamide, *N*-methylformamide, *N*-methylacetamide, *N*-methylbenzamide, and *N*-propylbenzamide) and investigated the kinetics and mechanisms of the reactions of amides with chlorine. Apparent second-order rate constants for the reactions of chlorine with the selected amides at pH 8 were in the range of 6.6×10^{-3}-0.23 $M^{-1}s^{-1}$. Hypochlorite (^{-}OCl) dominates the reactions of amides with chlorine. The reaction products of chlorinated amides were observed to react with electron-rich moieties (e.g., phenolics, β-dicarbonyl acid) with apparent second-order rate constants in the order of 10^{-3}-10 $M^{-1}s^{-1}$ at pH 8. Furthermore, the activation energies of the reactions of amides with chlorine were obtained by temperature-dependent reaction kinetics (64.8-71.0 kJ/mol). Based on these results, the chlorine stability in the presence of amides can be modeled as a function of pH and temperature. The knowledge obtained in this study will provide guidance to apply handwashing systems for safe water reuse.