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How Actionable Research in Chemistry can promote Sustainability

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Advances in chemistry have improved human well-being, most notably by increasing the food supply through the development of synthetic nitrogen fertilizer. At the same time, chemical innovations have resulted in environmental degradation that threatens human health. Current global challenges, such as climate change and biodiversity loss, call for solution-oriented, actionable research that should inform environmental policy as well as practice in chemical industry and in environmental protection. Designing effective actionable research requires serious attention to the needs and interests of potential implementation partners (and ideally direct involvement of their representatives) at formative stages of project development. Time and resources must also be budgeted for knowledge exchange, which may benefit from involvement of (non-academic) knowledge brokers. Examples will be presented to illustrate the impacts of actionable research in environmental chemistry as a model and motivation for the broader adoption of actionable research in chemistry.

Safe and sustainable by design: A computer-based approach to redesign chemicals for reduced environmental hazards

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Persistency of chemicals in the environment is seen a pressing issue as it results in accumulation of chemicals over time. Persistent chemicals can be an asset in a well-functioning circular economy where products are more durable and can be reused or recycled. This objective can however not always be fulfilled as release of chemicals from products into the environment can be inherently coupled to their use. In these situations, chemicals should be designed for degradation. In this work, a systematic and computer-aided workflow was developed to facilitate the chemical redesign for reduced persistency. The approach includes elements of Essential Use, Alternatives Assessment and Green and Circular Chemistry and ties into goals recently formulated in the context of the EU Green Deal. The organophosphate chemical triisobutylphosphate (TiBP) was used as a case study for exploration of the approach, as its emission to the environment was expected to be inevitable when used as a flame retardant. Over 6.3 million alternative structures were created in silico and filtered based on QSAR outputs to remove potentially non-readily biodegradable structures. With a multi-criteria analysis based on predicted properties and synthesizability a top 500 of most desirable structures was identified. The target structure (di-n-butyl (2-hydroxyethyl) phosphate) was manually selected and synthesized. The approach can be expanded and further verified to reach its full potential in the mitigation of chemical pollution and to help enable a safe circular economy.

Systematic, computer-aided approach to redesign for less persistent chemicals
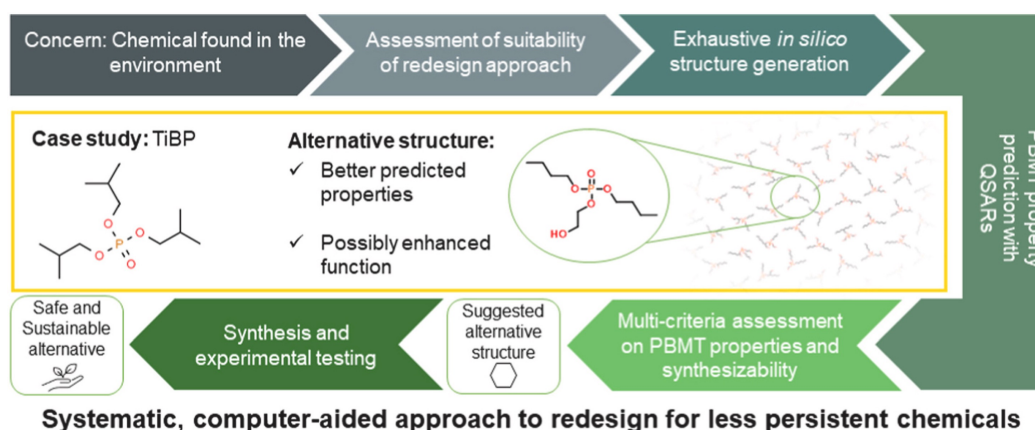
[1] van Dijk, J., Flerlage, H., Beijer, S., Slootweg, J. C., & van Wezel, A. P. (2022). Chemosphere, 296, 134050.

Insights into the storage aging effects on dimer esters and other oligomers in beta-pinene secondary organic aerosol samples

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Collection of secondary organic aerosol (SOA) onto filters is often used in combination with LC-MS for detailed chemical characterization. Studies have shown that a large fraction of laboratory-generated SOA can be attributed to high molecular weight oligomeric compounds. Often there is a significant delay between sample collection and analysis which may lead to changes in the chemical profile of the samples.

In this study beta-pinene SOA was generated by O3 and OH oxidation and collected onto filters, which were either extracted in a mixture of water and acetonitrile or left on the filter, to investigate changes in the overall chemical composition profile over time up to one month. The samples were analyzed by UHPLC-ESI-MS in negative polarity mode. An untargeted approach led to several thousand detected compounds and principal component analysis indicated a significant difference between the samples stored on filters or as extracts. In order to understand these differences, further focus was put on previously identified carboxylic acids, dimer esters and other oligomers tentatively assigned to the ester class.

The signal intensity for oligomers in the chromatograms decreases over time in extracts, which can be explained by hydrolysis causing decomposition of esters and other components. On the other hand, the signal intensity on filters shows a strong increase for dimers and trimers, which suggests a further chemical aging of the SOA particles (or "film") deposited on the filters which allows further reactions of SOA monomer compounds to form dimers and trimers. The two different storage conditions represent two atmospheric processing conditions: (1) the aging of SOA under dry conditions favoring oligomerization over long time scales of days and (2) the effects occurring when SOA partitions into cloud droplets where water is promoting hydrolysis and decomposition of oligomers back to monomers.
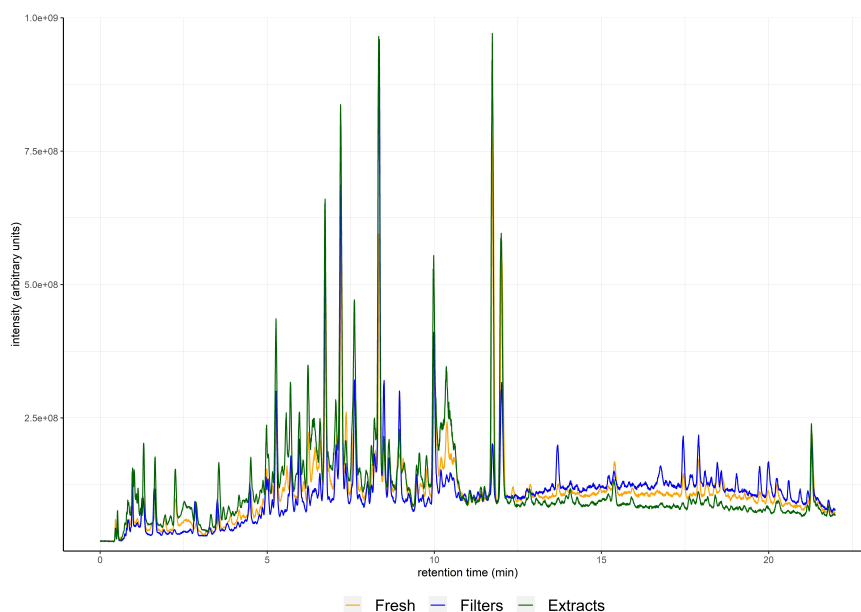

Figure 1: Total Ion Chromatogram representing fresh (orange), 4-week-old filter (blue) and extracts (green). Monomers elute at a retention time between 2-12 minutes and oligomers between 12-22 minutes.

Assessing melt effects on aerosol tracers in a firn core with non-target screening

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Natural archives, for example, high-alpine glacier ice cores, allow the reconstruction of past trends in the composition and concentration of atmospheric aerosols. Unfortunately, these archives are heavily affected by climate change, and the chemical impurities are prone to relocation, thereby limiting the chemical signal interpretation. So far, mainly the signal preservation of inorganic ions was studied. The majority of the organic aerosol tracers have not been investigated, let alone their behaviour in firn/ice influenced by melting. Our goal is to narrow this knowledge gap and provide a more comprehensive understanding of organic aerosol tracer preservation in firn and ice.

Here, we present data from a firn core collected on the Corbassière glacier (Grand Combin, Swiss Alps) in 2020. The firn core was dated by annual layer counting using stable oxygen isotope ratio ($\delta^{18}O$). We analysed organic tracers with a hybrid target/non-target screening approach optimised for determining oxidation products of volatile organic compounds. As these tracers are usually present at low concentrations, we performed solid-phase extraction as a pre-concentration step. The samples were analysed with high-performance liquid chromatography coupled with high-resolution mass spectrometry, using Electrospray Ionisation and Orbitrap technology. This approach allowed the identification of a wide range of compounds at low concentrations through the comparison of their MS/MS spectra with spectral libraries (e.g., mzCloud) and reference standards.

To reduce data complexity, we conducted hierarchical cluster analysis, enabling the identification of profiles that share similar sources (e.g., biogenic, or anthropogenic) and/or are affected by similar processes (e.g., melting). Our results indicate that one cluster shows a periodicity, i.e., is mostly preserved. Whereas, the other clusters display varying degrees of meltwater influence. Overall, this investigation provides a unique and comprehensive assessment, for the first time, of the impact of melting on the preservation of organic aerosol tracers within a firn matrix. This knowledge is crucial for understanding and interpreting ice core records in the context of global warming.

The Photo Transformation of C1 Compounds; Methanol, Formaldehyde and Formic Acid via Natural Water Components

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The photochemical transformation of naturally occurring organic molecules in the aquatic environment is an essential component of element cycling processes and important in ecosystem function. Photochemistry is not only involved in the buildup of organic molecules through photosynthesis in these systems, but also in their degradation. The degradation of dissolved organic matter (DOM) via photoirradiation can lead to an increase in biologically labile DOM (lower molecular weight components) and can thus provide a key source of growth substrates for naturally occurring microbial communities at the base of the food chain. Despite decades of environmental photochemistry research, we still do not understand the processes involved in the photoproduction and phototransformation of simple, ubiquitous compounds, such as methanol and other lower molecular weight acids in natural waters. Without deeper mechanistic insight, it is difficult to explain the reasons for these variations and how they may change, for instance, due to climate change.
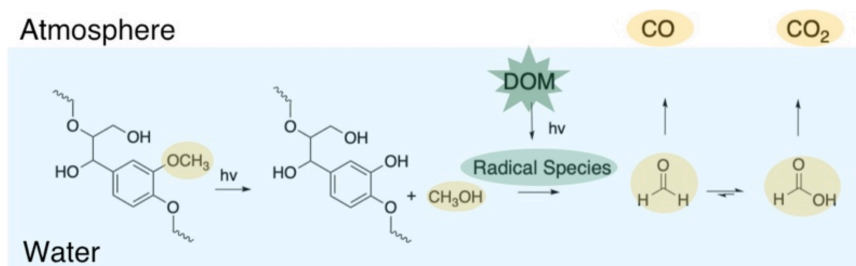
Previous research has demonstrated a link between the irradiation of sea water/DOM and observed the production of carbon monoxide and lower molecular weight acids. Our group further investigated this feature by irradiating a variety of lignin monomers to try and observe potential patterns of CO production and relating it to their chemical structure. We found that upon irradiation of lignin monomers in MQ water, the system produced methanol and CO, and the amount of these products was dependent on the presence of a methoxy group (observed in figure above) on the ring. Although a question remained, how did methanol convert to CO in a system only containing a lignin monomer and MQ water, and how may this represent a photochemical implication for these small compounds in environmental systems.

Upon irradiation of methanol and DOM over the period of 48 hours, we observed four key products; formaldehyde, formic acid, CO and CO_2. The order in which they appeared gave us insight on the pathway and intermediates of complete or partial mineralization of methanol in potential aquatic environments. We observe that methanol reacts with OH radical as predicted whereas formic acid and formaldehyde are more sensitive to singlet oxygen. We also were able to observe different rates of CO/CO_2 production during the experiments which helped us relate which products could be pre-cursors for what could end up in the atmosphere. We showed that formate oxidation led to production of CO_2 when irradiated with DOM, whereas formaldehyde was the precursor to both CO and formate. These findings will be used to elaborate photochemical models of carbon cycling. We believe the transformations of C1 compounds play an important role in the photomineralization of C-substrates in the upper, well-lit zones of aquatic ecosystems.

Climeworks – removing CO$_2$ from the Earth's atmosphere through direct air capture

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Removing carbon dioxide from the atmosphere—legacy emissions and future unavoidable emissions—has become a must to meet climate goals, as pointed out by the latest IPCC report,[1] and is set to become common practice within the next decades. However, the marathon to build a carbon removal industry that successfully operates at gigaton scale has only just begun.

Climeworks was founded in 2009 and has since grown to be the leader in technological carbon removal through direct air capture (DAC). Much of Climeworks' focus has been on building plants and advancing engineering and sorbent technologies. Here, we present Climeworks' synergies between engineering, materials science, and chemistry to advance CO$_2$ capture from air and its permanent storage. This effort is built on a platform for material development with many of the tools that modern chemistry can provide us.

[1]   https://www.ipcc.ch/report/ar6/syr/; accessed on May 16 **2023**.

An on-site sample preparation approach for plant eco-metabolomics and its application to agroecosystems in East Africa

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Mass spectrometry-based plant metabolomics is frequently used to identify novel naturally occurring molecules or study the effect of specific treatments on a plant's metabolism. Reliable sample handling is required to avoid artifacts, which is why most protocols mandate immediate shock freezing of plant tissue in liquid nitrogen and an uninterrupted cooling chain to preserve labile molecules. However, the logistical challenges of acquiring liquid nitrogen and establishing an uninterrupted cooling chain make this approach infeasible for some studies. Especially for research on environmental or ecological systems, permanent cooling can pose a challenge, which is why frequently dried leaf tissue is used instead. While this approach works for stable molecules, the drying process has a significant impact on the overall metabolite profile.

In preparation for a metabolomic study of an agroecosystem in sub-Saharan Africa, we screened ten extraction and storage approaches for plant metabolites retrieved from maize leaf tissue across two cropping seasons to find a method which can be implemented for large sample quantities under logistically challenging conditions. The methods were evaluated across a two-month storage period and directly compared to samples obtained from shock-frozen leaf tissue. We show that our on-site liquid-liquid extraction protocol provides a good compromise between sample replicability, extraction efficiency, material logistics, and metabolite profile stability and is a viable alternative for metabolomics analyses of environmental or ecological systems.

Our on-site sample preparation was then used to study neighbourhood effects in a push-pull intercropping system. The samples were collected from farmer fields in Kenya, Rwanda, Ethiopia, and Uganda, and extracted on-site before shipment to Switzerland for mass spectrometry measurements. Our approach could differentiate maize plants grown under push-pull systems from plants grown with conventional agricultural practices and molecular classification is currently ongoing.

We demonstrated the feasibility of using an on-site liquid-liquid extraction protocol for plant metabolites from maize leaf tissue. We conclude that our method provides a reliable alternative for logistically challenging conditions regarding sample quality and stability as well as ecological scalability. This protocol allowed us to identify differences in the metabolite profiles of maize plants grown under different agricultural practices, highlighting the potential of this method for ecological studies.

Tracing soil sorption and plant uptake by spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) of five antibiotics – experimental test with spiked soil

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Antibiotic residues are widely detected in agricultural soils and animal manure fertilizers, and thus have the potential to be taken up by plants cultivated in such soils. The fate of five antibiotics were studied in an experimental greenhouse trial. The antibiotics of interest were applied as a mixture into a model agricultural soil, representative for Swiss agricultural soils, at increasing concentrations (0, 0.1, 1, and 10 mg/kg for each individual antibiotic). The selected antibiotics consisted of clarithromycin (CLA), enrofloxacin (END), chlortetracycline (CTC), sulfamethoxazole (SMZ) and trimethoprim (TMP), which represent a range of characteristics including cationic (CLA), zwitterionic (END, CTC) and anionic (SMZ, TMP) species dominating under the experimental conditions (soil pH 7.4). Spinach (*Spinacia oleracea*) and radish (*Raphanus sativus*) were grown in the spiked soil, under controlled environmental and climatic conditions for 6 weeks, after which time the crops were harvested. Collected soil and plant samples were extracted for antibiotics with QuEChERS (**Qu**ick, **E**asy, **Ch**eap, **E**ffective, **R**ugged, and **S**afe) method (potassium phosphate buffer: acetonitrile with 5% formic acid, 1/1 vol/vol and acetonitrile with 1% acetic acid correspondingly). The soil LOQs were 3.2 µg/kg for CTC, and < 0.5 µg/kg for the CLA, END, SMZ, and TMP. The absolute recovery for CTC was 70%, and for other antibiotics with isotope labelled available the relative recoveries ranged between 100 and 107%. Pore-water was collected by separating it from the soil by centrifugation. Soil and pore-water samples collected in the course of the experiment (day 0, 2 days, 1 week, 3 weeks and 6 weeks), showed different degradation behaviour between the antibiotics. For example, in the 1 mg/kg concentration half-lives of CTC, SMZ, TMP were 0.9, 3 and 8 days, respectively. However, the concentrations of CLA and END remained constant throughout the experiment, and as a result their concentrations were the highest after six weeks of exposure (CLA>END>CTC>SMZ>TMP). The measured soil pore-water concentrations from the same treatment (1 mg/kg) were highest for CLA and SMZ, followed by TMP, whereas CTC was not detected. The sorption coefficients (Log Kd) for CLA, TMP and SMZ after 6 weeks were 1.9, 0.9 and 0.8, respectively. Based on the differences in the antibiotic sorption behaviour and pore-water concentrations, differences in the uptake and translocation of the antibiotics in plants can be expected. The extractions of the plant above- and belowground fractions are currently ongoing.

Novel Identification of Human Pharmaceutical Metabolites in Untreated Wastewater by Wide Scope Suspect Screening

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Humans are exposed to a multitude of chemical compounds, including pharmaceuticals. Upon intake, they are often metabolized in order to increase polarity and facilitate their excretion. Detection of these metabolites in the influent of wastewater treatment plants (WWTPs) can give information on the exposure of a large fraction of the human population. Many human metabolites arrive at WWTPs in higher amounts compared to their parents, still many studies analyze the parent compounds or focus on already identified metabolites of single compounds. Therefore, this study aims to identify and analyze metabolites originating from a broad range of pharmaceutical parent compounds by online-SPE-LC-ESI-HRMS/MS in combination with suspect screening. For this purpose, untreated wastewater of three Swiss WWTPs was sampled for one week in early 2022 during dry weather conditions. The suspect list was generated based on the yearly consumption amounts of parent pharmaceutical compounds in Switzerland. To complete the suspect list with the respective human metabolites, literature search, mainly with Drugbank and Swiss medical compendium, was performed. The resulting list encompasses around 1100 metabolites of which 80 were covered by a targeted approach. Feature detection and suspect list filtering were performed with Compound Discoverer. To elucidate the structures of the prioritized features, a combination of database search with mzCloud, MassBank and NIST as well as *in silico* prediction with MetFrag, SIRIUS/CSI:FingerID and FISh scoring was applied. Additional confidence was gained by molecular networking, employing the fact that structural similarity between parent and metabolite can lead to similarity in MS2 spectra. Overall, more than 50 metabolites with confidence levels 2 or 3 could be identified in wastewater, several for the first time. Analytical reference standards were purchased for confirmation.
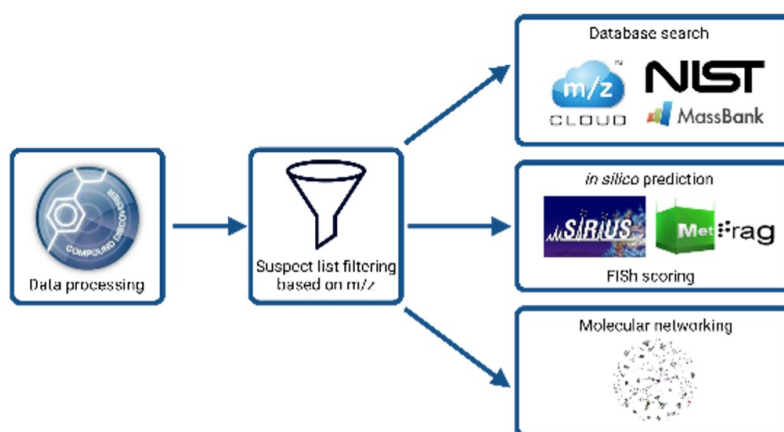
Applied suspect screening workflow using database search, *in silico* prediction tools and molecular networking for human metabolite identification.

Exploring the Metabolomic Alterations in Diatom *Cyclotella meneghiniana* in Response to Hg(II) and MeHg Exposure

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Mercury pollution in aquatic systems is of significant concern for human and environmental health due to its ability to bioaccumulate and to biomagnify (in particularly as methylated form) within the trophic food web. Phytoplankton, including diatom species, are crucial for primary production and the functioning of global biogeochemical cycles. Located in the basis of aquatic food webs, perturbations in these organisms can pose a significant impact on the entire ecosystem. Despite this, our current understanding of how mercury species, such as Hg(II) and MeHg, affect these organisms is limited. Although previous research has identified certain toxic effects of mercury on phytoplankton, the specifics of metabolomic disturbances in diatoms are not well understood. Therefore, the present work aims to study the metabolic alterations in diatom *Cyclotella meneghiniana* induced by short-term exposure to subletal concentrations of Hg(II) and MeHg. For that, this study employed a combination of targeted metabolomics, biological accumulation, and physiological response assays to elucidate the metabolomic disturbances in diatom *Cyclotella meneghiniana*, following a 2-hour exposure to Hg(II) ($8.3 \times 10^{-9} \pm 4.4 \times 10^{-10}$ M and $8.4 \times 10^{-8} \pm 5.1 \times 10^{-10}$ M) and MeHg ($6.5 \times 10^{-9} \pm 6.9 \times 10^{-10}$ M and $7.9 \times 10^{-8} \pm 3.3 \times 10^{-9}$ M).

Findings revealed that Hg(II) and MeHg exposure resulted in metabolism disturbances concerning amino acids, nucleotides, fatty acids, carboxylic acids, and antioxidants, but not carbohydrates. The extent of these alterations was concentration-dependent for Hg(II), with higher Hg(II) concentrations causing more significant metabolomic disturbances. For MeHg treatments, no apparent concentration dependence was found, with both MeHg concentrations inducing metabolomic perturbations.

This research presents the first evidence of the primary metabolomic alteration induced by short-term exposure to Hg(II) and MeHg in the diatom species *Cyclotella meneghiniana*. Our findings highlight the potential advantages of using targeted metabolomic approaches to detect early-stage perturbations caused by metal exposure in the phytoplankton species before physiological endpoint detection.

Keywords: inorganic mercury (Hg(II)), monomethylmercury (MeHg), metabolomic perturbations, diatom species, *Cyclotella meneghiniana*, targeted metabolomic, physiological response assays

Interspecific biotransformation of micro-pollutants in fish from Swiss watercourses with different contamination levels

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The biotransformation of chemicals encompasses biological processes that are triggered in response to chemical exposure to support detoxification and the elimination of xenobiotics. Such processes are likely to vary among species due to factors related to gene conservation and inducibility. However, the influence of these factors towards differential sensitivity to exposure remains understudied. In addition, environmental and anthropogenic factors may alter biotransformation activity and the ability of species to cope with pollution. In the present study, fish species that are representatives of Swiss biodiversity were collected in watercourses with different levels of pollution and surrounded by different land use. Their livers were used to isolate S9 enzymatic fractions and comparative assessments were conducted to assess enzymatic activity and biotransformation rates of different micro-pollutants. Among species, brown trout (*Salmo trutta*) presented the highest activity for enzymes considered gold-standard biomarkers, including CYP1A and Glutathione-S-transferase, particularly in sites with high levels of anthropogenic influence. However, the pumpkinseed (*Lepomis gibbosus*), an invasive species from North America, presented significant activity of other biotransformation enzymes, like CYP3A4, and the highest biotransformation rates for micro-pollutants. Compared to brown trout and pumpkinseed, bottom-dwelling species, like the European bullhead (*Cottus gobio*) and the common barbel (*Barbus barbus*), displayed the lowest enzymatic activity and micro-pollutant biotransformation. These observations underline major species sensitivity differences towards pollution and highlight the influence of environmental and anthropogenic factors that could play a significant role in altering biodiversity in aquatic ecosystems.

Characterization of the main European mineral water brands based on the ion composition

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The history of the mineral water consumption goes back to early legends. Already then, in addition to physiological needs, their beneficial effects were also used in medicine. The composition of each mineral water varies according to its origin, the minerals, salts, gases and radioactive elements it contains and the quantities involved. Chemically, mineral water is a complex liquid.

In our research, statistical methods were used to analyze the chemical composition of the macro-parameters indicated on the labels of European bottled and commercial mineral waters. A total of 692 mineral waters from 13 countries were analyzed. Furthermore, mineral waters were classified according to their evaporation residue and ionic content. Correlation coefficients were used to study the relationship between the chemical composition of rocks and mineral waters.

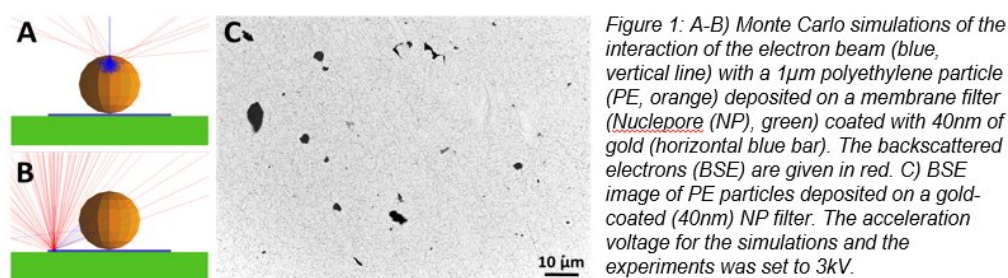Statistical analysis was carried out on the cations Ca^{2+}, Mg^{2+}, Na^+, K^+, and on the anions HCO_3^-, Cl^-, SO_4^{2-}. Piper diagrams of the studied mineral waters were prepared by country, as well as box-plots and Spearman correlation and heat map analysis.

Detection of microplastic particles (1-10µm) in soil matrices

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Quantifying the number of small microplastic particles (MP) in complex matrices is challenging. We, therefore, developed a method based on automated scanning electron microscopy (SEM) to assess MP between 1 and 10µm. We suspended 1-10µm sieved polyethylene (PE), polyvinylchloride (PVC) and Lufa 2.4. soil in different proportions as proxies for contaminated soils. These suspensions were filtered through 40nm gold-coated membrane filters (Nuclepore, Whatman) and imaged using an SEM operated at an acceleration voltage of 3kV. These experimental conditions were derived from Monte Carlo simulations of the interaction of the electron beam with solid materials using the software code CASINO (v. 3.3.0.4) [1] (Figure 1). Particle detection, based on the backscattered electron signal and elemental analysis, using a windowless energy dispersive x-ray (EDX) analysis system (X-TREME, Oxford Inst.), were automated using the software code 'feature' (Oxford Inst.). The classification was based on the carbon to oxygen ratios and on the presence of elements such as silicon or chlorine (Cl).

Figure 1: A-B) Monte Carlo simulations of the interaction of the electron beam (blue, vertical line) with a 1µm polyethylene particle (PE, orange) deposited on a membrane filter (Nuclepore (NP), green) coated with 40nm of gold (horizontal blue bar). The backscattered electrons (BSE) are given in red. C) BSE image of PE particles deposited on a gold-coated (40nm) NP filter. The acceleration voltage for the simulations and the experiments was set to 3kV.

Pure suspensions: In the PVC sample, 70% of the particles were identified as PVC and 15% as PE and soil particles, each. In the PE sample, 85% were identified as PE and 15% as soil particles and in the pure soil sample, 93% of the particles were classified as silicates and 7% as PE.

MP mixtures in soil: The dynamic range of the method was assessed by mixing MP (stock suspension containing equal amounts of PE und PVC MP) with soil suspensions in a 1:1 and a 1:10 ratio. The quantified ratio between PE and PVC in all experiments (pure MP mixtures, 1:1 and 1:10 mixtures with soil particles) ranged between 0.7 and 1.2. The obtained ratios between soil and MP in 1:1 and 1:10 mixtures were 1.1 and 8.5, respectively. These results demonstrate that the MP were correctly identified also in the presence of a 10-fold excess of soil particles. The reduced accuracy of the PVC identification is probably caused by the volatility of Cl under the electron beam. We are currently developing sample preparation protocols to enrich the MP content in soils, which will allow assessing the contents of small MP in field samples.

[1] Demers, H., et.al. (2011), Three-dimensional electron microscopy simulation with the CASINO Monte Carlo software. Scanning, 33: 135-146

Formation kinetics and hydrolysis properties of organic peroxides from monoterpene-derived Criegee intermediates with various organic acids

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It is well recognised that secondary organic aerosols (SOA) represent a major fraction of tropospheric fine particles that can contribute to serious air pollution, damage human health and affect Earth's climate. SOA are typically originated from complex atmospheric (photo)chemical oxidation processes of volatile organic compounds (VOCs), which are emitted from natural and man-made sources. It has been suggested that organic peroxides (ROOR, where R denotes H or an organic group), as a major class of SOA components, can significantly contribute to aerosol toxicity and related health effects. This is mainly due to their oxidising properties, which is also regarded as so-called reactive oxygen species (ROS). Despite their atmospheric and health importance, the analytical identification of compound-specific organic peroxides in atmospheric aerosols is highly challenging, due to their labile properties, complex composition and limited availability of standards. This represents a significant knowledge gap that limiting our understanding of atmospheric processes of organic peroxides and further assessment of their health effects.

In this study, we synthesize a number of atmospheric relevant organic peroxides through liquid phase ozonolysis. Specifically, large excess of ten selected individual carboxylic acid (i.e., cis-pinonic acid, cis-pinic acid) was added into acetonitrile solvent containing either α-pinene or 3-carene. High concentrations of O_3 were bubbled through these solutions resulting in the formation of stabilized Criegee intermediates (SCIs), which can subsequently react with the added carboxylic acid to form target α-acyloxyalkyl hydroperoxide (AAHP), as shown in Fig. 1. The synthesized AAHP standards (ca. 20) were identified individually by means of liquid chromatography coupled to a high-resolution mass spectrometer. The AAHP formation kinetics were also obtained by tracking the temporal profiles of individual carboxylic acids in the same liquid phase ozonolysis process, and the relative rate constant for SCI with various carboxylic acids generally varied small within a factor of 2-3. The synthesized AAHP solution was further used for hydrolysis purpose, and the difference among their hydrolysis rate can be up to two orders of magnitude. As a final proof-of-concept, four AAHPs were unambiguously identified and semi-quantified in the laboratory generated α-pinene SOA and 3-carene SOA samples, and their mass contribution to total SOA was semi-quantified as 0.28% and 0.21% respectively. Our results improve the molecular-level understanding of organic peroxides in SOA and useful for more accurate assessment of their environment fate and health impact.
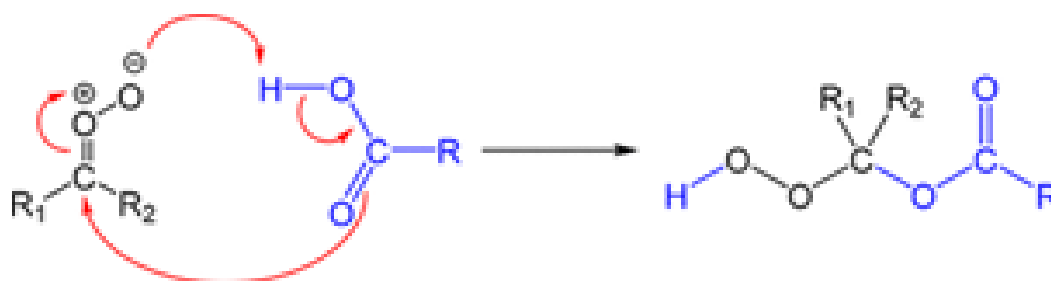
[1] Zhao, R. et al., *Environ. Sci. Technol*., **2018**, 52(4), 2108-2117.
[2] Wang, S. et al., *Chemical Reviews,* **2023**, 123, 4, 1635–1679.
[3] Chhantyal-Pun, R. et al., *ACS Earth and Space Chemistry*, **2018**, 2(8), 833-842.

Direct Irradiation of Aromatic Methyl Thioether Compounds

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Dissolved organic compounds containing photolabile moieties are susceptible to photochemical transformations in aquatic systems. For example, compounds containing reduced sulfur are generally prone to photolytic reactivity. This study focuses on aromatic S-compounds having a methyl thiyl group. This group was proposed to be a precursor to the photoproduction of methane sulfonic acid, a crucial component of the sulfur biogeochemical cycle.[1] However, little is known about their photodegradation pathways that lead to methane sulfonic acid production. In this work, we selected two model aromatic methyl thioethers for in-depth mechanistic analysis and product identification. The first is thioanisole, a pollutant detected in the wastewater of an oil production site.[2] The second is 3-(methylthio)benzoic acid, like thioanisole in structure, but it has a meta-substituted carboxylic group. We observed that the aromatic methyl thioethers in this study undergo direct photolysis in the UVB region. The role of their triplet-excited states was significant in this process. The main products formed were the corresponding sulfoxides through an oxidation pathway. In addition, a cleavage pathway occurs, confirmed by the products identified, revealing the bond break between the aromatic ring and the sulfur methyl group. This work provides insight into the photochemistry of aromatic methyl thioethers and shows that the role of light can be crucial in elemental cycling, sulfur cycling in this case.

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Towards Streamlined Environmental Persistence Assays for Trace Organic Contaminants: Preliminary Findings from High-Throughput Biodegradation Testing

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The 2022 European Commission framework entitled "Safe and Sustainable by Design chemicals and materials" emphasizes the need for early assessment of the hazardous properties of chemicals during their design. However, evaluating the environmental persistence of the large number of candidate molecules generated through the design process requires innovative methods that are high-throughput, automatable, and time-efficient. This poster presents preliminary findings on the adaptation of standard large-volume biodegradation tests into a small-volume 96-well plate format suitable for automation. We carried out comparative biodegradation tests in activated sludge at multiple scales using a test set of 30 chemicals, mainly agrochemicals, selected due to their reproducible degradation behaviour in activated sludge experiments.[1] Tests were conducted over a 48-hour timeframe using reverse phase liquid chromatography (LC) tandem high-resolution mass spectrometry (HRMS). We discuss the variability observed across different experimental scales and evaluate the replicability of results within the 96-well plate setup.
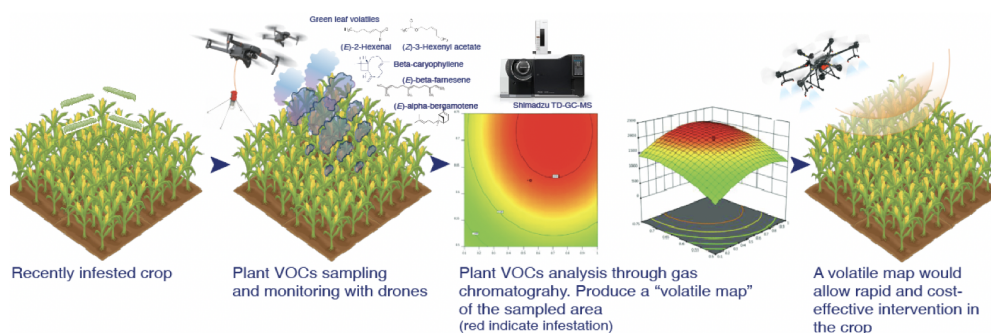
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Development of plant-volatile-based remote sensing for early detection of insect pest presence and crop protection

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Currently, global agriculture is challenged to provide food for an increasing human population while facing climate change and a negative environmental footprint due to chemical pollution. Early identification of plant stress enables fast intervention to limit crop losses, and optimized application of pesticides and fertilizer to reduce environmental impacts. Current image-based remote sensing technologies identify plant stress responses days or weeks after the stress event, usually only after substantial damage has occurred and visual cues become evident. In contrast, plant volatiles are released seconds to hours after stress events, and can quickly indicate both the type and severity of stress. An automated and non-disruptive sampling method is needed to enable the use of plant volatiles for monitoring plant stress in precision agriculture. Here, we present the development of a sampling pump that can be deployed and collected with an uncrewed aerial vehicle. We observed comparable volatile recovery from a blend of 6 to 7 analytical standards between our sampler and a commercial portable pump at low air flows (i.e, 150-200ml/min). Furthermore, our sampler was capable of sampling at the higher flow rates 300, 400, and 500ml/min, which depending on the chemical class of the volatiles -as in the case of the green leaf volatiles (GLVs)-, could be advantageous in outdoor sampling conditions (yet to be tested). Moreover, under indoor sampling conditions of still air, we found that our sampler is capable of recovering volatiles when the distance between the volatile emission point and the sampler is at 1m, 2m, and 4m distance without significant reduction of the volatiles collected. On the other hand, the air downwash of a drone hovering at 1m, 2m, and 4m above the sampler and the volatile emission point significantly reduced the quantity of volatiles recovered. The possibility of robotic collection of plant volatiles is a first and important step towards the use of chemical signals for early stress detection and opens up new avenues for precision agriculture beyond visual remote sensing.

Recently infested crop — Plant VOCs sampling and monitoring with drones — Plant VOCs analysis through gas chromatograhy. Produce a "volatile map" of the sampled area (red indicate infestation) — A volatile map would allow rapid and cost-effective intervention in the crop

Online Quantification of Oxidative Potential from Residential Wood Combustion (RWC) and Car Exhaust Aerosol

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Air pollution particles are the single highest environmental health risk and have adverse effects on human health with over 7 million premature deaths per year. Despite these negative effects, many physical and chemical properties of particulate matter (PM) and their effect on human health still remain unclear. The oxidative potential (OP) has widely been suggested as proxy to measure toxicity in PM. Different assays have been developed to quantify OP over the recent years. Most of them measure the OP offline from aerosol that is collected on a filter and analyzed with a time delay from days to month.

We could show for a biogenic secondary organic aerosol using α-pinene as precursor, that the OP-active compounds decay with a half-life from seconds to hours, leading to the assumption that the OP in filter samples, is potentially highly underestimated. Therefore, we built an online instrument that can quantify OP with a high time resolution using a physiological relevant assay. With this online instrument and the corresponding offline assay, we characterized several aerosol types, where we could show that there is not only an OP decay during the offline analysis, but that this decay is also highly variable for different aerosol systems.

With the online instrument we also measured primary (fresh) and secondary (aged) emissions from RWC and car exhaust to investigate the differences in aging times and compositional toxicity of the different aerosol systems. We could show a highly time resolved signal as well as that for RWC high photochemical ages lead to a lower mass-normalized OP, compared to car exhaust emissions where a higher aging leads to a slightly higher OP. Aged RWC gives, compared to aged car exhaust, an order of magnitude higher OP showing that aged RWC is potentially more toxic.

The fate of heavy metals in industrial recycling facilities of e-waste

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Occupational hygiene (respirable and inhalable airborne dust, settled dust and wipe samples) and human biomonitoring samples (urine and blood) were collected. Exposed workers were recruited who worked in industrial recycling of e-waste. Four target activities within e-waste processing were identified to have associations with exposure to chromium, cadmium, mercury and lead, (i) sorting of e-waste (ii) dismantling of e-waste, (iii) shredding and pre-processing e-waste, and (iv) metal processing for example melting for re-use. Workers were grouped into the following exposure groups: batteries, metals and plastics, white goods (such as refrigerators and washing machines), brown goods (such as TV, audio equipment and similar household appliances) and miscellaneous e-waste. Samples were also collected from workers who were not occupationally exposed to chromium, cadmium, mercury and lead through e-waste processes to form a comparison control group. Urine samples were collected from exposed workers at the beginning (pre-shift) and end (post-shift) of the workweek. Hair samples were collected in the morning preferably before the start of the workweek. Venous blood samples were collected towards the end of the workweek. Chromium, cadmium, mercury and lead has been analysed in urine samples and hair samples. Venous blood samples were collected for the analysis of cadmium and lead in whole blood and chromium in red blood cells. Air and wipe samples are used to identify exposure routes and risk reducing measures. Wipe samples were collected at the beginning and end of the air measurements (ca. 8h) to investigate the increase in dermal contamination. Settled dust samples workplace. Both inhalable and respirable personal dust measurements, hand wipes and settled dust samples were collected for the analysis of chromium, cadmium, mercury and lead.