Inhalt

Instrumental Analytical Chemistry

Dear friends and colleagues,

Last year I announced that transitions of 2019 would become fully active in 2020. At the time of writing, I did not at all though think of the much more impacting effects of a virus pandemic hardly anybody knew about a year ago. In the end, therefore, 2020 truly was different than anticipated. From March on, almost no meetings in presence as a central part of communication in science could take place. The one lucky exception for us was the successful MWAS 2020 in September that fell into a timeslot of less strict restrictions and was welcomed by everybody. Organized mainly by IWW, we could demonstrate how one can host such a meeting with 150 participants under all required safety and hygiene precautions even in times of the pandemic. However, right now, the conference would be impossible. This was also true in May 2020 when we had to cancel our annual water chemistry conference for the first time since 1948 – like so many other events with a long tradition. Of course, we all have been active in finding virtual substitutes that can partially compensate for the lack of direct exchange. And video-based meetings also have their advantages in some cases. I am sure that in the future, after the hoped-for effect of vaccination and relief of restrictions, we will still see more frequent use of all these tools to replace long travels for short meetings partially. However, personal face-to-face contacts, including a drink at the bar, cannot be fully substituted. The same holds true for teaching, where in enormous speed, we have established digital formats after many years of steady but slow growth. And many students may even prefer these formats, in particular, if it allows asynchronous learning. So we should try to merge the best of two worlds in the realm of teaching in the post-pandemic future and thus may at least have won something from the crisis. At the end of 2020, I would specifically like to thank my fabulous team at IAC that helped to master all the additional challenges posed by the pandemic.

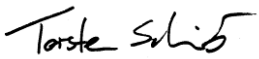
I do not want to mention only SARS-CoV-2, though. 2020 has also seen many successes. In January 2020, water research has finally been endorsed as the fifth research profile area at UDE organized by our Centre of Water and Environmental Research (ZWU). After a very successful online evaluation of our CRC proposal RESIST in September, DFG finally granted the proposal in November, and we will start with the work in early 2021. Finally, the first two projects of the FutureWaterCampus have been granted and allow for the initiation of research work, although approval of the building itself had to be further postponed to next year.

After finishing his external Ph.D. thesis on microplastics analysis in Krefeld, Dr. Gerrit Renner switched fully to IAC as a new group leader in the area of Data Processing and Analysis. In his work on IR spectroscopy of polymers in the environment (see summary of his thesis below) but also in our strengthened focus on the use of high-resolution mass spectrometry at IAC, we have identified data processing as highly relevant for

future research with remaining deficits compared with technological developments. I am sure that Gerrit will be very successful in establishing this junior research group. With Dr. Anam Ashgar, we host a Humboldt fellow since February who works in the area of oxidative processes. I hope that in the long run, she may continue the work in that area at IAC as another junior research group leader, still in close collaboration with her predecessor Holger Lutze, now a professor at TU Darmstadt.

We did not only manage the pandemic in 2020 but were again successful in publishing results of our research in 25 papers in international journals, many of which appeared in the premier journals of
the field. Three of them appeared in a topical collection of Analytical and Bioanalytical Chemistry on "Environmental Analysis of Persistent and Mobile Organic Compounds – An Environmental Challenge" that I guest-edited together with my colleagues Thomas Knepper and Thorsten Reemtsma. Several new projects commenced or continued in 2020 that will be summarized on the next pages to give you an idea of our current activities at the university. Not included here but very important as part of the group activities are the projects by external Ph.D. students at IWW, IUTA, and various other research institutes and in industry.
The all-time record of nine Ph.D. students successfully finished their theses and were awarded their doctoral degrees. Furthermore, 6 Master and 2 Bachelor students completed their thesis work at our department or at an external partner institute with a home supervisor at IAC.
Finally, I would like to thank all group members and students again for their excellent work at IAC and all partners from academia, industry, and funding agencies for their great support and fruitful collaborations.

I hope you are interested in our IAC report and welcome very much feedback or collaboration interests for the future. I wish all of you the best for 2021 and all of us quick relief from the Corona burden. In the meantime, stay healthy!



Torsten C. Schmidt

Instrumental Analytical Chemistry Group Members (autumn 2020)

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Prof. Dr. Torsten C. Schmidt

Secretarial Office
Lydia Vaaßen

Regular Staff

Dipl.- Ing. Gerd Fischer	Project Administration, IT Administrator
Dr. Maik Jochmann (AOR)	Stable Isotope Analysis/Sample Preparation and Gas Chromatography
Dr. Klaus Kerpen	2D-Fluorescence Spectroscopy/Advanced Oxidation Processes/Laser Commissioner
Dipl.- Ing. Robert Knierim	Laboratory equipment/Glassware/Support of guest scientists
Dr. Holger Lutze (until 02/20)	Advanced Oxidation Processes
Robert Marks	Technical support
Dr. Gerrit Renner (from 05/20)	Data Processing and Analysis
PD Dr. Ursula Telgheder	Ion Mobility Spectrometry/2D-Fluorescence Spectroscopy/Expert advice for course of studies/Radiation Protection Commissioner
Claudia Ullrich	Laboratory assistant/Safety officer

Apprentices

Anna Spehr	Laboratory assistant
Tasja Herrmann	Laboratory assistant

Ph.D. Students

Internal

Mohammad Sajjad Abdighahroudi	An investigation of Pharmaceutical and Personal Care Products (PPCPs) as potential precursors for Nitrogenous Disinfection Byproduct (N-DBPs)
Tobias Hesse	Liquid chromatographic methods for stable isotope analysis
Lotta Hohrenk	Suspect and non-target screening of diffuse immissions into aquatic systems
Katharina Hupperich	Influence of organic matter on oxidative transformation processes
Sasho Joksimoski	Novel coupling techniques for the determination of organic compounds in complex samples by ion mobility spectrometry
Wiebke Kaziur-Cegla	Development of a generic protocol for automated sample preparation in GC-MS
Daniel Köster	Development of a wet-chemical interface for online nitrogen isotope analysis of organic compounds using liquid chromatography-isotope ratio mass spectrometry (LC-IRMS)
Seyed Mohammad Seyed Khademi	Direct immersion SPME Arrow – Corona discharge IMS for the determination of pesticides in water samples
Nerea Lorenzo Parodi	Aromatic amines as biomarkers in human urine: Analytical method development and epidemiological studies
Valentina Merkus	Characterization of transformation processes using high-resolution mass spectrometry
Xenia Mutke	Treatment of membrane concentrates by oxidative processes
Nenad Stojanovic	Development and application of advanced stable isotope methods to study compound degradation at real field sites
Jens Terhalle	Transformation processes and Isotope effects in natural and technical aqueous systems
Sarah Willach	Stable isotope analysis to characterize oxidative and photochemical transformation processes
Vanessa Wirzberger	Oxidative water treatment: mechanistic aspects and matrix effects

External

Alexander Augustini	Chemical characterization of the ingredients of electronic cigarettes and the inhaled products.
Anastasia Barion (Günter)	Disk SPE-based sensitive determination of organochlorine pesticides and polybrominated diphenyl ethers in water
Nico Bätz	Effect-directed identification and reduction of diffuse immissions in rivers
Sandro Castronovo	Examination of micropollutant degradation in biological wastewater treatment: a proteomics approach
Matin Funck	Development of a Sampling-Procedure allowing subsequent qualitative and quantitative Pyrolysis-GC/MS analysis for Subµ-Plastics in the Aquatic Environment
Lina Gessner	Hemoglobin based blood volume estimation for the (semi-) quantification of methadone, opiates, cocaine and metabolites in Dried Blood Spots (DBS), deposited on non-standardized materials, via GC/MS-MS
Vanessa Hinnenkamp	Development and application of suspect and non-target screening of water samples using high resolution mass spectrometry (HRMS)
Jana Hinz	Development and application of multidimensional GC-IMS methods for the analysis of volatile and semivolatile substances in safety and health research
Oliver Höcker	Characterisation of anaerobic processes in biogas generation using non-target screening
Frank Jacobs	Development of an automated microextraction technique
Sarah Klaes	Development and optimization of an electrochemical flow cell and coupling with the multi-elemental analysis
Kjell Kochale	Automated hyphenation of effect-based and instrumental analysis
Susann Pristat	Development of procedure tests for hot and cold coils considering the optimization of transport logistics of slabs
Kirsten Purschke	Suspected Target Screening of organic compounds in industrial wastewater
Gerrit Renner	Development of new spectroscopic and multivariate chemometric methods for the characterisation of (micro)plastics in the marine environment
Sara Schäfer (Saß)	Oxidative transformation of organic compounds in ultrapure water by ozonation and UV photolysis

Fabian Ude	Non-radioactive, energetically variable ionization unit for pollutant analysis in building materials based on FAIMS technology
Tobias Werres	Microfluidic characterisation of high performance liquid chromatography systems with the main emphasis on the intrinsic efficiency

Research and Teaching Assistants

Felix Drees

Simon Nikutta

Christina Sommer

Felix Niemann

Kaliyani Wickneswaran

Guest Scientists

Prof. Sina Dobaradaran,

Bushehr University of Medical Sciences, Iran

- Comprehensive study on environmental emissions/sorption of PAHs by cigarette butts (CBs)
- Study of the kinetics of PAHs release from the cigarette butts into the aqueous solutions
- Improvement of a method for detection of PAHs contents of CBs by GC-MS (my next project)

Dr. Cheolyong Kim,

Pusan National University, South Korea

- Formation mechanisms of halogenated by-products from dissolved organic matter (DOM) during the sulfate radical based oxidation process

Dr. Anam Asghar

Postdoctoral Research Scientist
Alexander-von-Humboldt Georg Forster

Project Title: Oxidation of Micropollutants: Synergistic effects of ozone integrated peroxymonosulfate (PMS) oxidative processes

With the research expertise in oxidative processes, the main aim of this visit is to further advance my research exposure and investigate the fundamental mechanism of oxidative wastewater treatment processes. The first phase of this project focused on the yields of oxidants (i.e., hydroxyl and sulfate radicals) in ozone and ozone/peroxymonosulfate (PMS) processes. The synergetic effects of these oxidants were evaluated with the main focus on the targeted screening of transformation products formed as a result of oxidative degradation of micropollutants (MPs) in pure and mixed water matrix. In continuation to current research activities, this work in its second phase, further intends to focus on the degradation of MPs and subsequent formation of transformation products in heterogeneous oxidative processes. In such processes, the experimental protocol demands similar challenges as that of homogenous processes but the special challenge would surely be the activity of catalyst in the presence of water matrix.

Awards

Valentina Merkus

On June 05, 2020 was awarded at the university-wide Dies Acdemicus for the best master degree in the faculty of chemistry 2019. Due to Corona restrictions at the time, the Dies for the first time had to take place online and the awards were not handed out in person.

Dr. Fabian Itzel

Young Scientist Award 2020, Centre for Water and Environmental Research (ZWU) for his PhD thesis "Investigation of agonistic and antagonistic endocrine activity during full-scale ozonation of waste water". Due to Corona restrictions, the YSA could not be handed out in presence.

Michelle Klein

Young Scientist Award 2020, Centre for Water and Environmental Research (ZWU) for her master thesis "Ecotoxicological impact of nitrogen-containing micropollutants and their oxidation products"
Due to Corona restrictions, the YSA could not be handed out in presence.

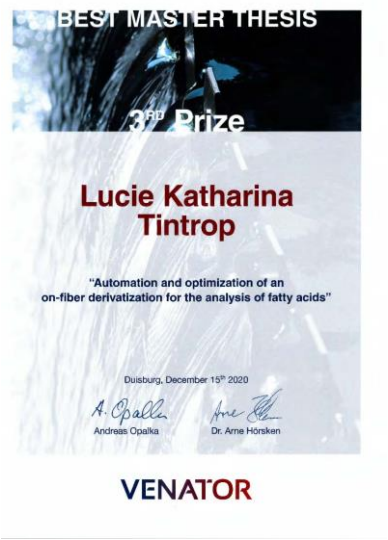
Wiebke Kaziur-Cegla

on September 17, 2020 received the 2nd poster award on the 4th MWAS (Mülheimer Wasseranalytisches Seminar) for her poster entitled

"Automated Solid Phase Microextraction Arrow for Determination of Phosphorous Flame Retardants in Water".

Felix Drees

Award of the best Bachelor Degree in Water Science (December 16, 2020)



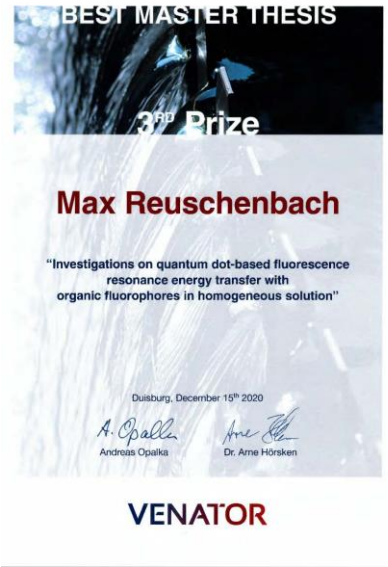
Lucie Tintrop

Water Science Awards for best master theses:
"Automation and optimization of an on-fiber derivatization for the analysis of fatty acids"
3rd Venator Water Award

Mischa Jütte

Water Science Awards for best master theses:
"Oxidation of nitrogen-containing micropollutants with chlorine dioxide in surface water"
3rd Venator Water Award

Max Reuschenbach



Water Science Awards for best master theses:
"Investigations on quantum dot-based fluorescence resonance energy transfer with organic fluorophores in homogeneous solution"
3rd Venator Water Award

Robert Marks

Evonik Operations GmbH Award for the best master theses:
„Gezielte Oberflächenmodifizierung mit Raman-kodierten Nanopartikeln“
(December 16, 2020)

Kittitouch Tavichaiyuth

Water Science Awards for best master theses:
"Investigation of the nitrogen-free phosphonate antiscalants in oxidation process: reaction kinetics and degradation rate"
2nd Venator Water Award

Max Reuschenbach

On December 15, 2020 Max Reuschenbach was awarded for best performance in analytical chemistry during the Water Science Master program by GDCh, Division of Analytical Chemistry.

Data Processing & Analysis: A New Junior Research Group

Group leader: Dr. Gerrit Renner

> *"Many laboratory scientists view data analysis as a hobby—the last thing performed when writing up a paper or report on a Friday afternoon. They often spend months or years acquiring data and at the very last minute produce some sort of statistical analysis to include in their paper to please referees and editors." — Richard G. Brereton, A short history of chemometrics: a personal view*

Brereton's quite provoking statement addresses all of us, and we have to admit that he has hit the nail on the head. Over the years, measurement data became more extensive and more complex, and looking at the developments of digitalization, processing and analyzing measurement data will become more and more crucial. However, the number of chemometric methods is almost infinite, but unfortunately, there is a vast lack of standardization. Taking the right decision highly depends on the initial research question you want to answer and on the data's structure. And in many cases, after searching in vain, we use methods we are already familiar with, knowing full well that they are of limited use in answering our questions. In the end, it is a pity, as we do not manage to unfold the full potential of our scientific experiments, and to that end, the IAC established a new junior research group that will challenge data processing and analysis. The new group will work closely with all IAC scientists, develop new chemometric workflows, and realize automation concepts to handle large or big datasets.

The first project will focus on liquid chromatography high-resolution mass spectrometry (LC-HRMS) non-target analysis (NTA) data. In this context, Lotta Hohrenk-Danzouma et al. from the IAC already confirmed the assumption that NTA results are spiked with a significant number of false-positives. Moreover, results evaluated with algorithm A do not match with results evaluated with algorithm B or C. However, the conventional algorithms for NTA are not insufficient, but the study pointed out that it is hard to impossible to setup and optimize all evaluation parameters for the individual algorithms. Additionally, most algorithms for NTA do not come up with any information about result reliability. Therefore, the project will aim to find new and more robust ways for NTA evaluation and develop a new supporting output variable that will contain information about result reliability.

Another aspect the new group will be looking for is comparing different samples, which is a data analysis process. Of course, one can compare two samples based on a set of properties that both samples have in common in an ideal world. However, this is hardly the case in the real world, and you have to challenge how to compare apples with oranges. The main question here is how we define similarity and dissimilarity. How will we treat the fact that some samples have properties that other samples do not have, e.g., they consist of partly different chemical substances? The new group will investigate and develop new similarity analysis methods based on pattern recognition, neural networks, and machine learning.

Last but not least, the data processing and analysis junior research group would like to sensibilize the relevance of data evaluation within the analytical process.

Running Projects at IAC 2020

NRW Graduate School Future Water: Global water research in the metropolitan region Ruhr (Future water)

Involved staff: Lotta Hohrenk (IAC PhD student), Vanessa Wirzberger (IAC PhD student), Dr. Holger V. Lutze, Claudia Freimuth (Coordinator), Prof. Dr. Torsten C. Schmidt (Speaker)

Partners: Prof. Dr. Bernd Sures, Prof. Dr.-Ing. André Niemann, Prof. Dr. Martin Denecke, Prof. Dr. Rainer Meckenstock, Prof. Dr. Jens Boenigk, Prof. Dr. Nicolai Dose (University of Duisburg-Essen), Prof. Dr. Marc Wichern (Ruhr-University Bochum), Dr. Jochen Türk, Nico Bätz (IUTA), Michelle Klein (IUTA), Prof. Dr. Sigrid Schäfer (EBZ Business School Bochum), Prof. Dr. Mark Oelmann (HRW Mülheim), Dr. Steven Engler (RUB) and many mentors and collaborators from the water and wastewater sector

Funding: Ministry for Culture and Science of the State of North-Rhine Westphalia (NRW) through the joint project "Future Water: Global water research in the metropolitan region Ruhr"

The multiperspectivity of inter- and transdisciplinary approaches allows to conduct innovative and path-breaking research. Combining knowledge and methods across disciplines makes possible to identify hitherto unnoted research questions. Tackling questions from different and novel angles allows to find answers that have not been conceived before. The integration of practitioners into these processes can enhance the relevance of the research questions, the fit of the methods applied, the effectiveness of research processes and the applicability and outreach of the results.

This approach is at the very heart of the graduate school "Future Water", which is located in the Ruhr metropolitan area in Western Germany.

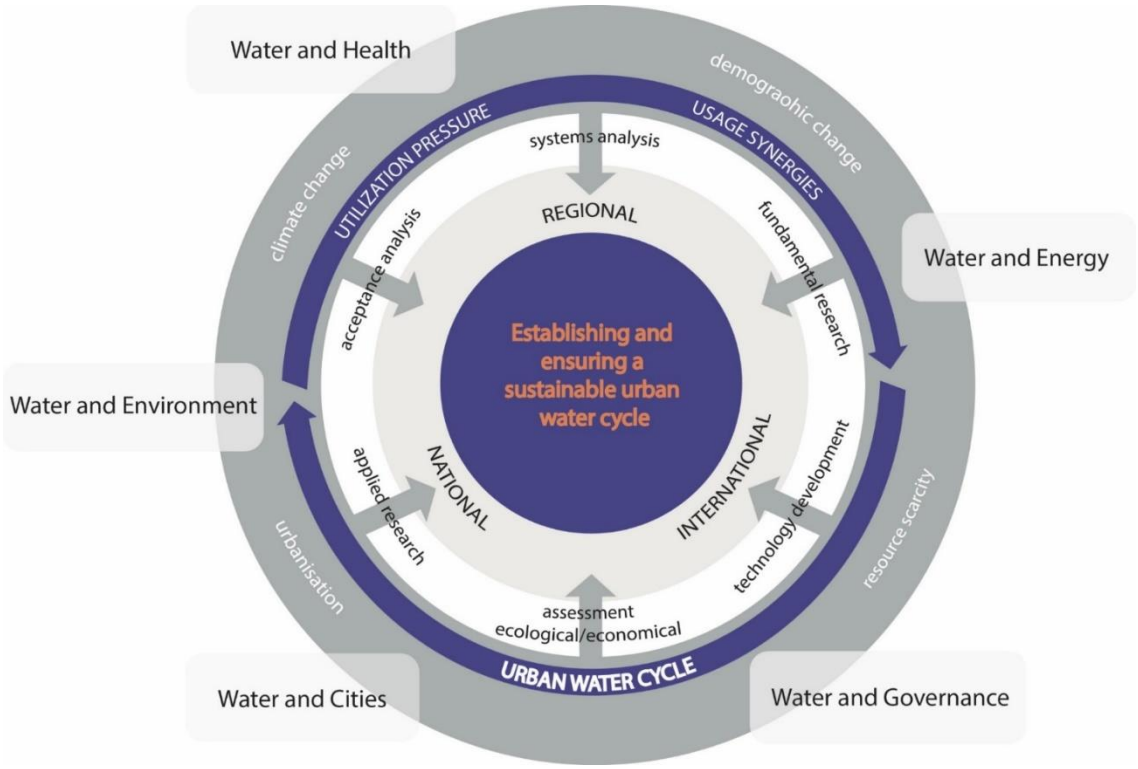
In 2014, a variety of academic and applied institutes joined forces to develop strategies for a sustainable water management with a special focus on the urban water cycle. The following figure describes the many facets of that work. The wide array of disciplinary backgrounds represented in the graduate school made building bridges between the natural sciences, applied engineering and social sciences both possible and necessary. Altogether, in Future Water 12 PhD students and a coordinator position are funded. Coordination is done by the Centre for Water and Environmental Research (ZWU) at UDE. In 2019, continuation of the graduate school in a second funding phase 2019-2022 was granted.

At IAC, one project (Lotta Hohrenk-Danzouma) focuses on the analysis of micropollutants introduced by diffuse sources with nontarget screening. Nontarget screening is based on high resolution mass spectrometry and offers the potential of detecting broad range of analytes at low concentrations in one full scan measurement. By that it provides a more complete overview about compounds present in a sample, enables the identification of formerly unknown contaminants and reveal temporal or spatial trends.

Especially small streams can be affected by diffusive introduction of pollutants like agricultural run-off due to smaller dilution ratios and peak exposures after heavy rainfalls. Passive samplers accumulate organic micropollutants over a certain time period, by that a more comprehensive monitoring is possible and episodic pollution events are less likely to be missed compared to spot samples.

With nontarget anlysis approaches a large number of data are recorded and extensive data processing is necessary. Different chemometric tools can be further used for data mining and prioritization of relevant pollutants.In the current project passive sampling extracts are analysed with a LC-HRMS based nontarget screening method and temporal- and spatial trends are explored by chemometric methods.

Another project at IAC (Vanessa Wirzberger) deals with reaction mechanisms of nitrogen containing compounds (in detail diclofenac, metoprolol and isoproturon) during ozonation with special focus on the reaction with matrix components and the formation of transformation products. Transformation products are identified with LC-HRMS and tested in regards of their toxicity to aquatic organism (D. magna).



Selection of the ZIM cooperation project "LUKE" (project partners: Fabricius Pro Terra GmbH and Instrumental Analytical Chemistry) as an example of success

Involved staff: Sasho Joskimoski, Michelle Lüling, Dr. Klaus Kerpen, PD Dr. Ursula Telgheder

On June 10, 2020 the ZIM cooperation project "Development of a combined in-situ remediation and monitoring method for the treatment of contaminated groundwater (Luft-Untergrund-Kontamination-Erfassung "LUKE")" was published by the AiF as an example of success.

The aim of the project was the development of a low-cost in-situ process for the remediation of BTEX-contaminated groundwater. For this purpose, Fabricius Pro Terra GmbH realized a special multiparameter lance system for the installation of a gas injection system, for continuous sampling and for the direct determination of the parameters pH-value, O_2-content, conductivity and moisture in the aquifer. This technology also allows an efficient remediation of low polluted aquifers by oxygen input, which activates microbiological and chemical processes for the degradation of pollutants. Coupled with the system is a modified Field Asymmetric Ion Mobility Spectrometry (FAIMS) spectrometer, which allows continuous monitoring of the pollutant concentration in the observation level. This monitoring system was developed in the Department of Instrumental Analytical Chemistry, Faculty of Chemistry at the University of Duisburg - Essen.

Further information can be found under:

https://www.zim.de/ZIM/Navigation/DE/Infothek/Erfolgsbeispiele/erfolgsbeispiele.html

Characterization of the metabolome of P. aeruginosa in biofilms as a lung infection model

Involved staff: Timo Köhler (AAC), PD Dr. Ursula Telgheder

Partners: Prof. Dr. Oliver Schmitz, Applied Analytical Chemistry, University of Duisburg – Essen,
Dr. Jost Wingender, Environmental microbiology and biotechnology, University of Duisburg – Essen

Funding: German Research Foundation (DFG)

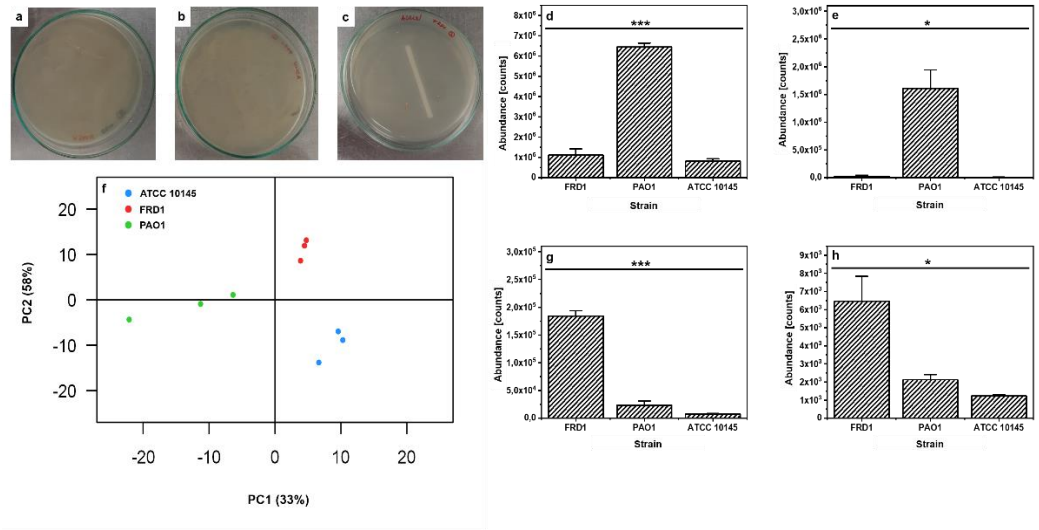


Figure: Cultivation of *P. aeruginosa* ATCC10145, PAO1, FRD1 in an *in vitro* biofilm model (CF-like conditions) and subsequent TD-GC-qMS analysis. Fig. a - c: confluent biofilm growth; Fig. f: scores plot; Bar charts of the significance analysis, d: 2-octanone (confidence level: *); e: 2-tridecanol (*); g: butyric acid n-butyl ester (***); h: 2-amino-1,3,5-triazine (*).**

Cystic fibrosis (CF) is an autosomal recessive hereditary disease that leads to the production of thickened mucus in the infected organ (e.g. lung). Conditions in the infected lung favour polymicrobial infections, such as chronic lung infections with *Pseudomonas aeruginosa*. *P. aeruginosa* is the major pathogenic bacterium colonizing CF lungs at the end of the lifetime of CF patients. [A. Folkesson, Nat Rev Microbiol, 2012;10:841–51]

Using the *in vitro* biofilm model and the developed TD-GC-qMS method, *in vitro* studies of the extracellular volatile metabolome (mVOCs) of *P. aeruginosa* were performed under CF-like conditions. Sampling of mVOCs was performed by thin-film microextraction. Using a solid artificial sputum medium (developed together with the project partners), confluent biofilms of *P aeruginosa* ATCC 10145, PAO1 and FRD1 were cultivated under CF-like conditions (see Figure, a - c). The comparison of the mVOCs of the three bacterial strains using a PCA shows a variance in the metabolome (see figure f). In comparison of the CF-relevant strains *P. aeruginosa* FRD1 and PAO1, a total of 31 metabolites were identified in which a significant increase or decrease in peak intensity was observed. As an example, this is shown for four selective metabolites in the figure d, e, g and h in form of bar charts.

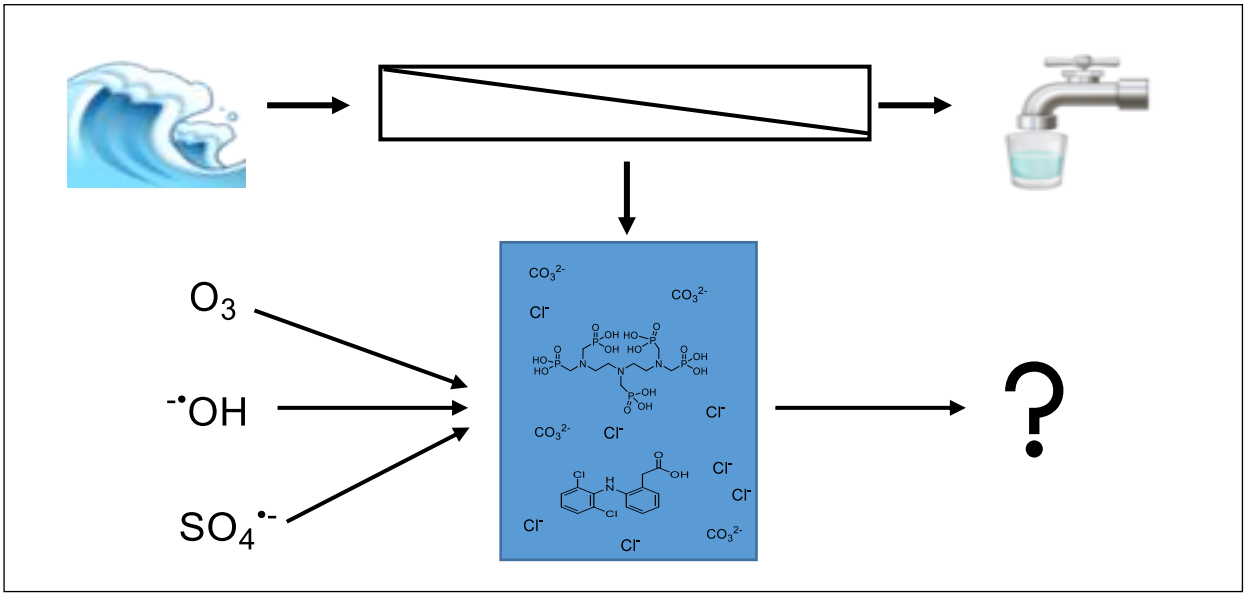
Further *in vitro* studies on the extracellular volatile metabolome of other CF-relevant bacterial pathogens will be performed in the future. The aim of these studies is the identification of bacterial pathogens from CF sputum based on selective metabolites and the variance of the peak intensity of these metabolites. Furthermore, the results will be used for the development and establishment of a clinical non-invasive "at-bedside" breath analysis method for CF patients.

Membrane processes in drinking water supply (KonTriSol)

Part: Membrane concentrate treatment with oxidative processes

Involved staff: Xenia, Mutke, Prof. Dr. Holger V. Lutze (TU Darmstadt), Prof. Dr. Torsten C. Schmidt
Involved students: Kittitouch Tavichaiyuth, Felix Drees, Orkan Akin
Partners: IWW Water Centre, TZW, University Frankfurt, Technical University Berlin, Technical University Hamburg, Cornelsen Umwelttechnologie, Delta Umwelt-Technik, Lagotec, Lanxess, Solenis,
Funding: Federal Ministry of Education and Research (BMBF)

The project KonTriSol deals with the technical, legal and economic solution approaches for the usage of nanofiltration (NF) and reverse osmosis (RO) processes. Over the next years, ten project partners will work on elimination steps for technical and permission barriers of NF/RO technology in drinking water treatment.



NF and RO membrane technologies enabling the reduction of water hardness, inorganic water constituents, natural organic substances, and anthropogenic substances. The resulting concentrates contain a high concentration of these substances and additional a high concentration of antiscalant chemicals added during the treatment processes. The direct disposal of concentrates to the environment could be hazardous to aquatic organisms and increase the micropollutant contamination of water bodies.

The aim of the IAC project part is to investigate the application of oxidative processes to concentrates of membrane processes. Focus of the study is the reactivity of antiscalants in regard to different oxidizing agents like ozone, hydroxyl radicals and sulfate radicals. Furthermore, the influence of high matrices (high chloride, calcium, carbonate sulfate, silicate, and NOM content) on the degradation efficiency of antiscalants, pharmaceuticals and perfluorinated compounds will be investigated.

Influence of organic matter on oxidative transformation processes

Involved staff: Katharina Hupperich, Prof. Dr. Holger V. Lutze (TU Darmstadt), Prof. Dr. Torsten C. Schmidt
Involved students: Kaliyani Wickneswaran
Funding: German Research Foundation (DFG)

It was shown that matrix components can affect the transformation product (TP) formation during oxidative processes. This was firstly observed in the transformation of dimethylsulfamide to the cancerogenous compound *N*-nitrosodimethylamine (NDMA) which required presence of bromide. Yet, such effects of the water matrix on transformation processes are hardly investigated. The present project deals with matrix effects on transformation processes governed by natural organic matter (NOM). In the reaction of *N*-containing pollutants, reactive intermediates are such as aminyl radicals and nitroxide radicals can be formed and their reaction to final products (Figure 1) are hardly studied yet, which is one major task in the present project.

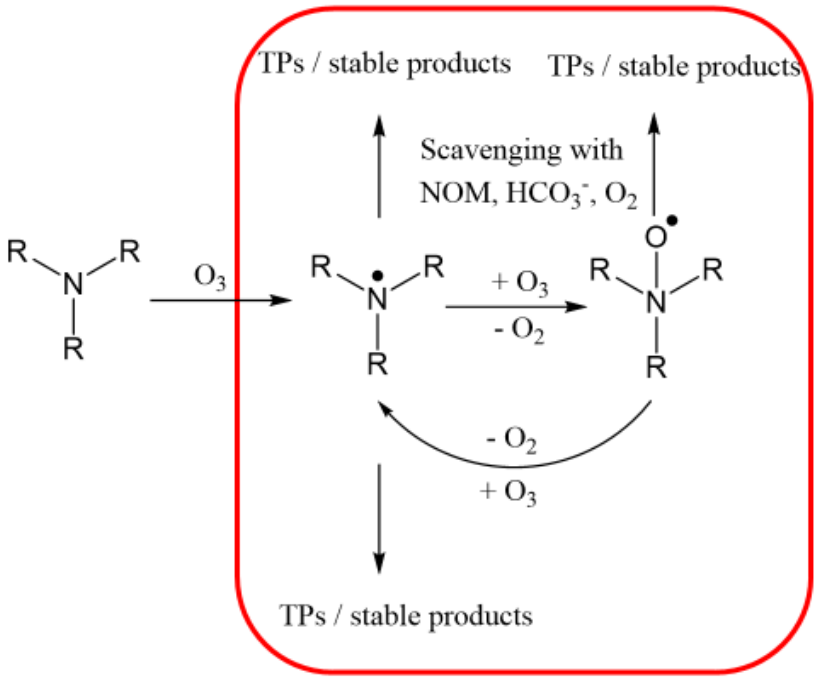


Figure 1: Possible reaction pathway of nitrogen containing compounds with its reaction of matrix compounds

Thereby kinetics of the reaction with aminyl radicals with simple model compounds representing reactive sites of matrix will be investigated, using laser flash photolysis coupled with time resolved UV-Spectroscopy (ICCD Camera).

Furthermore, the structural changes of NOM upon reactions with oxidants used in water treatment (O_3 and ClO_2) is investigated using excitation emission measurements/matrices (EEM). Thereby, the EEM measurements give signals which are specific for the molecular structure, enabling to identify a change in the chemical structure of NOM upon oxidation reactions (Figure 2). Therefore, a method to process the data to qualify and quantify these changes will developed.

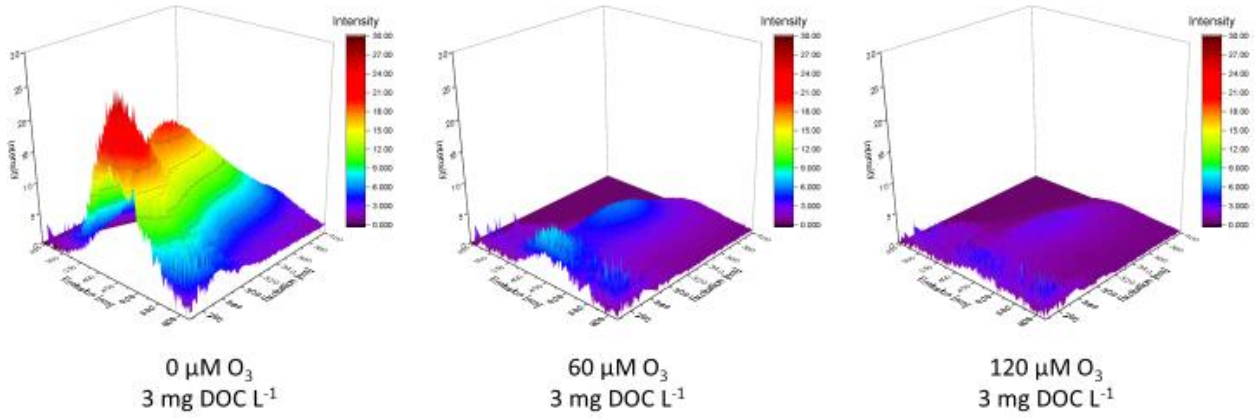
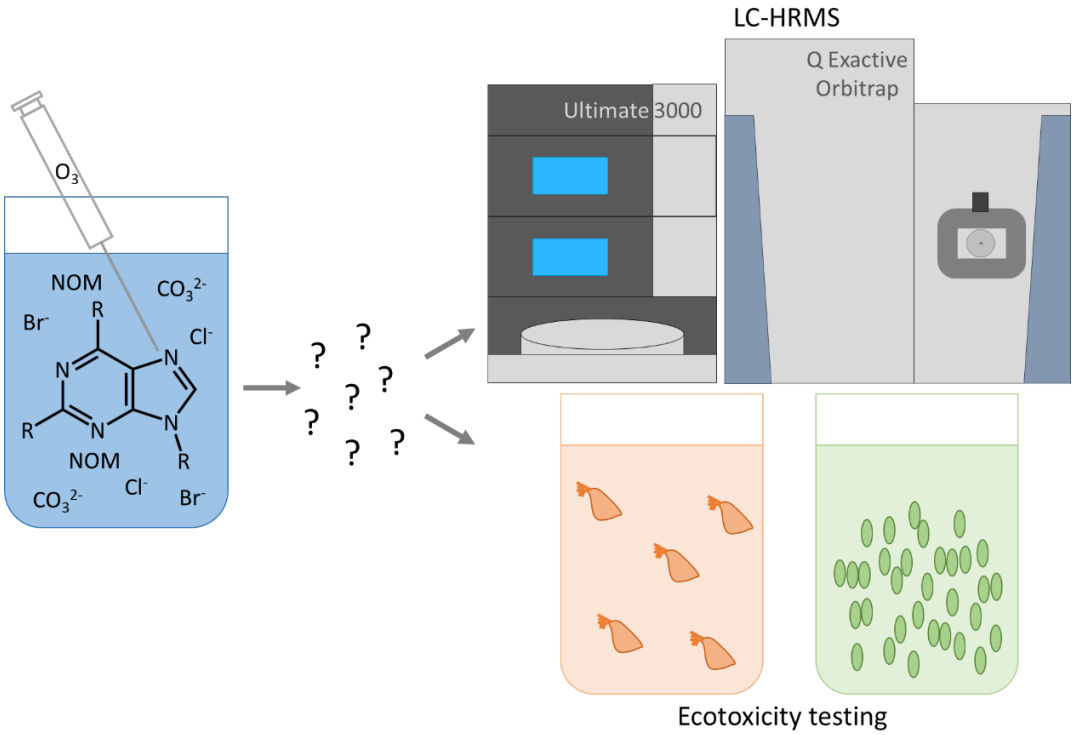


Figure 2: EEMs after eliminating Raman and Rayleigh scattering of Suwannee River NOM (3 mg DOC L^{-1}, 5 mM phosphate buffer, pH 7) without ozonation and ozonated with 60 and 120 µM)

Characterization of transformation processes using high-resolution mass spectrometry

Involved staff: Valentina Merkus, Prof. Dr. Torsten C. Schmidt
Involved students: Christina Sommer
Funding: Fonds der Chemischen Industrie (FCI)



Ozonation of sample compounds in defined water matrices to unknown products (left) followed by transformation product identification by LC-HRMS (top right) and ecotoxicity testing (bottom right).

Oxidation processes are widely used in wastewater treatment for the removal of micropollutants, although there is still a lack of knowledge of the ongoing mechanisms. It is known that organic substances are transformed to reaction products. These transformation products may then reach the environment instead of the original pollutants. Here they may cause several negative impacts like ecotoxicological or endocrine effects. Hence, there is special interest in the identification of transformation products of widely spread contaminants and in the understanding of their formation in various water matrices.

However, examinations are barely possible for all single compounds due to the high number of detected pollutants in wastewater. Therefore, the ozonation of small, general structures and related more complex structures including environmentally relevant pollutants is investigated in this project. Special attention is given to the influence of the water matrix components alkalinity, organic matter, and inorganic anions such as chloride and bromide. The aim of this work is to predict the ozonation of micropollutants on their general structure and in dependence of the water matrix. Purine, its derivates guanine and adenine, and the two antiviral guanine derivates acyclovir and penciclovir were chosen as example substances. The project includes general examinations of their ozonation like stoichiometry, reaction kinetics and quantification of target products. Nevertheless, the main focus is the identification of the transformation products using high resolution mass spectrometry.

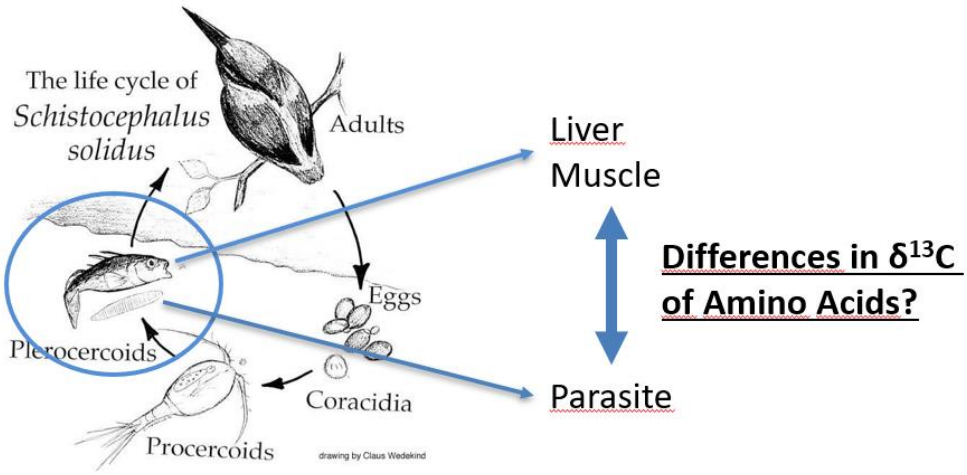
The second part of the project is the ecotoxicological examination of the ozonation of ibuprofen, which showed increased toxicity to algae compared to the parent compound solely. Ecotoxicity is studied by standardized test systems such as acute toxicity testing on *Daphnia magna* and the freshwater algae test. Simultaneously, transformation products are identified and their formation and degradation depending on the ozone dosage are examined by high resolution mass spectrometry. Parameters such as pH and the presence of scavengers can be changed to affect the formation of oxidation products and therefore possibly also the ecotoxicity of the ozonated mixture. This coupling of methods allows to identify the toxic products, for which no standards are available, or exclude products from further toxicity testing.

Compound specific carbon isotope analysis of amino acids and sugars via LC-IRMS to investigate host-parasite interactions

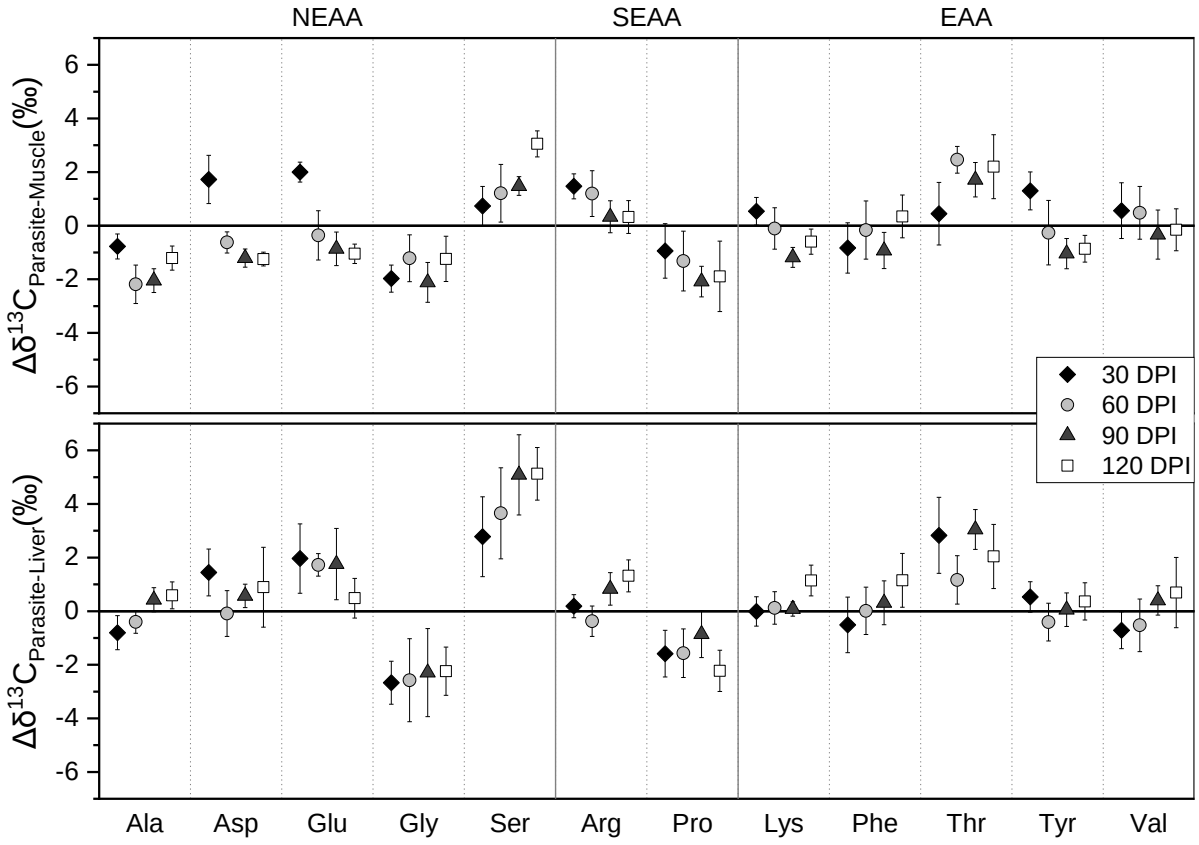
Involved staff: Tobias Hesse, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt
Involved students: Shaista Khaliq
Partners: Dr. Milen Nachev, Prof. Dr. Bernd Sures, Aquatic Ecology
Funding: Internal

Parasites are present in almost all types of ecosystems and they employ the most popular lifestyle on earth. There are hardly any species which are not part of a parasitic lifecycle, to a point where even parasites have parasites. Yet scientists struggle to incorporate parasites into classical food web approaches not only because of their small size, but also because of the complexity of their trophic transmissions and lifecycles. However, the biomass of parasites in a given ecosystem can exceed that of top predators and neglecting them will falsify not only link density and connectance in a food web, but also estimates for energy and nutrient transfer.

This project focuses on the analysis of carbon stable isotope signatures to investigate the metabolic relationship between a host and its intermediate parasite. Stable isotope analysis has been recently recognized as a powerful but underutilized tool to examine host-parasite interactions and our focus will be on amino acids and glucose as metabolic compounds for energy and nutrient transfer. Samples are drawn from a feeding experiment in which three-spined-sticklebacks (*Gasterosteus aculeatus*) were experimentally infected with the tapeworm *Schistocephalus Solidus*. Individual infected and non-infected (control) fish were dissected on a monthly basis and samples were taken from muscle, liver and parasite tissue. Compound specific isotope analysis (CSIA) of amino acids and glucose was carried out using an LC IsoLink™ interface (Thermo Scientific™) coupled to an isotope ratio mass spectrometer (DeltaV Advantage, Thermo Scientific™) and using established methods for compound hydrolysis and chromatographic separation.



Three-spined sticklebacks only act as an intermediate host of the parasite and represent one part of its complex life cycle. Samples were taken from fish liver, muscle and parasite tissue over a course of four months and analyzed with regard to differences in their carbon isotope signature of individual amino acids.



Carbon isotope values of individual amino acids are plotted as the difference between parasite and fish muscle (liver) over a period of 120 days after infection (DPI). Amino acids can be divided into non-essential (NEAA), semi-essential (SEAA) and essential (EAA), based on the ability of an organism to synthesize those compounds.

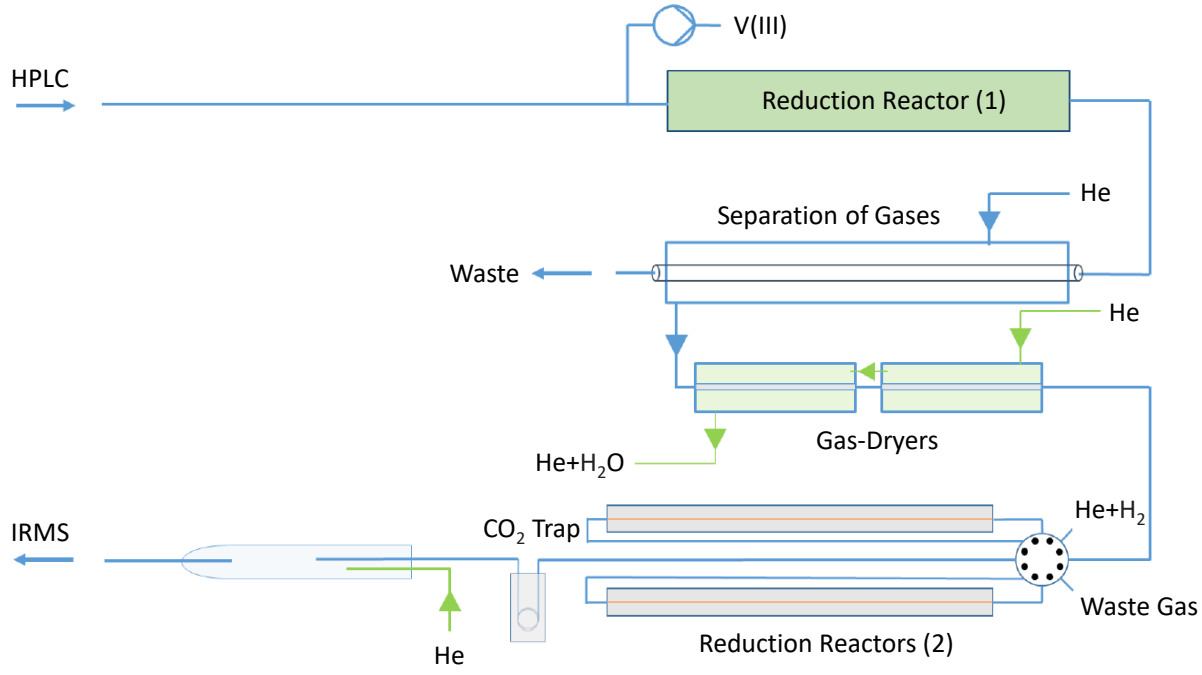
First results show that most of the essential amino acids show little to no fractionation between parasite and the host's muscle or liver tissue. This is a common observation, as these compounds cannot be synthesized *de novo* and have to be taken up through diet. The only exception is threonine, which shows enriched carbon isotope values between parasite and host for both liver and muscle. Threonine can be extensively metabolized in animals to yield glycine, which is an important amino acid for both cell growth and energy metabolism. Non-essential amino acids show higher amounts of isotope fractionation, as these substances can be synthesized in organisms. Glycine and serine show the highest differences over the whole sampling period. The same applies for glutamic and aspartic acid at the beginning of the experiment after 30 DPI. Threonine, glycine and serine are closely linked, not only because threonine can be metabolized to yield glycine, but also because glycine and serine are interconvertible and closely related to gluconeogenesis, which is probably used by the parasite to synthesize high amounts of glucose for reproduction in the adult life stage. Therefore, we believe that isotope analysis of glucose will complement our results, which is the current focus of our research to finalize our observations and gain a deeper insight into host-parasite relationships.

Development of a modified interface to determine stable nitrogen isotope ratios of nitrate by LC-IRMS

Involved staff: Tobias Hesse, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt
Involved students: Felix Niemann
Funding: Internal, ZWU

Human activities have led to an increasing release of reactive nitrogen species into the environment, with N_2 fixation and the combustion of fossil fuels as the most important anthropogenic sources. Impacts on the global nitrogen cycle are a matter of rising concern, and nitrate is an important intermediate in this cycle. One of the known consequences of nitrate release into aquatic freshwater systems is a decrease in biodiversity and adverse health effects on humans and especially infants. Stable isotope analysis of nitrogen and oxygen is an effective way to identify the source and fate of nitrate pollution. However, current methods are limited and labor-intensive.

The aim of this project is to modify an LC-IRMS system to determine the stable nitrogen isotope ratios of nitrate in water samples. Complex sample preparation, as needed in popular methods, should become unnecessary. The quantitative conversion of nitrate to nitrogen takes place online in a two-step process involving a vanadium(III) reactor, reducing nitrate into N_xO_y-species and a subsequent copper oven reducing these species into elemental nitrogen. The product will be analyzed in an IRMS for its stable nitrogen composition.



Setup of the modified interface for online reduction of nitrate to elemental nitrogen. Conversion takes place in a two step process: 1) Nitrate is reduced in the liquid phase with vanadium(III) to N_xO_y-species and 2) N_xO_y-species are further reduced in the gas phase using hot copper wires. The resulting nitrogen is introduced into an isotope ratio mass spectrometer for isotope analysis.

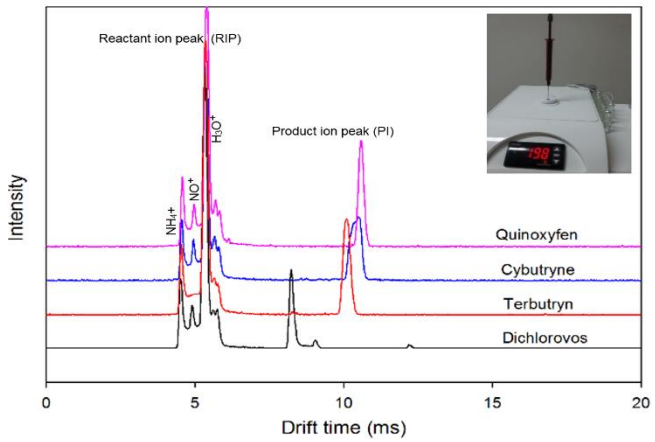
The setup is currently tested in our laboratory and first results look promising. Nitrogen peaks from nitrate could be detected after reduction and were separated from the injection peak using a Hypercarb™ PGC chromatographic column (Thermo Scientific™). We are currently evaluating the efficiency of nitrate reduction with vanadium(III) after the first reduction reactor by quantifying the remaining nitrate concentration of a stock solution using ion chromatographic methods. Further optimization will be necessary before we will determine precision, accuracy and detection limits using international nitrate reference materials. Finally, we will use the modified interface to determine nitrogen isotope signatures of nitrate from real water samples for source allocation and make further developments to measure nitrogen isotopes online from organic compounds.

Direct immersion SPME Arrow – Corona discharge IMS for the determination of pesticides in water samples

Involved staff: Seyed Mohammad Seyed Khademi, PD Dr. Ursula Telgheder
Funding: Internal

The application of Ion Mobility Spectrometry (IMS) in analytical chemistry as a fast, sensitive, low-cost and simple technique for the determination of explosives, pharmaceuticals and environmental samples such as surface water has been introduced in the last three decades, whereas no more studies were presented for the determination of pesticides contaminants by IMS technique in water samples. The implementation of IMS for the analysis of pesticides in real water samples is under challenge due to the interfering of water clusters during detection, complexity of surface water matrix and trace amounts of pesticides existing in real water samples.

Within this thesis, direct immersion-solid phase microextraction Arrow interfaced with an IMS was investigated to overcome the limitation of sensitivity for the determination of pesticide contaminants in real water samples. Furthermore, the extraction optimization procedure of SPME Arrow was performed using GC-Mass spectrometry and a modified corona discharge (CD) IMS. The injection port which is compatible with the Arrow device was constructed for the analysis of contaminated water samples.



Analysis of selected pesticides (Quinoxyfen: 4 mg/L, Terbutryn: 300 µg/L, Dichlorovos: 300 µg/L und Cybutryne: 1 mg/L) in water by direct immersion SPME Arrow-CD IMS

The theoretical study of ionization of the target pesticides dichlorovos, cybutryne, terbutryn and quinoxyfen in the positive mode of corona discharge ionization source of the IMS was investigated using density functional theory and B3LYP method as well as Gaussian09® software. Using computational chemistry, it was possible to assign the peak in the IMS spectrum to the selected pesticides.

Detection limits of 13-124 µg L^{-1}, RSD from 5.2-7.5%, recovery ranged from 99-103% were calculated using the developed SPME-Arrow - IMS method. In conclusion, the SPME-Arrow as a simple sample preparation method coupled with the CD-IMS can be introduced as a low-time consuming, inexpensive and simple method for the determination of selected pesticides at concentration levels of µg L^{-1} in surface water. The proposed method can be applied as an early-warning alarm system in water treatment plants where the fast detection of pesticides discharged into water resources may occur.

Reactions of chlorine dioxide with nitrogen-containing compounds

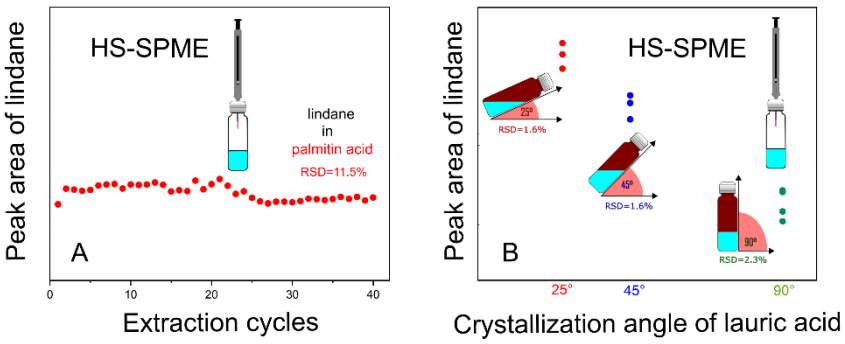
Involved staff: Mohammad Sajjad Abdighahroudi, Prof. Dr. Holger V. Lutze (TU Darmstadt), Prof. Dr. Torsten C. Schmidt
Funding: German Academic Exchange Service (DAAD) via the Federal Ministry for Education and Research (BMBF) Program "Sustainable Water Management"

Reaction of the disinfectant chlorine dioxide with nitrogen-containing compounds
Chlorine dioxide is used for the treatment of water for several decades. However, reaction mechanisms of pollutant degradation are hardly known. With the support of a DAAD scholarship, reactions of nitrogen-containing compounds with chlorine dioxide are investigated. Organic pollutants, though, are very complex and that aggravates their investigation. Hence, the present project focuses on the transferability of knowledge from model compounds to existing micropollutants. Simple model compounds such as N-heterocycles (e.g., piperidine, imidazole, etc.). will be used as surrogates for ritalinic acid, dexmedetomidine and other potential micropollutants that contain these moieties. In this regard, the following studies will be carried out for compounds: Reaction kinetics with ClO2 and HOCl, yields of different chlorine products and stoichiometry
The project has shown that chlorine dioxide reacts fast with saturated *N*-heterocycles (amines) and
rather slow with aromatic *N*-heterocycles. Since only deprotonated amines react with chlorine dioxide, the kinetics increases with pH. Two moles of chlorine dioxide are consumed per mole model compound transformed. In this reaction, chlorine dioxide gives rise to chlorite (electron transfer) and a radical cation. The radical cation may cleave H^+ and undergo an extremely fast second reaction with ClO_2 following different possible mechanisms. This behavior of chlorine dioxide was already observed by other researchers for aromatic compounds (e.g., phenol), and it was postulated that hypochlorous acid could be formed as the product of the second reaction. The results have shown that for saturated N-heterocycles, a second electron transfer reaction with the second nitrogen forms another chlorite. This was confirmed with more than 80% formation of chlorite as the primary ClO_2 transformation product. However, in the case of aromatic *N*-heterocycles (pyrrole and imidazole), the second attack did not form chlorite as its yield was only around 46% and 50%, respectively. The missing fraction of chlorine mass balance was indeed measured to be mostly HOCl, indicating an oxygen transfer reaction. The same behavior was also observed for micropollutants containing these moieties.

Multi-Ion - Non-radioactive, energetically variable ionization unit for fast and selective pollutant analysis in building materials based on FAIMS technology

Involved staff: Sasho Joskimoski**,** Dr. Klaus Kerpen, Fabian Ude, Robert Marks, PD Dr. Ursula Telgheder
Involved students: Dionisio Tzimis
Partners: Schumann Analytics GmbH
Funding: Federal Ministry for Economic Affairs and Energy (BMWi) by the Central Innovation Programme for SMEs (ZIM)

The aim of this project is to develop a cost-effective and efficient analytical device that allows the rapid on-site analysis of toxicologically relevant substances in both older, already installed (waste wood) and new building products (mostly modern insulation materials). The substances are to be reliably detected both qualitatively and quantitatively. Furthermore, an alternative calibration method to the time-consuming, unstable and cost-intensive calibration gas method used so far was to be developed within the scope of this project. The current state of the art is that only the calibration of single substances or isotope-labeled internal standards can be performed. This requires trained personnel and is associated with high costs for the internal standards and a high expenditure of time. A promising approach is to spike and retain a standard mixture of organic compounds on a composite sorbent matrix for the controlled generation of a standard in a fluid over the doped matrix in either a gaseous or an aqueous phase. Reusable, cost-effective vials for production of reproducible amounts of analytes (pestizides) in the gas-phase were investigated. The idea behind involved the implemetation of such vials for on-site analysys i.e. quick and robust calibration control of headspace or HS-SPME (headspace solid-phase microextraction) methods in combination with IMS (**I**on **M**obility **S**pectrometry) and FAIMS (**F**ield **A**symmetric **I**on **M**obility**S**pectrometry).



A) Long term extraction

B) Surface dependant extraction

For this purpose lindane as a model pestizide was used for preliminary measurements alongside long chain fatty acids serving as a mixing matrix for additional pestizides. Small amount of lindane was added to a standard vial already filled with palmitic or lauric fatty acid. The vial was closed and stirred with a magnet at a temperature higher than the melting temperature of the fatty acid. Afterwards, relatively quick crystallization of the matrix occurred at room temperature. The produced vials were then ready for testing with HS-SPME GC/MS as shown. Standard GC/MS was used to test the signal stability of the gas phase with increased extraction cycles for longer periods of time. The samples were heated at a constant temperature until dynamic equilibrium between the amount of lindane in the gas phase and the liquid matrix was supposed. Subsequent crystallization is done after which the vial was sampled. In this way, through crystallization of the matrix, the signal originating from the fatty acid was avoided. Improvement of the initial results is expected after implementation of more controlled crystallisation parameters. For example, signal intensity is relatively dependable on the crystall surface (as shown), therefore crystallisation should be done under controlled conditions for ensuring higher reproducibility.

Theses completed in 2020

PhD Theses

20.02.2020

Vanessa Hinnenkamp

"Analytical strategies for the investigation of organic micropollutants in aqueous matrices by target, suspect and non-target screening analysis"

Summary

The occurrence of organic micropollutants in raw water used for drinking water production and in the drinking water itself causes a constant monitoring of the water quality to comply with the quality requirements. Commonly applied targeted approaches are based on gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) or liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), which have been established as sensitive and robust methods. Nevertheless, with these methods the recognition of unexpectedly emerging contaminants usually stays off. With the development and commercialization of high-resolution mass spectrometers (HRMS), comprehensive screening approaches can be applied, meaning that high numbers of micropollutants can be detected and HRMS data can be useful to identify unknown substances.

Therefore, this thesis deals with the development and application of analytical strategies, including target, suspect and non-target screening analysis for the investigation of known and unknown organic micropollutants in aqueous samples. An analytical method by means of ultra-performance liquid chromatography coupled to an ion mobility quadrupole time-of-flight mass spectrometer (UPLC-IM-Q-TOF-MS) was developed for a sensitive detection of contaminants over a large polarity range. Additionally, for non-target screening analysis a data evaluation workflow was created. In order to use HRMS data beside a suspect or non-target screening, a quantitative screening method was developed and validated for the detection of more than 140 micropollutants. Especially for water suppliers, the quantitative information is important in order to have the information on the relevance of a substance and additionally, this information can be useful for the selection of validated target methods.

The usage of collision cross section (CCS) values, which can, e.g., contribute to the identification during suspect or non-target screening approaches, was investigated in relation to the question how far CCS databases with CCS values derived by different instruments (drift tube IM-MS and traveling wave IM-MS) can be used reciprocally. This comparative study was based on measurements of more than 120 substances with both systems and revealed mean values of absolute percentage errors of 1.0% for $[M+H]^+$ and 1.1% for $[M+Na]^+$ ions, meaning that a good correlation of CCS values derived with both instrument types resulted. However, the high deviations up to 6.2% obtained in isolated cases showed that a full comparability

between both instruments does not exist. Different LC and MS settings had no significant impact on the resulting CCS values of exemplarily tested substances. Only for karbutilate changes in the drift spectrum by drift tube IM-MS measurements were observed by using different LC settings, which could be caused by different protonation sites in the molecule.

A drinking water production process was investigated by a combined analytical approach by means of target, suspect and non-target screening analysis. Beside the known, also unknown substances could be identified or tentatively identified by database searches. Since for many unknown substances, comparisons with databases failed, it was investigated on example of an unknown feature with a mass-to-charge-ratio (m/z) of 326.1751 encountered by UPLC-IM-Q-TOF-MS measurements of a river Rhine sample, how extensive this feature can be characterized or even identified. In a comprehensive structural characterization by means of different analytical methods it was found that aromatic structures as well as a primary or secondary amino function is probably contained in the structure of the unknown feature. However, a possible molecular structure could not be proposed, which demonstrates the difficulty in identification attempts of unknown micropollutants.

Overall, this thesis demonstrated, that the combined approach of target, suspect and non-target screening analysis for the prioritization of known and unknown contaminants and identification of unknowns by databases can be successfully applied and has therefore a great potential for the future water monitoring. With regard to the identification of unknowns, extensions of the freely accessible databases are required in order to identify further unknown organic micropollutants more easily and quickly in further studies. Additionally, in further studies, the workflow, in particular those of non-target screening, should be further developed to be more feasible in a shorter time to enable that changes in raw and drinking water can be quickly recognized because the workflows developed so far require a lot of time.

26.02.2020

Gerrit Renner

"Development of new spectroscopic and multivariate chemometric methods for the characterization of microplastics in the marine environment"

Summary

Microplastics are ubiquitous and gain increasing attention in research as well as media and politics worldwide. In many cases, the presence of microplastics in different environmental compartments was reported and the risk potential was discussed. However, there is a lack of standardization starting with a clear definition of microplastics up to suitable analytical methods for their detection and characterization. Consequently, this work reviewed the literature to determine the status quo of microplastics analysis, and developed new suitable analytical and chemometric methods for microplastics identification and characterization.

Based on the studies reviewed, Fourier Transform Infrared Spectroscopy (FTIR) was confirmed as the most used method to identify microplastics. However, it could be obtained that the documentation of the microplastics identification process itself was mostly underrepresented, which indicated a lack of awareness of this important aspect. Therefore, a practical guide was developed that addressed data evaluation for spectroscopic data of microplastics. Moreover, a critical examination of the principles of infrared spectroscopy with special regard to the analysis of microplastics was presented.

In its core, this work focused on a new chemometric concept to identify microplastics based on FTIR spectroscopy, which is called µIDENT. The developed algorithm automatically extracts accurate vibrational band lists of individual spectra using a very robust and fast multi component curve fitting approach. In a second step, every list is transformed into a peak intensity ratio pattern. This is highly robust and characteristic for each polymer, and is the basis for reference pattern library search to identify microplastics. Furthermore, a rapid and intelligent method for chemical imaging using µFTIR (µMAP) was developed to challenge the problem that those kinds of measurements are very time consuming. Therefore, the µFTIR scans a defined area step-by-step, and only stops to start a detailed infrared measurement, if microplastics are at the current spot. This significantly reduces the number of measurements, which saves up to 92 % of the total measurement time. The method development is concluded by presenting an innovative concept for separation of microplastics from sediment samples for analytical purposes (µSEP). In this context, microplastics adhere to fine air bubbles and are transported onto a filter, while matrix components remain in the closed loop like approach. In contrast to other separation concepts, the presented prototype requires only water and air, which reduces costs and lowers the risk of losing microplastics due to aggressive substances.

To all method developments made, there were similar contributions by other research groups. However, this work especially addressed highly practical, automatable and robust concepts.

The focus was always on the application of the methods, which was underlined, for example, by publishing all source codes. In conclusion, the tools provided could improve current microplastics analysis, and could play an important role in future challenges in this area.

15.06.2020

Daniel Köster

"Applications for liquid chromatography coupled to isotope ratio mass spectrometry and evaluation of the oxidation processes towards compound specific $\delta^{15}N$ analysis"

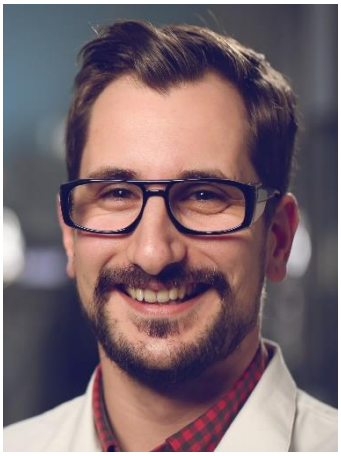
Summary

LC-IRMS has become a valuable tool in analytical chemistry since it was established in 2004. With more than 70 published applications in peer reviewed journals in the past 15 years, the main fields of application are in authenticity control, degradation of environmental contaminants, and the measurement amino acid in the context of nutrition, archeology, or forensics. As demonstrated in the present work by the elucidation of the plant origin of xylitol in chewing gums, compound specific $\delta^{13}C$ analysis by LC-IRMS is able to deliver precise carbon isotopic information with a simple sample preparation procedure and an online combination of analyte separation and measurement. With the developed method and sample preparation, xylitol in chewing gum formulations based on wood material could be discriminated from the cheaper substituent which is based on corn husks. Many applications using $\delta^{13}C$ analysis could benefit from an additional determination of the $\delta^{15}N$ information, which can increase the power to discriminate between analyte sources or serve as an additional information in the monitoring of the degradation of pollutants. To develop a LC-IRMS system based on the persulfate oxidation process in combination with a membrane gas separation unit for $\delta^{15}N$ measurements, the oxidation process in the interface under standard $\delta^{13}C$ measurement conditions was thoroughly evaluated. Special focus of the work on the oxidation efficiency was on the interaction of the interface oxidation parameters, as these are commonly not evaluated in existing publications. The obtained results show that accurate isotopic signatures for carbon can be obtained even though the transformation to CO_2 is not 100 % complete if the principle of identical treatment of the analytes and reference substances is applied. In addition, the common assumption that a linear correlation between analyte concentration and signal intensity in LC-IMRS indicates complete conversion of the analyte could be disproved. Only with the developed combination of TOC measurement and the LC-IRMS interface or separate referencing with a carbonate standard, exact information about the oxidation efficiency in the interface can be obtained. Based on the standard oxidation conditions in the interface, batch experiments with nitrogen containing model analytes were performed in a large scale reaction vessel to obtain a time resolved speciation of the nitrogen containing reaction products formed during the mineralization. For the analysis of the remaining organic analyte, the total bound nitrogen, ammonium, nitrate, and nitrite, analytical methods were developed on a combined TOC/TN_b instrument and two IC systems for anion and cation chromatography. The main challenge for the method development were the high

background of sodium or potassium as well as sulfate and persulfate that originates from the oxidation agent which is present in large excess (g L^{-1} for the oxidation agent vs. low mg L^{-1} for the nitrogen containing mineralization products). The TN_b measurement was strongly affected by the presence of persulfate especially for ammonium and organic nitrogen, whereas nitrate was not affected at the tested conditions.

Based on the TOC and the ion chromatography based measurements, nitrate and ammonium could be identified as the main products of the mineralization. The results were evaluated with a nitrogen mass balance approach which indicated, that for the tested model compounds, overall nitrogen recoveries between 91 and 102 % could be obtained. Under the standard oxidation conditions, ammonium oxidation to nitrate was not fast enough for the application in an online-reactor setup, which could be applied for the $\delta^{15}N$ measurement by LC-IMRS.

As a result of the mixed production of ammonium and nitrate under acidic conditions the reaction conditions had to be adapted and oxidation of nitrogen containing analytes in an alkaline medium was evaluated. Initially, ammonium and nitrate were observed as the main reaction products, but the subsequent oxidation of ammonium to nitrate is comparably faster at alkaline conditions. The alkaline oxidation conditions were transferred from the batch reactor system to the LC-IMRS interface. At combined system flow rates of 275 µL min^{-1}, more than 62.5 % of the initially introduced nitrogen could be recovered with a setup using a commercially available interface. For amino acids e.g. glycine, nitrate recovery rates of 85.5 % could be obtained. It could be shown, that increased residence times in the oxidation reactor (by reduction of the system flow) could lead to increased recoveries for the model compounds. Based on the evaluation of the persulfate oxidation reaction in the LC-IRMS interface and the results obtained for the oxidation under alkaline reaction conditions, nitrate could be utilized as an intermediate species used for quantitative conversion of the analyte nitrogen to an IRMS measureable gaseous form. The problem of the formation of two intermediate species (ammonium and nitrate) as observed for the oxidation under acidic conditions could be overcome by the new reaction conditions. The alkaline oxidation was successfully tested for model compounds in a commercially available LC-IRMS interface.



19.06.2020

Matthias Dumm

"Reactions of cyanides in Blast furnace gas wash water"

Summary

Blast furnace gas washing water is a cyanide containing wastewater, produced in large quantities in gas cleaning systems of big iron production sites. During the washing water treatment a naturally ocurring cyanide degradation could be observed. Since cyanides are toxic compounds, which are under regulatory control, exact knowledge of existent species, their origin and especially their reactions is crucial. Therefore, using FTIR spectroscopy, in this work it is shown, that blast furnace gas contains 41 mL m3 gaseous HCN on average, from which 12 % is transferred into the washing water. This accounts for 34 % of the dissolved cyanide compounds in the water phase. The remaining 66 % are brought in via flue dust. In addition to CN– and HCN, tetracyanozincate and hexacyanoferrate (II) can be identified as dominating cyanide species by analysis of the gas and water phase (UV/Vis, ICP-OES, FTIR und CFA). An almost complete degradation of weak acid dissociable cyanide takes place in the water cycle. Therefore, 40-90 % can be traced back to HCN volatilization by water analysis (CFA) and gas phase analysis (FTIR). Another 10-60 % of the degradation is based on a thiocyanate forming reaction between CN– and an unknown sulfur compound, which is characterized using various analytical techniques (CFA, ICP-OES, XRD, GC-MS an Q-TOF LC-MS), but cannot be definitely identified in the context of the presented work.

26.06.2020

Sarah Willach

"Oxidative processes – Insights in reaction mechanisms gained by high resolution and isotope ratio mass spectrometry"

Summary

Oxidative and phototransformation processes frequently contribute to micropollutant degradation in natural or engineered systems. For the remediation of contaminated sites or water treatment processes these may be, e.g., ozone (O_3), hydroxyl radicals ($^{\bullet}OH$), chlorine dioxide (ClO_2) or UV/vis light if the micropollutants contain one or more chromophores. However, the corresponding reaction mechanisms which are important to assess the formation of undesired transformation products (TPs) are mostly unknown. Currently, TP studies are regularly performed with the analysis by high-resolution mass spectrometry (HRMS) which enables the derivation of the TP sum formulas based on the exact masses. However, the reactive site and point of attack, respectively, remain mostly unknown. Here, compound-specific stable isotope analysis (CSIA) may be a useful tool to enlighten and further investigate reactions of micropollutants since degradation processes may reveal specific isotopic fractionation, which are related to the site of primary attack. Therefore, this study investigates the use of CSIA and HRMS as complementary tools to characterize various oxidative and phototransformation processes in order to elucidate the underlying reaction mechanisms. The sulfonamide antibiotic sulfamethoxazole (SMX) is chosen as a model compound in order to systematically investigate the pH dependent transformation caused by the oxidative and phototransformation processes listed above. SMX is a widely detected micropollutant in surface, ground- and wastewaters which may occur as neutral or anionic specie at typical pH values of water treatment or in natural waters.

In case of the oxidative processes, O_3 in presence and absence of $^{\bullet}OH$ and ClO_2, the reaction stoichiometry, product formation and reaction mechanisms were systematically investigated for reactions with SMX. Two moles of ClO_2 and approximately three moles of O_3 were consumed per mole SMX degraded. As revealed by HRMS, the oxidation of SMX with O_3 and ClO_2 leads to six major TPs in both cases. Tentatively formulated TP structures from other studies could partly be confirmed by CSIA. However, for one TP, a hydroxylated SMX, by HRMS alone it could not be decided whether hydroxylation occurred at the aromatic ring, as suggested in literature before, or at the anilinic nitrogen. By additional means of CSIA and an analytical standard it was possible to identify sulfamethoxazole hydroxylamine unequivocally as one of the TPs of the reaction of SMX with O_3 as well as with ClO_2. H-abstraction and electron transfer at the anilinic nitrogen are suggested as likely initial reactions of O_3 and ClO_2, respectively, leading to its formation. The oxidation of anionic SMX with O_3 did not show any significant isotopic fractionation whereas the other reactions studied resulted in a significant carbon isotope fractionation (e.g., $\varepsilon_C(O_3) = -2.2 \pm 0.1$ ‰ and $\varepsilon_C(O_3 + {}^{\bullet}OH) = -1.2 \pm 0.1$ ‰).

For the investigation of the phototransformation reactions of the two relevant SMX species, four different irradiation scenarios were employed, i.e., a low, medium, and high pressure Hg lamp as well as simulated sunlight. The observed phototransformation kinetics were faster for the neutral than for the anionic SMX species (from 3.4 (LP lamp) up to 6.6 (HP lamp) times). Furthermore, four phototransformation products (with m/z 189, 202, 242, and 260) were detected by HRMS that have not yet been described for direct photolysis of SMX. Isotopic fractionation occurred only if UV-B and UV-A wavelengths prevailed in the emitted irradiation and was most pronounced for the neutral species with simulated sunlight (ε_C = −4.8 ± 0.1 ‰). The phototransformation of SMX with UV-C light did not cause significant isotopic fractionation. Consequently, it was possible to differentiate sunlight and UV-C light induced phototransformation of SMX. Thus, CSIA might be implemented to trace back wastewater point sources or to assess natural attenuation of SMX by sunlight photolysis. In contrast to the wavelength range, pH-dependent speciation of SMX hardly impacted isotopic fractionation. However, regarding phototransformation no further comprehensive insights in the underlying reaction mechanisms could be gained by CSIA. This is attributed inter alia to the presence of sulfur and nitrogen as reactive sites in SMX and the current inability to determine any other but C-isotope values by liquid chromatography isotope-ratio mass spectrometry (LC-IRMS).

Consequently, much simpler model compounds without nitrogen or sulfur-containing moieties, i.e. benzene and its methylated and methoxylated analogs, were used in order to further systematically characterize the abiotic oxidative processes using O_3, $^{\bullet}OH$ or ClO_2 with CSIA. Carbon isotope enrichments factors (ε_C) were determined for reactions with O_3 (ε_C = −3.6 ‰ to −4.6 ‰) and $^{\bullet}OH$ (ε_C = < −1 ‰). The differences in isotope fractionation may be used to elucidate the contribution of the reactions with O_3 or $^{\bullet}OH$ to the overall transformation. Subsequently, apparent kinetic isotope effects (AKIEs) were derived for the reaction with O3. This was nontrivial due to challenges in assigning reactive positions in the probe compounds for the monodentate attack leading to an O_3 adduct. Several options for this step are presented and the outcome is compared to quantum chemical characterizations of O_3 adducts. The data show that a general assignment of reactive positions for reactions of O_3 with aromatic carbon in ortho, meta or para positions is not feasible and that AKIEs of this reaction should be derived on a compound-by-compound basis.

In conclusion, this work has illustrated the potential added value of CSIA to characterize oxidative and phototransformation processes. Simultaneously, it became obvious that the chemistry of allegedly simple reactions is not yet fully understood and that further research is required to enable us to understand reaction mechanisms and isotopic fractionation on a more holistic level.

18.08.2020

Kirsten Purschke

"Environmental Forensics of Industrial Wastewater based on Non-Target Screening"

Summary

The discharge of industrial wastewater into surface water requires constant monitoring of the water quality to comply with specifications and quality requirements. Furthermore, it must be ensured that individual approvals for the production plants are obtained when industrial wastewater is discharged into the wastewater treatment plant (WWTP). For this reason, the influent of the WWTP is continuously monitored for trace organic compounds (TrOCs). These compounds are usually determined using liquid- (LC) or gas chromatographic (GC) target methods coupled to low-resolution mass spectrometers. However, these methods monitor only a small part of TrOCs in wastewater. Only a limited number of compounds can be detected in a single run and many compounds are ignored in the analysis as they are not part of the target list. Thus, unknown TrOCs neither can be detected nor identified in wastewater samples using these methods, even if they are present in high concentrations. Therefore, high-resolution mass spectrometers (HRMS) have become more and more common in water analysis to carry out more extensive monitoring by detecting both known and unknown compounds. Besides, in combination with a non-target screening (NTS), the generated HRMS data additionally enable the identification of unknown compounds.

The application of LC-HRMS in NTS related to industrial wastewater data is described in this work. Sample treatment procedures and an analytical LC-HRMS method are developed which enable the sensitive and reliable monitoring of TrOCs in a broad polarity range. Additionally, the development of a reliable data processing algorithm for NTS is part of this work. A large amount of data is produced in LC-HRMS that cannot completely be evaluated. Thus, prioritisation methods are required, enabling data reduction. As a result, three prioritisation strategies were developed, which make it possible to extract relevant features (a combination of a particular mass-to-charge ratio, the associated retention time and intensity) from the data for identification. The relevance of each feature depended on the prioritisation strategy.

The first prioritisation method selects these features, whose intensities followed rising or falling trends over time-series measurements. As a result, influences on industrial wastewater through the different production processes in an industrial park were recognised. This method was carried out by principal component analysis (PCA) and group-wise PCA (GPCA). 130 of initially 3303 detected features were prioritised in the WWTP influent samples. In addition to prioritisation, the introduced method enabled componentisation (grouping of several features into one TrOC). As proof-of-concept, one feature with an increasing trend over five months was identified as N-methylpyrrolidone.

In the second trend-related prioritisation method, the time series investigations were linked to spatial trends. For this purpose, several sampling sites before and after the WWTP were sampled and analysed over five months. This allows evaluating the treatment procedure of industrial wastewater over time. Besides, site-specific features were detected. In future studies, these features could serve as a fingerprint in the monitoring of the wastewater streams.

In contrast to the first two, the latter prioritisation method shows a more technical approach. TrOCs, which were repeatedly detected in the influent of the WWTP by the routine monitoring, but which were initially not identified ('*known unknowns*') are prioritised and identified by an (offline) two-dimensional LC coupled to two kinds of detection techniques (ultra-violet detection and MS). The identification of these '*known unknowns'* is of high interest for the operators of the WWTP. LC-UV peaks from wastewater samples were fractionated manually in the first dimension and elucidated in the second dimension, the LC-HRMS, by NTS. By applying this method, the analysis of only one sample fraction led to sampling purification and therefore, data reduction. As an example, the '*known unknown'* with the retention time of 41.1 minutes and the maximum UV absorption of 240 nm in the first dimension was successfully identified as a dichlorodinitrophenol isomer.

All in all, this work shows that the use of HRMS data, in combination with NTS and the application of the presented prioritisation methods, extends the monitoring of industrial wastewater and permits an evaluation of the WWTP processes. It indicates great potential for future establishment in routine monitoring.

27.10.2020

Lina Gessner

"Hemoglobin based blood volume estimation for the (semi-) quantification of methadone, opiates, cocaine and metabolites in Dried Blood Spots (DBS), deposited on non-standardized materials, via GC/MS-MS“

Summary

The analysis of Dried Blood Spots (DBS) has been challenging for the forensic toxicological casework in the past years. The broad range of advantages concerning the usage of DBS, including analyte stabilizing effects, reduced infection risks, simplified sampling and storage have led to many successful approaches to establish DBS analytics in routine analysis, but some issues remain. There are only few publications and studies dealing with the quantification of analytes in DBSs on non-standardized materials, which underlines the need for a suitable method. The unknown blood volume is the biggest challenge. Several methods for the blood volume determination have been developed, but have always been limited by the uncertainty of variable hematocrit (hct) concentrations in blood. The following work therefore addresses the analyte quantification of common drugs of abuse and their metabolites in DBS on non-standardized carrier materials. Since these might be found at a scence of crime, there is a need for a simple determination method for the blood spot volume that allows a parallel analyte measurement and consequently the quantification of analytes.

In the first part of this work a GC-MS/MS method for the (semi)-quantification of benzoylecgonine (BE), ecgoninemethylester (EME), methadone, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP), codeine, morphine and dihydrocodeine (DHC) has been validated successfully for DBS on commonly available printer paper. Since a case-near sample treatment was aspired, DBS were dried at ambient air without protection against environmental conditions. Validation was performed with respect to the guidelines of the GTFCh (Gesellschaft für Toxikologische und Forensische Chemie) by evaluating linearity, selectivity, accuracy, stability, extraction efficiency and the limits of quantification (LOQ) and detection (LOD). Hereby, long-term stability was evaluated after the samples were exposed to different storage temperatures (-20 °C, 4 °C, 20-22 °C ambient temperature (AT) and 40 °C). The method was also examined with regard to the influences of different extraction buffer amounts (1 mL, 2 mL or 3 mL), different spot volumes (25 µL, 200 µL or 500 µL) and the usage of hct-adjusted blood specimens (hct 34 % or 51 %) on the analyte quantification. The results indicated that the variability of data concerning the stability of analytes and the influences of the amount of blood volume and consequently the amount of extraction buffer were analyte specific. Nevertheless, the method was demonstrated to be suitable for the (semi-)quantification of the analytes in DBS on printer paper.

In the second part, the applicability of the GC-MS/MS method was tested for DBSs deposited on other non-standardized materials, including cotton, elastane and cotton-elastane composite fabrics, carpet, tile and a wood panel. Selectivity, accuracy and extraction efficiency were investigated at a spot size of 500 µL. Again, the GC-MS/MS method was shown to be sufficient for the (semi-)quantification of the analytes on the various carrier materials, with the results indicating that the carrier material has an impact on the analyte quantification. The analytes revealed different reactions to the materials used which resulted in varying degrees of analytes losses.

In part three, a method for the blood volume estimation of a DBS was investigated in parallel to the first and second part. For this purpose the well-known cyanhemigloin method (HiCN) was used, which enabled a photometric hemoglobin (hb) determination. The hb content was found to correlate with the used amount of blood, so that the initial blood spot volume could be estimated. A standardized correction factor (CF) and specific dilution factors for each spot could be calculated and applied to the samples of accuracy and extraction efficiency to assess the suitability of the HiCN method in connection with the analyte quantification method. Furthermore, blood samples with adjusted hct levels (hct 34 % and 51 %) were examined to assess whether the HiCN method is suitable to overcome the challenging ´hct problem´. The application of the blood volume estimation to the data of analyte quantification revealed variable results. The different materials produced inconsistent data with respect to blood volume estimation. Nevertheless, the HiCN method was also successfully semi-validated with regard to GTFCh guidelines for blood samples and corresponding DBSs in a physiological hct range (36-50%). Although the suitability of the combination of the GC-MS/MS method and HiCN method was demonstrated for some analytes, the data showed a strong dependency on hct. It was observed that blood samples with highly increased or decreased hct have major impact on the assessment of quantification data.

In the last section of this work, 20 authentic blood samples from post-mortem cases containing relevant analyte concentrations of the investigated substances were used to prepare DBSs on printer paper, cotton-elastane fabric and tile. Analyte concentrations were analyzed in DBS and liquid samples and compared to each other. HiCN method was also applied. Hereby, highly variable results were reported, indicating that various influences, including the post-mortem interval, putrefaction or post-mortem redistribution of drugs have substance specific impacts. Thus, it was concluded that the assessment of DBSs from post-mortem samples is delicate, as the circumstances of death cannot always be assessed precisely. With respect to the alternative matrix, the results indicated that the use of DBSs was not sufficient to completely cease degradation or other processes affecting the analyte quantification. Nevertheless, correct analyte (semi)-quantification could be performed for most of the selected analytes including BE, methadone, codeine and morphine.

15.12.2020

Wiebke Kaziur-Cegla

"Automated and solvent-free microextraction techniques for the GC-MS analysis of food and environmental samples"

Summary

Sample preparation is one of the most time-consuming steps in analytical chemistry, whose purpose is the transfer of analytes into solution, the removal of interfering matrix compounds, the enrichment of analytes for trace analysis, and sometimes the derivatization to a more suitable structure for successful separation or detection. Automation, reliability, minimizing the use of toxic solvents and increasing the sensitivity are some of the demands for sample preparation. Microextraction techniques fulfill these demands and are valuable alternatives for conventional used extraction techniques like liquid-liquid extraction (LLE) or solid-phase extraction (SPE). The aim of the thesis was to investigate, validate and expand the use of fully automated and solventless microextraction techniques to show new alternatives for the analysis of water and food samples. Therefore, gas chromatography mass spectrometry (GC-MS) based methods were developed, optimized and validated, using in-tube extraction dynamic headspace (ITEX-DHS) and solid phase microextraction (SPME) Arrow. Chemometric methods were used for the method optimization (design of experiments, DoE) and for data evaluation (linear discriminant analysis, LDA).

ITEX-DHS is a dynamic extraction approach, in which the headspace is pumped multiple times through a sorbent bed. As ITEX-DHS is only applied for headspace analysis, only volatile analytes can be analyzed, but matrix interferences can be avoided. Therefore, more complex matrices like viscous, oily or sticky matrices could be analyzed without problems. In this thesis, ITEX-DHS based methods in two areas of food analysis were developed and validated. In the first method, ITEX-DHS was optimized for the analysis of 21 volatile organic compounds (VOCs), commonly present in extra virgin olive oil (EVOO). The monitoring of EVOOs is of special interest, as it is one of the most important targets in food fraud. 31 EVOOs from five different geographical origins were measured and LDA was used for classification. The second method shows the use of ITEX-DHS for the analysis of honey samples. Honey is often mislabeled and has a high potential for food fraud. ITEX-DHS allows a quick, easy and robust analysis of VOCs, which are responsible for the aroma of honey and which can be linked to the botanical and geographical origin of honeys. Therefore, 14 VOCs were quantified with ITEX-DHS with method detection limits ranging from 0.8-47 ng g^{-1} and repeatabilities shown as relative standard deviations of below 8%. 38 honey samples were measured to show the applicability of the method and to give an overview how this method could be used for future work.

SPME is one of the most famous microextraction techniques. However, the fiber is very fragile, and the mechanical stability of the device is not very satisfactory. To overcome these

drawbacks, the SPME Arrow was developed. Its mechanical stability is increased by an Arrow shaped tip and the sorbent material is coated around a stainless-steel rod. Furthermore, the larger sorbent volume leads to more sensitivity. In comparison to ITEX-DHS, not only headspace sampling is possible, as the SPME Arrow can be placed into the aqueous sample for direct immersion sampling. Both options are presented in this thesis, and in total, three different SPME Arrow based methods were investigated, optimized and validated for a more sensitive analysis of the target analytes. The first presented use of SPME Arrow is the automated derivatization of fatty acids to fatty acid methyl esters directly on the sorbent material of the SPME Arrow. The fatty acids were extracted from acidified water via direct immersion sampling. Subsequently, the SPME Arrow was moved to another vial, containing a mix of methanol and sulfuric acid. The derivatization takes place on the fiber material and the fatty acids are methylated and afterwards thermally desorbed in the GC injector. For the analysis of taste and odor compounds in water, a SPME Arrow headspace method was optimized using DoE, and then validated. The achieved LODs were below the thresholds of the target analytes and varied from 0.05-0.6 ng L^{-1} with satisfactory repeatabilities (RSDs < 11%). Compared with conventional approaches, this method showed a significant enhancement in sensitivity, and outstanding robustness and stability. Furthermore, the required sample volume was reduced in comparison to other methods, and the method was able to detect seven analytes at very low concentrations. To show the option of direct immersion sampling, phosphorous flame retardants were analyzed directly from different water samples, using SPME Arrow. Again, the method was first optimized using DoE and was then validated. The limit of quantification (LOQ) ranged from 0.2-1.2 ng L^{-1} and thus, showed again great sensitivity for the application of SPME Arrow. Furthermore, the analysis was carried out completely automated, resulting in a more time-efficient method than LLE or SPE, which are very labor-intensive. This method showed to be the most sensitive analytical approach for the determination of phosphorous flame retardants in water.

All in all, this thesis presents five new options for the use of ITEX-DHS and SPME Arrow, as examples for modern, solvent-free and fully automated microextraction techniques. It demonstrates the potential of microextraction techniques for routine analysis as robust, sensitive and non-hazardous alternatives for commonly used extraction techniques, which often deal with large amounts of organic solvents.

18.12.2020

Vanessa Wirzberger

"Oxidative water treatment: mechanistic aspects and matrix effects"

Summary

The main emission sources of micropollutants (MPs) found in the aquatic environment are wastewater treatment plant (WWTP) effluents but also diffuse sources such as agricultural run-offs. An opportunity to reduce the load of MPs in WWTP effluents is the application of ozonation in order to degrade undesirable substances. Especially nitrogen containing (*N*-containing) substances, including many pharmaceuticals and pesticides, react fast with ozone. However, the degradation of these substances via ozone does not lead to mineralization but rather to a formation of transformation products (TPs) that can have a higher toxicity than the parent substance. Until now, reaction pathways of *N*-containing substances with ozone are still not completely understood, because they are depending on various factors such as the matrix composition. Therefore, the formation of TPs and their ecotoxicological potential is hardly predictable. Most studies investigating the degradation of MPs with ozone and the formation of TPs are performed in ultrapure water excluding the influence of matrix components.

Hence, this study wants to overcome the gap between mechanistic studies and the investigation of matrix influence. This was performed via the determination of TP formation during ozonation of three environmentally relevant substances (diclofenac (DCF), metoprolol (METO) and isoproturon (ISO)). The formed TPs were determined via target analysis, suspect and non-target screening and the toxicological potential towards aquatic organisms was evaluated. Various matrix compositions were investigated in terms of TP formation during the ozonation of DCF, METO and ISO. These included ultrapure, drinking and surface water, two different concentrations of non-purgeable organic carbon (NPOC: 2.35 mg/L and NPOC: 0.63 mg/L), two different scavengers (dimethyl sulfoxide (DMSO) and tertiary butanol (*tert*-BuOH)) and wastewater.

Within all these matrices the degradation of the three parent substances and detected stoichiometries were similar. However, even if the formation profiles of the TPs were similar (increasing formation until a certain ozone dosage and decreasing with higher ozone dosages) the yields differed among the water matrices. High differences in the TP formation were detected in the presence of scavengers. For two TPs a continuous formation without any degradation was determined either for DMSO or *tert*-BuOH but not for the other scavenger. This was striking as both scavengers are frequently applied in laboratory setups, assuming that both are leading to the same results. As this study was the first to compare the two

scavengers in terms of TP formation and revealed that the chosen scavenger can highly influence this formation further research is highly recommended.

Additionally, the influence of hypobromous acid (HOBr) formed in the reaction of bromide with ozone and the direct influence of bromide on the formation of TPs were investigated, as bromide is omnipresent in wastewater. It could be shown that HOBr and also low concentrations of bromide can influence the formation of TPs and that similar TPs could be detected in the direct reaction with HOBr compared with the samples containing bromide. This was striking as the reaction of ozone with the substances should be favored over the reaction of ozone with bromide. However, even low concentrations of bromide influenced the formation of TPs, leading to the detection of TPs not reported before.

All examined water matrices (except NPOC, drinking and surface water) in terms of TP formation were also investigated regarding the toxicity towards *D. magna*, showing that matrix composition can influence the toxic potential. After ozonation of the parent substances in ultrapure water and for all parent substances and target TPs no effect was detected. Only for the diclofenac TP 2,6-dichloroaniline an effect concentration leading to 50 % immobility of 1.02 mg/L after 48 h was observed and ozonation of DCF in the presence of DMSO led to an immobility of 95 % (48 h) of the daphnids. The reaction of HOBr with the parent substances did not reveal an effect for ISO but for metoprolol (100 % immobilization (48 h)) and diclofenac (95 % immobilization (48 h)).

Preliminary investigations performed in this study showed that simply structured *N*-containing substances, 2,2,6,6-tetramethylpiperidine and *cis*-2,6-dimethylpiperidine, do not react with ozone at pH 2 but pH 7. These two substances were chosen as they were expected to form aminyl radicals. However, stoichiometries above one have been determined for both substances at pH 7 and pH 11 which supports a postulated ozone consuming chain reaction, leading to a high ozone consumption with only low substance degradation.

The results of this study showed that even if the reaction mechanisms of *N*-containing substances during ozonation seem to be understood quite well, matrix components can highly influence these mechanisms and also the formation of TPs. Even for very well investigated substances the use of different scavengers revealed new observations within this study, underlining that further detailed research is still needed to achieve a better understanding of the influence matrix components can have on the formation of TPs and also on the toxicological potential towards aquatic organisms.

Master Theses

Pascal Kaiser
“Electrochemical studies to elucidate and evaluate the corrosion phenomena of zinc alloys”

Simon Nikutta
"The effect of different pH levels and kinetics on the magnitude of isotopic fractionation during the ozonation of phenol and phenol derivates"

Max Reuschenbach
"Investigations on quantum dot-based fluorescence resonance energy transfer with organic fluorophores in homogeneous solution"

Kittitouch Tavichaiyuth
"Investigation of the nitrogen-free phosphonate antiscalants in oxidation process: reaction kinetics and degradation rate"

Lucie Katharina Tintrop
"Automation and optimization of an on-fiber derivatization for the analysis of fatty acids"

Dionisios Tzimis
“Development of in-vial pesticide calibration methods for micro extraction-GC/MS analysis”

Bachelor Theses

Felix Drees

"Investigation of the N-containing organophosphonate NTMP in oxidative processes: reaction kinetics and degradation rate"

Sarah Rockel

“Analytical methods for the determination of perfluorinated and polyfluorinated alkyl substances in water and soil samples”

Publications

Peer-reviewed Journals

1. K. Purschke, M. Vosough, J. Leonhardt, M. Weber, T. C. Schmidt:
   Evaluation of Non-Target Long-term LC-HRMS Time Series Data using Multivariate Statistical Approaches
   Anal. Chem. **92** (2020), 12273-12281
   DOI: 10.1021/acs.analchem.0c01897
2. M. S. Abdighahroudi, T. C. Schmidt, H. V. Lutze:
   Determination of free chlorine based on ion chromatography - application of glycine as a selective scavenger
   Anal. Bioanal. Chem. **412** (2020), 7713-7722 (Paper in Forefront)
   DOI: 10.1007/s00216-020-02885-1
3. J. Li, C. Rumancev, H. V. Lutze, T. C. Schmidt, A. Rosenhahn, O. J. Schmitz:
   Effect of ozone stress on the intracellular metabolites from Cobetia marina
   Anal. Bioanal. Chem. **412** (2020), 5853-5861
   DOI: 10.1007/s00216-020-02810-6
4. K. Hupperich, X. A. M. Mutke, M. S. Abdighahroudi, M. Jütte, T. C. Schmidt, H. V. Lutze:
   Reaction of chlorine dioxide with organic matter - Formation of inorganic products -
   Environ. Sci.: Water Res. Technol. **6** (2020), 2597–2606
   DOI: 10.1039/D0EW00408A
5. W. Kaziur-Cegla, A. Salemi, M. A. Jochmann, T. C. Schmidt:
   Optimization and Validation of Automated Solid-Phase Microextraction Arrow Technique for Determination of Phosphorus Flame Retardants in Water
   J. Chromatogr. A **1626** (2020), 461349
   DOI: 10.1016/j.chroma.2020.461349

6. M. S. Abdighahroudi, H. V. Lutze, T. C. Schmidt:
Development of an LC-MS method for determination of nitrogen-containing heterocycles using mixed mode liquid chromatography
Anal. Bioanal. Chem. **412** (2020), 4921–4930
DOI: 10.1007/s00216-020-02665-x

7. O. Höcker, T. Bader, T. C. Schmidt, W. Schulz, C. Neusüß:
Enrichment-free analysis of anionic micropollutants in the sub-ppb range in drinking water by Capillary Electrophoresis-High Resolution Mass Spectrometry
Anal. Bioanal. Chem. **412** (2020), 4857–4865
DOI: 10.1007/s00216-020-02525-8

8. P. R. Martin, D. Buchner, M. A. Jochmann, S. B. Haderlein:
Stable carbon isotope analysis of polyphosphonate complexing agents by anion chromatography coupled to isotope ratio mass spectrometry: method development and application
Anal. Bioanal. Chem. **412** (2020), 4827-4835
DOI: 10.1007/s00216-019-02251-w

9. S. Willach, H. V. Lutze, H. Somnitz, J. Terhalle, N. Stojanovic, M. Lüling, M. A. Jochmann, T. B. Hofstetter, T. C. Schmidt:
Carbon isotope fractionation of substituted benzene analogs during oxidation with ozone and hydroxyl radicals: How should experimental data be interpreted?
Environ. Sci. Technol. **54** (2020), 6713–6722
DOI: 10.1021/acs.est.0c00620

10. B. M. Gilbert, M. Nachev, M. A. Jochmann, T. C. Schmidt, D. Köster, B. Sures, A. Avenant-Oldewage:
Stable isotope analysis spills the beans about spatial variance in trophic structure in a fish host – parasite system from the Vaal River System, South Africa
Intern. J. Parasit.: Parasites Wildlife **12** (2020), 134-141
DOI: 10.1016/j.ijppaw.2020.05.011

11. R. Akhbarizadeh, S. Dobaradaran, T. C. Schmidt, I. Nabipour, J. Spitz:
Worldwide bottled water occurrence of emerging contaminants: A review of the recent scientific literature
J. Hazard. Mat. **392** (2020), 122271
DOI: 10.1016/j.jhazmat.2020.122271

12. B. M. Gilbert, M. Nachev, M. A. Jochmann, T. C. Schmidt, D. Köster, B. Sures, A. Avenant-Oldewage:
You are how you eat: differences in trophic position of two parasite species infecting a single host according to stable isotopes
Parasitol. Res. **119** (2020), 1393-1400
DOI 10.1007/s00436-020-06619-1

13. S. Dobaradaran, T. C. Schmidt, N. Lorenzo-Parodi, W. Kaziur-Cegla, M. A. Jochmann, I. Nabipour, H. V. Lutze, U. Telgheder:
Polycyclic aromatic hydrocarbons (PAHs) leachates from cigarette butts into water
Environ. Pollut. **259** (2020), 113916
DOI: 10.1016/j.envpol.2020.113916

14. M. Funck, A. Yildirim, C. Nickel, J. Schram, T. C. Schmidt, J. Tuerk:
Identification of microplastics in wastewater after cascade filtration using Pyrolysis-GC-MS
MethodsX **7** (2020), 100778
DOI: 10.1016/j.mex.2019.100778

15. K. Purschke, C. Zoell, J. Leonhardt, M. Weber, T. C. Schmidt:
Identification of Unknowns in Industrial Wastewater using Offline 2D Chromatography and Non-Target Screening
Sci. Tot. Environ. **706** (2020), 135835
10.1016/j.scitotenv.2019.135835

16. F. Itzel, N. Baetz, L. L. Hohrenk, L. Gehrmann, D. Antakyali, T. C. Schmidt, J. Tuerk:
Evaluation of a biological post-treatment after full scale ozonation at a municipal wastewater treatment plant
Water Res. **170** (2020), 115316
DOI: 10.1016/j.watres.2019.115316

17. G. Renner, A. Nellessen, A. Schwiers, M. Wenzel, T. C. Schmidt, J. Schram:
Hydrophobicity-Water/Air-Based Enrichment Cell for Microplastics Analysis Within Environmental Samples: A Proof of Concept
MethodsX **7** (2020), 100732
DOI:10.1016/j.mex.2019.11.006

18. G. Renner, T. C. Schmidt, J. Schram:
Automated Rapid & Intelligent Microplastics Mapping by FTIR Microscopy: A Python-Based Workflow
MethodsX **7** (2020), 100742
DOI: 10.1016/j.mex.2019.11.015

19. C. Becker, M. A. Jochmann, T. Teutenberg, T. C. Schmidt:
A nebulizer interface for liquid chromatography - Flame ionization detection: Development and validation
Talanta **206** (2020), 120229
DOI: 10.1016/j.talanta.2019.120229

20. A. Tekle-Röttering, S. Lim, E. Reisz, H. V. Lutze, M. S. Abdighahroudi, S. Willach, W. Schmidt, P. R. Tentscher, D. Rentsch, C. S. McArdell, T. C. Schmidt, U. von Gunten:
Reactions of pyrrole, imidazole, and pyrazole with ozone: Kinetics and mechanisms
Environ. Sci.: Water Res. Technol. **6** (2020), 976 – 992.
DOI: 10.1039/c9ew01078e

21. C. Becker, M. A. Jochmann, T. Teutenberg, A. A. Deeb, T. C. Schmidt:
Determination of Liquid Chromatography/Flame Ionization Detection Response Factors for N-heterocycles, Carboxylic Acids, Halogenated Compounds and Others
Anal. Bioanal. Chem. **412** (2020), 171-179
DOI: 10.1007/s00216-019-02222-1

22. L. L. Hohrenk, F. Itzel, N. Baetz, J. Tuerk, M. Vosough, T. C. Schmidt: Comparison of Software Tools for LC-HRMS Data Processing in Non-Target Screening of Environmental Samples
Anal. Chem. **92** (2020), 1898-1907
DOI: 10.1021/acs.analchem.9b0409

23. T. Koehler, I. Ackermann, D. Brecht, F. Uteschil, J. Wingender, U. Telgheder, O. J. Schmitz:
Analysis of volatile metabolites from in vitro biofilms of Pseudomonas aeruginosa with thin-film microextraction by thermal desorption gas chromatography-mass spectrometry
Anal. Bioanal. Chem. **412** (2020), 2881–2892
DOI: 10.1007/s00216-020-02529-4

24. P. Sauerbier, R. Köhler, G. Renner, H. Militz:
Plasma Treatment of Polypropylene-Based Wood–Plastic Composites (WPC): Influences of Working Gas
Polymers **12** (2020) 1933
DOI: 10.3390/polym12091933

25. P. Sauerbier, R. Köhler, G. Renner, H. Militz:
Surface Activation of Polylactic Acid-Based Wood-Plastic Composite by Atmospheric Pressure Plasma Treatment
Materials **13** (2020) 4673
DOI: 10.3390/ma13204673

Conferences and Meetings

Organization

mwas2020
Mülheimer Wasseranalytisches Seminar

4. Mülheimer Wasseranalytisches Seminar (with IWW), Mülheim, September 16-17, 2020

The fourth MWAS in 2020 was a large success that was not fully anticipated due to the uncertainties imposed by the Corona pandemic. The meeting was again co-chaired by Dr. Ulrich Borchers (IWW) and Prof. Torsten Schmidt (UDE-IAC and IWW). 150 scientists and practitioners gathered and discussed intensively for two days new developments in water analysis. Of course, the situation was very special since safety and hygiene regulations had to be strictly obeyed, thus attendance was limited and fully booked. Although the exhibition was already sold out in 2019, many company representatives were not allowed to travel and had to cancel. In the end, this was one of the rare occasions in 2020 to meet in presence and all participants enjoyed this unique opportunity to leave their home office screens for a short while. Everybody agreed that face-to-face discussions cannot be fully replaced by virtual meetings. In 2020 special emphasis was laid on analytical methods for persistent and mobile organic compounds (PMOC), the determination of poly- and perfluorinated compounds (PFAS) and on digitalization and data processing.

Invited Lectures

T. C. Schmidt:
Trends in der Wasseranalytik – wie wird sich das zukünftige Monitoring von organischen Spurenstoffen verändern?
digitale IWAR-Vortragsreihe, TU Darmstadt
Darmstadt, December 14, 2020 (Invited Lecture)

Institute Colloquium

20.01.2020	**Prof. Dr. Marja Lamoree, VU Amsterdam** Effect-Directed Analysis: adding another dimension to toxicant identification
03.02.2020	**Dr. Thomas Eichmann, University Graz** Explorative Lipidomics
	No colloquia later in 2020 due to travel restrictions and partial lockdowns

Teaching

At IAC we are involved in teaching mostly in the Bachelor and Master program "Water Science" that is a unique science-based curriculum with a focus on chemistry, analytics and microbiology (see details at https://www.uni-due.de/water-science/). All courses are also optional for students in the Bachelor and Master program "Chemistry", some are also offered as elective courses for chemistry students studying towards a teacher's degree and for students of the related Master programs "Environmental Toxicology" (offered in the faculty of biology) and "Management and Technology of Water and Wastewater – MTW3" (offered in the faculty of engineering).

Summer term

Lecture and Tutorial "Water Chemistry" (B.Sc. Water Science, in German)

Lecture "Water – The Lecture" (B.Sc. Water Science, in German)

Excursion to Wastewater Treatment Plant Duisburg-Kaßlerfeld (B.Sc. Water Science, in German)

Lecture and Tutorial "Oxidative Processes" (M.Sc. Water Science, in English)

Lecture and Tutorial "Stable Isotope Analysis" (M.Sc. Water Science, in English)

Laboratory Practical "Stable Isotope Analysis" (M.Sc. Water Science, in English)

Lecture and Tutorial "Quality Management" (M.Sc. Water Science, in English)

Laboratory Practical "Environmental Analytics" (M.Sc. Environmental Toxicology, in English)

Excursion to the Institute for Reference Materials and Measurements, Geel (B) (M.Sc. Water Science, in English)

Winter term

Lecture and Tutorial "Water Analysis" (B.Sc. Water Science, in German)

Laboratory Practical "Analytical Chemistry" (B.Sc. Water Science, in German)

Laboratory Practical "Water Chemistry and Analysis" (B.Sc. Water Science, in German)

Lecture and Tutorial "Water Chemistry" (M.Sc. Water Science and Environmental Toxicology, in English)

Lecture, Tutorial and Seminar "Chemometrics and Statistics" (M.Sc. Water Science, in English)

Individual Practical Projects "Analytical Chemistry" (M.Sc. Water Science, in English)

Excursion to the Drinking Water Treatment Plant incl. Ultrafiltration, Roetgen (M.Sc. Water Science, in English)

Miscellaneous

Births

Bennet Drees , 13.08.2020

Wedding

Wedding Lotta Laura Hohrenk-Danzouma, 11.12.2020 with Husband Bala and Daughter Nabila Ina.