# UNIVERSITÄT
# DUISBURG
# ESSEN

*Open*-Minded

**2023**

**Jahresbericht**

**Annual Report**

# Content

# Instrumental Analytical Chemistry

### Dear friends and colleagues.

Every year is special. Once again, 2023 had some unique challenges on scales from global to university level and has shown us how important teaching and research are on the long path towards sustainable development and fair society. Natural sciences are and will remain an important building block on that path, which, unfortunately, is not currently reflected in the number of students in our faculty. Nevertheless, so far, we luckily always found highly qualified and motivated people who are the core of our research group. That is how we could continue our successful work at IAC, thanks to my fabulous team, and we are pleased to give you an overview of our activities in 2023 with this annual report.

We participated actively in several conferences and meetings in 2023 and picked up our long-term scientific exchange with the groups of Holger Lutze and Thomas Ternes, organized for the first time in Darmstadt. We started the year with the established Hohenroda Ph.D. seminar luckily back to presence that already saw two students receiving awards; Robert Marks was honored with the Ernst-Bayer award of the working group separation science, Max Reuschenbach received a formidable second place in the participants' voting for the best oral presentation. Later in the year, Sarah Rockel won an award for the best oral presentation at the German stable isotope conference (details to be seen later). Congratulations to all of them and the other IAC members who did a splendid job. This includes the seven PhD students at IAC who successfully defended their theses. Thanks mostly to the active Ph.D. students and postdocs, we have surpassed the already high number of publications from 2022 and set another all-time high with 36 papers in internationally peer-reviewed journals, most of which appeared in the field's premier journals. In addition, Sina Dobaradaran, our longstanding external IAC member from Bushehr, Iran, published another 21 papers without other contributors from IAC.

Last year has also seen some successful proposals. Maryam Vosough got a proposal accepted by DFG that will fund her work on HRMS data processing and analysis for the next two years, and another DFG project was accepted in the area of 2DLC for stable isotope analysis. Our profile-building project, "Natural Water to Hydrogen" was favorably reviewed in summer. It started in November 2023 and last for three years. Anam Asghar is involved in that project as a postdoctoral researcher. Finally, our excellence cluster proposal REASONS was submitted, and we have been eagerly awaiting the results of the first-round review early February 2024. And hooray! We obviously could convince the international expert panel and have been invited to submit a full proposal in August 2024 that was will keep us very busy in the coming months. But we also received some sad news last summer. Prof. Alfred Golloch, former head of the IAC and co-founder of the Bachelor and Master Water Science degree programs, passed away on August 2, 2023, at age 85. An obituary can be found at the end of this annual report.

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 and success in 2024, for which I can extend my wishes from last year for a more peaceful near future that allows us to focus more on all the challenges posed by climate change.

# Group Members



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## Head of Chair
Prof. Dr. Torsten C. Schmidt

## Secretarial Office
Lydia Vaaßen

## Regular Staff

| | |
|---|---|
| Dr. Anam Asghar | Advanced Oxidation Processes |
| Simone Bettinger | Laboratory engineer, Instrument, and Lab Supervision |
| Dr. Maik Jochmann | Stable Isotope Analysis, Sample Preparation, and Gas Chromatography |
| Dr. Klaus Kerpen | 2D-Fluorescence Spectroscopy, Advanced Oxidation Processes, Laser Commissioner, IT Administrator |
| Dipl.- Ing. Robert Knierim | Laboratory Equipment, Glassware, Support of guest scientists |
| Dr. Gerrit Renner | Analytical Data Science, Project Administration |
| 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
Maximilian Budweg

Jo-Ann Wollenberg

## Research, Teaching, and Technical Assistants
Rukiyye Abis

Isabel Halbhuber

Alina Hofrath

Daniel Höhn

Janina M. Pytlik

Anna Mangels

Isabell Schelhorn

## Ph.D. Researchers

Dr. Amir Salemi

General topic: Development and Optimization of Sample Preparation and Chromatographic Analysis methods

During the past year, I collaborated in writing two review papers (on green sample preparation and passive sampling methods) and two other papers on the newly developed HLB-SPME and the NTA of surface water using data fusion and MCR. Furthermore, an SPE-LC-Orbitrap MS for selected biomarkers was developed and implemented for a wastewater-based epidemiology project. I am currently working on the greenness evaluation of standard analytical methods and collaborating in the determination of phenolic compounds released from cigarette butts. Finalizing the automated derivatization technique is also among the planned projects of 2024.

## Ph.D. Students (Internal)

Felix Drees

Data Processing in Non-Target Screening

Tobias Hesse

The Potential of LC-IRMS: Carbon stable isotope analysis of amino acids in a host-parasite system and a proof-of-principle study for $\delta15N$ measurements of nitrate

Katharina Klein

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

Shaista Khaliq

Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids

Nerea Lorenzo Parodi

Aromatic amines as biomarkers in human urine: Analytical method development and epidemiological studies

Michael Leupold

Investigations of transformation reactions of antibiotics by photocatalysis in aqueous systems

Robert Marks

Coupling techniques in the field of isotope ratio mass spectrometry

Valentina Merkus

Characterization of transformation processes using high-resolution mass spectrometry

Xenia Mutke

Treatment of membrane concentrates by oxidative processes

Felix Niemann

Isotope fractionation associated with abiotic Imidacloprid degradation

Max Reuschenbach

Automated data processing and data analysis in high-resolution mass spectrometry

Sarah P. Rockel

Development and evaluation of a 2D-LC-IRMS coupling for the use of conventional reversed-phase chromatography in component-specific stable isotope analysis

Lucie K. Tintrop

Automated and miniaturized sample preparation in gas chromatographic analysis

Duaà Tahboub

Studies on electrochemical treatment processes for the decomposition of Persist Organic Pollutants (POPs) in contaminated ground and surface water

## Ph.D. Students (External)

| | |
|---|---|
| Reyhaneh Armin | Non-target analysis of organic micropollutants in industrial wastewater |
| Alexander Augustini | Chemical characterization of the ingredients of electronic cigarettes and the inhaled products. |
| Indra Bartels | Analysis of suggested SARS-Cov-2 treatment pharmaceuticals in surface waters |
| 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 |
| Joanna Flottmann | Analysis of highly polar trace substances in water with LC-HRMS(/MS) |
| Matin Funck | Development of a Sampling-Procedure allowing subsequent qualitative and quantitative Pyrolysis-GC/MS analysis for Subµ-Plastics in the Aquatic Environment |
| Annika Fechner | Kopplung eines miniaturisierten Thermodesorptionschips und einer µ-Plasma-Ionisierungsquelle zur Analyse flüssiger Proben mittels Ionenmobilitätsspektrometrie |
| Jana Hinz | Development and application of multidimensional GC-IMS methods for the analysis of volatile and semivolatile substances in safety and health research |
| Malte Hübchen | Automated sample preparation and gas chromatographic analysis in the field of food and consumer goods |
| Frank Jacobs | Development of an automated microextraction technique |
| Michelle Klein | Effect-directed analysis for monitoring and evaluation of surface and wastewater |
| 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 |
| Lars Reinders | Analytical monitoring of personalized drugs containing monoclonal antibodies: An alliance of patient and personnel safety |
| Sara Schäfer | Oxidative transformation of organic compounds in ultrapure water by ozonation and UV photolysis |
| Hannah Schanzmann | Schnelle, nicht-invasive Identifikation nosokomialer Infektionen |
| Fabian Ude | Non-radioactive, energetically variable ionization unit for pollutant analysis in building materials based on FAIMS technology |
| Mike Wenzel | Determination of microplastics in soils and mosses |
| Tobias Werres | Characterization of extra-column volumes in capillary high-performance liquid chromatography |
| Modestus Wigger | Methoden der digitalen Sensorik von Lebensmitteln basierend auf der Ionenmobilitätsspektrometrie |

# Guest Scientists

**Prof. Sina Dobaradaran**
Long-term visiting scientist
Bushehr University of Medical Sciences, Iran

A comprehensive study on environmental emissions of primary aromatic amines by cigarette butts and compare with unsmoked cigarette levels.

Study of the kinetics of aromatic amines release from cigarette butts into the water environments

Determining the acute toxicity of CBs leachates for aquatic organisms (my next project)

**Prof. Dr. Maryam Vosough**
Long-term visiting scientist
Chemistry and Chemical Engineering Research Center of Iran
(CCERCI)

Department of Clean Technologies, Chemometrics laboratory

Development of chemometrics-based approaches for Non-Target analysis of micropollutants in water environment using LC-HRMS/MS

One clear challenge with high-resolution mass spectrometric-based instruments is the generation of massive quantities of data ("big analytical data") and their pre-processing and processing steps. So, developing post-acquisition data handling tools is increasingly critical for reliable non-targeted analysis workflows. In particular, this is the case for non-targeted environmental data, as the goal is to track and identify trace quantities of organic micropollutants and their transformation products in the presence of strong matrix effects and generally in a more extensive chemical space than metabolomics study. Chemometrics, a powerful interdisciplinary field that uses mathematical, statistical, and machine learning tools to analyze high-dimensional and complex chemical information, can be appropriately incorporated in different environmental non-targeted analysis workflow stages.

**Adrien Tanti**
Student Intern from the UNIVERSITE D'AIX-MARSEILLE, MARSEILLE, France
Duration: (May 29, 2023 to July 28, 2023)
Internship Tutor: Anam Asghar

Topic: To investigate the stimulatory and/or inhibitory effects of dissolved organic matter on sulfate radical-mediated oxidation process

# IAC News

## Instrumental Analytical Chemistry Launches Newly Redesigned Website

Instrumental Analytical Chemistry (IAC) is delighted to announce the successful completion and launch of our completely redesigned website. The new site, now live, boasts an enhanced interface and a wealth of resources tailored for established researchers and those interested in analytical chemistry. In line with our commitment to fostering knowledge and innovation in analytical chemistry, the redesigned website provides a platform that seamlessly combines aesthetics and functionality. It has been constructed with the needs of our diverse audience in mind, featuring improved navigation, accessibility, and streamlined content. The website is live now and can be accessed at **https://www.uni-due.de/iac/**. We encourage everyone to explore the new site and take advantage of the wealth of information it provides.
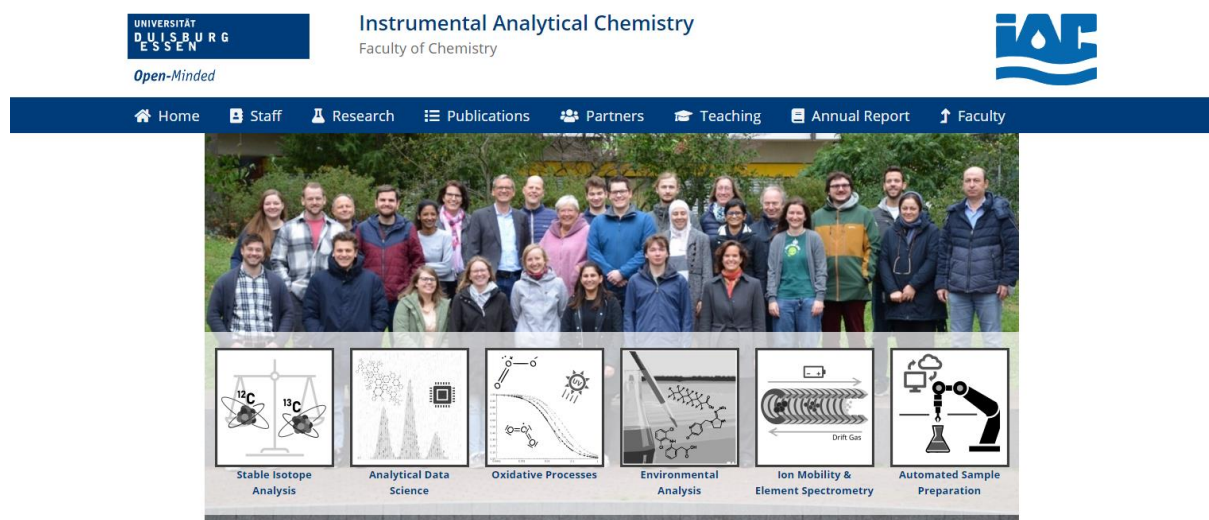
# Awards



## Ernst-Bayer Award
**Robert Marks**

For the outstanding scientific publication:

Marks, R. G., Jochmann, M. A., Brand, W. A., & Schmidt, T. C. (2022). How to couple LC-IRMS with HRMS– a proof-of-concept study. *Analytical Chemistry, **94**(6), 2981-2987.*
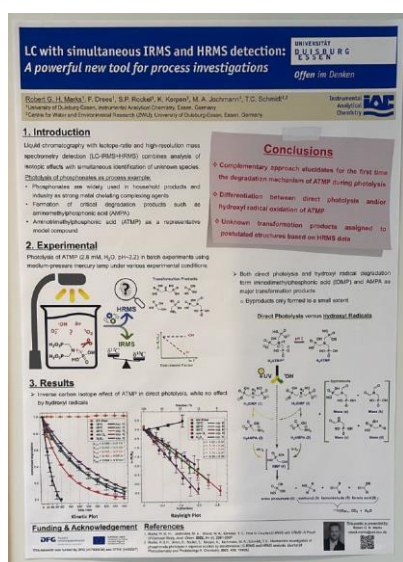


## Best Presentation Award (Doctoral seminar of the AK Separation Science)
**Max Reuschenbach**

For the outstanding scientific talk:

Reuschenbach, M., Schmidt, T. C., Renner, G. (2023). How to increase the confidence in results from Non-Target Analysis with HPLC-HRMS? Development of a Data Quality Score. *33rd Doctoral seminar of the AK Separation Science*



## HPLC 2023 Best Poster Award
**Robert Marks**

For the outstanding scientific poster:

Marks, R. G., Drees, F., Rockel, S. P., Kerpen, K., Jochmann, M. A., Schmidt, T. C. (2023). LC with simultaneous IRMS and HRMS detection: A powerful new tool for process investigations. *HPLC 2023, 51st Internation Symposium on High-Performance Liquid Phase Separations and Related Techniques*

### Best Presentation Award (German Association for Stable Isotope Research)
**Sarah Rockel**

For the outstanding scientific talk:

Rockel, S. P., Jochmann, M. A., Schmidt, T. C. (2023). Two-dimensional LC-IRMS – The future of CSIA? *ASI Annual Conference 2023*

### Axel-Semrau Award
**Janina Marie Pytlik & Leonardo Solazzo**

For their outstanding Bachelor theses:

Pytlik, J. M. (2023). Acute Ecotoxicological Effects of Industrial Wastewater on the aquatic Environment

Solazzo, L. (2023). Charakterisierung eines hydrophilic-lipophilic balanced SPME Materials zur Anreicherung von Analyten aus wässrigen Proben

### Water Science Award (UDE) & Student Award Analytical Chemistry (GDCh)
**Anna Mangels**

For the best performance in analytical chemistry (bachelor) in 2023.

# Running Projects

## Overview

1. Photocatalysis of the β-lactam antibiotic amoxicillin and clavulanic acid for the prevention of the spread of antibiotic resistances: Kinetics, matrix effects, and transformation processes.

2. Development and evaluation of a 2D-LC-IRMS coupling for the utilisation of conventional reversed-phase chromatography in component-specific stable isotope analysis.

3. Inhibitory and/or stimulatory role of dissolved organic matter in advanced oxidative processes.

4. Natural Water to Hydrogen- Understanding the dynamics of active sites in electro-catalytic hydrogen production from unpurified water.

5. Unraveling Non-Target Screening Variability: A Deep Dive into Chemical Process Characterization.

6. Development of a pipe reactor system controlled by on-site TOF detection for the remediation of PFAS-containing fire extinguishing water by means of perfluoroAd precipitation (TOFfloc).

7. Development of a new method for the determination of N-nitrosamines in the air at the workplace in the context of occupational safety - NNOccSafe.

8. Development of a method for the analysis of the extracellular volatile metabolome of nosocomial pathogens by thermal desorption GC-MS and GC-IMS.

9. Non-radioactive ionization for spectrometry and spectroscopy.

10. Studies on electrochemical treatment processes for the decomposition of Persistent Organic Pollutants (POPs) in contaminated ground and surface water.

11. Development of Chemometrics/Machine learning-based approaches for non-target analysis of micropollutants in water environment using LC-HRMS/MS.

12. Development of a Data Quality Score for the Processing of Non-Target-Screening Data generated by HPLC-HRMS.

13. Membrane processes in drinking water supply (KonTriSol).

14. Isotope-labeling in situ derivatization and HS-SPME arrow GC-MS/MS for simultaneous determination of fatty acids and fatty acid methyl esters in water.

15. Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids (A13: CRC RESIST).

16. Investigation of Stable Isotope Fractionation during Abiotic Imidacloprid Degradation.

17. Determination of atmospherically deposited microplastics in moss: Method development and performance evaluation.

18. AutoExtrakt – Development of a fully automated microextraction device and its application for the analysis of substances in complex matrices from food and environmental origin.

## Photocatalysis of the β-lactam antibiotic amoxicillin and clavulanic acid for the prevention of the spread of antibiotic resistances: Kinetics, matrix effects, and transformation processes

**Involved staff:** Michael Leupold, Isabell Schelhorn, Dr. Anam Asghar, Prof. Dr. Torsten C. Schmidt
**Partners:** Dr. Lukas Fischer
**Funding:** Zentrum für Wasser- und Umweltforschung, Stiftung Zukunft NRW

The research project aims to remove antibiotics and antibiotic resistance genes in hospital wastewater by photocatalysis to counteract the global contamination of the environment and the associated loss of efficacy of antibiotic agents. In urban areas, antibiotics and resistance genes enter the environment through wastewater. Since wastewater treatment plants are not optimized to remove pharmaceuticals or resistance genes. Resistance genes in the environment threaten human health, as they can travel from there back to the population (Westphal-Settele et al., 2018). If nothing is done, antibiotics will soon become ineffective in combating infectious diseases, which is predicted to lead to 10 million annual deaths worldwide by the middle of this century (O'Neill, 2016). One solution strategy is to treat wastewater using photocatalysis (Nosaka et al., 2017). Whether universal antibiotics and antibiotic-resistance genes can be removed in complex matrices is unclear. Nevertheless, photocatalysis is promising because, compared to other treatment methods, it can be expected to produce high yields of reactive oxygen species that can effectively degrade pharmaceuticals.

A photocatalytic reactor for testing photocatalytic materials was developed during the research project. It will show how artificial matrices influence the kinetics and transformation of product formation using the two beta-lactams, amoxicillin, and clavulanic acid. In addition to the analytical methods of coupling liquid chromatography with high-resolution mass spectrometry, parameters relevant to the degradation, such as dissolved organic carbon, pH, and dissolved oxygen, will be measured. A schematic overview of the reactor and the planned online, inline, and at-line measurements are attached to the figure. The knowledge gained will then be used halfway through the research project to study amoxicillin and clavulanic acid and their corresponding resistance genes in hospital wastewater. Since many different antibiotics and corresponding resistance genes can be expected to be found in hospital wastewater, a group of ten relevant antibiotics and their corresponding resistance genes will also be selected according to their relevance, quantified in samples, and tested for photocatalytic degradability. The group should contain antibiotics from all important substance classes. The research data will be published in the form of lectures, poster contributions, and publications, as well as in suitable databases.
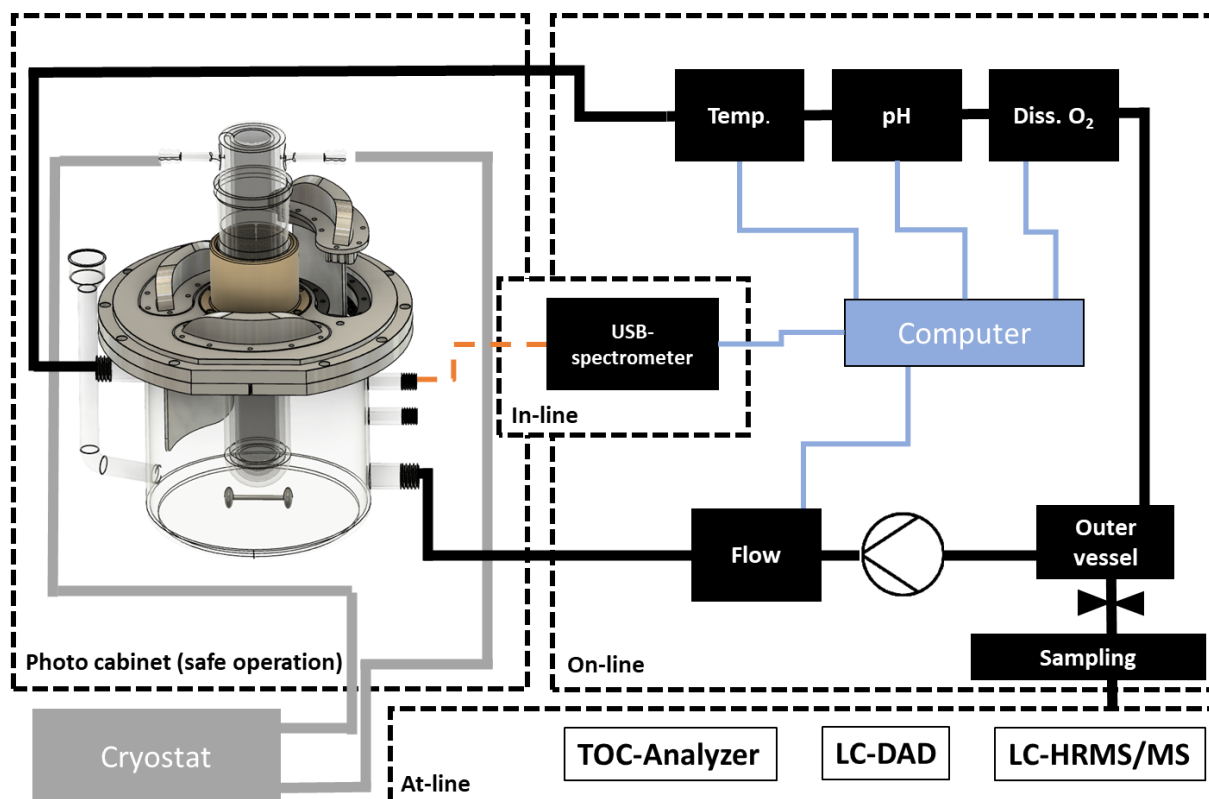
*Figure Caption: Schematic overview of the reactor and planned on-line, in-line, and at-line measurements.*

Literature:

Nosaka, Y., & Nosaka, A. Y. (2017). Generation and Detection of Reactive Oxygen Species in Photocatalysis. Chemical Reviews, 117(17), 11302-11336. https://doi.org/10.1021/acs.chemrev.7b00161

O'Neill, J. (2016). Tackling drug-resistant infections globally: final report and recommendations.

Westphal-Settele, K., Konradi, S., Balzer, F., Schönfeld, J., & Schmithausen, R. (2018). Die Umwelt als Reservoir für Antibiotikaresistenzen. Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz, 61(5), 533-542. https://doi.org/10.1007/s00103-018-2729-8

## Development and evaluation of a 2D-LC-IRMS coupling for the utilization of conventional reversed-phase chromatography in component-specific stable isotope analysis

**Involved staff:** Sarah P. Rockel, Robert G. H. Marks, Dr. Klaus. Kerpen, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt

**Partners:** -

**Funding:** German Research Foundation (DFG) Project Grant 537343248

Compound-specific stable isotope analysis (CSIA) can be applied in many fields, including evaluating sources and transformation processes of micropollutants or verifying food authenticity. When coupling liquid chromatography (LC) to an isotope ratio mass spectrometer (IRMS), the stable carbon isotope signature of analytes in water samples can be assessed. Limitations of this method occur due to the wet chemical oxidation of carbon in the LC-IRMS interface, where all oxidizable carbon is transformed into carbon dioxide ($CO_2$). Because of this, the use of organic substances as eluents, buffers, or modifiers can lead to falsifications in the determination of the carbon isotope signatures of the analytes and has to be avoided. This

limits the use of already established chromatographic separations based on organic eluents, which comprise over 90 % of applied LC methods. Only inorganic buffers and temperature can be used for method development, which makes it difficult and time-consuming, especially for more complex samples. A possibility to overcome this limitation is offered by combining two-dimensional-LC (2D-LC) with LC-IRMS (see figure).
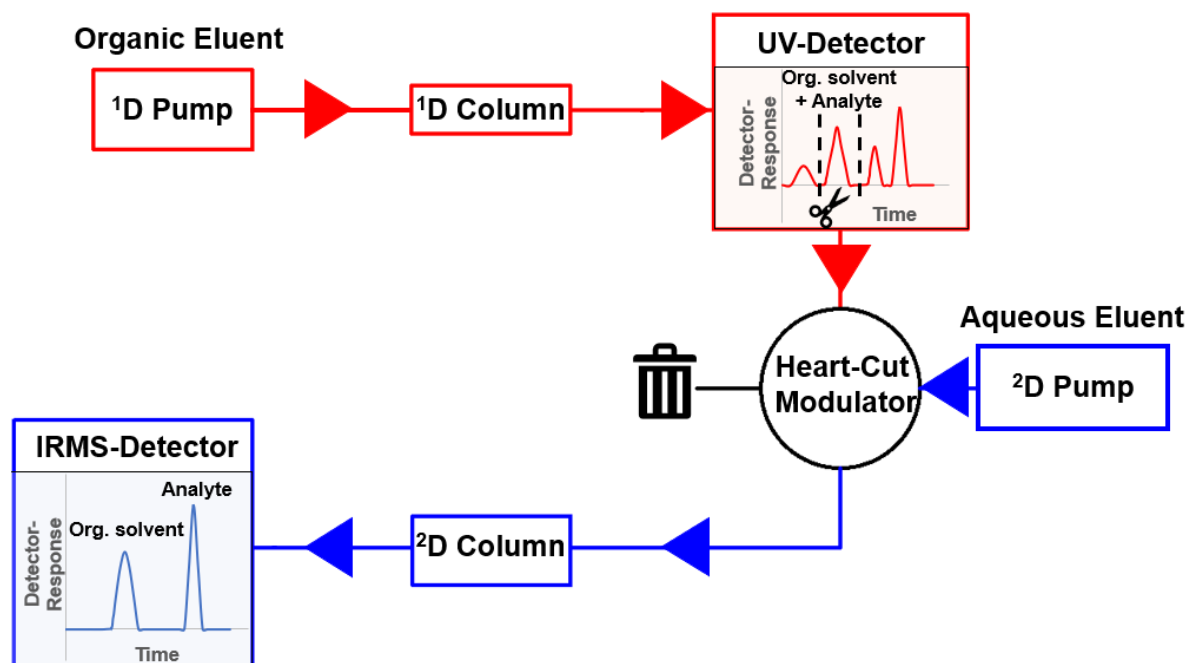


*Figure Caption: Two-dimensional LC-IRMS system, with organic-containing eluent stream (red) in 1D and fully aqueous eluent stream (blue) in 2D*

Conventional 2D-LC works with two chromatographic columns with different separation mechanisms. This way, peak capacity can be significantly increased, allowing chromatographic separation of compounds that coelute in only one dimension. Adapting this system to LC-IRMS allows LC methods taken from the literature to be used with organic additives in the first dimension without any method development. The analyte of interest is then transferred via heart-cut modulation, using a sample loop transfer onto the second dimension, where the organic solvents are separated from the analyte before oxidation.

This study investigates the potential of heart-cut-2D-LC coupled with IRMS to make CSIA more accessible for a broader spectrum of applications. Therefore, caffeine, which is well-studied in CSIA, is used for initial method development and validation. Parameters such as peak shape, retention time, reproducibility, and carbon isotope signatures are considered for the method validation. To open up various applications, we aim to vary chromatographic parameters, such as column materials and modulation techniques. The long-term goal is to apply this instrumentation in mechanistic investigations and measuring real-life samples.

## Inhibitory and stimulatory role of dissolved organic matter in advanced oxidative processes

**Involved staff:** Dr. Anam Asghar, Dr. Klaus Kerpen, Prof. Dr. Torsten C. Schmidt
Partners:  -
**Funding:** internal

The degradation of organic micropollutants (OMPs) by advanced oxidation processes (AOPs) poses a significant challenge due to the complexity and diversity of water matrices. Water matrix constituents, mainly dissolved organic matter (DOM), impact their effectiveness. DOM is a complex mixture of heterogeneous compounds with a continuum of functional groups and molecular sizes. The reactivities and concentrations of such functional groups determine the extent of the NOM-oxidant interactions and, thus, induce promoting and inhibiting effects. Therefore, during the application of AOPs, DOM can block light penetration, scavenge radicals/oxidants, and enhance the formation and reactivity of valuable reactive oxidative species to eliminate OMPs, thereby altering the transformation pathways. Therefore, the research needs to advance the structural and practical understanding of how DOM can be exploited to enhance the synergistic properties effects of DOM and improve the performance of oxidative processes.

It is necessary to look at the underlying mechanisms probably by choosing appropriate surrogates or model DOM/NOM model compounds of different sizes and functional groups and subsequently investigate their role in oxidative processes to develop a comprehensive understanding of multiple roles of DOM in the application of AOPs. Therefore, this project aims to pitch the idea of using different NOM/DOM model compounds with different molecular sizes and functional groups to understand the mechanisms governing DOM's synergistic and inhibitory properties in AOPs.

## Natural Water to Hydrogen- Understanding the dynamics of active sites in electro-catalytic hydrogen production from unpurified water

**Involved Staff:** Dr. Anam Asghar, Prof. Dr. Torsten C. Schmidt
**Partners:**  Prof. Dr. Corina Andronescu, Prof. Dr. Katrin Domke, Jun.-Prof. Dr. Kai Exner, Jun.-Prof. Dr. Anzhela Galstyan, Prof. Dr. Stephan Schulz, Prof. Dr. Mathias Ulbricht, Prof. Dr. Harry Hoster, Prof. Dr.-Ing. Stefan Panglisch, Prof. Dr. Christof Schulz, Prof. Dr. Ing. Doris Segets, Prof. Dr. Richard Kramer Campen
**Funding:** Ministerium für Kultur und Wissenschaft NRW



The "Natural Water to Hydrogen" research profile is an initiative undertaken by the University of Duisburg Essen (UDE). Its primary goal is to enhance the sustainability of hydrogen ($H_2$) production through water electrolysis. This is achieved by establishing a platform for gaining fundamental insights into the processes occurring at electrodes and membranes within aqueous environments. This understanding will allow us to determine the precise water quality requirements for electrolysis, which can vary depending on the catalyst and membrane used. This will be achieved through comprehensive efforts that draw upon expertise from water research, electrocatalysis, and membrane technology.

The IAC project aims to collaborate with involved groups to understand the impact of water quality parameters on the performance of the electrolysis process and the membrane and catalyst activity. However, analyzing them will be challenging due to the high alkalinity of water samples. Therefore, we will focus on developing analytical techniques to analyze the water quality parameters, which include cations ($Na^+$, $Ca^{2+}$, $Mg^{2+}$), anions ($Cl^-$, $SO_4^{2-}$, and $NO_3^-$, $HCO_3^-$/$CO_3^{2-}$), and dissolved organic matter (DOM) in concentration typically present in drinking water samples. Additionally, the project scope will be extended to perform downstream water analysis and evaluate the overall process performance regarding catalyst leaching and inactivation of the membrane.

## Unraveling Non-Target Screening Variability: A Deep Dive into Chemical Process Characterization

**Involved staff:** Felix Drees, Prof. Dr. Maryam Vosough, Prof. Dr. Torsten C. Schmidt
**Partners:** -
**Funding:** internal

Non-Target Screening (NTS) is an analytical chemistry technique employed to comprehensively analyze samples, identifying compounds present, including those not initially targeted or expected. This method enables the identification of unknown compounds, offering a more realistic depiction of the chemical composition. The increasing use of NTS for monitoring and process characterization has been notable in recent years. However, the well-established issue of different NTS approaches yielding significantly varied results prompts an examination of its implications for process characterization.

This work investigates the potential impact of diverse NTS approaches on process characterization, mainly focusing on whether distinct approaches yield similar data patterns and consequently prioritize the same chemical components. Two markedly different NTS approaches were applied to the same dataset, generated through liquid chromatography coupled to high-resolution mass spectrometry (HPLC-ESI-MS) while sampling a mesocosm setup incorporating treated wastewater into river water.

Following both NTS approaches, namely Regions of Interest Multivariate Curve Resolution Alternating Least Squares Analysis (ROI MCR-ALS) and MZmine3, exploratory Principal Component Analysis (PCA) was employed. Subsequently, Analysis of Variances Simultaneous Component Analysis (ASCA) was applied to consider the process design, evaluating the essential components for the constructed model based on their bootstrapped loading values. Finally, Partial Least Squares Discriminant Analysis (PLS-DA) was utilized to prioritize chemical components derived from the preceding information.

Results indicate that both NTS approaches initially extracted similar chemical information from the raw data, revealing a generally similar but not congruent data pattern related to the experimental design (Figure 1).
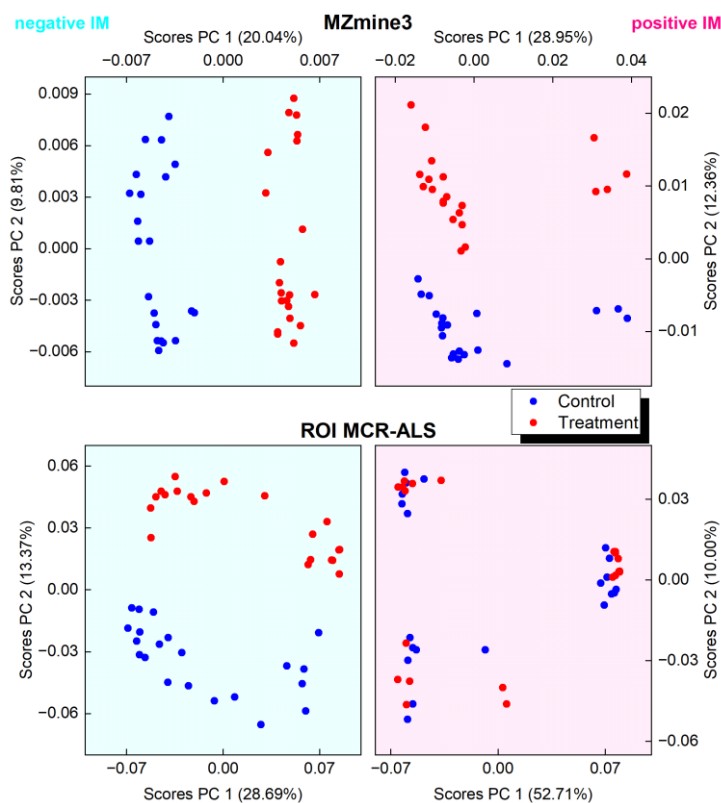
*Figure 1: Scores on PC 1 & 2 obtained from PCA of feature and component list by MZmine3 and MCR ALS in negative and positive ionization mode. The color code indicates sample types, control (blue), and treatment (red).*

However, despite employing different prioritization strategies, the observed data patterns were not associated with the same chemical information, as shown in Figure 2 for ASCA results.
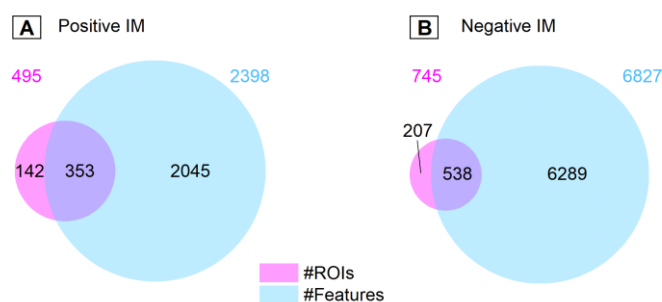


*Figure 2: Comparison of ROIs and Features, which are prioritized in ASCA modeling due to their bootstrapped loading values. Results are visualized in a Venn diagram for positive and negative ionization modes (IM). Masses within an allowed tolerance of 0.005 amu are assumed to correspond. Features that are associated with the injection peak are excluded in this comparison. Considering ROIs that quantitatively contribute to 5% or more to a component's mass spectrum is included.*

This underscores the robust potential of an NTS approach for characterizing processes, yet the challenge of inconsistent data processing results hampers consensus on the causative components.

## Development of a pipe reactor system controlled by on-site TOF detection for the remediation of PFAS-containing fire extinguishing water using perfluoroAd precipitation (TOFfloc)

**Involved staff:** Dr. Klaus Kerpen, Simone Bettinger, PD Dr. Ursula Telgheder
**Partners:** Cornelsen Umwelttechnologie GmbH
**Funding:** Federal Ministry for Economic Affairs and Climate Protection (BMWK) by the Central Innovation Programme for SMEs (ZIM)

Perfluorinated and polyfluorinated alkyl substances are a group of chemical substances of anthropogenic origin. Their unique properties, such as their thermal and chemical stability, or their water and grease-repellent properties, have made their use attractive in many areas of industry for over 60 years, including for use in firefighting. However, their extraordinary properties also ensure that they are very stable in the environment and can hardly be degraded, so they are ubiquitous worldwide and pose a danger to humans and the environment due to their toxic properties.

The project aims to develop an automated pipe reactor system for cleaning PFAS-containing wastewater, e.g., cleaning the extinguishing agent tanks of fire engines and stationary extinguishing systems based on the PerfluorAd process. The process parameters, such as flow velocity, dwell time, dosing rates, etc., must be adjusted to automate the system. The dosing of the specific precipitant PerfluorAd is controlled via an on-site analysis process based on detecting the total organic fluorine compounds (TOF). The basis of the analysis procedure is the thermal conversion of the organic fluorine compounds into elemental fluorine or polyatomic fluorine species with subsequent spectrometric detection. The device-specific parameters such as geometry and material of the connections, temperature program, and gas flows must be adapted so that sensitive spectrometric analysis of the resulting species is made possible by coupling with a helium plasma with barrier discharge at atmospheric pressure (BDP) and a CCD spectrometer.

The spectrometric analysis after converting the organic fluorine compounds into elemental or polyatomic fluorine species represents a promising approach. The conversion of the organic fluorine compounds is carried out thermally using a miniature evaporator. The device-specific parameters such as geometry and material of the connections, temperature program, and gas flows are to be adapted to make a sensitive spectrometric analysis of the resulting species possible by coupling with a suitable detector. After optimization and validation of the developed process, it will be integrated and adapted into the tubular reactor prototype.

## Development of a new method for the determination of N-nitrosamines in the air at the workplace in the context of occupational safety - NNOccSafe

**Involved staff:** Jana Hinz, PD Dr. Ursula Telgheder
**Partners:** Bonn-Rhein-Sieg University of Applied Sciences
**Funding:** German Social Accident Insurance (DGUV)

Continuing from the results presented in the 2022 yearly report, research within the framework of the 'NNOccSafe Project", funded by the German Social Accident Insurance (DGUV), was pursued according to the defined working packages. The overall aim of the work is to develop a method based on the coupling of gas chromatography (GC) and ion mobility spectrometry (IMS) that supersedes the current state of the art for nitrosamine analysis regarding sensitivity, selectivity, economy, and ease of operation. The focus in 2023 was sampling airborne nitrosamines on Tenax TA and their breakthrough volume.

The breakthrough volume of a substance for a specific adsorbent such as Tenax is defined as the volume of carrier gas/sampling volume per gram of adsorbent that causes the analyte to migrate through the packing of the thermal desorption tube and out the other end. A setup has been prepared where the analytical GC column has been replaced by a stainless-steel thermal desorption tube connected to the injector and detector by a capillary guard column to determine the parameters needed for the calculation of the breakthrough volume of N-nitrosamines (retention times of the analytes after traversing the sorbent at different temperatures).



Breakthrough Volume Plot NDMA on Tenax TA

$$y = -0.0162x + 1.8132$$
$$R^2 = 0.9743$$
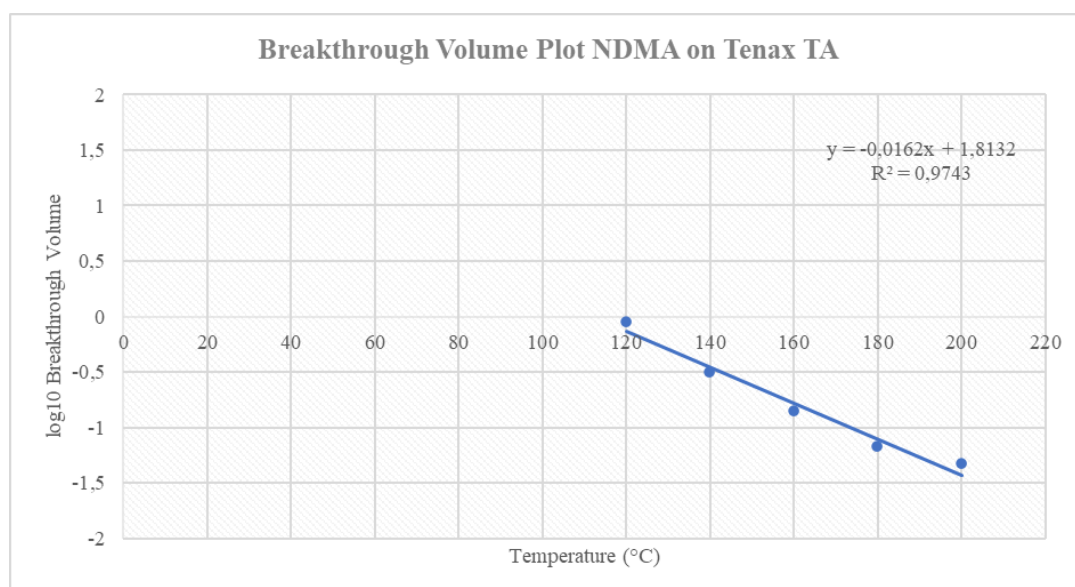
*Figure Caption: Breakthrough volume plot for NDMA Tenax TA (60/80 mesh, 200 mg) at temperatures between 120 and 200 °C with a synthetic air carrier gas flow rate of 108.9 mL/min.*

The breakthrough volume plot for NDMA on Tenax TA (60/80 mesh, 200 mg) at temperatures between 120 and 200 °C with a synthetic air carrier gas flow rate of 108.9 mL/min.

As can be seen from the regression coefficient, the linearity appears to be sufficient to extrapolate the data to room temperature (approximately 20 °C). Similar regression coefficients – between 0.979 and 0.9987 – were determined for the remaining six N-nitrosamines.

The following breakthrough volumes for seven N-nitrosamines on Tenax TA 60/80 mesh adsorbent were determined using the generated regression equation:

*Table Caption: Overview of calculated breakthrough volumes (per gram and 200 mg of Tenax TA 60/80 mesh) at room temperature (20 °C) for each N-nitrosamine*

| Nitrosamine | Molecular mass (g/mol) | $Bv$ 1 g Tenax TA (L) | $Bv$ 200 mg Tenax TA (L) |
|---|---|---|---|
| NDMA | 74,08 | 30,85 | 6,17 |
| NMEA | 88,10 | 31,20 | 6,24 |
| NDEA | 102,13 | 50,44 | 10,09 |
| ND-iso-PA | 130,18 | 305,21 | 61,04 |
| ND-n-PA | 130,18 | 1033,95 | 206,79 |
| NMOR | 116,11 | 114,50 | 22,90 |
| NPYR | 100,12 | 233,40 | 46,68 |

As a standard, thermal desorption tubes are filled with 50 – 1000 mg of adsorbent. The cartridges used in this experiment contained 200 mg of Tenax TA adsorbent. For low molecular, high volatility N-nitrosamines, such as NDMA and NMEA, the sampling volume for these tubes is around 6 L. The values for the other N-nitrosamines appear to increase with their molecular weight, with ND-n-PA showing the highest breakthrough volume. ND-n-PA is the unbranched isomer of the ND-iso-PA molecule and possesses a greater spacial size and higher boiling point, which may account for its greater absorbance to the resin bed.

As there is little information on N-nitrosamine breakthrough volumes on Tenax, the results of this experiment cannot be compared to any literature values.

These theoretical breakthrough volume values are verified by connecting thermal desorption tubes sequentially and determining the recovery of NDMA (the lead substance) on the second tube after the breakthrough airflow volume has been reached and superseded.

## Development of a method for the analysis of the extracellular volatile metabolome of nosocomial pathogens by thermal desorption GC-MS and GC-IMS

**Involved staff:** Hannah Schanzmann, PD Dr. Ursula Telgheder
**Partners:** Hamm-Lippstadt University of Applied Sciences, ION-GAS GmbH, Witten/Herdecke University with Helios University Hospital Wuppertal
**Funding:** Bundesministerium für Bildung und Forschung, Grant No. 13GW0428C

Hospital-acquired infections, like nosocomial pneumonia, are one of the most significant challenges in inpatient care. They lead to increased mortality, longer stays, higher treatment costs, and, thus, a socioeconomic burden. Therefore, a rapid and reliable diagnostic is crucial for starting targeted antibiotic therapy. However, culture-based diagnostic procedures often take up to 48 hours to identify the causal pathogen.

Hence, a technology enabling faster detection of specific pathogenic agents must be

developed. The project presented here aims to identify pathogens based on their specific microbiological volatile organic compound (mVOC) profiles in exhaled air. A benchtop system consisting of a thermal desorption (TD) gas chromatograph with a mass spectrometer (MS) is established to measure these mVOCs from bacterial reference cultures and human breath. In addition, an ion mobility spectrometer (IMS) was coupled as a second detector so that the MS and the IMS shared the same flow line using a flow splitter. Nearly identical retention times can be achieved within the range of up to 30 minutes with slight deviations of 0.06 to 0.24. This enables the identification of unknown compounds in the IMS chromatogram using unambiguous mass spectral identification. The coupling of TD-GC-MS-IMS has been built up for the first time.

To find specific mVOCs as a benchmark of selected known pathogens such as Pseudomonas aeruginosa, Staphylococcus aureus, Streptococcus pneumonia, Legionella pneumophilia, Acinetobacter baumannii complex, and Escherichia coli grown in vitro the volatiles in the culture's headspace were extracted onto TD tubes using a self-made sampling chamber. Then, the TD tubes were subsequently measured with the TD-GC-MS-IMS. Initial measurements of selected pathogens demonstrate the great advantage of the new coupling: identifying unknowns in the IMS measurements using the mass spectrometric database, as there are still no databases for IMS available. For example, Indole, a product of its tryptophan metabolism, can be found in the headspace of Escherichia coli cultures. We could show that specific peaks can be detected already after six hours of incubation.

To assess the system's efficacy for the field of breath analysis, characteristic VOCs such as ethanol, isoprene, acetone, 2-propanol, and 1-propanol were successfully identified in exhaled air using the dual detector system due to the match of the corresponding IMS and MS spectra.

The next step will be performing a proof of principle trial in the clinical setting, examining a patient's breath profile with nosocomial infections, and comparing the volatile fingerprints obtained in the in vitro studies.

## Non-radioactive ionization for spectrometry and spectroscopy
**Involved staff:** Annika Fechner, PD Dr. Ursula Telgheder
**Partners:** Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V.
**Funding:** -

Ion Mobility Spectrometry (IMS) is a crucial analytical tool for detecting volatile organic compounds (VOCs). In IMS sample analysis, ionization is a crucial step. As commercialized IMS relies on radioactive sources for ionization, exploring a non-radioactive alternative is essential. The Flexible Microtube Plasma (FμTP) is being evaluated as a potential substitute. Developed by the Miniaturization working group at ISAS e.V., this highly miniaturized ionization source is well-suited for coupling with the compact structure of an IMS. This project validates and optimizes the coupling of FμTP with a commercial IMS. The setup involves adapting and 3D-printing components in the commercial IMS. Post-adaptations, the successful connection of the FμTP to the IMS has been achieved, showcasing impressive ionization efficiency.

Ongoing optimization ensures the long-term stability of the FμTP-IMS coupling. Additionally, FμTP aims to replace the standard ionization source in a commercial gas chromatography-IMS (GC-IMS). Components of the GC-IMS have been redesigned and manufactured using 3D printing. The adaptation and functionality of the GC-FμTP-IMS coupling are developed and

currently optimized. Another focus of the project is clarifying the ion chemistry of the FµTP and the characterization of the negative mode. The developed couplings are utilized and optimized for analyzing various biologically relevant samples, including metabolites and signal molecules of bacteria. A thermal desorption chip (TDC) has been employed for liquid sample application. Designed for enriching and controllably releasing complex sample mixtures, the TDC offers a miniaturized form of pre-separation and sample evaporation for the IMS through adjustable temperature programs. It has shown significant potential for directly measuring liquid sample mixtures and concentrating the samples up to a factor of 10 using IMS. The developed system will be used to monitor food safety control. Despite stringent hygiene regulations, food-borne illnesses persist in Germany primarily due to pathogenic bacteria like Campylobacter and Salmonella. Poultry meat is a significant source of human Campylobacter infections, and poultry and pork are familiar sources of salmonellosis. An automated inline analytical method is employed for monitoring using the developed (TDC-) FµTP-GC ion mobility spectrometry. This method investigates microbial secondary metabolites and bacterial communication molecules of poultry germs, specifically Campylobacter and Salmonella. The goal is to quickly and cost-effectively determine microbial entry into the slaughter chain and associated carcass contamination.

## Development of Chemometrics/Machine learning-based approaches for non-target analysis of micropollutants in water environment using LC-HRMS/MS

**Involved staff:** Maryam Vosough, Sarah Philomena Rockel, Dr Amir Salemi, Janinna Marie Pytlik, Felix Drees, Dr Gerrit Renner, Prof. Dr. Torsten C. Schmidt
**Partners:** -
**Funding:** German Research Foundation (DFG)

The first part of this project, funded by the DFG, was focused on developing an efficient data processing protocol for the non-targeted screening (NTS) of complex surface water samples using data independent acquisition-all ion fragmentation (DIA-AIF) mode in HPLC-Orbitrap-MS/MS. As part of the work, we proposed to process fused LC-MS1 and LC-MS2 AIF data sets extracted from LC-HRMS/MS measurements in NTS workflows using extended multivariate curve resolution-alternating least squares (MCR-ALS). This enables straightforward assignment between precursor ions of trace organic pollutants obtained from resolved MS1 spectra and their corresponding "resolved" MS2 spectra. Some follow-up studies will utilize this strategy, complemented by advanced multi-way decomposition algorithms to enhance the NTS capabilities and expand MS2 spectral coverage for complex datasets.

The upcoming phase will also see the implementation of different ML algorithms, further refined with feature selection algorithms. This will enable the effective classification of LC-HRMS data from various water samples. The output of these methods will be compared with the prioritized list of pollutants provided by latent projection models. Finally, by developing a quantitative method based on authentic standards for highly ranked pollutants, reliable information about the concentrations of potentially hazardous pollutants (referred to as "mixture exposure") in a set of surface water will be obtained, as well as environmental interpretations that can be used for further environmental monitoring and risk assessment.

## Studies on electrochemical treatment processes for the decomposition of Persistent Organic Pollutants (POPs) in contaminated ground and surface water

**Involved staff:** Dua'a M.F. Tahboub, PD Dr. Ursula Telgheder
**Partners:** -
**Funding:** The German Academic Exchange Service (DAAD)

The persistent organic pollutants in water are a severe environmental problem affecting human health and the ecological system. The per- and polyfluoroalkyl substances (PFAS) and phosphonate compounds are persistent, non-biodegradable compounds released into water and groundwater in large quantities. Their degradation, removal, and detection are a significant challenge in analytical and environmental chemistry. The primary purpose of this research project is to develop and optimize an electrochemical degradation (ED) method for water pollutants (PFCs and phosphonates) using electrochemical techniques before qualitative and quantitative analysis using LC-MS/MS.

In this study, Amino tris (methylene phosphonic acid) (ATMP) is a model substance of phosphonates. The ED of ATMP in aquatic systems generates hazardous and toxic transformation products such as imino di (methylene)phosphonate (IDMP) and amino tris (methylene phosphonic acid) (AMPA). The ED of ATMP is performed by cyclic voltammetry (CV) using graphite electrodes and glassy carbon electrodes vs. Ag/AgCl (3M KCl) in aqueous media. Additionally, we will perform long-term CV to achieve complete ATMP degradation and detect the transformation products using LC-HRMS-Orbitrap.

A state-of-the-art boron-doped diamond electrode (BDD) flow cell manufactured by (CONDIAS GmbH, Germany) was employed for the ED of three different PFAS compounds under acidic, basic, and neutral pH solutions. The solution is placed in a glass reservoir and circulated through the cell using a pump. The cell electrodes are connected to a power supply and monitored by applying suitable potential. All PFAS will be quantitative/ qualitative measured using LC-MS/MS system and finally measuring the electrochemical degradation efficiency.
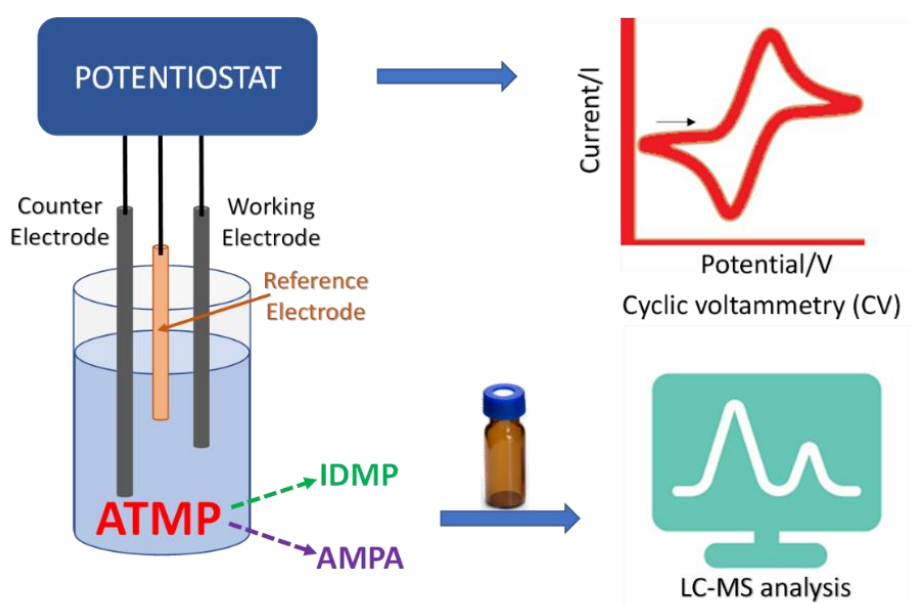
## Development of a Data Quality Score for Processing Non-Target-Screening Data generated by HPLC-HRMS

**Involved staff:** Max Reuschenbach, Dr. Gerrit Renner, Prof. Dr. Torsten C. Schmidt
**Partners:** -
**Funding:** Friedrich-Ebert-Stiftung e.V. and internal

Non-target screening (NTS) is a pivotal tool in water monitoring, offering broad-scale chemical characterization capabilities from complex measurement data. Despite its potential, NTS faces significant challenges in data processing due to its reliance on intricate, multidimensional strategies and the necessity for robust, automated data handling. A notable difficulty arises in comparing interlaboratory or inter-software results, given their dependency on varying measurement systems, samples, and processing algorithms, leading to often incomparable outcomes.

A critical gap in NTS data processing is the reporting of result uncertainties, notably the uncertainties of feature properties extracted from workflows, i.e., Δrt or Δm/z. Conventional methods seldom incorporate uncertainty propagation in subsequent evaluation steps, if at all. Moreover, the human factor in algorithm parameter setting contributes to the prevalence of false positives in feature lists, complicating their differentiation from true positives.

Our research addresses these challenges and introduces a new generation of NTS data processing algorithms. These algorithms eliminate the need for user input parameters and integrate statistical uncertainty propagation as a core component in processing and reporting. This approach not only streamlines the process but also aids in prioritizing features and identifying false positives. This work presents our latest research results on developing a new, robust, fast, and fully automated peak detection and characterization algorithm for chromatographic data from NTS.

As its vital principle, this algorithm is grounded in curve fitting, employing a unique peak model based on linear regression - a method inspired by Caruana et al. (1986) for its efficiency. Our model, a linearized modification of a Gaussian function, accommodates symmetric and asymmetric peak shapes and is shown in Eq. 1

$$
\begin{array}{ll}
\textit{Linearized Gaussian Model}: & \textit{NEW}: \textit{Modified Linearized Gaussian Model}: \\[1em]
\ln y = \beta_0 + \beta_1 x + \beta_2 x^2 & \ln y = \beta_0 + \beta_1 x + \begin{cases} \beta_2 x^2 \ for \ x \in \mathbb{R}, x < 0 \\ \beta_3 x^2 \ for \ x \in \mathbb{R}, x \geq 0 \end{cases}
\end{array} \tag{1}
$$

Where y is the intensity profile along the retention time x, the regression coefficients β0,1 describe the peak's standard offset and linear term. In contrast, β2,3 describes the quadratic term of the left and right sides separately. Moreover, the plotted function can be obtained from Figure 1 to understand better how our new model is constructed. This diagram shows two typical scenarios that the new model can handle.

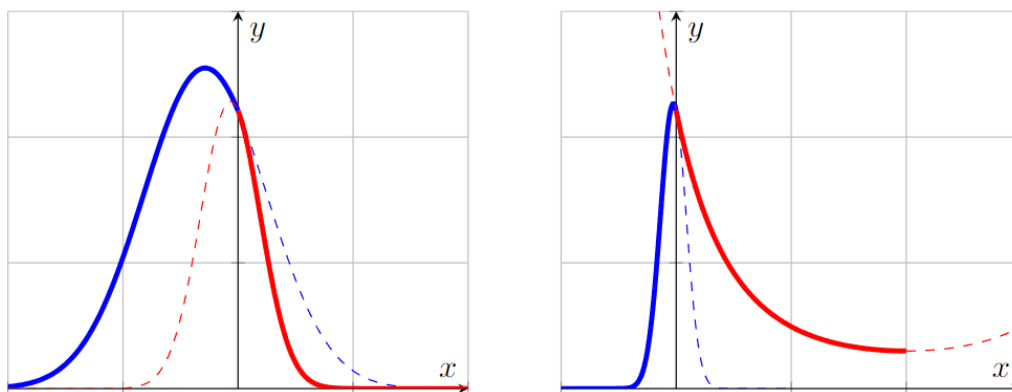*Proposed Peak Model*          *Proposed Peak Model (with Valley Point)*

*Figure 1: Visualization of the proposed peak model, which contains a case-sensitive merge of two half-peaks. The valid data is shown in straight lines, while the imaginary parts are shown as dashed lines. The latter is invalid due to the case sensitivity and will not be considered in the regression.*

In contrast to conventional nonlinear peak regression approaches, this new model does not require any initial parameters or an iterative approximation of the optimized model fit but provides the unique analytical solution of the best regression by design. Moreover, it extracts fundamental peak properties like retention time and peak area. It provides associated uncertainty metrics, aiding in identifying statistically significant peaks and reducing false positives by well-established statistical tests (t-test). The latter is primarily only possible for this new approach of peak regression and cannot be applied to conventional nonlinear peak regression.

Our peak extraction algorithm can handle peak detection and peak characterization at once by combining the analytical peak function with a new search engine, conducting multiple regressions across extracted ion chromatograms using a moving window approach. Similar to convolution or continuous wavelet transform, this method filters results based on validity and statistical significance, ensuring the most accurate peak representation for each chromatographic profile, as exemplified in Figure 2.

When applied to water sample data, we compared our algorithm to other feature extraction methods or peak pickers like *Centwave*, especially regarding feature list overlap and inter-algorithmic robustness. In this context, we could demonstrate that the inter-algorithmic robustness of feature extraction in NTS is connected to data quality. The better a peak model fits to measurement data, the more robust these features are, even with other feature extraction algorithms. This observation highlights the importance of extracting data-quality information and underlines the benefit of our strategy. In this context, we describe the quality of chromatographic peaks by their uncertainties like retention time, peak width, or height. Moreover, we combine these pieces of information to obtain a compact data quality scoring ($DQS_{peak}$).
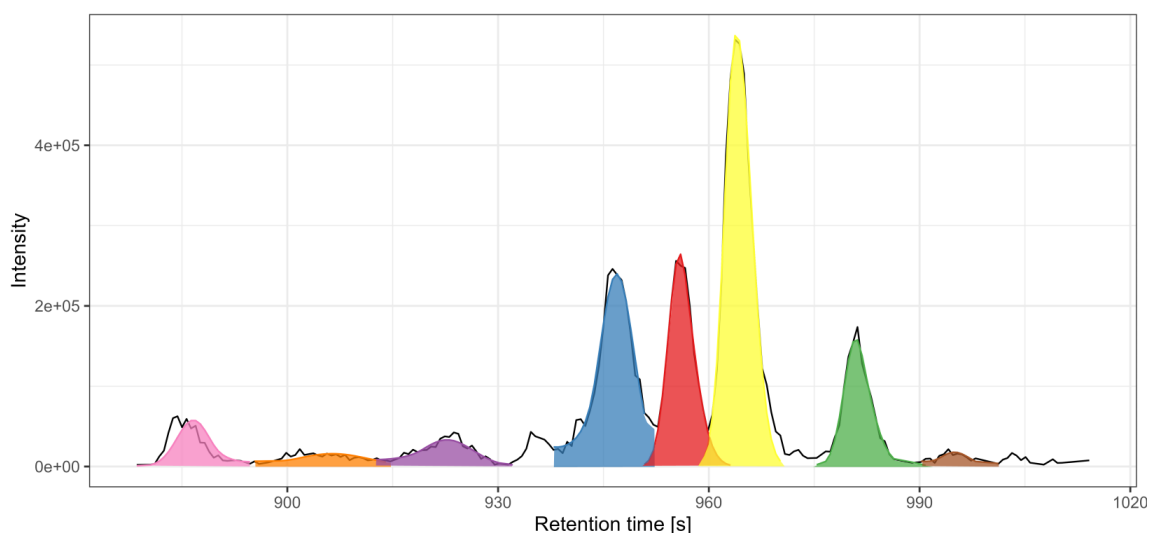
*Figure 2: Example of the automated peak detection and characterization based on an extracted ion chromatogram from a river sample. All chromatographic peaks shown here as colored patches pass all the statistical tests and describe the respecting chromatogram ranges at best.*

In former studies, we established those DQS metrics for other steps, i.e., centroiding HRMS and binning to create extracted ion chromatograms. The news DQS expands the data quality monitoring toolbox, and in total, this allows a very comprehensive and detailed look at individual aspects of data quality during the NTS data processing workflow.

Furthermore, we coupled our workflow with an in-house machine-learning model to distinguish between false and true positives. We achieved an accuracy of 91%, a sensitivity of 91%, and a specificity of 91% when applied to more than 150,000 extracted ion chromatograms. We are poised to release the algorithm as an R-package and C++ Library on GitHub, integrating it into NTS data processing platforms such as Streamfind and MZmine. With our work on automated and statistics-driven peak detection, we hope to provide the NTS and other analytical communities with new, efficient tools that will help them better understand the evaluation process and improve result interpretation and comparison.

## Membrane processes in drinking water supply (KonTriSol)

**Involved staff:** Xenia Mutke, Prof. Dr. Holger V. Lutze (TU Darmstadt), Prof. Dr. Torsten C. Schmidt
**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)
**Funding:** Bundesministerium für Bildung und Forschung

The KonTriSol project presents a detailed examination of the reaction kinetics between organophosphonates—specifically HEDP, PBTC, ATMP, and DTPMP—and oxidizing agents like ozone, hydroxyl, and sulfate radicals within the pH range of 5 to 7. This range is crucial for drinking water treatment processes and environmental considerations. The study's findings highlight a distinct difference in ozone reactivity between nitrogen-containing phosphonates (ATMP and DTPMP) and those without nitrogen (HEDP and PBTC), indicating that HEDP and PBTC exhibit resistance to ozone but can be degraded through the action of hydroxyl radicals produced during the ozonation process. The reactivity of organophosphonates with hydroxyl and sulfate radicals suggests a sufficient potential for their successful elimination, with no

observed pH dependency and increased reactivity correlating with the number of potential reaction sites.

In exploring the elimination of organophosphonates, the project delved into ozonation and advanced oxidation processes (AOP) based on sulfate radicals (Persulfat/UV) oxidation. The investigation covered the influence of matrix components on the elimination performance, utilizing eleven synthetic matrices designed after authentic concentrate compositions to simulate the water treatment environment accurately. This methodology enhanced the understanding of oxidative treatment applications in concentrate processing. The research noted that high ozone dosages were insufficient for complete mineralization of phosphonates to orthophosphate, with PBTC ozonation showing minimal transformation to orthophosphate, indicating the formation of phosphate-containing by-products that compete with PBTC for oxidative species, thereby reducing PBTC elimination. The presence of hydroxyl radical-consuming substances (NOM, Hydroxyl radical scavenger addition) led to decreased elimination of phosphonates.

Furthermore, the innovative UV-based sulfate radical process (UV/$S_2O_8^{2-}$) was evaluated for its potential to degrade ubiquitously occurring perfluorinated alkyl substances. However, matrix components significantly reduced the elimination performance of this process due to the substantial consumption of oxidants. A comparison between ozonation and UV/persulfate processes revealed that the energy demand for UV/persulfate oxidation was too high to be considered energy-efficient. On the other hand, ozonation's energy requirement for treating HEDP, ATMP, and DTPMP was within a realistic range, indicating its potential for practical application.

The project also investigated the elimination of trace substances using ozonation and the UV/persulfate process, targeting compounds listed in the B-2017 recommendations for trace substance elimination by the Spurenstoffkompetenz-Zentrum Baden-Württemberg. Through literature review and experimental determination of reaction kinetics, the project aimed to predict the degradation of selected trace substances theoretically. The comparison between theoretical and actual elimination rates provided insights into the reactivity of these substances with ozone and hydroxyl radicals, highlighting the challenges and potentials for their effective removal from water. The study assessed the bromate formation potential in both oxidative processes, finding a lower risk associated with UV/persulfate treatment than ozonation, especially at higher ozone dosages. This aspect is crucial for ensuring the safety and compliance of water treatment methods with environmental standards. The energy requirements for the 80% elimination of specific substances (Sulfamethoxazole, Benzotriazole, and Iohexol) were calculated, demonstrating the significant energy efficiency differences between the ozonation and UV/persulfate processes, with the latter showing a lower energy demand for specific compounds.

This comprehensive analysis provided by the KonTriSol project significantly enhances our understanding of the dynamics involved in eliminating organophosphonates and trace substances in water treatment processes. It offers valuable insights into optimizing treatment strategies to achieve high water purity levels while minimizing environmental impacts and energy consumption. The findings underscore the importance of considering the complex interplay between chemical reactivity, process efficiency, and environmental safety in developing and applying water treatment technologies.

## Isotope-labeling in situ derivatization and HS-SPME arrow GC-MS/MS for simultaneous determination of fatty acids and fatty acid methyl esters in water

**Involved staff:** Lucie K. Tintrop, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt
**Partners:** -
**Funding:** Internal

The demand for green analytical methods is increasing. Microextraction methods pose the green alternative to large-scale extractions in research and in standard methods. The world's most used and well-accepted microextraction technique, solid-phase microextraction (SPME), is solvent-free, miniaturized, simple to handle, and automatable. The drawbacks of SPME, such as the poor mechanical resilience and small phase volume, were rectified by its further development SPME arrow. For water analysis using gas chromatography-mass spectrometry (GC-MS), the choice of the extraction method is a critical step in terms of analytical performance and greenness.

Nevertheless, the standardization of microextraction methods is still lacking. Therefore, this thesis investigates the applicability of SPME and SPME-arrow for GC-MS water analysis in industrial process surveillance for analyzing fatty acids and fatty acid methyl esters and non-targeted wastewater monitoring. Moreover, several challenges are addressed, such as combining microextraction and derivatization, fiber cleaning, and extracting analytes with different polarities. The optimization of the critical extraction parameters, such as time, temperature, and pH, by the design of experiments significantly increased the gained response in all the applications and is discussed in detail to minimize the effort for future use and development of the methods. A chemical-thermal fiber cleaning procedure was developed, substantially reducing the carry-over effect. The method detection limits obtained in this study ranged from low ng L-1 to low µg L-1, which is lower than achieved by several research studies. With SPME headspace operation, no pre-treatment was necessary, even though the samples possess complex matrices. Selective tandem mass spectrometry implemented additional reduction of sample matrix-based analysis interferences for target analysis. A non-target approach using GC time-of-flight mass spectrometry with parallel electron ionization (EI) and chemical ionization (CI) was tested in combination with a prototype hydrophilic-lipophilic balanced (HLB) SPME with a particular focus laid on the identification of substances using the complementary dataset from EI and CI. The approach extracted and analyzed analytes with very different polarities, expecting the HLB to become the new use-one-for-all material in SPME. For the investigated research fields, SPME and SPME-arrow performed well. Consequently, their future implementation in standard methods is supported by the results.

## Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids (A13: CRC RESIST)

**Involved staff:** Shaista Khaliq, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt
**Partners:** University of Duisburg-Essen, Ruhr-Universität Bochum, Leibniz Institute of Freshwater Ecology and Inland Fisheries, University of Cologne, Kiel University, University of Koblenz-Landau and Helmholtz Centre for Environmental Research
**Funding:** German Research Foundation (DFG)

Throughout 2023, I was deeply involved in various academic pursuits and collaborative ventures to advance research in stable isotope analysis and aquatic systems. In terms of publications, I authored and submitted a comprehensive review paper titled "Stable Isotope Analysis of Amino Acids in Aquatic Systems – Problems, Challenges, Solutions: A Review" in December 2023. This paper was submitted to an invited special issue of the Journal "Trends in Analytical Chemistry." My engagement extended to participation in two significant conferences: the DGMS conference in Dortmund from May 14 to 17, 2023, where I delivered a talk, and the GASIR conference in Bayreuth from September 27 to 29th, 2023, where I presented a poster. Additionally, I undertook two research stays to enrich collaborative efforts and gain valuable insights. The first was at Magdeburg with collaborative Partner group A12 (RESIST: Prof. Dr. Markus Weitere and Alex) in May 2023. The second was at NIOZ (Royal Netherlands Institute for Sea Research) Texel from September 4 to 22nd, 2023. Internally, I fostered collaborations with various groups within the RESIST consortium, including the A02 group (RESIST) for DOC measurement of samples and the A12 and A09 groups (RESIST) for updates on project scenarios and sample exchange. My involvement in academic events included participation in the University Duisburg-Essen summer school from May 8 to 12th, 2023, and the Annual retreat from October 1 to 5th, 2023.

Additionally, I attended the monthly RESIST doctoral seminar, the CRC colloquium, and the CRC annual meeting, where I delivered a talk. Lab work was a significant aspect of my activities, involving extensive work with GC-IRMS for Compound-specific isotope analysis of Amino Acids (AAs) of standards and samples. Overall, these endeavors have contributed to advancing knowledge in our field and facilitated valuable collaborations and networking opportunities within the scientific community. I remain committed to continuing these efforts and advancing our research goals in the coming year.

## Investigation of Stable Isotope Fractionation during Abiotic Imidacloprid Degradation

**Involved staff:** Felix Niemann, Dr. Maik A. Jochmann, Prof. Dr. Torsten C. Schmidt
**Partners:** -
**Funding:** Internal

Despite political efforts to ban neonicotinoids like Imidacloprid, it is still found ubiquitously in surface waters around the world. Originally designed as an insecticide for sucking pests, its toxic effects on non-target organisms like pollinators and aquatic organisms are particularly worrying. In the environment, it can undergo physical and (bio-)chemical transformation processes that facilitate mineralization but potentially produce more hazardous substances than the starting substance. This highlights the importance of characterizing the transformation

processes, estimating their contributions, and identifying factors influencing them.

This study focuses on abiotic imidacloprid degradation, such as hydrolysis and photolysis, as they contribute significantly to its natural attenuation in water soil systems. In laboratory experiments, influences like spectral distribution, dissolved oxygen content, pH value, and addition of photosensitizers and quenchers can be investigated.

The novelty of this study is the use of compound-specific stable isotope analysis (CSIA) as a tool to identify characteristic isotope effects for individual transformation processes. This technique has been proven to grant valuable insights into reaction mechanisms. Polar compounds such as Imidacloprid are challenging analytes for CSIA, as they are not directly analyzable by gas chromatography. Therefore, liquid chromatography coupled with a conversion interface and an isotope ratio mass spectrometer (LC-IRMS) separated it from its transformation products. The developed method uses only aqueous eluents, is robust, and could be tested successfully on samples generated in laboratory batch experiments. A recently introduced system that allows for simultaneous high-resolution mass spectrometry (HRMS) by Orbitrap-MS allows the assignment of structural proposals to unknown peaks. This information complements stable carbon isotope data gained by the IRMS detector.
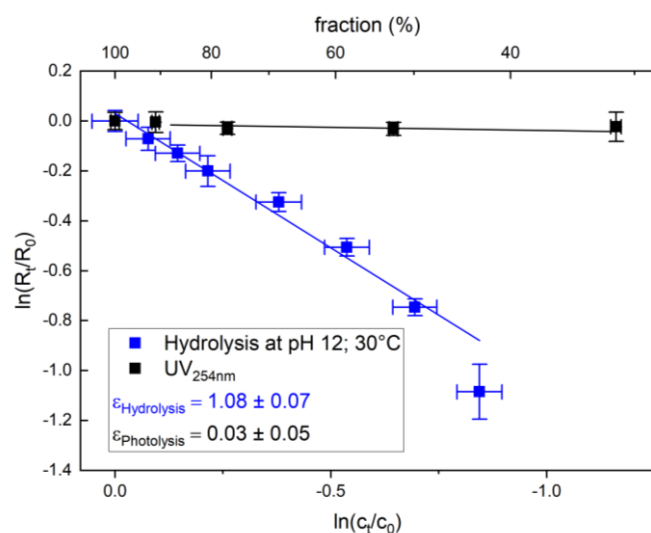


*Figure 1: Rayleigh-Plots of Imidacloprid photolysis and hydrolysis. Carbon enrichment factors are estimated by linear regression analysis of the double-logarithmic plot.*

## Determination of atmospherically deposited microplastics in moss: Method development and performance evaluation

**Involved staff:** Mike Wenzel, Gerrit Renner, Torsten C. Schmidt
**Partners:** Justus Schoettl, Laura Pruin, Björn Fischer, Carmen Wolf, Christine Kube, Jürgen Schram, Jochen Türk
**Funding:** Federal Environment Agency (European Moss Survey 2020/2021) FZK 3720632010

Microplastics, defined as plastic particles and fibers ranging from 1 µm to 5 mm, have been increasingly detected across various environmental matrices, including water, soil, and air. In this study, we introduced a novel sample preparation method called µPEEL (microplastics extraction through exfoliation), developed to accurately determine atmospherically deposited microplastics on moss. Our study underscores the necessity for accurate qualitative and quantitative analysis methods to comprehensively assess the fate of microplastics in the environment. Traditional analytical approaches, such as Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy, provide qualitative data on microplastics, while thermoanalytical methods like thermal extraction desorption-gas chromatography-mass spectrometry (TED-GC-MS) offer both qualitative and quantitative insights. However, these methods often require extensive sample preparation to mitigate matrix interferences and improve analytical accuracy. The study critically evaluates the µPEEL method against oxidative digestion using Fenton's reagent, a commonly employed sample preparation technique for organic-rich and moss samples.
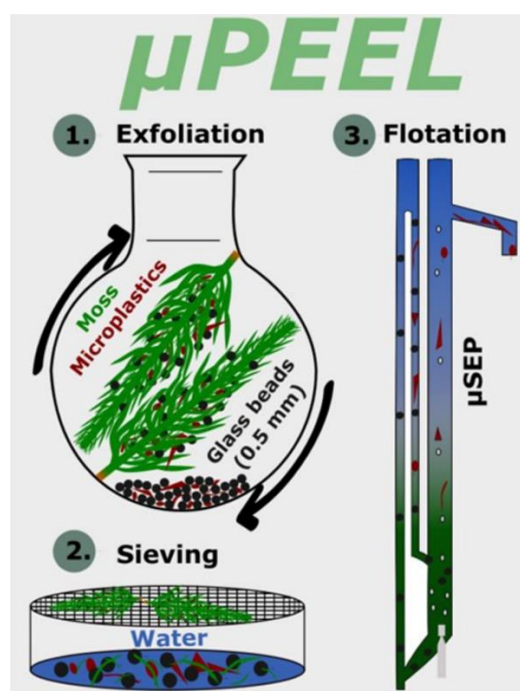


*Wenzel, M., et al. (2023). Green Analytical Chemistry, 7, 100078.*

The µPEEL method involves three primary steps: (1) exfoliation of microplastics from the moss surface using glass beads, (2) sieving of the exfoliated sample, and (3) separating microplastics from the glass beads and moss abrasion through flotation. The hydrophobicity-water/air-based enrichment cell for microplastics (µSEP) was used for flotation. This innovative approach aims to reduce sample matrix interferences, facilitating more accurate mass- and particle-based analyses. The research meticulously details the experimental procedures, including sample

preparation, analytical methodologies (TED-GC-MS and light microscopy), and data evaluation techniques employed to assess the efficiency of the µPEEL method. Results from the study indicate that the µPEEL method achieves high recovery rates for different polymers (PET, PP, PE, and PS), with minimal matrix interferences observed during TED-GC-MS analysis. This contrasts with the oxidative digestion method, which exhibited substantial retention time shifts and signal suppression, potentially leading to inaccurate microplastic quantification. The functionality of the µPEEL method was also demonstrated through light microscopy, showing its capability to facilitate contrast-based particle identification due to the high separation quality achieved. This is particularly advantageous for microplastic analysis utilizing Raman microscopy (µRaman), where the high measurement-time effort and sample throughput are critical concerns.

Furthermore, the green analytical chemistry assessment using the software tool AGREEprep revealed that the µPEEL method outperforms oxidative digestion regarding environmental impact, primarily due to its reduced use of hazardous chemicals, sustainability of materials, and lower waste production. The study concludes that µPEEL offers a robust and environmentally friendly sample preparation method for microplastic analysis and minimizes matrix effects, enabling more accurate and reproducible results. The study underscores the urgent need for improved analytical workflows and underlines the importance of sample preparation approaches. By developing and evaluating the µPEEL method, the researchers offer a viable and green solution for accurately detecting and quantifying microplastics in complex environmental samples. The findings highlight the potential of the µPEEL method to advance research concerning atmospheric microplastics and demonstrate that the method's greenness can be reconcilable with the method's functionality.

## AutoExtrakt – Development of a fully automated microextraction device and its application for the analysis of substances in complex matrices from food and environmental origin

**Involved staff:** Frank Jacobs, Dr. Klaus Kerpen, PD Dr. Ursula Telgheder
**Partners:** GERSTEL GmbH&Co.KG
**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 fully automated and efficient extraction technique that enables the sensitive analysis of toxicologically relevant substances in environmental samples as well as in food samples. The substances are to be reliably detected both qualitatively and quantitatively. The extraction technology to be developed will enable laboratories for environmental and food controls to sensitively detect and quantify residues of environmental pollutants or aromatic substances in an automated process.

A new sample preparation technique based on SBSE (Stir bar Sorptive extraction) is being developed. Key characteristics of SBSE as a technique have been kept. Some of those characteristics are the high sensitivity of the sorptive phase, the full immersion capability, and the ability to be used as a passive sampler, have been transferred to the automated version.

The motivation for this project was to automate the complete sample preparation process by using an x/y/z-sampler. Because of the new form factor, the agitation of the sample was done in a revised vertical shaking unit so that the tray could be cooled and heated. A wash and drying

station is implemented to clean and dry the sorbent after extraction. The loss of analytes is minimized by featuring a centrifuge for drying the sorbent. An online conditioning station has also been introduced for complete automatization of the process.

The Setup of the System consists of a MPS Autosampler (GERSTEL Gmbh&Co.KG, Mülheim, Germany) configured with a QuickMix, Wash/Drying-Station, Thermal Desorption Unit (TDU2) and Agilent 7890B GC with 5977B MS. A DoE approach was chosen for determining interdependency of parameters like sample extraction time, salt concentration and extraction temperature. The concentration range for calibration of 22 pesticides described in DIN 27108 was determined by the DIN calibration method from 1-10ng/L. Each measurement was performed in a triplet. Blank measurements were done to ensure no carryover was present. For comparison, an SPME extraction following the DIN27108 method was done.

Method development by Design of Experiments resulted in optimized parameters: 90 minutes of extraction time, 70°C, 30% of NaCl (w/w). Results showed LODs in single-digit ng/L concentrations for most analytes for the automated SBSE. Only two substances where not detected. Only five of the 22 analytes were found for the SPME method, which demonstrated a higher sensitivity for the automated SBSE method.

Further experiments must be done to compare the automated versus the non automated version to ensure that analytical performance is the same. Furthermore, the automated SBSE has to be applied to new applications.

The results of the pesticide analytics will be published at a later date.

# Theses Completed

Chlorine dioxide ($ClO_2$) is one of the oxidants used for disinfection and micropollutant abatement in water treatment. Amines are one of the reactive moieties toward ClO2, which is not well investigated in the literature. Thus, the reactions of $ClO_2$ with nitrogen-containing heterocycles (NCHs) are investigated in this research.

In $ClO_2$ oxidation of organic compounds, free available chlorine (FAC) can be produced as a secondary oxidant. A new method is developed to selectively scavenge intrinsically formed FAC by glycine. The product of the scavenging reaction, *N*-chloroglycine, was measured using ion chromatography with a conductivity detector and post-column reaction with UV detection. The results were compared with the standard *N,N*-diethyl-*p*-phenylenediamine (DPD) method. The *N*-chloroglycine method showed LOQ of 24 and 13 µg $L^{-1}$ $Cl_2$ for conductivity and UV detector, respectively. The *N*-chloroglycine method also showed 102 and 105% recovery of the FAC in the drinking water matrix relative to the DPD method. However, for the measurement of intrinsic FAC formed in the reaction of $ClO_2$ with phenol, the *N*-chloroglycine method performed considerably better, with twice the recovery of the DPD method due to the interference of other oxidative species in the latter method.

To understand the process of NCHs oxidation with $ClO_2$, it is necessary to monitor NCHs' degradation. However, NCHs are polar and ionic bases with high water solubility; thus, analyzing these compounds is challenging for reversed-phase liquid chromatography. Using a mixed mode phase with both reverse and ion exchange interactions in hyphenation with mass spectrometry, a method was developed to analyze NCHs. The results show that the governing interaction depends on the $pK_a$ of the NCHs. Those with $pK_a$ < 2.5 mainly display reversed-phase interaction through their neutral species, and those with higher $pK_a$ show a mixture of reversed-phase/ion exchange/HILIC separation mechanisms. The method's MDLs for NCHs were between 3-6 µg $L^{-1}$ with low matrix effects and recoveries in the range of 77-96%, except for pyridazine exhibiting 32%. Additionally, NCHs degradation during ozonation was monitored, revealing that the relative degradation increases in the order of imidazole > pyrazole > piperidine > pyridine > pyridazine.

The *N*-chloroglycine and LC-MS method was utilized to investigate $ClO_2$ reaction with aromatic and saturated NCHs. Aromatic NCHs such as pyridine, pyrimidine, and azoles are moieties frequently found in micropollutants and the environment. Investigation of aromatic NCHs showed a difference between six-membered and five-membered aromatic NCHs, in that the former is unreactive and the latter is reactive toward $ClO_2$. The rate constants for all six-membered aromatic NCHs were < $10^{-3}$ $M^{-1}$ $s^{-1}$. Imidazole, a five-membered aromatic NCH, showed a pH-dependent reaction rate due to its species' different reaction rate constants. Cationic species are unreactive due to the inaccessibility of electron pair; neutral species showed a rate constant of around 0.05 $M^{-1}$ $s^{-1}$ while anionic species exhibited a high rate

constant of $(2.08 \pm 1.4) \times 10^6$ $M^{-1}$ $s^{-1}$. However, imidazole's apparent reaction rate constant at pH = 7 was only $6.7 \times 10^{-2}$ $M^{-1}$ $s^{-1}$ since the anionic species fraction is very low at this pH ($pK_a$ = 14.4). For pyrrole, the rate constant was $(1.18 \pm 0.3) \times 10^3$ $M^{-1}$ $s^{-1}$ independent of pH since pyrrole does not dissociate in water. It was also observed that FAC could form in yields up to 45% and 37% in $ClO_2$ oxidation of imidazole and pyrrole, respectively. Dexmedetomidine, an NCH-containing pharmaceutical, was also investigated to compare its behavior with the model compound. Dexmedetomidine behavior was almost identical to imidazole, with the anionic species being the reactive species with a rate of $(7.3 \pm 4.6) \times 10^7$ $M^{-1}$ $s^{-1}$ and forming 35% intrinsic FAC.

Saturated NCHs are among the most common moieties of micropollutants, especially pharmaceuticals. The reaction of $ClO_2$ with cetirizine and ritalinic acid, two micropollutants with saturated NCH moieties, shows that rate constants are pH-dependent due to the speciation of their NCHs moiety. This was also observed for their corresponding model compounds, piperidine, 2-methylpiperidine, piperazine, and dimethylpiperazine. For micropollutants and model NCHs, the neutral amine species had reaction rates of 800 to 3200 $M^{-1}$ $s^{-1}$, while cationic amines were not reactive with rate constants < 0.01 $M^{-1}$ $s^{-1}$. Above 80% of $ClO_2$ was transferred to chlorite in this reaction, and consumption of 5 and 4 $ClO_2$ per degraded ritalinic acid and cetirizine was observed, respectively. Chlorite formation results from electron transfer in $ClO_2$ reaction, proving that all investigated NCHs mostly react by this mechanism. Using the rate constants of model NCHs the degradation of ritalinic acid and cetirizine in a surface water matrix could be predicted with -8 to -15% and 13 to -22% error, respectively. The results show that micropollutants that have only piperidine as reactive moiety are not degradable due to low reaction rate constants at pH values relevant for the water treatment process ($k_{app}$ = 0.072-0.14 $M^{-1}$ $s^{-1}$, at pH = 7), while piperazine-containing compounds can be moderately degraded ($k_{app}$ = 5-55 $M^{-1}$ $s^{-1}$, at pH 7).

**2023-02-06**

**Dr. rer. nat. Tobias Hesse**

**The Potential of LC-IRMS: Carbon stable isotope analysis of amino acids in a host-parasite system and a proof-of-principle study for δ15N measurements of nitrate**

Stable isotope analysis is an established technique in scientific branches like geology, meteorology, archaeology, food authenticity, and ecology. Different instruments have been developed, and although the measurement of stable isotope signatures by LCIRMS is not the most widely used method, it still bears significant advantages over other, more common instrumentations. It is frequently used for δ13C analysis of carbohydrates, amino acids, and compounds of environmental interest. This is demonstrated by compound-specific isotope analysis of individual amino acids in a controlled feeding/infection experiment using a parasitic cestode (Schistocephalus solidus), its second intermediate host (three-spined stickleback, Gasterosteus aculeatus), and protein-rich fish diets to advance our understanding of trophic fractionation and nutrient transfer. The system accurately measured thirteen individual amino acids' carbon stable isotope signatures with little sample preparation over an extensive sampling period. While trophic fractionation of amino acids in sticklebacks was low due to

isotope routing on high protein diets, it was possible to see different trends in δ13C values over time in liver and muscle tissue, induced by a subtle carbon isotope shift of dietary sources between sampling days. Biosynthesis of non-essential amino acids in the liver was indicated from minimal amounts of dietary lipids and highlighted the strength of this technique combined with multivariate data analysis. A similar approach was used to show increased Δδ13CAA values of infected compared to uninfected sticklebacks on the same diet, indicating that the metabolic burden on host organisms induced by parasitic infection is reflected in the carbon isotope signature of amino acids through extensive catabolism, likely to fuel an ongoing immune response and to sustain parasitic growth. Compound-specific isotope analysis has been highlighted as a powerful tool to study host-parasite interactions, and precise measurements of carbon isotope signatures from small amounts of different sample materials enabled resource allocation in the parasite S. solidus, which pointed towards nutrients being assimilated from host liver tissue. The parasite accumulates large amounts of glycogen for maturation, and it was further possible to measure the carbon isotope signature of glucose from parasite tissues with little sample preparation and chromatographic separation. Biosynthesis of parasitic glucose from alanine, asparagine, and glutamine was indicated by constant fractionation of -2 to -3 ‰ from enzymatic reactions.

In contrast, the possible conversion of threonine and serine to glycine for one-carbon metabolism and parasitic growth calls for further research using isotopically enriched materials to get more detailed information and quantify the nutrient transfer. To advance the field of LC-IRMS and show its potential for future applications, a modified interface for δ15N nitrate analysis was developed and tested in a first proof-of-principle study. Reduction of nitrate to measurable N2 gas was facilitated with V(III)Cl3 and elemental copper using established techniques, while already reported improvements for the LC-IRMS interface were implemented to increase the precision and lifetime of the ion source. The system could measure δ15N values from 10 μL injections of nitrate standards and reference materials with a concentration of 50 mgL-1Nand with a precision better than 1.4 ‰. In contrast, the linearity between δ15N values was sufficient to measure natural abundance levels. The biggest problems were high nitrogen background signals from the mobile phase, isotope shifts, and nonlinear signal intensities from standards with different concentrations. However, applying this new technique to samples from an isotope enrichment experiment in a small river was already possible, where 15N-enriched ammonium chloride was administered over time to mark the surrounding environment isotopically through natural nitrification processes.

In contrast to our expectations, no increase in the δ15N signature of nitrate was measured from downstream water samples during the first two weeks. However, the δ15N values of unknown nitrogen species eluting early during the injection peak were highly enriched in 15N. This could be attributed to nitrite, although measurement errors due to the early stage of the interface cannot be disregarded entirely. Further research and developments are overall necessary, but the system already shows promising results. It could enable fast and reliable isotope analysis of nitrate for anthropogenic source allocation and increase the scope of LC-IRMS in the future by enabling δ15N analysis of organic compounds.

**2023-05-03**

**Dr. rer. nat. Tobias Werres**

**Characterization of extra-column peak broadening in capillary high-performance liquid chromatography**

Ensuring reasonable energy prices, establishing reliable supply chains, ensuring the availability of resources, and, last but not least, taking environmental protection into account are future global challenges. Corresponding challenges also play an increasingly central role in everyday analytical laboratory work. The search for countermeasures to these challenges is also becoming increasingly prevalent in the analytical laboratory. Miniaturization, as one of the cornerstones of Green Analytical Chemistry (GAC), can help save resources in the form of solvents, energy, and laboratory space, especially in the field of capillary liquid chromatography (cLC), without reducing the integrity of analytical data and even increasing sample throughput in the process. Despite advances in cLC development and research in recent years and the disruptive nature of the technology, market penetration has still not been achieved. This is partly because there is a persistent assumption that the systems are unsuitable for routine operation due to a lack of robustness. In addition, although the number of commercial systems is increasing, current research is often not consistently implemented, for example, by sticking to the modular concept. This creates unnecessary capillary paths and increases the extra-column volume, which results in peak band broadening and, thus, poorer chromatographic efficiency. Therefore, this work aims to investigate the influence of different factors on the extra-column band broadening in cLC to lower barriers to implementing cLC and developing a new system.

The first part of the Ph.D. thesis was mainly devoted to quantifying the influence of different extra-column volumes on peak band broadening and served to answer open questions in the current literature. Initially, the influence of injection volume and pre-column volume was investigated for both isocratic and gradient elution as a function of the retention factor. Subsequently, the focus was shifted to the influence of the post-column volume. For this purpose, different commercially available concentration-dependent and mass flow-dependent detector systems were investigated. In addition, the ratio of the column's inner diameter to the system volume on the band broadening during isocratic and gradient elution was compared. The knowledge gained from the previous research was used in the second part of the thesis to advance the development of new separation phases based on bead cellulose and a portable measurement system for on-site monitoring of contaminants in aqueous matrices based on online enrichment and cLC coupled with ion mobility spectrometry.

**2023-05-05**

**Dr. rer. nat. Lars M. H. Reinders**

**Analytical monitoring of personalized drugs containing monoclonal antibodies: An alliance of patient and personnel safety**

The drug and dose are adapted to the patient in modern cancer therapy. As a result, pharmaceutical specialists do not manufacture the required preparations on a large scale but individually. The pharmaceutical active substances are usually cytostatics and monoclonal antibodies with carcinogenic, mutagenic, or reproduction-toxic (CMR) properties. This leads to an area of tension between patient safety and occupational safety.

A sampling concept was developed under occupational safety for the quality assurance of personalized preparations. With this concept, five cytostatic drugs and three monoclonal antibodies in preparations were tested for identity and content. It was shown that 96% of the cytostatic preparations (n=136) and 100% of the monoclonal antibody preparations (n=10) met the legal requirements. The quality of the preparations can thus be assessed as very good.

Affinity chromatography with immobilized FcγRIIIa was performed to characterize the monoclonal antibodies further. To enable the coupling of affinity chromatography with high-resolution mass spectrometry (HRMS), 2D-HPLC was used for online desalting. It was shown that monoclonal antibodies with glycan modifications with higher galactose or lower fucose content have a higher affinity for the receptor.

Furthermore, it was demonstrated that monoclonal antibodies can be characterized using affinity chromatography, 2D-HPLC, and HRMS and distinguished from their biosimilars.

As part of the work on occupational safety, a method was developed for quantifying airborne monoclonal antibodies in the trace range. It was possible to show that there is a potential for release during patient-specific production using this method. This is triggered by the piercing of the drug containers and the occurrence of a pressure equalization process. The release could be quantified to 15 ng. An unintentional release can be prevented using pressure equalization systems (spikes). As part of the method developed, the antibodies are quantified at the peptide level, which requires enzymatic digestion. Since it is time-consuming and may take several hours, the digestion step was automated using immobilized enzymes and coupled online with mass spectrometric detection. This reduced the required digestion time by 98%.

**Treatment of phosphonate based antiscalants and micropollutants in reverse osmosis concentrate by oxidative processes**

Reverse osmosis (RO) is an advanced membrane process used to produce potable water from various water sources, including surface water, seawater, and wastewater. The yield of the product water from the RO systems is increased by adding antiscalants, which prevent the membrane from scaling calcium and other ions. Removing antiscalants from the RO concentrate can induce the precipitation of oversaturated scale-forming substances, enable additional water recovery from RO concentrates, and reduce the risk of eutrophication after concentrate disposal into the receiving water (e.g., river water). Furthermore, the oxidative treatment of RO concentrates reduces the discharge of micropollutants into the environment.

The aim of this study was to provide a better insight into oxidation reactions of the N-free phosphonate antiscalants 1-hydroxy ethane-1,1-phosphonic acid (HEDP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) and of the N-containing phosphonate antiscalants amino trimethylene phosphonic acid (NTMP/ATMP) and Diethylenetriamine penta(methylene phosphonic acid) (DTPMP) regarding reaction kinetics with ozone, hydroxyl radicals ($^{\bullet}OH$) and sulfate radicals ($SO_4^{\bullet-}$).

In addition, the efficiency of eliminating pharmaceuticals, corrosion inhibitors, x-ray contrast media, and perfluorinated compounds from RO concentrates during ozonation and UV/persulfate processes was investigated. Second-order rate constants for the reactions of candesartan, irbesartan, methyl-benzotriazole, and chloro-benzotriazole with $SO_4^{\bullet-}$ were determined for the first time. Besides kinetic experiments, the ozone exposure and hydroxyl radical exposures, and degradation rate in different water matrices and real RO concentrates were investigated. Additionally, the by-product formation was determined and the energy demand for antiscalant elimination with the process of ozonation and UV/persulfate was calculated.

The kinetic results showed that HEDP and PBTC are ozone-refractory at pH 7, while NTMP and DTPMP are highly reactive with ozone. The second-order reaction rate constants with $^{\bullet}OH$ and $SO_4^{\bullet-}$ are in the typical range for organic compounds and showed no pH dependency.

The matrix degradation experiments evinced an increased HEDP degradation rate in sulfate, silicate, and chloride matrices during ozonation. Whereas carbonate and chloride hindered PBTC ozonation, and NOM inhibited both HEDP and PBTC degradation through scavenging of $^{\bullet}OH$. Due to their high reaction rates with ozone the ozonation of NTMP and DTPMP was not affected by inorganic water constituents. Only the addition of NOM reduced the degradation to a small extent. The $SO_4^{\bullet-}$ radical-based oxidation process of the antiscalants was mainly inhibited by bicarbonate, chloride, and NOM. The highest inhibitory effect of bicarbonate on this AOP by scavenging of $SO_4^{\bullet-}$ and $^{\bullet}OH$ was observed for N-free organophosphonates.

This study has shown that ozonation and UV/persulfate oxidation are promising tools to remove organophosphonates from RO concentrates. HEDP could be degraded up to 60% with ozone and UV/persulfate application, whereas the oxidation of PBTC is limited to 10% degradation for

both processes. NTMP and DTPMP ozonation showed the same extent of degradation in the concentrates as compared to the buffered experiments. DTPMP degradation with UV/persulfate was around 45%, whereas NTMP could be degraded up to 65% at a fluence of about 65 kJ m$^{-2}$.

UV/persulfate eliminated all micropollutants to a higher extent than ozonation in RO concentrates due to the higher yield of oxidative species and photolytic degradation. Compounds with electron-rich moieties like carbamazepine, diclofenac, metoprolol, and sulfamethoxazole were eliminated with small ozone doses (< 0.5 mg O$_3$ / mg DOC) and with a small fluence (< 5000 J m$^{-2}$) in UV/persulfate processes. Photosensitive compounds with high reactivity towards $^\bullet$OH and SO$_4^{\bullet-}$ like the x-ray contrast media iopamidol, iohexol, and amidotrizoic acid were successfully eliminated with small fluence in UV/persulfate, whereas these compounds persist in ozonation at common ozone dosages.

Comparing the application of both oxidative processes to the RO concentrate, ozonation has the disadvantage of higher formation of by-products like bromate. In the presence of N-containing organophosphonates the formation of bromate is decreased due to enhanced ozone consumption. The energy demand of both processes strongly depends on the target compounds to be eliminated. For the elimination of compounds such as HEDP, NTMP, DTPMP, and sulfamethoxazole, ozonation is an economical technique, whereas UV/persulfate is better suited for the elimination of ozone-refractory compounds such as x-ray contrast media. In general, oxidative process treatment of RO concentrates could be applied to partly abate micropollutants before discharge.

**2023-08-03**

**Dr. rer. nat. Valentina I. Merkus**

**Comprehensive investigation of the ozonation of pharmaceutical micropollutants**

Due to insufficient removal of organic micropollutants in conventional wastewater treatment, ozonation is discussed as additional treatment step to reduce the pollutants' load. This oxidative process is also applied in drinking water treatment mostly for disinfection. Although research on ozonation has been performed for years, there is still a lack of knowledge because of various occurring transformation mechanisms depending on the pollutants' structures. However, ozonation of micropollutants has to be understood entirely to evaluate the applicability of this treatment option. Most ozonation research focuses on specific compounds. However, this procedure is not efficient due to the continuously increasing number of applied chemicals. Hence, understanding of ozonation mechanisms of fundamental structures is crucial. Moreover, the joint evaluation of different ozonation characteristics provides deeper insights into the oxidation reactions that would remain hidden considering only separated aspects.

The nucleobases adenine and guanine are the fundamental structures of various antiviral agents, which are regularly detected in the water cycle. Both base on purine, an aromatic, heterocyclic compound consisting of a fused imidazole and pyrimidine moiety. To investigate the ozonation characteristics and check the transferability of gained knowledge, examinations

were performed with the three archetypes and the two guanine based antivirals acyclovir and penciclovir. Reaction kinetics and ozone consumption ratios were covered in this study besides the identification of transformation products. As important matrix factors the influences of organic matter and bicarbonate were explored. Generally, reaction rates with ozone increased in the order purine < adenine < guanine. Vice versa the ozone consumption needed for complete degradation decreased pointing to the main ozone attack at a nitrogen moiety in purine, at a carbon moiety in guanine and both sites in adenine. A Hammett correlation of the reaction rates with substituent constants in the pyrimidine moiety showed potential to indicate sites of initial ozone attack. Despite a small number of data points and negligence of structures outside the considered aromatic moiety, our results of the correlation match with conclusions from ozone consumption experiments. Due to the slow reaction kinetics of purine and adenine with ozone, formed carbonate radicals contribute to the degradation of both compounds. Results for guanine and the two examined derivatives were similar indicating that findings are transferable to more complex micropollutants if considering mesomeric and inductive effects of substituents. Cyanuric acid was confirmed as product resulting from the ozonation of purine and adenine. Examination of several purines allowed the compilation of a comprehensive suspect list including analogues to previously described products. Application of this list led to the observation of 49 ozonation products. Additionally, a non-target approach revealed several further potential reaction products. Two prioritisation methods, principal component analysis and overlaps of features of the basic structures, pointed to the importance of product groups containing a 2-imino-5-oxoimidazole structure at neutral and basic pH and a group containing a 4-amino-2,4-imidazolinedione structure or 2,4-diamino-1,3-oxazol-5(2H)-one structure at acidic pH for guanine derivatives. Additionally, during the ozonation of the archetypes one molecule ($C_4H_8O_3$) was observed at neutral and basic conditions and another one ($C_3H_2N_2O_3$) at neutral and acidic pH. Due to structural complexity, noticeably more products were detected for the examined micropollutants. However, similarities were observed between the products of the structural motif representatives, allowing at least partial transfer of knowledge to related pollutants. Matrix effects on the formation and degradation of products were observed such as promotion or scavenging of hydroxyl radicals or the reaction of carbonate radicals with organic structures. Formed intermediates of organic matter are also suspected to react with analytes or their products.

One drawback of ozonation is the formation of potentially ecotoxic products. The analgetic ibuprofen, which is omnipresent in the aquatic environment and was previously shown to induce toxic effects during ozonation, was chosen as example compound for a new approach combining analytical and ecotoxicological testing to identify toxic transformation products from ozonation experiments. During chemical analysis seven products were confirmed with reference standards, of which two were reported for the first time for ozonation. However, five products previously suggested could be rejected. Ecotoxicity was determined by the model organisms *Daphnia magna* and *Desmodesmus subspicatus* during ozonation at acidic and neutral pH. While daphnids were inhibited by the ozonated mixture at pH 3, an increased effect on the growth of green algae was observed at pH 7. Although ecotoxic effects correlated with the formation of several products, assignment to one specific compound was impossible. Thus, the mixture of compounds might be relevant for the observed effect pointing out that evaluation of ecotoxicity during ozonation should always rely on ozonated samples, best in the respective matrix, instead of examining single transformation products. Additionally, the results underline the importance of performing toxicity testing with several model organisms, which could be affected differently, and not just trust in toxicity prediction tools as they were shown to only

allow rough estimations and ignore mixture toxicity.

The applied workflow combines investigations of various ozonation characteristics and thus provides information on reaction fundamentals, environmental impacts and the feasibility of ozone treatment with consideration of matrix influences. Checking a micropollutant motif generates knowledge transferable to a wide range of micropollutants. Deeper understanding of effects by different functional groups in organic matter on ozonation and the definition of a test battery for ecotoxicological testing covering multiple aspects such as trophic levels or exposure times can further improve the procedure.

**2023-09-05**

**Dr. rer. nat. Sasho Joksimoski**

**High-field asymmetric ion mobility spectrometry (FAIMS) study for on-site monitoring of aromatic volatile organic compounds in groundwater and their degradation in the presence of ferrous iron and carbonate**

Possibilities and limitations of remediation of VOC-contaminated groundwater and its analytical monitoring are the focus of this dissertation. Focal points are the development of a novel, continuous sample introduction system in combination with APPIFAIMS for on-site monitoring of contamination, site-specific assessment analyses and introduction of a possible additional remediation step by oxygen implementation (e.g. with a permeable membrane) in iron- and carbonate-rich groundwater environments. For this purpose, the possibility of using a low-cost, stand-alone, continuous real-time FAIMS system for on-site monitoring of groundwater was determined. The effects of high humidity and humidity variations on the signal in the analysis of aromatic VOCs were investigated for two different ion sources (APPI, APCI). To reduce the influence of humidity, a novel gas-water separation unit coupled to the FAIMS was implemented. Signal-specific values were determined from the maximum signal intensity at a given compensation voltage (CVmax) and a given dispersion field strength (DF) for selected aromatic VOCs, including BTEX from water. Successful calibration of the aromatic VOCs as a single analyte was performed with the gas-water separation APPI-FAIMS from spiked water samples. The limit of detection (LOD) of benzene, toluene, ethylbenzene, o-xylene and indane in water was 0.1, 0.9, 1.1, 0.3, 0.8 mg L-1 at 0% DF and 0.1, 0.9, 1, 0.4, 0.7 mg L-1 at 36% DF, respectively. The effectiveness of the sample introduction system (i.e. the gas-water separation unit) and the repeatability of the APPI-FAIMS signal were confirmed by monitoring of aromatic VOCs in water/groundwater samples under laboratory conditions. Similarly, an aromatic VOCs sum-signal was used to monitor contamination intensity at a groundwater contamination site. The sum-signal was enabled due to the low humidity provided by the gas-water separation unit. This allowed effective charge transfer and minimized influence of humidity on the signal in the analysis of aromatic VOCs. The results were validated with HS-GC/MS.

The geochemical composition of the remediation site was investigated, including the iron concentration and the concentration of BTEX pollutants in the groundwater. In addition to BTEX, other groundwater pollutants such as indane were also determined. Furthermore, a membrane-supported oxygen injection (OxyTech) was used as a non-standard remediation method and its effect on the redox conditions in the remediation well was investigated. In order to determine the

short-term effects of the oxygen addition to anoxic groundwater on the contaminants, the previously described gas-water separation APPI-FAIMS method was applied for on-site aromatic VOC monitoring. The results were confirmed with HS-GC/MS. In addition, the general properties and oxygen permittivity of OxyTech (silicone) membrane were determined. Further aspects involving ferrous iron oxidation followed by subsequent, induced •OH production and aromatic VOCs oxidation were carried out. This included the chemical potential involved in oxygenation in anoxic groundwater containing ferrous ions and carbonate/bicarbonate ions in high concentration. By using the coumarin detection method the formation of thereactive •OH radicals during the oxidation of the iron ions was confirmed. The possible oxidation products from the aromatic volatile organic groundwater contaminants were detected and identified after liquid-liquid extraction and direct analysis by GC/MS. Additionally, the oxidation capabilities of the system were confirmed on other water contaminants. Ibuprofen as a non-volatile organic water contaminant was also oxidized in presence of oxygen and ferrous ion in carbonate/bicarbonate rich water. In addition, the presence of one or more carboxyl groups was shown to play a special role in Fe-complex coordination and the formation of •OH radicals, as found when trisodium citrate dihydrate was used instead of sodium bicarbonate.

## Master Theses

**Nils-Jacob Fanke**
Determination of singlet oxygen yields during ozonation of nitrogen-containing compounds

**Maximilian P. Stapf**
Disintegration behavior of polymer compounds used in biodegradable mulch films (at Fraunhofer UMSICHT, Host supervisor: Dr. Stephan Kabasci)

**Shuai Tong**
Untersuchung der Fraktionierung stabiler Kohlenstoffisotope bei abiotischem Abbau von Imidacloprid

**Jannik Weber**
From Bottlenecks to Climate Neutrality: Modeling the Upscaling Potential of Photovoltaics in Germany and Identifying Critical Bottlenecks and Their Impact on Market Ramp-Up towards Climate Neutrality 2045 (at Fraunhofer Institute of Solar Energy ISE, Host supervisor: Dr. Charlotte Senkpiel)

## Bachelor Theses

**Emily Böckenholt**
Non-target Identification of Organic Compounds in Real-life Microplastics (at University of South Carolina, Host supervisor: Prof. Susan Richardson)

**Jannis Fischer**
Verbesserung der Erkennung und Eliminierung von Falsch-Positiven in Non-Target-Screening-Daten: Entwicklung und Anwendung eines Random-Forest-Modells zur Bewertung der Güte von Peak-Detektionsalgorithmen

**Anna Mangels**
Entwicklung und Anwendung einer Methode zur Analyse von per- und polyfluorierten Alkylsubstanzen (PFAS) in salzhaltigen Wassermatrices mit besonderem Fokus auf Trifluoressigsäure (TFA) (at TZW, Host supervisor: Dr. Karsten Nödler)

**Jan Oesterschlink**
Entwicklung einer Festphasenextraktionsmethode zur diskriminierungsarmen Anreicherung von Wasserproben anhand von Leitsubstanzen für die effektdirigierte Analytik (at IWW, Host supervisor: Dr. Jan Funke)

**Janina Marie Pytlik**
Acute Ecotoxicological Effects of Industrial Wastewater on the Aquatic Environment

**Leonardo Solazzo**
Charakterisierung eines hydrophilic-lipophilic balanced SPME Materials zur Anreicherung von Analyten aus wässrigen Proben

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# Invited Lectures

## Was uns stabile Isotopen über die Welt erzählen: Von grauer Vorzeit bis zu aktuellen Dopingsündern
**T. C. Schmidt**:
*Lecture Series „Die kleine Form", Essen, December 06, 2023 (invited)*

## Was sollen wir zukünftig messen? Bedarf und Trends in der Wasseranalytik organischer Spurenstoffe
**T. C. Schmidt**:
*Wissenschaftliches Kolloquium von BfG, Uni Koblenz und Hochschule Koblenz*
*Koblenz, December 05, 2023 (invited)*

## FutureWater meets FutureLab: was sind die nächsten großen Herausforderungen der (Wasser)analytik?
**T. C. Schmidt**:
*7. IUTA Analytik-Tag, Duisburg, November 09, 2023 (invited)*

## Sustainable sample pretreatment for microplastic analysis in environmental samples
**T. C. Schmidt, M. Wenzel, G. Renner, J. Tuerk**:
*25th International Symposium on Advances in Extraction Technologies (Extech 2023), Playa las Américas, Tenerife, Spain, July 21, 2023 (invited Keynote Lecture)*

## Simultaneous Determination of Fatty Acids and Fatty Acid Methyl Esters in Aqueous Samples by HS-SPME Arrow GC-MS/MS
**T. C. Schmidt, L. K. Tintrop, J. R. Lieske-Overgrand, M. A. Jochmann**:
*2nd ADVANCES IN SEPARATION SCIENCE: from extraction to chromatographic separation, Gembloux, Belgium, June 29, 2023 (invited Keynote Lecture)*

## LC with simultaneous IRMS and HRMS detection: A powerful new tool for process investigations
**T. C. Schmidt**:
*HPLC 2023, Duesseldorf, June 20 (invited Keynote Lecture)*

## Invited Short Course on "Miniaturized and automated sample preparation"
**T. C. Schmidt, S. Pedersen-Bjergaard**:
*HPLC 2023, Duesseldorf, June 18, 2023*

# Conferences and Meetings

## Ruhr-Rhine-Main Meeting

The Ruhr-Rhine-Main Meeting, a pivotal event fostering scientific exchange among research groups in the field of water and environmental analytical chemistry, was successfully organized by the Holger Lutze Group from TU Darmstadt and took place at their university's premises from November 30 to December 1, 2023. This gathering marked a significant collaboration between our group (IAC), colleagues from IUTA, the Bundesanstalt für Gewässerkunde (BfG), and the Holger Lutze Group (TU Darmstadt), focusing on research and developments in environmental sciences and analytical chemistry.

The network meeting underscored the importance of harmonizing non-target screening (NTS) data for aggregated analysis, a theme introduced in the first talk and echoed throughout the event. Presentations covered a broad range of topics, including the application of NTS in governmental water monitoring in Saxony, multi-way data processing of LC-HRMS/MS data for non-targeted screening of water samples, and innovative approaches to feature detection in NTS that eliminate the need for user-defined parameters, fully automating the process and prioritizing data quality.

A significant portion of the discussions was dedicated to environmental monitoring and the degradation of pollutants, with talks on investigating pesticides in Hessian waters and developing a circulating flow reactor for the photocatalytic degradation of antibiotic residues. Furthermore, the meeting delved into the chemical interactions of nucleotides with chlorine dioxide. It explored the effects of intrinsically formed free available chlorine on pollutant degradation during oxidative water treatment processes. The event facilitated a rich exchange of scientific knowledge and set the stage for future collaborations and research directions. It was announced that our group would organize the next meeting in 2024, promising another opportunity for advancing our collective understanding and methodologies in environmental science and analytical chemistry.

Despite the logistical challenges encountered by some attendees due to travel disruptions with Deutsche Bahn, the meeting achieved its objectives. It fostered a sense of community and collaboration among the participating researchers. The Ruhr-Rhine-Main Meeting exemplifies the vital role of scientific gatherings in promoting knowledge exchange, driving innovation, and addressing complex environmental challenges through collective expertise and interdisciplinary approaches.

# Teaching

At IAC, we are involved in teaching mostly in the Bachelor and Master program "Water Science," which 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)*

**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)*

## Winter term

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

**Laboratory Practical** "Analytical Chemistry" *(B.Sc. Water Science and Chemistry, 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 and Environmental Toxicology, in English)*

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

# Miscellaneous

## Group outing: Landschaftspark Duisburg-Nord
2023-10-04

Under the canopy of a gloriously sunny sky, our team embarked on an adventurous outing to the re-natured industrial splendor of the Landscape Park Duisburg-Nord. The day was marked not just by a friendly competition but also by the exploration of hidden gems throughout the park, adding an element of discovery to our spirited rally.

The event kicked off with the division into two teams, with Team "Odd" quickly emerging as the athletic powerhouse, their determination as palpable as the concentration of a meticulously prepared standard solution. In contrast, Team "Even" brought strategic prowess and analytical thinking to the table, embodying the precision of a finely tuned gas chromatograph. Among the day's highlights were three standout activities that truly captured the essence of our outing:

# A memory game that tested our ability to classify various amphibians, reminding us of the importance of accurate identification, whether in the field or our analytical work.

# A challenging mountain sprint that saw Team "Odd" leverage their athletic edge, embodying the efficiency of a rapid sample throughput.

# The creative construction challenge, where teams engineered boats to transport an egg across a river, echoing the innovative spirit of analytical chemistry in solving complex problems.

Uschi and Claudia, the masterminds behind the day's seamless organization, ensured that each competition not only tested our abilities but also fostered a sense of camaraderie and teamwork. Their oversight of the rally and competitions was akin to the meticulous attention to detail required in our laboratory analyses, ensuring every aspect of the day was perfectly calibrated for enjoyment and challenge. As the day drew to a close, an anticipated speech from the losing team to congratulate the victors went unsaid, yet the absence of formalities did not diminish the spirit of mutual respect and admiration among all participants. The outing concluded in a local bistro, where tales of the day's adventures were shared over a royal feast, cementing the bonds formed through friendly competition and shared experiences.

The day at Duisburg-Nord was a resounding success, a testament to the spirit of our team and the exceptional planning of Uschi and Claudia. Though Team "Odd" claimed the title with unmatched vigor, every participant left with a sense of achievement, contributing to a day filled with laughter, learning, and the joy of exploration.

## Obituary Prof. Dr. Alfred Golloch

It is with a heavy heart that we bid farewell to Prof. Dr Alfred Golloch, who passed away on 2 August 2023 at the age of 85.

After training as a laboratory technician and studying chemistry with a subsequent doctorate in Aachen, Prof Golloch began his academic career in 1972 in the Department of Chemistry at the newly founded Gesamthochschule Duisburg. After his habilitation in 1974, he was appointed Professor of Instrumental Analytical Chemistry. This made him one of the first university lecturers and pioneers of chemistry in Duisburg. After years of intensive teaching and research, Prof Golloch retired in 2003.

His research activities were characterised by the challenges of the structural transformation of the Ruhr region. The development of high-performance atomic spectrometric analysis methods and systems made a significant contribution to the progress of increasingly sophisticated element and species analysis in the coal and steel industry. He has written three books on the methods of spark, arc and laser atomic emission spectrometry. However, his research has also constantly focussed on environmentally relevant topics, such as work on reaction mechanisms in the field of oxidative processes for water treatment. He has published the results of his research activities in numerous publications and lectures in Germany and abroad. International co-operation has always been important to him.

Prof Golloch's diverse interests were also reflected in his scientific work. For example, he worked in the field of authentication of amber and wrote a book on craftsmanship in Myanmar.

It was not only his research work that was enriched by his open, life-affirming and future-orientated attitude, his teaching also benefited from this. Prof. Golloch was one of the founders of the international Bachelor's and Master's degree course in Water Science, which was offered for the first time in 2001 and, as a system-oriented course, takes into account all the important chemical, analytical and microbiological aspects of water research.

 *"One lives twice: the first time in reality, the second time in memory"*

> *Honore de Balzac*

Prof Golloch's memory will always have a permanent place with us.

*Klara Drees was born on October 8, 2023*