Institute of Hydrochemistry
Department of Chemistry
Technical University of Munich

Annual Report 2017

Institute of Hydrochemistry

Chair of Analytical Chemistry and Water Chemistry

Members of the IWC in December 2017

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Chair of Analytical Chemistry and Water Chemistry
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Editor: Dr. Thomas Baumann

Editorial

Dear colleagues and friends!

I am happy to welcome you for the first time as new director of the Institute of Hydrochemistry (IWC). In April last year, I had the pleasure to join a vibrant institute that had been shaping the research landscape of Analytical and Water Chemistry for decades, and which has continuously attracted new, innovative projects right until the “handover”. This was gratifying and challenging. When taking over there is the chance to build on traditions, but also to start in new directions to target the challenges in Water Science of tomorrow. For this endeavor, I see the IWC well-equipped.

In times of increasing population density and water scarcity, water reuse is becoming more and more important. Microarray-based bioanalytics in the group of PD Dr. Michael Seidel is not only able to detect pathogens very specifically and early on. In combination with unprecedented preconcentration by monolythic adsorption-filtration it also provides the opportunity to actively study the behaviour of pathogens in aquatic systems and during water treatment. This can help prevent infections by bacteria and viruses while optimizing water reuse. Studies on bacteria and pathogens are complemented by ongoing projects in the groups of Dr. Natalia Ivleva (focus on Stable Isotope Labeling) and Prof. Christoph Haisch. They are combining Raman microspectroscopy and surface-enhanced Raman (SERS) scattering to characterize bacterial physiology.

Raman Microspectroscopy in the group of Dr. Ivleva has played a critical role in responding to current societal concerns about microplastics in the environment. The group of Dr. Ivleva was not only among the first to develop analytical methods to distinguish polymer particles from other particles, fibers, and colloids (and to identify quartz particles that had previously been mistaken as microplastics). She is also active in three large coordinated projects, two of them coordinated from within TUM. One of them spearheads detection of sub-micrometer particles (SubµTrack, coordinator Prof. Drewes, TUM), and one addresses the question in what way microplastics behaves differently compared to the multitude of naturally occurring particles in the same size range (MiPAq, coordinator Prof. Geist, TUM). Both projects are an example of how Water Research at TUM is joining forces to address current challenges!

Compared to well-established management of surface waters, active management of subsurface storage capabilities is still underdeveloped. Challenges are posed by competing types of use (storage of water quality, geothermal energy, use as reservoirs) which warrant further exploration. With his core expertise in hydrogeology and many projects exploring the hydrogeochemistry of geothermal operations, the group of PD Dr. Thomas Baumann aims to bring together research areas in Water Science at the Technical University of Munich and is building bridges to the TUM Department of Civil, Geo and Environmental Engineering (Prof. Einsiedl).

An example that challenges in environmental science reach well beyond water

research is the current discussion about Diesel engine emissions. Here, the aerosol group (headed by Prof. Christoph Haisch) has tackled the need of reliable real-time measurements in air, and is contributing with innovative analytics of nitrogen oxides and particulate matter. Current research is pushing the limits in the endeavor to analyze even smaller particle sizes ("down to ten" (nm)). In acknowledgement of his scientific achievements Christoph Haisch was awarded the TUM Adjunct Professor (Apl.-Prof) title last year – Congratulations!

It is exciting to complement the IWC's research portfolio with yet another prominent research direction: chemical micropollutants in the water cycle. Isotope analysis of single organic compounds at natural isotopic abundance allows my Isotope Group (Dr. Rani Bakkour) to link changes in compound-specific isotope effects to underlying biochemical degradation mechanisms. Mechanisms of biodegradation can be elucidated in complex environmental systems and in living organisms down to the enzyme level. The same principles can be applied to study chemical reaction mechanisms in catalysis research. In an ERC Consolidator Grant we are currently exploring isotope effects to directly observe the onset of bioavailability limitations at low micropollutant concentrations. Through identifying thresholds of degradation we aim to contribute to better bioremediation strategies.

The upcoming year will bring new opportunities, but also major challenges. The move of our Institute by the end of the year will bring us closer to our colleagues in related disciplines – the Chair of Analytical and Water Chemistry will move into a newly refurbished floor in Chemistry at Garching campus, whereas the hydrogeology group will join the Geosciences at the downtown campus at Arcisstrasse and the aerosol research group will currently remain in Großhadern. This will also mean that a large part my research group, which is presently still located at the Helmholtz Zentrum München, will finally be able to join the IWC in Garching. On the other hand, for many members of IWC this means commuting over longer distances. In the long run, however, the move will offer opportunities for collaborative research projects in chemistry, and to join forces in the Water Cluster at TUM.

Last, but not least, I would like to thank my secretaries, our technicians, the group leaders and my predecessor Prof. Nießner for their help to have a good start at IWC. It was gratifying to enter a well-kept flagship running at full speed and to enjoy the stimulating atmosphere among all colleagues and Ph.D. students. Thanks for your great work and dedication!

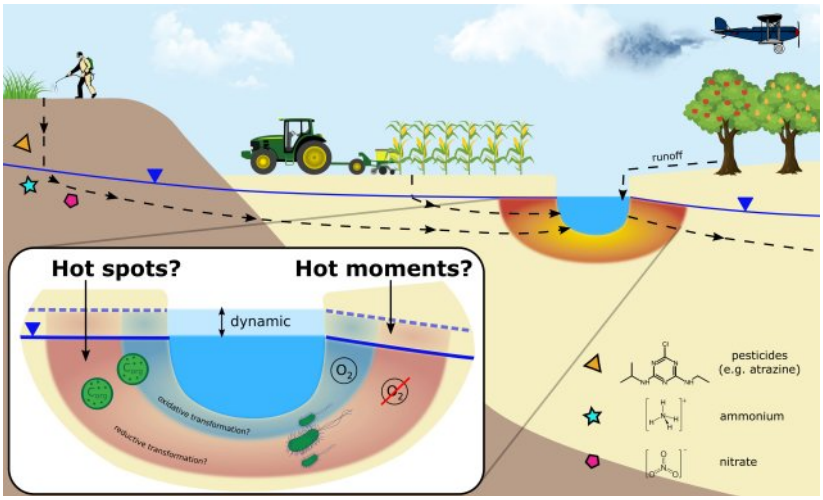
Kind regards,

Martin Elsner

Identifying the Turnover of Agricultural (Micro-)pollutants in Subcatchments using Compound-Specific Isotope Analysis (CSIA)

Diffuse pollution of groundwater by agricultural organic and inorganic compounds (N-species, pesticides) has become a worldwide environmental issue. In spite of extensive laboratory research, major knowledge gaps still exist regarding the fate and behavior of these pollutants on the catchment scale.

Research Rationale. Even though considerable progress has been made in identifying and quantifying degradation processes of agricultural pollutants in laboratory experiments, the biogeochemical drivers of pollutant transformations on the catchment scale are still insufficiently understood. As part of the Collaborative Research Center CAMPOS, we aim at evaluating the attenuation potential of the transition zone between groundwater and surface water of lower-order streams in the Ammer catchment between Herrenberg and Tübingen.



Conceptual model of the CAMPOS study area illustrating flow paths of agricultural (micro-)pollutants and the hypothesized reactive potential of the transition zone.

Due to the simultaneous occurrence of organic matter, steep redox gradients and high microbial activity, the transition zone provides advantageous conditions for the turnover of pollutants. Further, these biogeochemical regimes are prone to variations in time and space resulting in distinct zones and times relevant for biogeochemical transformation ("hot spots" and "hot moments"). Therefore, we particularly investigate processes and reactive potentials in this transition zone which affect pollutant turnover and subsequent flux to lower-order streams.

Analytical Approach. In order to gain conclusive evidence of degradation we measure stable isotopes at natural abundance by Compound-Specific Isotope Analysis (CSIA). CSIA is accomplished by the hyphenation of either a gas chromatograph (GC) or a liquid chromatograph (LC) with an isotope ratio mass spectrometer (IRMS).

The obtained isotope ratios can serve as *isotopic fingerprints* to evaluate the source of a contaminant. In addition, kinetic isotope effects associated with transformation processes lead to an enrichment of heavy relative to light isotopes (e.g. $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{2}H/^{1}H$ or $^{37}Cl/^{35}Cl$) in the remaining pollutant molecules. This isotopic footprint provides a concentration-independent evidence of degradation which we even can quantify. Finally, changes in isotope ratios are often reaction-specific, allowing us to distinguish between different transformation pathways.

David Glöckler, Rani Bakkour, Martin Elsner

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M. Elsner, G. Imfeld (2016) Compound-specific isotope analysis (CSIA) of micropollutants in the environment — current developments and future challenges. Curr. Op. in Biotechnol. 41, 60-72.

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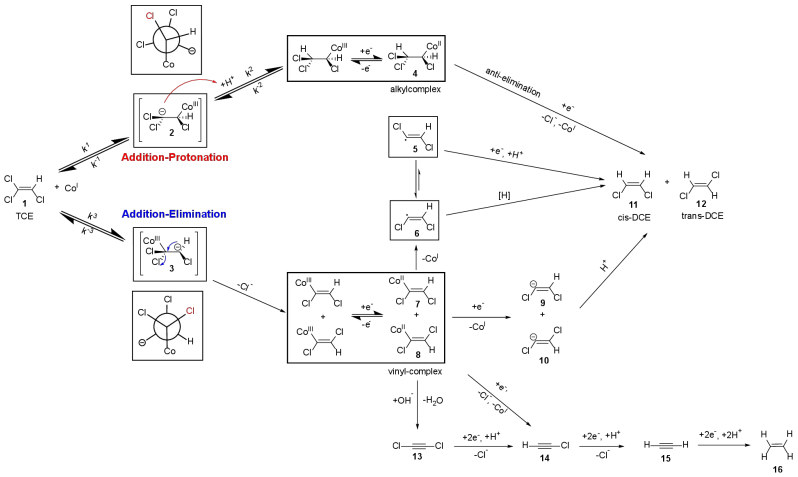
Prof. Dr. Jan Fleckenstein, Helmholtz Zentrum für Umweltforschung Leipzig; PD Dr. Tillmann Lüders, Helmholtz Zentrum München; Dr. Marc Schwientek, Eberhard Karls Universität Tübingen; Prof. Dr. Christian Zwiener, Eberhard Karls Universität Tübingen

Which Mechanisms of Chlorinated Ethene Transformation Lie at the Heart of Reductive Dehalogenases?

Chlorinated ethenes are the most frequent contaminants at polluted sites. With isotope-based analysis we decipher the transformation mechanism of their coenzymatic reductive dehalogenation.

State of the Art. Chloroethenes are commonly used in industrial applications, and detected as carcinogenic contaminants in the environment. Their dehalogenation is of environmental importance in remediation processes. However, a frequent problem is the accumulation of toxic degradation products such as *cis*-dichloroethylene (*cis*-DCE) at contaminated sites. Although numerous studies have addressed the reaction chemistry of reductive chlorinated ethene dehalogenation in organisms and in chemical model systems such as Vitamin B_{12}, underlying mechanisms are still a matter of controversial debate.



Integrating mechanism for competing pathways of chlorinated ethene dehalogenation by Vitamin B_{12}

Results. We bring forward new evidence from compound specific isotope effect analysis of carbon, chlorine and hydrogen. When isotope values of two elements are plotted against each other (e.g. carbon and chlorine), different slopes reflect different underlying mechanisms. Using this tool, Cretnik et al. 2013 [1] could show that microbial strains (*G. lovleyi* strain SZ, *D. hafniense* Y51) and the isolated cofactor cobalamin employ similar mechanisms of reductive dechlorination of TCE. Here we go further and compare chemical model systems with these strains and vitamin B_{12}.

Three possible mechanisms have been suggested for reductive degradation of chlorinated ethenes with vitamin B_{12}:
1. Nucleophilic substitution; 2. Nucleophilic addition; 3. Single electron transfer (SET).

Isotope effects observed in reactions with well-known outer sphere single electron transfer (OS-SET) reagents differed strongly from those with Vitamin B_{12} ruling out this mechanism for biodegradation of chlorinated ethenes [2]. A strong pH dependency of isotope effects in TCE combined with mass spectrometry detection of alkyl- and vinyl complexes of vitamin B_{12} further suggests a reaction sequence of 1) addition-elimination- (for PCE), 2) addition-protonation-elimination (for *cis*-DCE) and a pH-dependent transition between both mechanisms for TCE. These results reveal unprecedented insight into the mechanisms lying at the heart of reductive dehalogenation [3].

B. Heckel, M. Elsner

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Cooperation:
Prof. Dr. Kristopher McNeill, Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zurich

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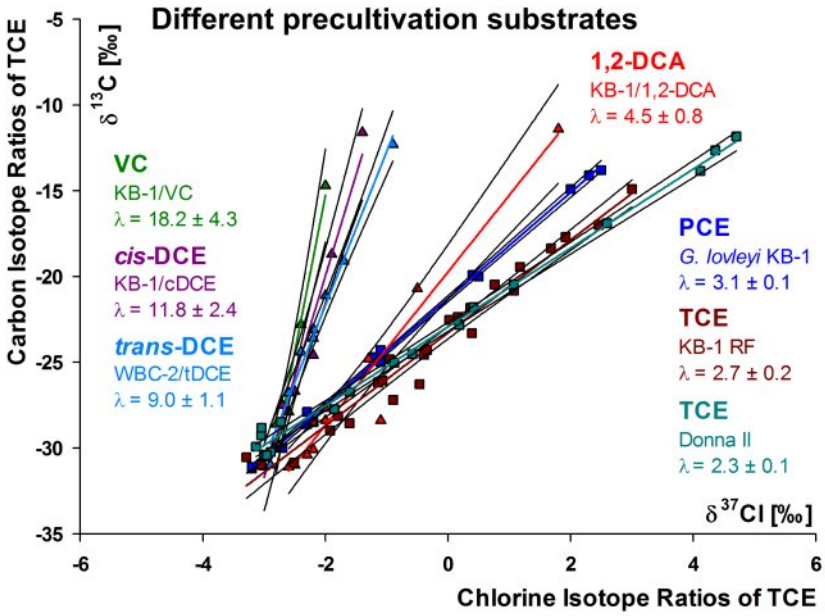
Mechanistic Dichotomy of Bacterial Reductive Dechlorination Revealed in Trichloroethene-Dehalogenating Cultures

Chlorinated ethenes are toxic pollutants threatening groundwater quality worldwide. Dual element isotope analysis revealed different underlying dehalogenation mechanisms of the same compound TCE for bacterial cultures and, finally, provides a plausible mechanistic explanation for the different degradability of TCE vs. *cis*-DCE at contaminated sites.

State of the Art. The widespread groundwater pollutant trichloroethene (TCE) can be reductively dehalogenated to harmless ethene by specialist microorganisms, particularly *Dehalococcoides*. However, the specific reaction mechanisms in reductive dehalogenase enzymes (RDases) have remained elusive. Furthermore, reductive dehalogenation often stops at toxic *cis*-1,2-dichloroethene (*cis*-DCE) or vinyl chloride (VC).

Our aim was to study the differences in cis-DCE and TCE microbial dechlorination and to explore the influence of culturing conditions and associated enzymes on TCE dechlorination mechanisms.

Experimental Approach. Compound-specific carbon ($\delta^{13}C$) and chlorine ($\delta^{37}Cl$) isotope fractionation of TCE and *cis*-DCE was measured in pure and mixed bacterial, organohalide-respiring, cultures. The magnitude of carbon relative to chlorine isotope effects, as expressed by the slope λ of $\delta^{13}C$ vs. $\delta^{37}Cl$ regressions, was used as a powerful tool to distinguish different reaction mechanisms.



Isotope fractionation trends of TCE dechlorination vary between microorganisms.

Results. The slope λ was larger in the transformation of *cis*-DCE by two *Dehalococcoides mccartyi* strains compared to TCE transformation by *Geobacter lovleyi* strain KB-1. λ was also larger for TCE transformation for enrichment cultures that had been precultivated on lesser chlorinated ethenes like *cis*-DCE, *trans*-DCE and VC. λ slopes of precultivated cultures match reported values for cob(I)alamin addition followed by protonation, whereas λ slopes for TCE-adapted cultures match values for cob(I)alamin addition followed by chloride elimination (see contribution Benjamin Heckel). These contrasting trends demonstrate the existence of distinct reductive dechlorination mechanisms, not only for specific substrates (*cis*-DCE vs. TCE), but also for the same substrate (TCE) in cultures preconditioned for different substrate utilization. This surprising mechanistic dichotomy indicates that RDases and their reaction chemistry are tailored to chemical target structures and may provide an answer to the long-standing question why chlorinated ethene remediation frequently stalls at *cis*-DCE.

Christina Lihl, Alfredo Perez de Mora, Armin H. Meyer, Martin Elsner

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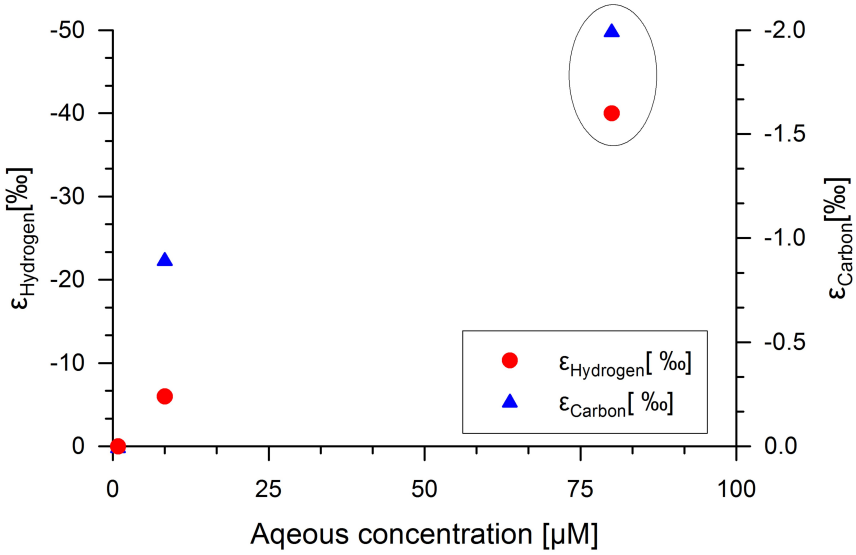
Direct Observation of Mass Transfer Limitations in Slow Anaerobic Biodegradation of 2-Methylnaphthalene (2-MN) Dissolving from an Oil Phase at Low Concentrations

Anaerobic biodegradation of polycyclic aromatic compounds (PAHs) dissolving from oil may take months in laboratory experiments, mimicking natural conditions. Can mass transfer be limiting under these conditions, even in a well-shaken system?

State of the Art. During biodegradation of organic compounds in the environment, mass transfer limitations are frequently invoked, but never verified. Anaerobic biodegradation of PAHs occurs over such long time scales that the limiting factors are uncertain: is it mass transfer or microbial physiological adaptations?

Compound-specific isotope analysis has recently emerged to enable a direct observation of bioavailability limitations [1]. In the absence of mass transfer limitations kinetic isotope effects are observable. In contrast, if diffusion is slow (e.g., out of an oil phase, or into bacterial cells) molecules will be quantitatively converted at the enzyme so that changes of $^{13}C/^{12}C$ will not observable outside in solution.



Hydrogen and carbon enrichment factors in anaerobic degradation of 2-MN by the sulfate-reducing enrichment culture NaphS2. Values in the circle are the enrichment factors at high concentrations in the absence of an oil phase, values to the left are in the presence of oil.

A recent study reported that mass transfer was not limiting in the presence of an oil phase if equilibrium concentrations of aqueous PAHs were between 50 and 100 µM [2]. Our goal was, therefore, to investigate whether isotope fractionation is masked at lower concentrations of the PAH 2-methylnaphthalene (2-MN).

Results. Carbon and hydrogen isotope enrichment factors were determined in anaerobic degradation of 2-MN by the sulfate-reducing enrichment culture NaphS2 in the presence and absence of a hexadecane phase mimicking oil. Values were greatest at high 2-MN concentrations in the absence of the oil phase (-2.1 ± 0.1 ‰ and -40 ± 7 ‰, for carbon and hydrogen, respectively) and lowest at low 2-MN concentrations in the presence of the oil phase (Figure 2). Even in a well-shaken system, this demonstrates that mass transfer from an oil phase into bacteria becomes limiting at low PAH concentrations implying this restriction applies also to low concentrations in nature.

Sviatlana Marozava, Armin H. Meyer, Mehdi Gharasoo, Alfredo Perez de Mora, Lin Zhuo, He Wang, Martin Elsner

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Cooperation:
Rainer U. Meckenstock, University Duisburg-Essen

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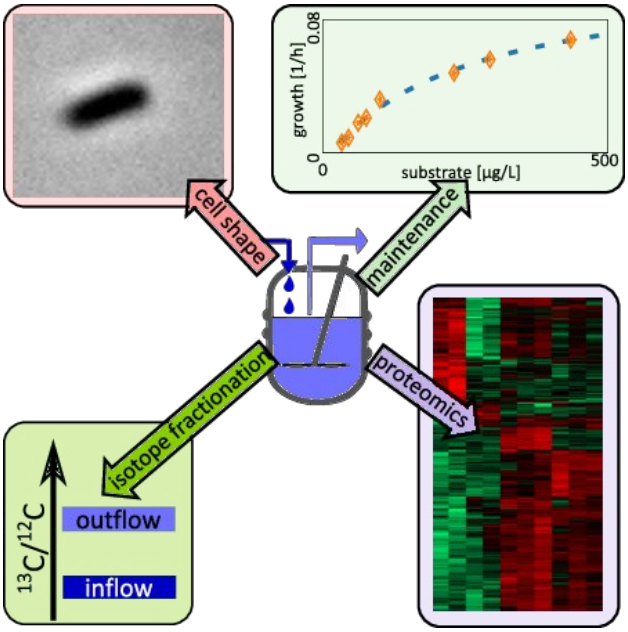
Rate Limiting Mass Transfer in Micropollutant Degradation Revealed by Isotope Fractionation

Persistent pesticides contaminate drinking water resources. What is the reason that their natural degradation fails at low concentrations?

Limits of Biodegradation. Biodegradation of persistent micropollutants like pesticides often stalls at low concentrations (µg/L) in the environment. Either mass transfer limitations (i.e. uptake into bacteria) or physiological adaptation (i.e. enzyme downregulation) are debated to slow down microbial degradation under these conditions. Bioavailability limitations have often been invoked, but not observed experimentally in the low concentration regime. Neither has the interplay of bioavailability limitations with physiological adaptation been addressed by proteomics. Compound-specific isotope fractionation analysis (CSIA) enables researchers to trace bioavailability limitations, but has failed so far to reach trace concentrations in typical batch degradation studies.

CSIA Reveals Rate Limiting Mass Transfer. Therefore, we accomplished CSIA for degradation of the persistent pesticide atrazine during cultivation of *Arthrobacter aurescens* TC1 in bioreactors (chemostat and retentostat) under different growth rates leading to steady state residual atrazine concentrations ranging from 12 µg/L to 440 µg/L. Isotope analysis of atrazine revealed a drastic decrease in isotope fractionation at low concentrations. At high concentrations $\delta^{13}C$ of the biodegradation with whole cells fully represented the isotope effect of the enzyme reaction. At low concentrations contrasting, smaller $\delta^{13}C$ indicated that this isotope effect was masked by rate limiting mass transfer across the cell membrane. This onset of mass transfer limitation was observable at concentrations resembling oligotrophic conditions, and was accompanied by physiological adaptations to nutrient limitation in the cell shape, maintenance energy, and in the proteome: The cells' transition to stationary growth phase was accompanied by drastic downregulation of basic cell functions and a transition from rod shape to coccus shape. This might lead to improved energy housekeeping and lower maintenance energy. We conclude that mass transfer limitations are important for biodegradation in the environment and that these limitations play a decisive role for bacterial adaptation to oligotrophic conditions.



Assessing biodegradation limitations with a comprehensive approach in bioreactors

Benno Ehrl, Kankana Kundu, Sviatlana Marzozava, Mehdi Gharasoo, Martin Elsner

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^{13}C and ^{15}N Isotope Analysis of Desphenylchloridazon by Liquid- and Gas-Chromatography Isotope Ratio Mass Spectrometry (GC/IRMS and LC/IRMS): Method Development and Lysimeter Field Study

Desphenylchloridazon (DPC), the main transformation product of chloridazon is detected with increasing frequency in groundwater. Can its further degradation be monitored by measuring its natural stable isotope ratios using compound-specific isotope analysis?

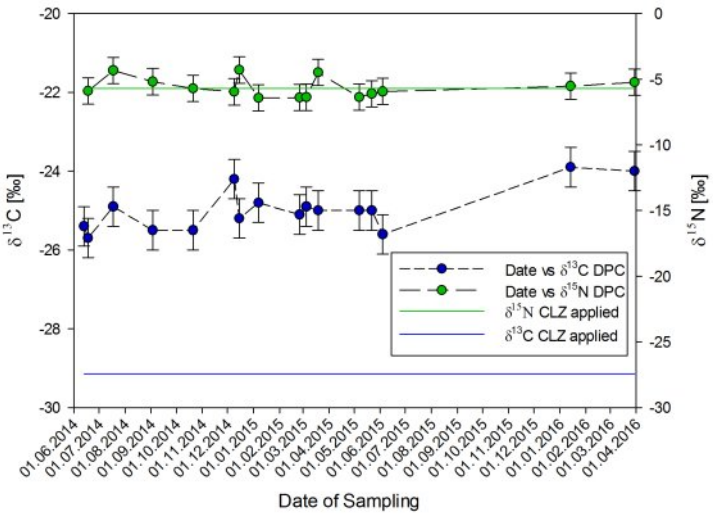
State of the Art. DPC has a high leaching potential and is more persistent than its parent compound chloridazon [1]. Investigation of stable carbon and nitrogen isotope ratios before and after degradation can give insights into mechanisms and environmental fate of DPC. In this study, a method for $\delta^{13}C$ and $\delta^{15}N$ analysis of DPC by liquid- and gas chromatography isotope ratio mass spectrometry (GC/IRMS and LC/IRMS) was developed, validated and applied to lysimeter field samples.

Results. To evaluate isotope analysis according to trueness and precision, $\delta^{13}C$ and $\delta^{15}N$-values of standards were determined by Elemental-Analyzer-IRMS.

LC-IRMS. Reproducible isotope results were achieved by injecting standards directly onto an Atlantis LC-column (3 µm x 100 mm).

GC-IRMS. Since DPC is not amenable to GC analysis, a derivatization method was tested and optimized to achieve precise isotope ratio measurements. At a temperature of 70 °C and with an excess of trimethylsilyl-diazomethane (TMSD) (160-fold $n_{TMSD}/n_{analyte}$), a nearly complete reaction with accurate $\delta^{15}N$ values was obtained. The limit of precise isotope analysis was identified as 2 µg of DPC on column.

Lysimeter field samples. DPC was enriched in ^{13}C by approximately 3 ‰ and 2 ‰ in gravel and moraine soil, respectively. In contrast, no changes in nitrogen isotope values were observed (figure 1). The measured $\delta^{15}N$-values of DPC corresponded to the $\delta^{15}N$ of the CLZ applied on the lysimeter. Hence, the $\delta^{15}N$ value of DPC found in environmental samples can be used as a fingerprint to retrace the manufacturer of CLZ.



Isotope values of DPC from lysimeter field samples, injection of CLZ in moraine soil

Aileen Melsbach, Christina Lihl, Martin Elsner

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Cooperation:
Violaine Ponsin, Clara Torrento, Prof. Daniel Hunkeler, University of Neuchâtel, Switzerland; Rani Bakkour, Thomas Hofstetter, EAWAG Zurich, Switzerland.

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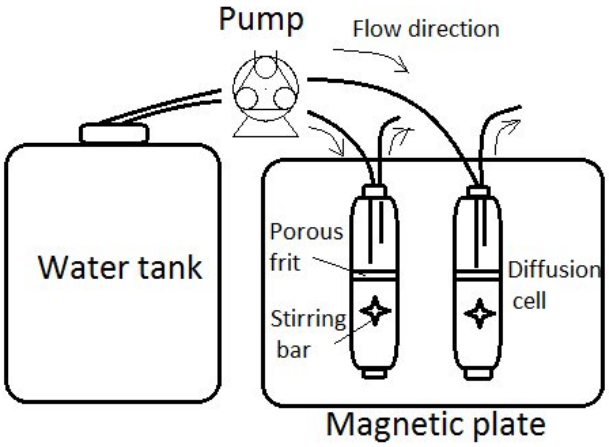
Hydrodynamic Dispersion-Induced Isotope Fractionation of 2,6-dichlorobenzamide (BAM) and Metolachlor at Natural Isotopic Abundance in Aqueous Systems

Compound specific isotope analysis (CSIA) is a novel approach to study the bottleneck of biodegradation of organic micropollutants in groundwater, based on changes in compound-specific isotope values. Can hydrodynamic dispersion bias such interpretation when compounds are analyzed at their natural isotopic abundance?

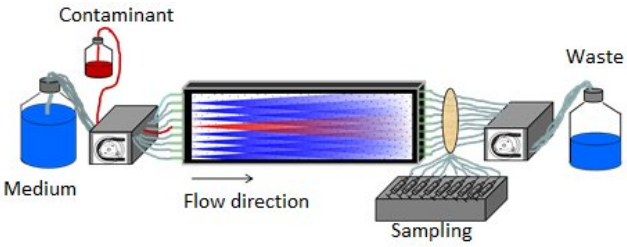
State of the Art. Biodegradation of organic micropollutants appears to stop at low concentrations. CSIA is applied to explore the bottleneck of low-level degradation (physiology vs. bioavailability) in this study. However, in contaminated sediments, observed isotope fractionation of substrate molecules in bulk solution may in addition be affected by dispersion and diffusion. Although isotope fractionation associated with these processes is generally assumed negligible, significant isotope fractionation by dispersion was recently observed with labelled compounds, in which labeled isotopologues have much larger mass differences than in real-world situations. Does this effect also need to be considered for compounds of natural isotopic abundance?

Diffusion Cell Experiment. A Diffusion cell experiment was conducted to study the isotope fractionation associated with the diffusion of BAM and metolachlor in aqueous phase. BAM (400 mg/L) and metolachlor (100 mg/L) continuously diffused from the lower compartment to the upper compartment through a porous frit. The measured concentrations of BAM and metolachlor in the lower compartment of the diffusion cell decreased with time, which followed Fick's law very well. And the isotope fractionations of C and N were smaller than 1‰, thus the isotope fractionation caused by diffusion in aqueous phase is negligible.



Schematic of the experimental setup for the diffusion cell experiment

Two-dimensional Sediment Tank Experiment. To further study isotope fractionation induced by hydrodynamic dispersion, an abiotic two-dimensional sediment tank experiment was conducted, where a concentration gradient was created by transverse dispersion. Solutions with BAM (400 mg/L) and metolachlor (100 mg/L) were injected via one center port of the inflow boundary.In this study, the isotope fractionation caused by hydrodynamic dispersion is also proven to be negligible (smaller than 1‰). This allows us to neglect these effects when CSIA to further study biodegradation of organic micropollutants with the aim to pinpoint bottlenecks of biodegradation.



Schematic of the experimental setup for the tank experiment

Fengchao Sun, Mehdi Gharasoo, Martin Elsner

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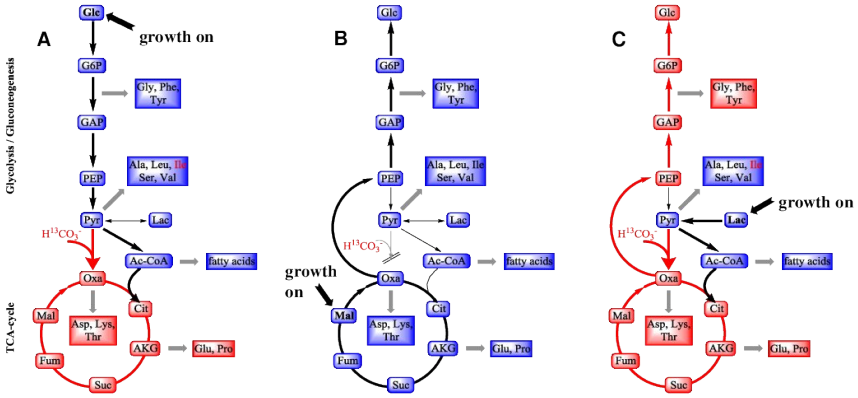
Cooperation:
Prof. Olaf Cirpka, Tübingen University; Dr. Martin Thullner, Helmholtz Centre for Environmental Research – UFZ

Heterotrophic $^{13}CO_2$-Fixation – A new Indicator for Microbial Dissolved Organic Carbon Utilisation?

Virtually all heterotrophs incorporate CO_2. So far no one made use of the fact that heterotrophic fixation of CO_2 depends on the organic substrate and thus this process has the potential to show which carbon source was utilised by the heterotroph.

Experimental Approach. *Bacillus subtilis* was grown in M9 minimal medium in the presence of $H^{13}CO_3^-$ and various organic substrates. The ^{13}C-incorporation into bacterial biomass was determined by EA-IRMS and the ^{13}C-distribution in protein-derived amino acids was measured by GCMS.

The enzyme pyruvate carboxylase (PC) catalyses the conversion of pyruvate to oxaloacetate via the addition of CO_2, thus replenishing the TCA-cycle. PC occupies a vital position in a metabolic hub of the central carbon metabolism, being responsible for the regulation of the carbon flux in the cell. Depending on the carbon source, we expect different ^{13}C enrichment patterns of metabolic products, with an indicative pattern for each carbon source.



(A) Carbon from CO_2 uptake ends up in metabolites and products of the TCA-cycle, if Bacillus subtilis W23 is grown on glucose. (B) Only negligible amounts of carbon from CO_2 uptake can be expected in the amino acids during growth on malate. (C) During growth on lactate, carbon from CO_2 uptake ends up in metabolites and products of gluconeogenesis and the TCA-cycle.

Results. We found that growth on substrates that are funnelled through glycolysis (A) led to enrichment in ^{13}C of up to 12% in the amino acids directly derived from TCA-cycle metabolites. In case of growth on substrates that enter the central car-bon metabolism "between" glycolysis and the TCA-cycle (C), the amino acids directly derived from TCA-cycle metabolites were enriched in ^{13}C as well as the amino acid glycine, which was derived from gluconeogenic metabolites. In both cases, the replenishment of the TCA-cycle through PC was crucial and we found the expected distribution of ^{13}C in the amino acids. In contrast, during growth on TCA-cycle metabolites (B) the replenishment of the TCA-cycle through PC is negligible. This clearly shows that the CO_2-fixation patterns are indicative for different carbon sources and can be used to differentiate amongst them.

Marina Spona-Friedl, Alexander Braun, Martin Elsner

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Erb, T.J. (2011) Carboxylases in Natural and Synthetic Microbial Pathways. Applied and Environmental Microbiology 77, 8466–8477

Funding:
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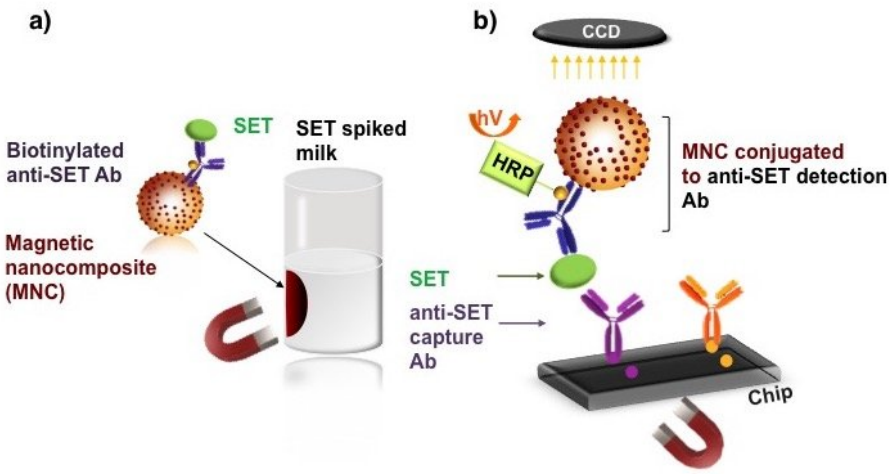
Cooperation:
Prof. Eisenreich, Chair of Biochemistry, TUM; Dr. Griebler, Institute of Groundwater Ecology, Helmholtz Zentrum München; Prof. Kappler, Center for Applied Geoscience, Universität Tübingen

Magnetic Nanocomposites for Rapid Biosensing of Staphylococcal Enterotoxin B in Milk

Staphylococcal enterotoxin B (SEB) is one of the most common causes of acute food poisoning, accounting for numerous foodborne-disease outbreaks all over the world. To ensure a fast surveillance and response to foodborne-disease outbreaks, a rapid method is required which enables a sensitive quantification of SEB in large volumes of milk.

State of the Art. Several approaches (e.g. ELISA, mass spectrometry) for the detection of SEB in complex food matrices have already been used. However, most of the current methods require a costeffective and time-consuming pre-enrichment and isolation of SEB in the food matrix. Additionally, only very low amounts of SEB are present in large quantities of food. Hence, analytical methods with a very low detection limit are needed. The combination of immunomagnetic separation based on superparamagnetic iron-oxide shell silica-core nanocomposites and microarray analysis is a promising tool to improve risk assessment in the food safety.

Experimental Approach. Magnetic nanocomposites conjugated to anti-SEB antibodies were preconcentrated and separated from the milk matrix by using a permanent magnet. After immunomagnetic separation, a sensitive quantification of SEB by chemiluminescence-based microarray analysis on the automated MCR 3 platform was performed.



Schematic illustration of a) immunomagnetic separation in milk samples and b) principle of chemiluminescence sandwich microarray immunoassay in combination with magnetic separation

Results. A novel synthesis approach of raspberry-shaped superparamagnetic iron oxide-shell silica-core nanocomposites was developed. Magnetic nanocomposites were fully characterized by various techniques (TEM, SEM, FT-IR, SQUID magnetometry, DLS, Raman and Moessbauer spectroscopy).After the functionalization of these magnetic nanocomposites with specific detection antibodies, immunomagnetic separation of SEB directly in large volumes of milk is feasible. For a sensitive quantification of proteotoxins, IMS was coupled with a chemiluminescence sandwich microarray immunoassay. An efficient magnetic separation was performed in 100 mL milk. The immunomagnetic separation coupled to chemiluminescence sandwich microarray immunoassay for the detection of SEB in 100 mL milk was successfully established on the flow-based microarray analysis platform MCR 3 with a detection limit of 0.4 ng/L

Angelika Nistler, Michael Seidel

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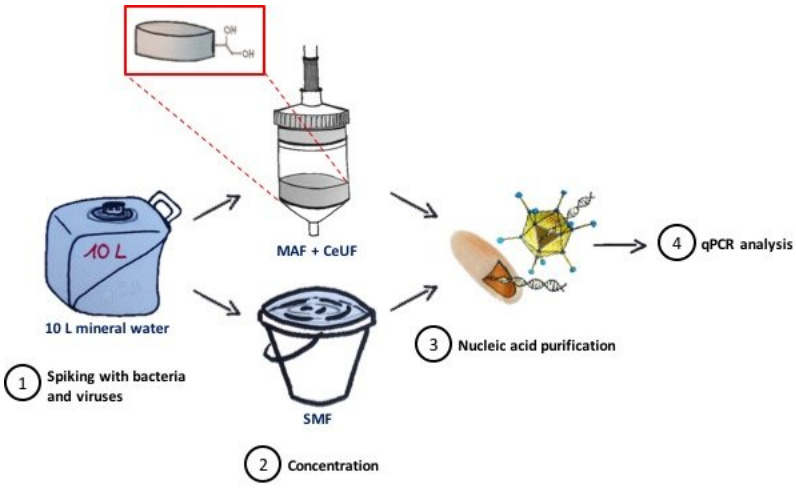
TUM International Graduate School of Science and Engineering (IGSSE)

Cooperation:
Prof. Dorner, Robert Koch Institute, Berlin, Germany; Prof. Haase, Dr. Gleich, TUM School of Bioengineering

Development of a Standard Operation Procedure (SOP) for the Concentration of Microbial Contaminations in Irrigation Water in Europe

The consumption of food of non-animal origin leads more and more frequently to diseases of consumers. Due to missing directives of quality one potential cause could be irrigation water contaminated with pathogens.

State of the Art. Water used for irrigation in agriculture represents a complex matrix. Germany uses surface and groundwater as the source for irrigation, whereas other countries with seasonal water shortages use desalted sea water as well as treated waste water. Depending on its origin, irrigation water contains a high composition of microbial contaminants. Even if the ratio of pathogens is often small, it is, nevertheless, sufficient to cause human diseases. Due to the World Health Organization (WHO) a reasonable explanation for infections caused by the consumption of food of non-animal origin could be the irrigation with contaminated water. To date, there is no European guideline defining quality standards for irrigation water. To protect consumer's health as well as to ensure the production of safe food screening, monitoring and controlling of microbiological hazards in irrigation water is highly needed.



Experimental overview. 10 L mineral water was spiked with different bacteria and viruses. Monolithic adsorption filtration (MAF) followed by centrifugal ultrafiltration (CeUF) or skimmed-milk flocculation (SMF) were used for the concentration of water samples. Nucleic acids were purified and quantified by qPCR

Experimental Approach. We compare two concentration methods, the monolithic adsorption filtration, established at TUM, and skimmed-milk flocculation, established at our Spanish partner laboratory in a European proficiency test setup. Therefore, experimental protocols for concentration and quantification of pathogens are harmonized as well as established in all partner laboratories. Bacteria and viruses are identified by species-specific genes via qPCR.

Results. 10 L mineral water was spiked with different amounts of bacteria and viruses, concentrated and quantified. Independently of the laboratory it was shown that monolithic adsorption filtration has a higher capacity of recovering viruses than skimmed-milk flocculation. Monolithic adsorption filtration enables the processing of water samples up to 100 L with a processing time of less than 30 min/10 L. In comparison, skimmed-milk flocculation is limited to a sample volume of 10 L with a processing time of more than 16 hrs/10 L. In addition to its short experimental time, monolithic adsorption filtration also represents a user friendly and space saving method. We could furthermore optimize the surface of our monolithic adsorption filtration disks. Now, water samples can even be processed at neutral pH, so that sample pre-conditioning is not needed anymore. In addition, monolithic adsorption filtration can also be applied for the efficient concentration of viruses from real water samples.

Sandra Schäfer, Michael Seidel

Funding:
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Cooperation:
Universitat de Barcelona (Barcelona, Spain), Universitat Politecnica de Valencia (Valencia, Spain), Universitat Rovira I Virgil (Tarragona, Spain), Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit (LGL), State General Laboratory (Cyprus), Technical University of Denmark (Copenhagen, Denmark)

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Hjelmsø, M.H.; Hellmér, M.; Fernandez-Cassi, X.; Timoneda, N; Lukjancenko, O.; Seidel, M.; Elsässer, D.; Aarestrup, F.M.; Löfström, C.; Bofill-Mas, S.; Abril, J.A.; Girones, R.; Schultz, A.C. Evaluation of Methods for the Concentration and Extraction of viruses from Sewage in the Context of Metagenomic Sequencing. PLOS ONE 2017, 1, e0170199

Culture-Independent Monoclonal Serotyping of *Legionella pneumophila* in Water, Aerosols and Urine Samples for Fast Screening of *Legionella*-Contaminated Sources

In future Legionella exposition cases outbreak sources can be identified faster with the LegioTyper. By serotyping in patients' urine, aerosol samples, and process water samples, infection markers can be compared and traced back to the source.

State of the Art. Due to increasing legionellosis cases within the last years an innovative fast and sensitive method for the detection of *Legionella pneumophila* is needed. The gold standard here, the culture method, takes 10 days for a positive result and can only type *Legionella spp*. By recommendation of the Federal Environmental Agency culture-independent screening methods are now allowed to identify sources in a shorter time. Furthermore a special focus lies on a complete serotyping of *L. pneumophila* serogroup 1-15 as legionellosis is mostly caused by the species *L. pneumophila* (90%). In outbreak cases caused by emissions from condensation cooling plants of *Legionella* containing aerosols to the environment it is essential to rapidly link infected patients to the outbreak source to start decontamination.

Microarray read-out device MCR Legiotyper (Image: GWK Präsizionstechnik GmbH).

Experimental Approach. A chemiluminescence sandwich microarray immunoassay was established based on the Dresden panel with 19 monoclonal and 1 polyclonal antibody immobilized on the microarray chip surface for the serotyping of *L. pneumophila* and subgrouping of serogroup 1 [1,2]. To optimize the manufacturing process and cost a new polycarbonate foil based microarray chip was developed. This allows a cost reduction from 20 € to 1 € per chip. Furthermore a new LegioTyper test device was established for flow-based measurements of complex matrices like e.g. urine or process water.

Results. In the course of the LegioTyper project it could be shown that measurements of patients' urine, environmental samples (waste/process/surface/tap water) and cultural samples are possible on the newly developed polycarbonate foil based microarray chip. In the last period of the project the concentrations of the capture antibodies on the surface are adjusted for the perfect compromise of maximum specific signal and least cross-reactivities. Furthermore all measurements can be performed on the same test device which makes the chemiluminescence sandwich microarray immunoassay applicable for both usage in clinical diagnostics and environmental hygiene control by health authorities.

Catharina Kober, Jonas Bemetz, Michael Seidel

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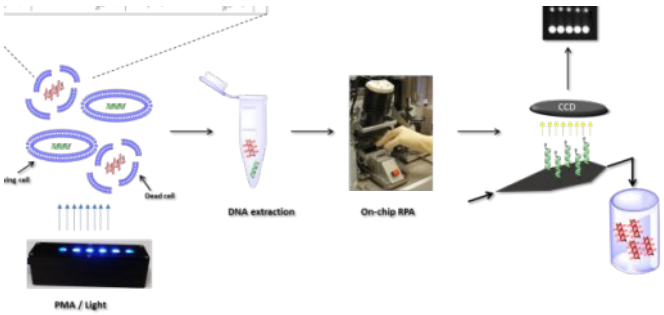
Funding:
BMBF LegioTyper (FKZ: 13N13698)

Cooperation:
Occupational and Environmental Health, Epidemiology, Bavarian Health and Food Safety Authority; Institute of Medical Microbiology and Hygiene, Institute of Virology, Medical Faculty "C. G. Carus", Technical University of Dresden; GWK Präzisionstechnik GmbH

Culture-Independent Detection and Quantification of Living *Legionella* for the Regular Monitoring of Water Samples

In condensation recooling plants it is obligatory to control the hygiene regularly. To prove the effect of biocide treatment the amount of viable and non-viable legionella are quantified by heterogeneous asymmetric recombinase polymerase amplification on DNA microarrays.

State of the Art. Due to new laws and guidelines (eg. 42. BImSchV, VDI-guideline 2047, sheet 2 and 3), the regular monitoring of *Legionella* in condensation recooling plants is of increasing importance. The culture method is still the gold standard for the detection of *Legionella*, though it takes 10 days and only a general detection of *Legionella spp.* is possible. Through recommendations of the Federal Environmental Agency culture-independent molecular biological methods like e.g. qPCR and isothermal nucleic acid amplification methods are becoming important for a fast and rapid quantification of *Legionella*. Nonetheless a viable/non-viable differentiation is necessary to monitor biocide effects.



Schematic procedure of the viability heterogeneous asymmetric recombinase polymerase amplification.

Experimental Approach. A chemiluminescence DNA microarray was established for the isothermal heterogeneous asymmetric recombinase polymerase amplification using the genomic sequences of 16S rRNA and mip gene for detection and differentiation of *Legionella spp.* and *L. pneumophila*, respectively [1]. For viable/non-viable differentiation the sample is pretreated with the DNA-intercalating dye propidium monoazide, which intercalates exclusively into the DNA of dead *Legionella* with permeable cell membranes. By subsequent heterogeneous asymmetric recombinase polymerase amplification only viable *Legionella* are detected. Without pretreatment the heterogeneous asymmetric recombinase polymerase amplification can quantify the total amount of viable and non-viable *Legionella spp*. and *L. pneumophila*.

Results. Calibration curves for quantification of viable and non-viable *Legionella* were obtained with specific RPA primers, reaching detection limits of 87 genomic units (GU) µL-1 for *Legionella spp*. and 26 GU/µL for *L. pneumophila*. With the viability heterogeneous asymmetric recombinase polymerase amplification, predefined proportions of viable *Legionella* could be measured in a range from 10^1 - 10^5 GU/µL with recovery rates of 81 to 133% [2]. A combination of both methods allows the quantification of the sum parameter of viable and non-viable *Legionella* and the determination of the proportion of viable *Legionella* in the sample on one microarray with two flow cells in less than one hour. By addition of preconcentration methods like monolithic adsorption filtration, condensation recooling plant water was measured within a few hours and the effect of biocides was demonstrated.

Catharina Kober, Michael Seidel

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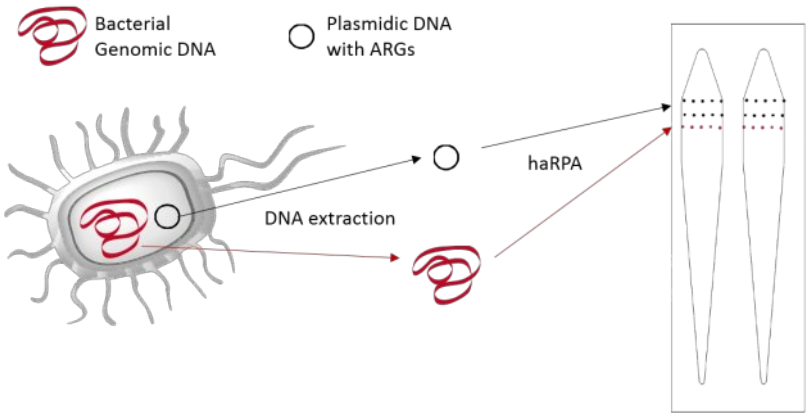
Funding:
IWC

Analysis of Extended-Spectrum β-Lactamase Gene CTX-M with a Heterogeneous Asymmetric Recombinase Polymerase Amplification on DNA Microarrays

Antibiotic resistant bacteria are an emergent research topic in the field of water research. Rapid and simultaneous detection of antibiotic resistance genes (ARGs) and pathogenic bacteria by DNA microarrays is important for water safety

State of the Art. Antibiotics are an effective way to treat bacterial infections. Over the last decades, antibiotic resistance has risen and multiresistant gram-negative bacteria have evolved. The current gold standard for detecting ARGs is cultivation followed by PCR which is time consuming and only feasible for culturable bacteria. To provide faster results the existing heterogeneous asymmetric recombinase polymerase amplification (haRPA) assay on the microarray chip [1] was adapted for the detection of extended spectrum β-lactamase (ESBL) gene CTX-M which is the most prevalent in most EU member states.

Experimental Procedure. The haRPA microarray enables the detection of specific DNA sequences in 40 min. For the assay the commercially available TwistAmp® basic RPA kit is used and specific forward and reverse primers are added together with sample DNA. After incubation, the detection of the amplified DNA-sequences is preferred on the automated flow-based microarray analysis platform MCR3 where chemiluminescence signals are analyzed.



Schematic overview of multiplex haRPA for detection of bacterial species and ARGs.

Results. For the first time haRPA for the detection of the ESBL gene CTX-M 15 was successfully established. Detection of CTX-M 15 *K. pneumoniae* positive in a concentration of 10^4 to 10^8 cells/mL of an overnight culture was possible with no cross-reactivities against other ESBL genes as well as non-resistant bacterial species (*Enterococcus faecalis*, *Pseudomonas aeruginosa*, and *L. pneumophila*). Within the Metawater project, a validation study will compare the haRPA assay with an already existing PCR assay at the LGL for the detection of CTX-M carrying gram-negative bacteria.

Future projects include using the viability haRPA method developed by Kober et al. [2] and further extending the DNA detection panel by multiplexing. This will make it possible to quantify bacterial species and ARGs simultaneously while also giving information about living bacteria from concentrated surface water and wastewater samples thus providing a full risk assessment in a short time.

Lisa Göpfert, Michael Seidel

References:
(1) A. Kunze; M. Dilcher, A. Abd El Wahed, F. Hufert, R. Niessner and M. Seidel (2015) On-chip isothermal nucleic acid amplification on flow-based chemiluminescence microarray analysis platform for the detection of viruses and bacteria. Anal. Chem. 88 (1), 898–905.
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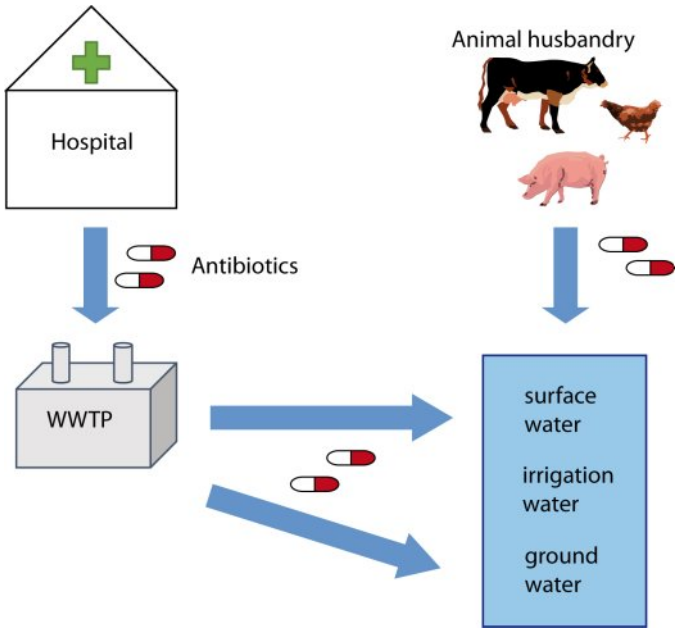
Funding:
BMBF METAWATER; (FKZ: WU1346A), JPI Water Project

Cooperation:
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit (LGL)

Detection and Active Reduction of Antibiotics in Water Samples

The amount of persistent antibiotics in the environment is a risk factor for antibiotic resistance. Therefore, rapid, inexpensive monitoring and characterization of sources and active reduction of emissions are crucial.

State of the Art. Antibiotics are used in human and veterinary medicine, enter the environment through different sources and end up in surface and ground waters. To monitor their distribution in the environment it is important to quantify their amount in real water samples. In addition, the reduction of antibiotic discharge to water by active and selective degradation is currently not done as a standard procedure but is an important approach to lower antibiotics amount in the environment. To aid in such efforts, an inexpensive and rapid approach that is promising for online monitoring of antibiotics, the indirect competitive regenerable chemiluminescence microarray immunoassay (CL-MIA) was further expanded.



Schematic overview of antibiotics entering different water resources.

Experimental Approach. CL-MIA allows the multiplex detection of several antibiotics in one analysis on the automated microarray analysis platform MCR3. An indirect competitive assay principle is used where the antibiotics in the sample are competing with the immobilized antibiotics on the chip. The secondary antibody is labelled with horseradish peroxidase, which catalyzes the chemiluminescence reaction between luminol and H_2O_2. To detect lower concentrations of persistent antibiotics e.g. sulfonamides in surface water, preconcentration by monolithic adsorption filtration (MAF) was conducted.

Results. The already existing antibiotic panel for the CL-MIA, which includes 15 different antibiotics used primarily in veterinary medicine, was successfully expanded to include kanamycin and cephalexin, two antibiotics used as standard treatment options for mastitis in dairy cows. Application of the assay for different matrices like urine from treated cows and surface water samples was successfully daccomplished. The analysis of samples collected from a river passing through a poultry farm gave positive results for a few of the tested antibiotics. However, due to the dilution with clean water from a nearby lake pre-concentration is needed to analyze antibiotics in low concentrations. To this end, MAF was tested and evaluated to enable sensitive analysis of antibiotics from environmental samples.

The active reduction of persistent antibiotics through selective degradation in a device that can be implemented at discharge sources such as wastewater treatment plants (WWTPs) is currently in development.

Verena Mayer, Lisa Göpfert, Michael Seidel

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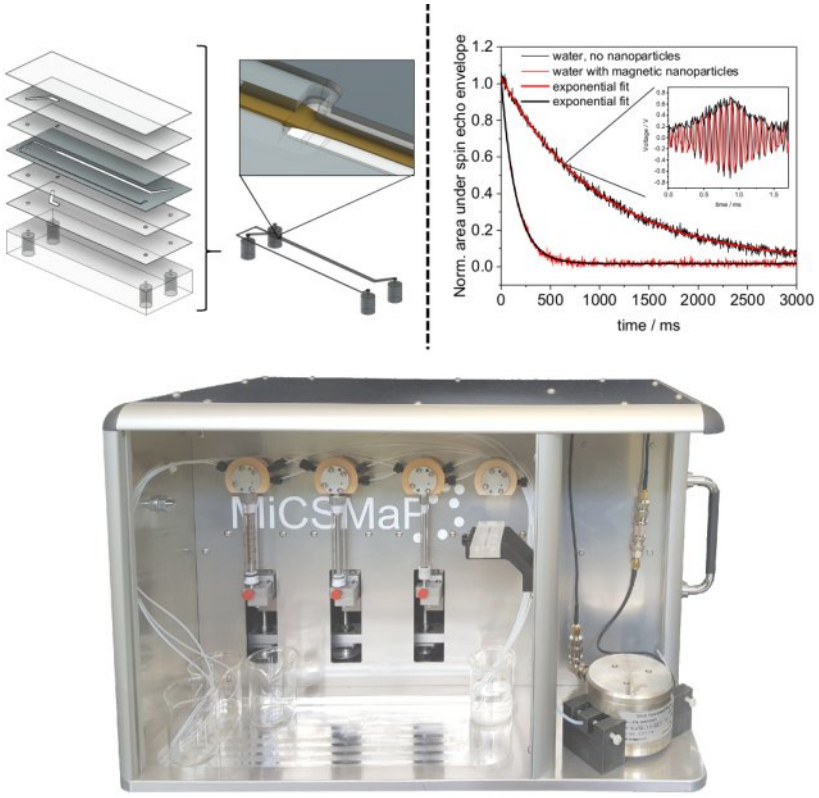
Funding:
Hanns Seidel-Stifung; IWC

Tape-based Microreactor for the Synthesis of Magnetic Nanoparticles and Integrated Characterization by T2-Relaxation

Small scale, continuous flow syntheses lie at the heart endeavor to favor chemistry for Industry 4.0. Especially the online-characterization and handling of solid nanomaterials still represent big challenges.

State of the Art. The use of miniaturized continuous-flow reactors is gaining importance for nanoparticle synthesis, especially for small-scale and decentralized production of nanomaterials, e.g. the synthesis of magnetic iron oxide nanoparticles. They have applications in analytical chemistry and imaging in biomedicine. Most synthesis protocols are based on batch syntheses, followed by lengthy analytical procedures for product characterization. The integration of analytical methods directly into a continuous synthesis process is important for fast synthesis optimization, quality- and process control, to share analytical data across systems and may pave the way for further application of nanomaterials in different fields.

Experimental Approach. Magnetic nanoparticles are synthesized by a co-precipitation reaction by 3D hydrodynamic flow focusing of an iron salt precursor solution into basic sheath streams. 3D microreactors were fabricated by stacking multiple layers of double-sided tape and polymer foils which makes the preparation process fast, low-cost and flexible to design changes. The microreactor is integrated into one machine with pumps and valves for sample handling and a miniaturized nuclear magnetic resonance (NMR) relaxometer for measurement of transverse (T2) relaxation time of hydrogen proton spins in water. The T2 time describes the decay of transverse magnetization in a static magnetic field after excitation by a radiofrequency pulse and is shortened in the presence of magnetic nanoparticles.



Exploded view of multilayer microreactor with schematic representation of 3D-flow focussing and experimental setup with integrated pumps and T_2-relaxometer

Results. Synthesis by 3D hydrodynamic flow focusing allows controlled synthesis of magnetic nanoparticles with defined size and suppresses solid deposition in the microchannel. Particle size, magnetic properties or aggregation state can be determined from T2 relaxation time directly during synthesis. This helps to optimize synthesis conditions for maximum T2 relaxivity for higher sensitivity and image contrast in applications of magnetic nanoparticles.

Jonas Bemetz, Michael Seidel

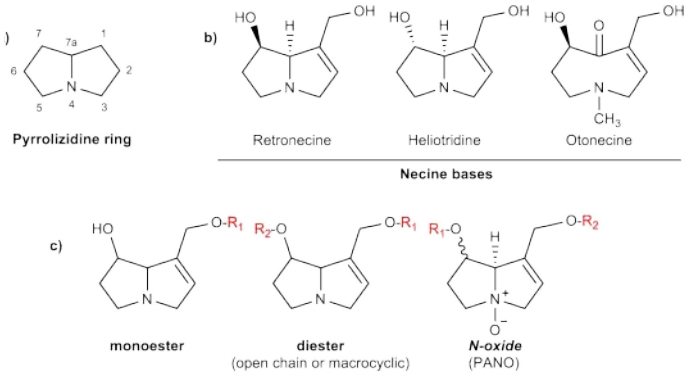
Funding:
TUM International Graduate School of Science and Engineering (IGSSE)

Cooperation:
Dr.-Ing. Bernhard Gleich, Munich School of BioEngineering (MSB), TUM

Development of an Immunological Screening Method for the Determination of Toxicologically Relevant Pyrrolizidine Alkaloids in Herbal Tea and Related Matrices

Toxic pyrrolizidine alkaloids (PAs) can be found as contaminants in a wide range of plant-based food sources. Currently, no defined limit concentrations for PAs in food exist but are probably introduced by European governments near-term. Therefore, food industries require an in-house method for rapid, easy and effective monitoring of unprocessed plant resources. In this context, bioanalytical methods based on immunological detection of the alkaloids are most suitable.

Background. PAs are so called secondary metabolites and naturally occurring alkaloids. They are produced by 3% of all flowering plants (e.g. Asteraceae, Boraginaceae, Fabaceae) as a constitutive defense mechanism against insect herbivores. Worldwide more than 660 PAs including corresponding N-oxides (PANOs) can be identified. Their chemical structure is based on a pyrrolizidine ring and each PA can be derived from one out of three basic bodies (necine bases) named Retronecine, Heliotridine and Otonecine. Esterification of the primary or secondary hydroxyl group, leading to mono-, diesterified or even cyclic structures (figure), results in a huge structural variety. Since PAs can be metabolized to highly reactive pyrrole esters, which form harmful DNA- and protein adducts, contamination of human food sources (e.g. herbal tea) are supposed to give rise to acute or chronic toxicity.



Chemical structures of relevant PAs
Pyrrolizidine ring (a); basic structures/necine bases (b); monoester, diester and PANOs (c)

Compared to standard mass spectrometry-based methods, bioanalytical methods based on immunological analyte detection facilitate parallel processing of many samples and require only minor training of staff. Moreover, they are cheap and do not require any costly sample preparation. Therefore, the aim of this project is to develop and validate an immunological screening method for the determination of toxicologically relevant PAs.

Experimental Approach. This work focuses on the generation of monoclonal antibodies. Based on the abovementioned necine bases, suitable antigens/haptens are designed and extensively characterized by ESI-MS. Derivatized basic bodies are coupled to protein carriers (e.g. BSA, OVA or TG) by using appropriate coupling chemistry and substitution grade is determined by MALDI-TOF MS subsequently. Generated protein conjugates are used for immunization of mice/rats, isolated splenic B lymphocytes are hybridized and resulting cell culture supernatants extensively screened for most suitable cell clones using direct and indirect competitive ELISA. Selected clones are used for the generation of monoclonal antibodies.

Results. After immunization of mice and rats using different hapten derivative-protein conjugates, a set of anti-hapten antibodies was obtained. Only few of them showed competitive binding behaviour, i.e. could be used to establish dose-response curves with the target analyte. Investigations are ongoing to identify the importance of the linking bridge structure of the immunogen for the observed antibodies' binding behaviour.

Katharina Stutzer, Dietmar Knopp

Funding:
FEI Research Association of the German Food industry (AiF 19010N)

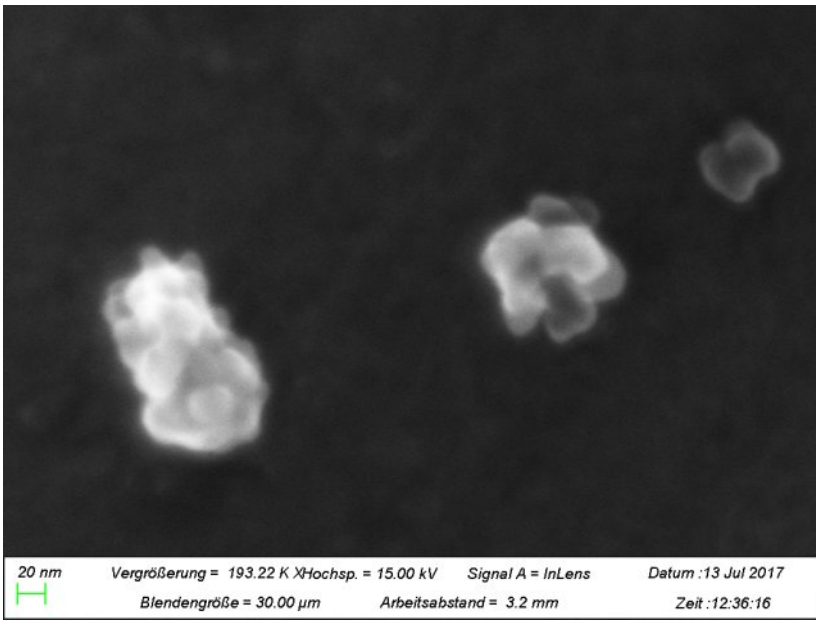
Cooperation:
Prof. M. Gareis, Dr. C. Gottschalk, Chair of Food Safety, Veterinary Faculty, Ludwig-Maximilians-University

Down to Ten - Characterization of Combustion Engine Exhaust Particles in the Size Range from 10 to 23 nm

Nanoparticles emitted from combustion engines are considered a significant health issue. While current legislation limits number of particles larger than 23 nm emitted from vehicles, knowledge about even smaller particles is sparse.

State of the Art. The DownToTen project seeks to develop a reliable and robust methodology to enhance the regulatory approach in the assessment of particle number emissions in the sub 23 nm region (down to at least 10 nm). The focus is set on state-of-the-art automotive powertrains with direct injection gasoline engines, but also diesel engines, under real-world operation conditions. To this end, DownToTen will first investigate and quantitatively describe the nature and the characteristics of nanoparticles <23 nm (formation, origin, physical and chemical characteristics), and will set up a synthetic aerosol bench for fundamental studies at instrument level for metrology and evaluation purposes. Existing and newly developed instruments will be evaluated against rigorous criteria for the measurement of sub-23 nm particles, with emphasis on their applicability as portable emissions systems (PEMS). Beside organic aerosol, the target is to analyze semivolatile and non-volatile particles. Inorganic particles <23 nm that are of particular environmental and toxicological interest have not been characterized so far. This deficiency results from a number of factors, such as the limited availability of routine analytical techniques allowing to determine elements at ultratrace levels and the lack of sampling strategies for <23 nm particles.

Results. Several methods for off-line chemical characterization of sub-23 nm particles have been tested: inductively coupled plasma mass spectrometry (ICP-MS), total reflection x-ray fluorescence (TXRF) or neutron activation analysis (NAA). The very minute sample amount is challenging for all these methods and the appropriate filter material is of crucial im-portance. Nevertheless, artefact-free sampling of nanoparticles is a challenge; hence, we also employ online analytical techniques, which are developed within the framework of the project. Mass spectrometry with a new ionization source from Plasmion, a high-tech start-up company founded by the IWC alumnus Dr. J.-C. Wolf, allows for direct online analysis of exhaust gas. It is combined with particle size fractionation and evaporation systems, thus allowing for the characterization of volatile and semi-volatile particles.



SEM image of sub-23 nm particles collected on an aluminum foil

Klemens M. Thaler, Christoph Haisch

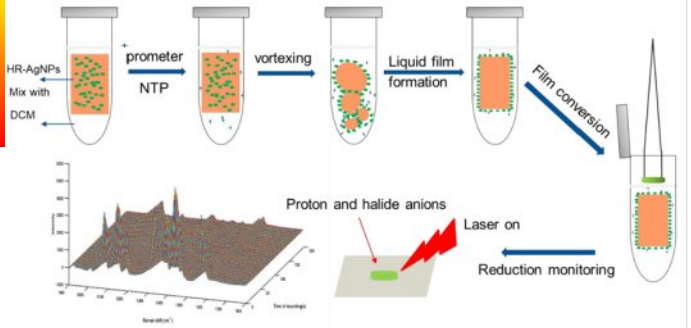
Funding:
EU

Cooperation:
Aristotle University of Thessaloniki; AVL List GmbH; Ricardo UK Ltd;Tampere University of Technology; Graz University of Technology; Joint Research Center; Centro Ricerche FIAT; Plasmion GmbH, Munich, Germany.

Simple SERS Substrate Application for Hot Electron-induced Reaction

Silver is a low-priced and highly efficient catalyst. In parallel, it can be used to excite surface-enhanced Raman scattering (SERS), a highly sensitive approach to monitor the catalytic conversion.

Experimental Approach. Double-sided adhesive tape was used to trap mobile silver films, forming at the interface of two immiscible liquids (such as aqueous phase and dichloromethane (DCM) phase), into freestanding films. These films are densely packed with silver nanoparticles and feature excellent SERS enhancement. Beyond the SERS studies, the freestanding silver films were employed to promote hot-electron-induced reduction without the addition of reducing agents. In the presence of Ag films, halide anions, 4-nitrothiophenol (4-NTP) can be reduced to 4-amino-thiophenol (4-ATP) by laser illumination without reducing agents. In this reaction, protons serve as hydrogen source. With increasing pH, reaction rates also increased.



Experimental procedure to investigate hot-electron-induced reduction of 4-nitrothiophenol.

Hydroxylamine reduced silver nanoparticles (HR-AgNPs) were applied to generate these liquid films. Because of their low stability, polyvinylpyrrolidone (PVP) was added. The densely packed silver particles were then transfered from liquid to solid state. Scanning electron microscope was employed to characterize the freestanding films. A time-resolved analysis of the reaction products is possible by surface-enhanced Raman spectroscopy. By using time series measurements, it is possible to analyze the relationship between catalytic reaction rate, laser power, and proton concentrations, respectively.

Results. Highly SERS-activie substrates were successfully prepared on double-sided adhesive tape. The films were optimized with respect to the amount of HR-AgNPs and the best stability, resulting in a highly reproducible, stable, and easy to generate substrate.

During the reduction of 4-NTP into 4-ATP, hot electrons, halide anions, and protons are the key factors for driving the reaction. The substrates are applied for monitoring the reduction. At certain proton concentration, 4-NTP reduced to 4, 4´-dimercaptoazobenzene (DMAB) and finally reduced to 4-ATP was detected. Reaction rates at different laser power and different proton concentrations were determined. The limitation of proton concentrations of 4-NTP converting to 4-ATP also was found out.

Two reaction routes can be suspected in this reduction: With sufficient protons, conversion of 4-NTP into 4-ATP is the dominant step. When the number of available protons is limited, conversion of 4-NTP into DMAB is the dominant reaction path.

Li Qiu, Christoph Haisch

References:
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Funding:
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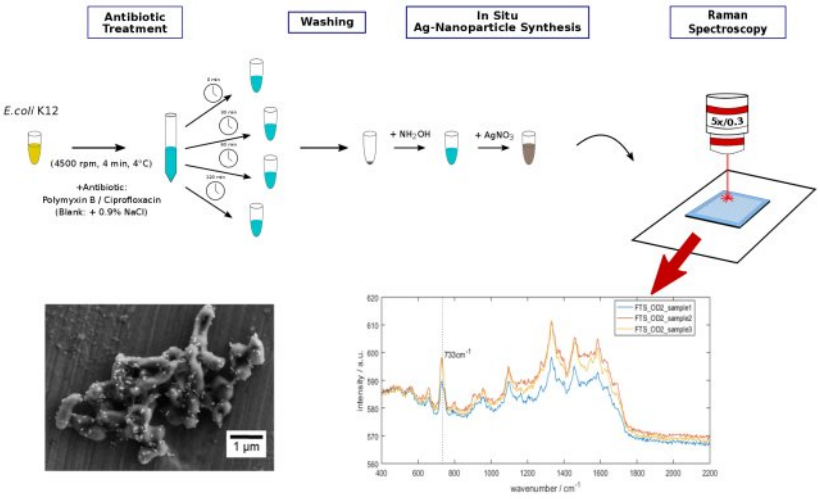
Antibiotic Resistance Testing of Urinary Tract Infection Bacteria by Surface-Enhanced Raman Spectroscopy

An alarming increase of bacterial resistancy against commonly used antibiotics urge for the development of faster antibiotic susceptibility testing methods. Raman spectroscopy and especially Surface Enhanced Raman Spectroscopy (SERS) are a promising suitable tool for that task.

State of the Art. Currently, the only clinically certified test methods for antibiotic susceptibility of bacteria, such as broth dilution and disc diffusion test, are time consuming due to the need of bacteria cultivation. It takes up to two days until a suitable treatment can be prescribed. Minimizing this time is the most urgent need to counteract spread and infection of life-threatening diseases through multiresistant pathogens.

While new genotypic methods for the application in microbiology, such as polymerase chain reaction or fluorescence in situ hybridization, come with a lack of information about the change of the phenotype microscopy is a standard tool used for identification and evaluation of microorganisms. In that context, a new setup, revealing additional information in biological research is Raman spectroscopy. The resulting spectra promise to give qualitative and quantitative information about a given sample with a high spatial resolution. In combination with surface enhancement, which can be obtained when silver nanoparticles are present, analysis can be even faster and more specific. A widely used and reliable approach is the in-situ reduction of silver nitrate with hydroxylamine in the presence of microorganisms. The resulting sample can then be analyzed by Raman spectroscopy. Using data analysis tools like principal component analysis (PCA) obtained spectra allow not only the reliable identification of the bacterial strains but also a distinguishable response after antibiotic treatment. Preliminary work showed that it even allows to distinguish alive from dead bacteria [1]. Thus prerequisites for the technique as application in antibiotic testing are fulfilled and reproducible protocols to analyze pathogens are being developed.



Scheme for antibiotic resistance testing of bacteria via SERS (inset: electron microscopic picture of the silver nanoparticle coated bacteria).

Results. Starting with the preliminary results published earlier [1], the scope of the project is to first, investigate further on the reliability of the method for relevant bacteria involved in urinary tract infections as well as optimization of the protocol regarding time efficiency. In close collaboration with the project partners. SERS will be used to screen the clinical samples and compare the results with tools from routine diagnostic. In case of success, a prototype setup capable of automatized measurements and thus useful for routine application shall be developed.

David Bauer, Christoph Haisch

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(1) H. Zhou, D. Yang, N. P. Ivleva, N. E. Mircescu, S. Schubert, R. Niessner, A. Wieser, C. Haisch (2015) Label-Free in Situ Discrimination of Live and Dead Bacteria by Surface-Enhanced Raman Scattering. Anal. Chem., 87 (13), 6553-6561.

Funding:
DFG

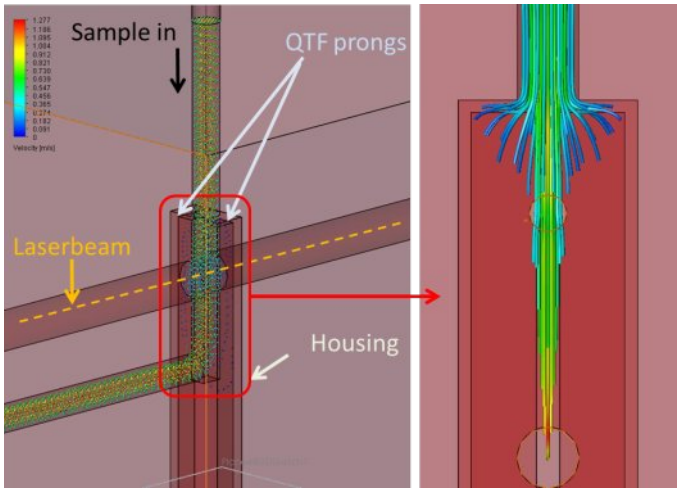
Cooperation:
Prof. Stief, Urologische Klinik der LMU München; PD Dr. Wieser, Max von Pettenkofer-Institut, LMU

Development of a GC Coupled, QEPAS-based CO_2 Isotope Detector

Isotope analysis of carbon dioxide (CO_2) has numerous applications in medical diagnosis, geochemistry and atmospheric chemistry. The most common technique for isotope analysis is isotope ratio mass spectrometry (IRMS) which provides an impressive level of precision, typically below 0.1‰. However, IRMS has several shortcomings, e.g., high cost, large size, complex sample preparation, and cross-sensitivity. Quartz-enhanced photoacoustic spectroscopy (QEPAS) offers a relatively cheap and simple strategy for isotope analysis.

Key Questions. QEPAS based sensors use a quartz tuning fork (QTF) as a sharply resonant acoustic transducer to detect weak photoacoustic excitation and to allow the use of extremely small volumes [1] At photoacoustic excitation the laser beam has to pass through the 300 µm gap between the prongs of QTF without touching them. Therefore good beam quality and precise focusing between prongs play a crucial role. The sample is injected into the QEPAS detector from a combustion furnace, so the aim is to reduce the temperature sensitivity of the sensor. During design it is important to avoid sample volume enlargements which can cause significant GC peak broadening.

Results. As a first step we selected the light source of the detector. The carefully chosen absorption line pair (near 4.3 µm) may provide sensitivity comparable to that of IRMS and ensure a low temperature sensitivity of $5 \cdot 10^{-4}$ ‰ /K. For the selected quantum cascade laser (QCL) we designed a laser mount which supports the temperature control of the laser. In addition, we designed and tested a laser focusing and spatial filtering optical system. The sensitivity of QEPAS detectors can be significantly increased using acoustic microresonators (AMR), but this configuration requires complicated optical alignment. Hence, we decided not to use an AMR. and for this detector configuration we carried out a SOLIDWORKS FloXpress flow analysis based on different sample introduction, sampling capillaries, and QTF housing. If the sample is vertically injected between the prongs of QTF, and the QTF is placed in a detector housing that has a flow cross sectional area comparable to the capillary cross-section, the flow remains laminar and similar to that in the sampling line. This type of housing can be implemented into a previously constructed and now available QEPAS cell what make the implementation of the detector easier. Instead of using an AMR, we were looking for alternative sensitivity-enhancement methods. All the preamplifiers dedicated for Quartz Enhanced PhotoAcoustic Spectroscopy (QEPAS) applications that have so far been reported in the literature have been based on operational amplifiers. The use of the voltage amplifier configuration is expected to result in an increase of QEPAS sensitivity by one to two orders of magnitude.



Schematic of the GC detector.

Noémi Utry, Christoph Haisch

Funding:
IWC

References:
(1) A.A. Kosterev; Y.A. Bakhirkin ; R.F. Curl; F.K. Tittel (2002) Quartz-enhanced photoacoustic spectroscopy. Opt. Lett., 27, 1902–1904.

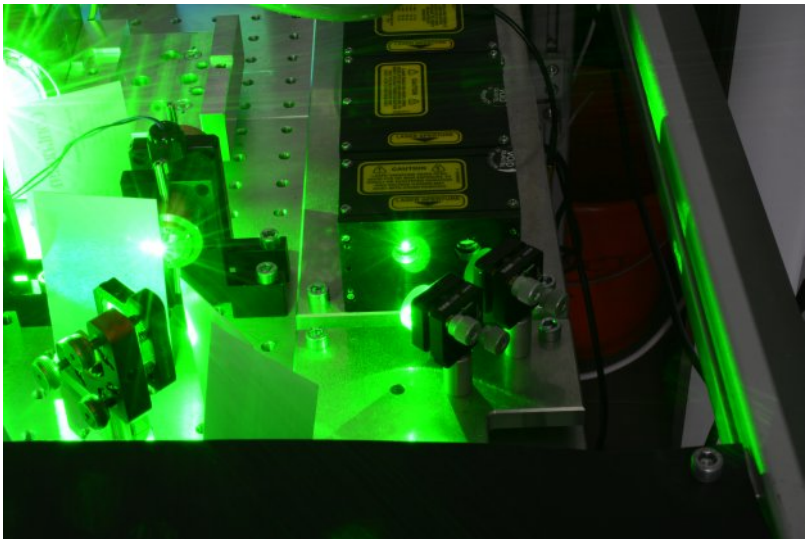
Development of a Mobile Time-Resolved Photoacoustic NO_2 and Soot Detector

Nitrogen oxides and soot particles emitted from combustion engines are considered the most prominent contaminants. Consequently, parallel monitoring of these two compounds with high temporal resolution and sensitivity helps to optimize low-emission engines.

Introduction. Current discussions on the air pollution in larger cities worldwide mostly focusses on particles and NO_x and particularly on NO_2, which are emitted from combustion engines. To further reduce the already low emission levels of these compounds, highly sensitive measurement procedures are required. Furthermore, significant emissions are generated not permanently, but only for very short time periods during the driving cycle, thus requiring a high temporal resolution and a large dynamic concentration range. Earlier developments showed that photoacoustic spectroscopy is the right tool for this challenging task [1]. In this project, we aim to improve the temporal resolution of a photoacoustic instrument significantly.

Results. A compact mobile photoacoustic detector for aerosol and gas analysis is developed. The detector is based on a rugged and compact frequency tripled Q-switched Nd:YAG-laser (Quantel Ultra 20) with second and third harmonic generator, which operates at a pulse repetition rate of 50 Hz. The three beams of the fundamental and the two harmonic wavelengths are separated and pass through photoacoustic cells. The pulse energy of the beams is in the range of 2 to 8 mJ. The acoustic signals are measured by microphones, amplified and analyzed by a mobile computer. Previous measurements with a similar photoacoustic cells have shown a sensitivity of up to 10^{-7} /m. Special attention was payed to the design of the photoacoustic cells in order to avoid or at least significantly reduce window contamination. First field tests of the new instrument are planned within the framework of our other projects, namely the Sub-Zero-Emissions- and the Down-to-Ten-project.

Peter Menzenbach, Christoph Haisch



Detail view of the photoacoustic cells during laser operation.

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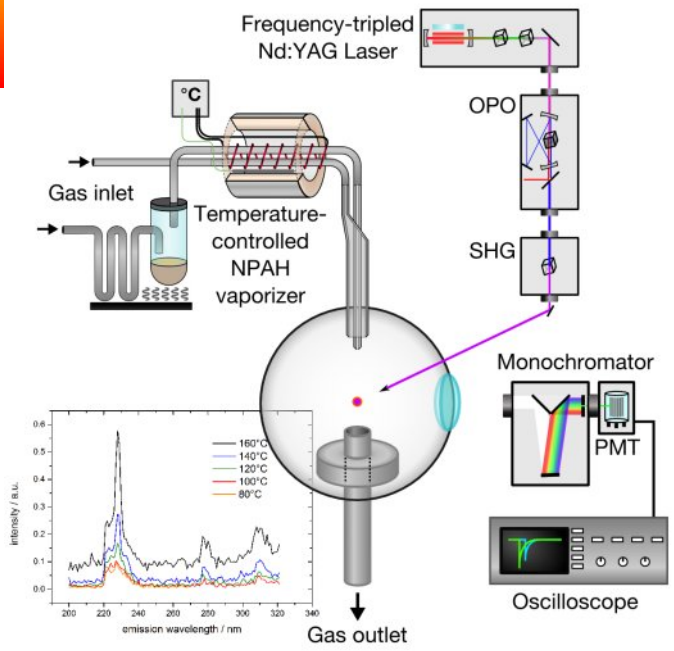
Funding:
IWC

Laser Photofragmentation for the Detection of Nitro-PAHs in Combustion Engine Exhaust

Nitro-PAHs emitted from a wide range of combustion processes are considered a significant mutagenic health issue. Photo-fragmentation has the potential to become highly sensitive detection technique of Nitro-PAHs.

Introduction. Nitrated polycyclic aromatic hydrocarbons (NPAHs), together with their parent com pounds, PAHs, are probably the abiotic class of substances, which is most harmful for human health, not only in the atmosphere, but in the total environment. More than a third of the mutagenic potential of ambient air is attributable to NPAHs. Our aim is to employ photofragmentation (PF), the process of breaking chemical bonds, for the on-line analysis of NPAHs. High sensitivities in the low ppb- or even ppt-range for PF-based gas phase analysis can be achieved. Different modalities shall be distinguished, regarding the fragmentation mechanism and the way of fragment detection. Resonant fragmentation allows for a rather straightforward system setup; a single laser pulse can be employed for fragmentation and photoionization.



Principle of NPAH via photofragmentation.

Experimental Approach. Depending on the photon energy employed, the fragments can be generated in an excited state, relaxing by optical emission. For nitrated aromatic compounds, a fragmentation process including elimination of nitrogen dioxide (NO_2) in an excited state and consecutive decay to excited atomic oxygen and excited nitric oxide (NO) is known. The excited NO molecules optically relax to the ground state. The source of the photons is a frequency doubled OPO, pumped by the third harmonic of a Q-switched Nd:YAG-laser.

Results. After extensive tests with different optical setups, we decided to stick to a rather simple detection system, comprising a grating monochromator and a photomultiplier tube. The optical setup of the existing detection system was optimized resulting in an increase of the beam intensity by a factor of 500. Special attention was payed to the design of the sampling cell, which needs to allow for laser excitation, laser pulse power monitoring, optical detection, pressure analysis in the cell, and sample gas in- and outlet including sheet flow.

Peter Menzenbach, Christoph Haisch

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M. Carrara, J. C.Wolf, R. Niessner (2010), Nitro-PAH formation studied by interacting artificially PAH-coated soot aerosol with NO_2 in the temperature range of 295-523 K, Atmospheric Environment 44, 3878-3885

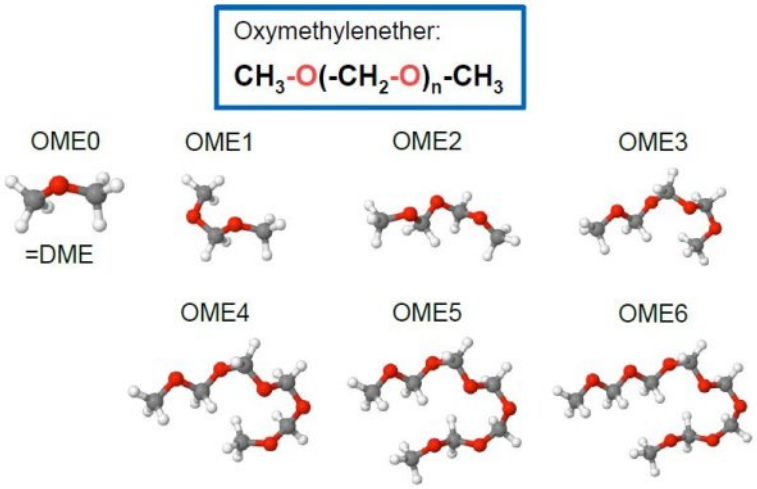
Funding:
DFG

Sub-Zero Emissions: Emission Control of Extremely Low Emission Engines

The much-debated gaseous and particulate emissions from combustion engines can be reduced significantly by the use of novel fuels. However, it has to be ensured that this approach does not result in the emission of other contaminants.

Introduction. Particulate and NO_x emissions are under critical discussion, banning of diesel-powered vehicles from cities is imminent. For various reasons, electro-mobility is not yet a real alternative, particularly not for heavy-duty vehicles. Fuels, which burn without the emission of soot, are an attractive alternative, since without the need for complex particle removing systems, the optimization of the whole engine and after-treatment system towards low gaseous emissions is possible. One highly promising candidate for a soot-free alternative for Diesel fuels is Oxymethylenether (OME), which also has the potential of CO_2 neutrality, as it can be produced completely from regenerative sources. As a combustion engine is in principle able to burn atmospheric particles, we are aiming for a combustion engine that does not emit any contaminants and even is able to clean particle-loaded intake air, based on the use of OME.

Obviously, this highly ambitious aim requires a thorough emission control with extreme sensitivity in order to proof the sub-zero-emission aim of the known contaminants, particularly soot and NO_x. However, the use of a new fuel also requires an extensive non-target screening for potential new contaminants. This analytical challenge needs to cover not only exhaust pipe analysis, but all process steps, as for example also potential emissions from degrading fuel constituents.



Molecular structure of the homologous series of the oxymethylen ethers (OMEs).

Experimental Approach. For the monitoring of particulate emissions, we intend to use an improved version of our photoacoustic soot sensor, which is meanwhile fully established as routine soot sensor for a wide range of applications. Other photoacoustic systems will be applied for the monitoring of N_2O and formaldehyde. Additionally, conventional particle analysis systems, optimized for ultrafine particles, will be employed.

In parallel, we are currently optimizing various offline sampling and analysis strategies, ranging from electron microscopy (SEM) coupled with EDX, ICP-MS, ion chromatography, to NAA and TXRF. The semivolatile organic fraction can be determined by means of a mass spectrometer. To enable direct analysis of the complex exhaust gas emission, we use a newly invented ionization source provided by our partners from Plasmion GmbH, a startup company founded in 2016 by an IWC alumnus. This MS system is currently equipped with a special evaporation system, which enables separation between gaseous, volatile, and semivolatile compounds associated with the particles.

Christoph Haisch

Funding:
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Cooperation:
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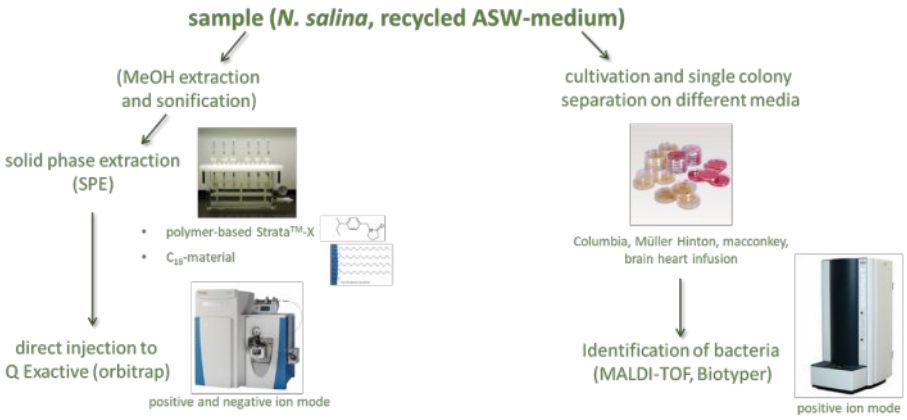
Chemical and Microbiological Analysis of Algae Growth Media

In the framework of the project “alpine algae kerosene”, algae can be squeezed to produce green kerosene. During the process of algae cultivation, secondary metabolites and bacteria can be accumulated in the cultivation medium, thus hindering algae growth and can lead to contamination of wastewater.

Introduction. The air traffic volume is predicted to increase at an annual rate of more than 5%, leading to a significant increase of kerosene consumption and CO_2 emission. Beyond increased efficiency of the air transport, the use of biogenic fuel can help archiving emission reduction despite the traffic increase. The partners in the project select and optimize microalgae in order to maximize the production of lipids, which are harvested and used to generate kerosene. While this approach is highly promising as it does not consume valuable clean water and agricultural area. Recirculation of the salty water further reduces consumption of raw material. However, it has to be made sure that during this recirculation, no algae toxins or other secondary metabolites hampering the cultivation, are produced. Growth of bacteria in the algae growth medium also has to be avoided. Our task in the project is monitoring of these components.



Schematic of the microbiological and chemical analysis of the algae growth medium.

Chemical Analysis. The complete sample, algae and medium, was first extracted by methanol and sonicated. Solid phase extraction by different extraction media was tested and then carried out by the polymere-based Strata-X SPE material. The extracted sample was then injected into the high-resolution mass spectrometer (ESI-Orbitrap). After the optimization of the MS analysis conditions, a continuous monitoring was carried out accompanying extensive algae growth experiments. As expected, no toxins were identified in these experiments, but it could be demonstrated that the MS method is also suitable to quantify typical fatty acids and chlorophyll.

Microbiological Analysis. Characterization of potential bacterial contaminants was carried out by a combination of cultivation with various media and subsequent identification by means of MALDI-TOF-MS, which then allows for the identification of the organisms based on the Biotyper-database. Different cultivation media, such as agar, Müller, BHI-Medium, macconkey were employed in order to avoid pre-selection by a selective medium. Typical organisms found in the in medium are *Exiguobacterium aurantiacum* und *Pseudomonas stutzeri*, aquatic microorganisms known to withstand various environmental conditions and saline media.

Christoph Haisch

Funding:
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Cooperation:
Werner Siemens-Lehrstuhl für Synthetische Biotechnologie, TUM; Lehrstuhl für Bioverfahrenstechnik, TUM; Lehrstuhl für Bioverfahrenstechnik, TUM; Bauhaus Luftfahrt e. V.

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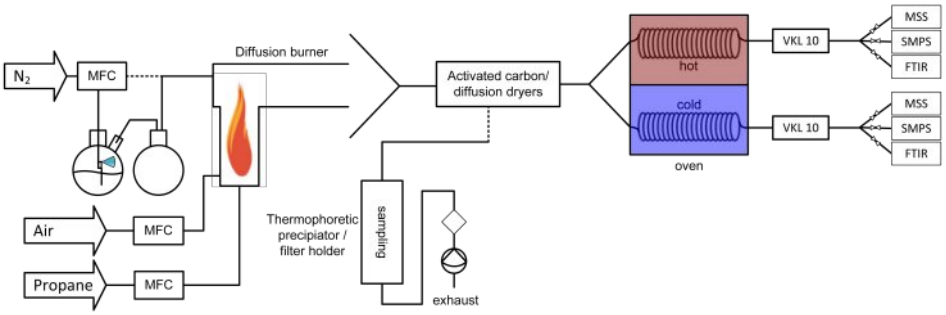
Gerssen A, Mulder PPJ, de Boer J (2011) Screening of lipophilic marine toxins in shellfish and algae: Development of a library using liquid chromatography coupled to orbitrap mass spectrometry. Anal Chim Acta 685 (2): 176-185.

Soot Oxidation Reactivity – Can it be Determined On-line?

Soot emissions are currently under constant discussion as soot impacts human health as well as the climate. There is a high need for a fast, on-line detection method for soot oxidation reactivity in order to remove soot particles from filters.

Introduction. Diesel soot is a major particulate pollutant and is classified as carcinogenic. Soot is theorized to have the second largest impact on global warming after CO_2. In North America and Europe, the main emitters of soot are diesel engines, which in consequence are equipped with particulate filters to minimize emissions. Regeneration of these filters is performed by oxidation (combustion) of the soot. Uncatalyzed oxidation requires temperatures > 600 °C in 5-10 Vol.-% O_2, resulting in poor fuel efficiencies. Surface coated catalysts or additives can lower these temperatures. Surface coated catalysts work, but show only loose soot-catalyst contact and are quite expensive. Additives are present during soot formation and lead to soot mixed internally with the catalyst and possible oxidation temperatures under 400 °C. As we have shown before, not only toxic Ferrocene- or Ce-based compounds can be used, but also cheap, inorganic and most likely non-toxic salts. Usually, soot oxidation reactivity is derived from temperature-programmed oxidation (TPO), microscopic techniques (i.e. HRTEM), Raman microspectroscopy (RM) or other spectroscopic techniques. Most of them require for filter sampling prior to the analysis, which is time-consuming and cost-intensive. Hence, there is a need for fast, online-capable method to characterize the oxidation reactivity of soot.



Schematic of our test system for the online soot reactivity monitor.

Experimental Approach. Our experimental setup for an online analysis essentially consists of an oven to treat the aerosols thermally. Downstream of the oven, we employed various detection systems, namely two scanning mobility particle sizer setups (SMPS), an infrared spectrometer (FTIR) and photoacoustic spectrometers (MSS, QuadPASS).

Results. The oven was first characterized using two SMPS systems in parallel, which let us to the conclusion that mean diameters are a good criterion to evaluate for soot oxidation reactivity. Highly reactive soot containing salt shows oxidation at lower temperatures compared to pure propane soot. We could also show that there is a clear temperature-dependent decrease in mass concentrations as measured by the photoacoustic spectrometers. In fact, we do not even need to observe full temperature programs like in TPO measurements, but can derive parameters related to the soot oxidation reactivity very fast and on-line by single-temperature measurements. This results in a huge reduction of measurement times, enables us to follow transient systems almost in real time, and gives rise to new possibilities regarding particle emission reductions.

Alexander Rinkenburger

Funding:
IWC

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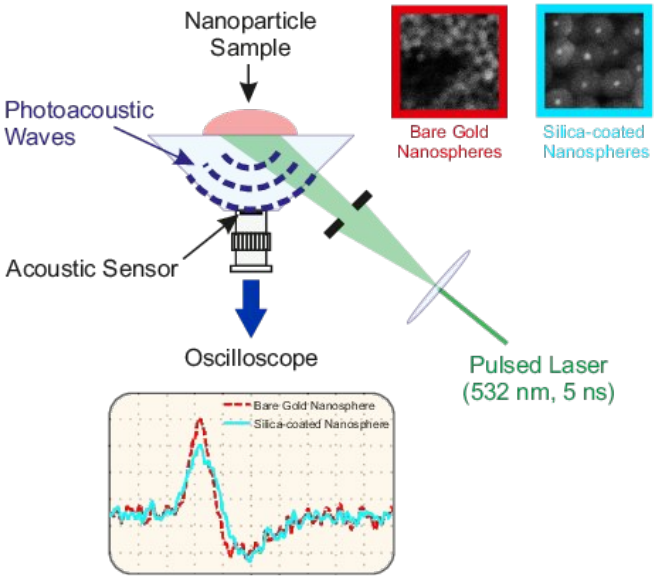
Experiment and Modeling of the Photoacoustic Response of Silica-coated Gold Nanospheres

Biomedical photoacoustic imaging applications can benefit from silica-coated gold nanoparticles. In this study, we demonstrate through complementary theoretical and experimental approaches the influence that silica coating on a gold nanosphere suspended in water has on the photoacoustic signal.

State of the Art. Biomedical photoacoustic imaging with nanoparticles enables targeted deep-tissue imaging. During photoacoustic excitation of nanoparticle colloidal suspensions, intensity-modulated light energy is absorbed by the nanoparticles, causing an increase in local particle temperature. The energy absorbed by the particle is rapidly transferred to the surrounding medium where the majority of the photoacoustic signal generation from thermoelastic expansion occurs.

Silica-coated gold nanoparticles introduce additional advantages in biomedical applications including increased colloidal stability, increased resistance to melting and increased surface area and porosity improving functionalization possibilities with targeting moieties. The effect of the silica coating on the fundamental photoacoustic signal generation process is still not theoretically well understood because the silica coating influences the energy transfer processes.



Photoacoustic sensor and sample measured signals from bare gold and silica-coated gold nanosphere suspensions

Results. We investigated theoretically and experimentally the photoacoustic signal generation by silica-coated gold nanospheres in water. Our theoretical model shows that the presence of a silica coating, which reduces the thermal resistance between the particle and water, reduces the photoacoustic signal amplitude. A broadening of the photoacoustic pressure pulse is also predicted from the presence of a silica coating. Our theoretical predictions are qualitatively consistent with our experimental results, where we excited suspensions of silica-coated gold nanosphere suspensions nanosecond-pulsed-laser illumination at 532 nm. Our measurements show the presence of silica coating on gold nanoparticles in suspension broadens the photoacoustic pressure pulse and reduces the measured photoacoustic signal amplitude.

Future work will examine sensitivity of the model to the level of porosity in the silica coating, and also extend the study to silica coating of gold nanorods.

Genny Pang, Christoph Haisch

References:
G. A. Pang, J. Laufer, R. Niessner, C. Haisch (2016) Photoacoustic Signal Generation in Gold Nanospheres in Aqueous Solution: Signal Generation Enhancement and Particle Diameter Effects. J. Phys. Chem. C, 120 (48), 27646-27656.

Funding:
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Cooperation:
Université Grenoble Alpes, CNRS, Lab. Interdisciplinaire de Physique. Grenoble, France

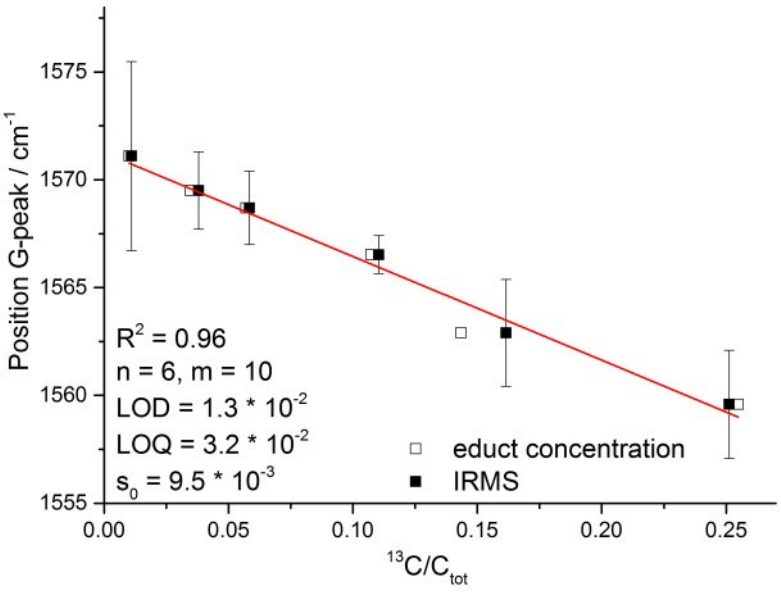
Stable-isotope Raman Microscopy for Analysis of Soil Organic Matter

The ability of soils to store rainwater is critical for agricultural yields. This ability is strongly linked to the amount and properties of soil organic matter.

State of the Art. Global climatic change is expected to alter the weather conditions leading to less frequent and more intense rainfalls. In order to ensure constant or increasing agricultural yields, soils need to be able to store as much water as possible. This ability of soil is linked to the amount and physicochemical properties of soil organic matter (SOM). While the addition of carbon sources (e.g. biochar) to soils can increase the ability of storing water in soil, the underlying mechanism remains unclear. If organic matter decays in soil, it is first transformed into humic substances, e.g. humic acids (HA). Therefore, the detection and characterization of HA in soil can help to gain a mechanistic understanding of the fate of added organic matter. For this, ^{13}C-stable isotope-labeled substances can be applied. The state-of-the-art methods for the analysis of soils, like ^{13}C nuclear magnetic resonance spectroscopy or nanoscale secondary ion mass spectrometry (NanoSIMS) can provide either the information on the structural composition of SOM or on the micro-scale resolved elemental and isotopic content However, the both methods are very time and cost intensive. Therefore, a fast and inexpensive method for spatially resolved analysis of SOM is required.

Analysis of ^{13}C-labeled Humic Acids. We examined the potential of stable-isotope Raman microspectroscopy (SIRM) for the evaluation of differently enriched ^{13}C-labeled humic acids as model substances for SOM. For this HA samples with known isotopic composition ($^{13}C/C_{total}$ ratios from 0.011 to 0.99) were synthesized.

By performing a pregraphitization, a suitable analysis method was developed to cope with the high fluorescence background. Results were verified against isotope ratio mass spectrometry (IRMS). The limit of quantification was 3.2 × 10^{-2} of $^{13}C/C_{total}$ for the region up to 0.25 of $^{13}C/C_{total}$ (see figure). The comparison with the NanoSIMS results suggests that SIRM can be used as a low-cost alternative for the analysis of soil samples. Thus, SIRM is well-suited for the quantitative analysis of stable isotope-labeled SOM with a spatial resolution in the micrometer range.



Linear regression for Raman data and $^{13}C/C_{tot}$.

Alexandra Wiesheu, Natalia P. Ivleva

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A. C. Wiesheu, R. Brejcha, C. W. Mueller, I. Kögel-Knabner, M. Elsner, R. Niessner, N. P. Ivleva (2017) Stable-Isotope Raman Microspectroscopy for the Analysis of Soil Organic Matter, Anal. Bioanal. Chem. 16th Anniversary Issue, DOI: 10.1007/s00216-017-0543-z.

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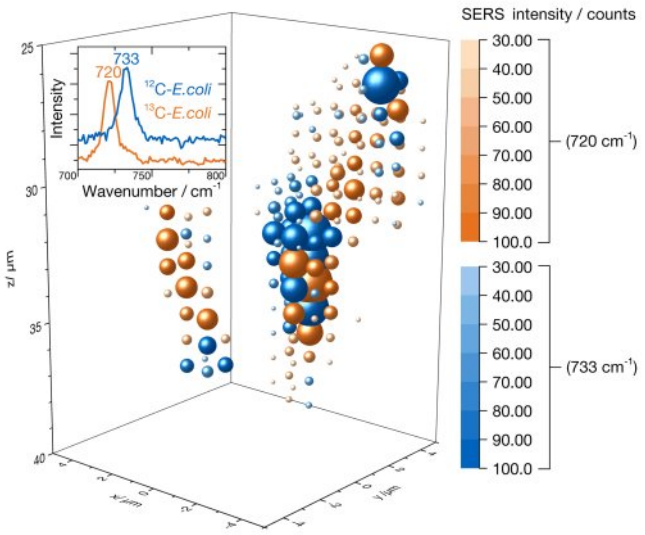
Cooperation:
Prof. Dr. I. Kögel-Knabner, PD Dr. C. Müller, Chair of Soil Science, TUM; R. Brejcha, Prof. Dr. M. Elsner, Helmholtz-Zentrum München (now at IWC-TUM); Prof. Dr. M. Wagner, Dr. M. Palatinszky, DOME, University of Vienna

3D Surface-Enhanced Raman Spectroscopy of Microbial Samples

Fundamental geochemical cycles are affected by microorganisms. As pathogens directly impact human health, sensitive detection and reliable characterization are mandatory for both public health as well as environmental studies.

State of the Art. Standard techniques for die discrimination of microorganisms include cell cultivation, fluorescence staining, immunoassays or genome sequencing. Spectroscopic approaches offer next to specific chemical information a high spatial resolution by combining spectrometry and optical microscopy. Raman micro-spectroscopy enables the discrimination of microbes at the single-cell level. Microorganisms appear under natural conditions in symbiotic communities. Hence, to decipher cellular heterogeneity, a combination of chemical information and spatial resolution is needed. Raman spectroscopy (RS) also provides evidence about the incorporation of stable isotopes through a typical red-shift of vibrational frequencies. Thus, the fate of isotopically labeled compounds can be traced. The low sensitivity of RS is due to the small scattering cross section of the Raman effect between incident photon and analyte. It can be improved by applying the effect of the surface-enhanced Raman scattering (SERS) which occurs in the immediate vicinity of nano-sized metal (Ag, Au) structures.



3D SERS image of $^{12}C/^{13}C$-labeled bacteria.

Analysis of ^{12}C and ^{13}C Cells. We examined the applicability of SERS to three-dimensional analysis of microbial samples. Therefore, bacteria were cultivated either at natural abundance of stable isotopes or with ^{13}C-labeled nutrients. By optical tweezing or embedding mixed cultures into a solid matrix, samples were tested for characteristic SERS signals and their red-shifted analoga. The three-dimensional visualization of artificial biofilms by SERS indicates the high potential of this analytical technique. The volume displayed in the image was measured in less than 5 minutes and yields information about the isotopic constitution of microbial cells three-dimensionally.

Experiments in a microfluidic setup proved the possible transfer of SERS onto sorting of microorganisms by optical trapping, reducing spectral integration times to 100 ms. Therefore, the implementation of SERS might facilitate microbial analysis.

Ruben Weiß, Natalia P. Ivleva

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Weiss R, Palatinszky M, Wagner M, Niessner R, Elsner M, Seidel M, Ivleva N P Surface-Enhanced Raman Spectroscopy of Microorganisms: Limitations and Applicability. Anal Chem (submitted).

Funding:
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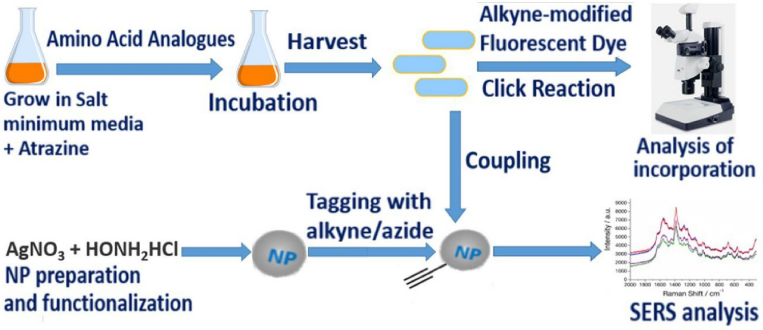
Cooperation:
Prof. Dr. M. Wagner, Dr. M. Palatinszky, DOME, University of Vienna

Development of Bioorthogonal Noncanonical Amino Acid Tagging – Surface Enhanced Raman Scattering (BONCAT-SERS) to Visualize Active Bacteria Responsible for Degradation of Organic Pollutants

Determination of active bacterial cells responsible for micropollutant degradation may help optimizing water treatment.

State of the Art. Removal of organic pollutants in water is crucial for drinking water quality and for aqueous ecosystems. Identification and characterization of microorganisms responsible for degrading organic pollutants is challenging and important for ensuring a sustained and cost efficient water treatment. State-of-the-art methods, like genetic screening, scanning electron and fluorescence microscopy do not disclose which bacteria are really metabolically active and growing. Stable isotope probing is expensive and may disturb the studied systems. Immunofluorescence analysis involves time- and cost-intense antibody production, and cannot explore uncultured microorganisms. Thus, a minimally invasive, rapid, and sensitive approach that combines visualization and characterization of active cells is warranted. The proposed approach pillars on a combination of bioorthogonal noncanonical amino acid tagging (BONCAT) with surface enhanced Raman scattering (SERS).



Schematic of the experimental coupling BONCAT and SERS

BONCAT and SERS Analysis. BONCAT relies on the in vivo incorporation of amino acids surrogates into bacterial biomass and is used to study individual cell response to external signals in situ. Amino acid analogues with modifiable tags are included into polypeptide chains by metabolically active cells. Active bacteria can subsequently be visualized by click chemistry: tags of the artificial amino acids are coupled to complementary chemical groups (azide-alkyne click chemistry) which facilitate visualization (fluorescent probes).

SERS is based on Raman spectroscopy and uses metal (Au or Ag) nanoparticles (NP) to enhance the Raman signal. SERS combines the ability of Raman microspectroscopy to deliver information about chemical structure at high spatial resolution with the advantage of specific visualization of cells in direct proximity to nanoparticles. The analysis is conducted in a rapid and non-destructive way.

Oleksii Morgaienko, Natalia P. Ivleva

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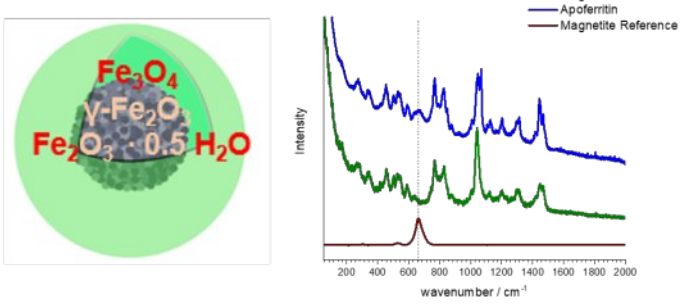
BIOMAG

Raman microspectroscopy is suitable for a non-invasive characterization of iron-containing proteins. A better understanding of the molecular processes of biomineralization mechanisms of the iron core in ferritin would be helpful for various promising applications.

State of the Art. Iron oxides with magnetic properties include magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) which have already been used as magnetic nanoparticles in many biological and medical applications such as magnetic cell tracking, hyperthermia and medical imaging. However, most of the current methods rely on chemically synthesized magnetic nanoparticles which have a negative effect regarding to their toxicity and biocompatibility. The use of iron-containing protein ferritin can help to overcome the aforementioned drawbacks. This protein is an intracellular spherical protein encapsulating an iron core inside the protein shell. Since the proposed crystalline structure of the iron core from natural ferritin is antiferromagnetic ferrihydrite like iron (III) oxide-hydroxide, it has aspired to modify natural ferritin into magnetoferritin by replacing ferrihydrite with magnetite and/or maghemite [1].

Characterization of Magnetoferritin. Raman microspectroscopy has shown to be an effective tool for an analysis of magnetite nanoparticles [2]. This method provides spectra which are unique to each compound and structure with a spatial resolution in µm-range. Hence, it is possible to distinguish between various iron oxides and hydroxides, as well as incorporated in ferritin despite of the complexity of the Raman signature of proteins.



Schematic drawing of Magnetoferritin (left) and Raman spectra of magnetoferritin (blue), apoferritin (ferritin without the core; green) and magnetite (red)

Differences in the Raman spectra of magnetoferritin and apoferritin can be seen. In the Raman spectrum of magnetoferritin we observe an additional broad band apart from the bands arising from molecular groups that belongs to the protein. This band has a maximum at 665 cm^{-1} which can be assigned to magnetite. As expected, this band cannot be seen in the Raman spectra of apoferritin, which is the protein without the iron core.

Further improvement of RM set up hold potential for a reliable and detailed analysis of iron modified protein complexes. Hence, it would help several studies, for instance, to get a knowledge of the origin and progress of neurological diseases (e.g. Alzheimer's disease).

Carolin Hartmann, Natalia P. Ivleva

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TUM International Graduate School of Sciencen and Engineering (IGSSE)

Cooperation:
Prof. G. Westmeyer, Chair of Biological Imaging, TUM

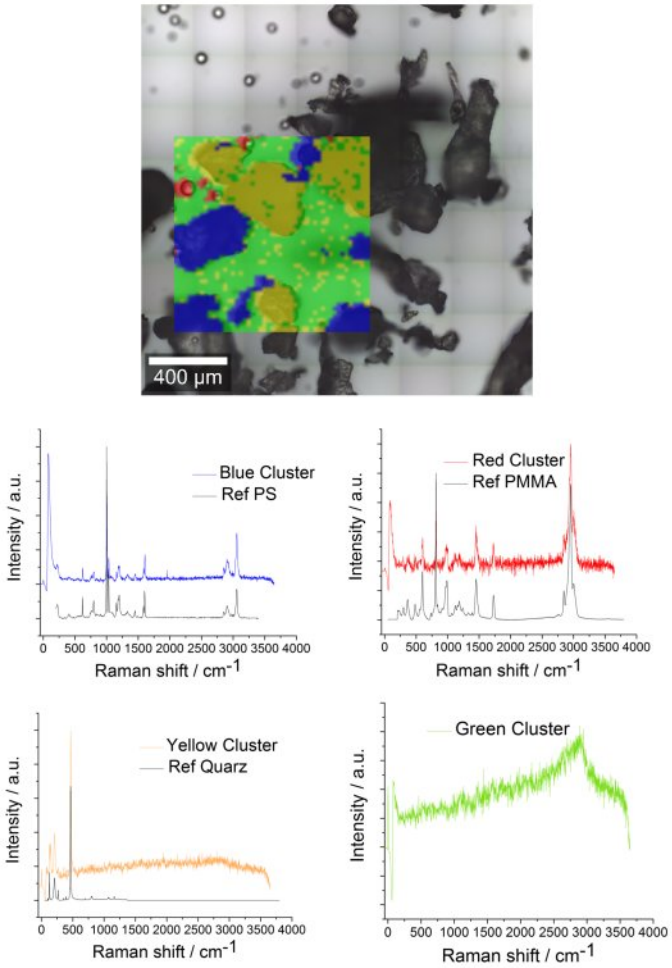
Microplastic in Environmental Samples – Selective Analysis with Raman Microspectroscopy

Microplastic particles are recognized as an environmentally relevant contaminant. For the estimation of its impact reliable and representative analytical methods are needed.

Background. The term Microplastic (MP) describes synthetic polymers in the form of particles, flakes or fibers within a size range of 1 µm – 5 mm. They are found in the aquatic and terrestrial environment and origin mostly from littering and subsequent degradation of bigger plastic waste. In the scientific community the hazard potential of MP is controversially discussed which is reflected by a great number of publications, both supporting and neglecting toxic patterns. To estimate the toxic potential, the information on the number and the size distribution of MP in different environmental bodies like freshwater habitats is needed. The BMBF project MiWa (microplastics in the water cycle) aims *inter alia* on the development and harmonization of analytical techniques. At the Institute of Hydrochemistry we focus on Raman microspectroscopy (RM).

RM Enables Differentiation Between MP and Non-MP Particulate Matter. The whole analytical process starting from sampling to sample preparation and ending with identification and data evaluation has been spearheaded in this project. The identification of MP with RM is unambiguous which is shown by the spectra in the lower part of the figure. Applying a laser on the sample results in inelastic scattering which is unique for each chemical bond and its molecular environment. Therefore, each polymer gives a characteristic fingerprint spectrum which enables a differentiation between polymer and other particulate matter, e.g. quartz. The figure shows a Raman Image. Each color corresponds to a Raman spectrum and thereby to a compound of the sample. The orange-colored quartz particles are thus distinguishable from the polymer particles which would not be possible from the optical image alone.

Philipp M. Anger, Natalia P. Ivleva



Raman Image and corresponding spectra of polymer and quartz particles.

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N. P. Ivleva, A. C. Wiesheu, R. Niessner (2017) Microplastic in Aquatic Ecosystems, Angew. Chem. Int. Ed. 56, 1720-1739.

Funding:
BMBF (MiWa – Microplastics in the Water Cycle)

Cooperation:
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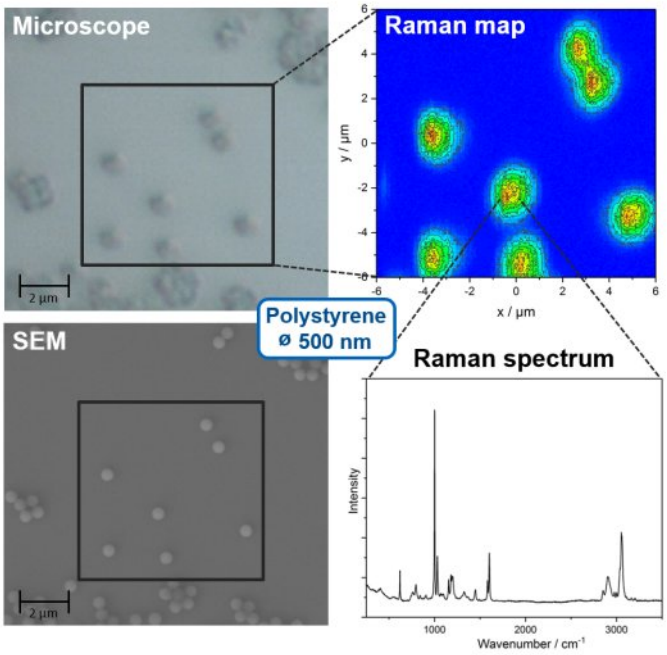
Raman Microspectroscopy for the Analysis of Nanoplastic Pollution

Even though very small plastic particles potentially pose a high toxicological risk, there is no established protocol for their detection. We employ Raman micro-qspectroscopy and field flow fractionation for the analysis of submicrometer plastic particles in environmental matrices.

State of the Art. Plastic is an omnipresent material in our modern society, which inevitably leads to a release into the environment, especially into marine and limnic systems. Here, plastic waste breaks down to microplastics (1 µm – 5 mm), subµplastics (0.1 µm – 1 µm) and nanoplastics (< 100 nm). Due to their small size, subµ and nanoplastics are suspected to have negative effects on the environment and organisms.



Raman spectrum and SEM image of 500 nm polystyrene spheres.

Raman Analysis of Sub-µm-Particles. The analysis of plastic particles can be performed by Raman microspectroscopy (RM), which is used for quantification and chemical identification. RM has been shown to be applicable to the analysis of particles up to 1 µm. We strive to extend its applicability to the sub-µm-range, supported by scanning electron microscopy (SEM). Initially, polystyrene particles of well-defined size are used as reference material for the Raman analysis (see figure). These studies are the foundation for preparing the method for the analysis of samples from environmental matrices.

Field Flow Fractionation. For the separation of particles from the sample matrix, we will use asymmetric flow field flow fractionation (AF^4), which is an established method in the analysis of engineered nanoparticles. AF^4 is easily coupled with other detection methods that are suitable for nanoparticle analysis, such as light scattering detectors. In this project a coupling of AF^4 and Raman microspectroscopy will be developed including a flow cell for the online Raman analysis of fractions in the effluent flow, combining the separation capabilities of AF^4 with the chemical identification of RM.

Christian Schwaferts, Natalia P. Ivleva

References:
N. P. Ivleva, A. C. Wiesheu, R. Niessner (2017) Microplastic in Aquatic Ecosystems, Angew. Chem. Int. Ed. 56, 1720-1739.

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BMBF SubµTrack

Cooperation:
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Raman Microspectroscopic Analysis of Microplastic Particles in Bivalve Samples

Bivalves taking up microplastic may be useful as bioindicators.

Background. Bivalves are used as bioindicators e.g. for 11 priority substances according to Directive 2008/105/EC (EC 2008) and 2013/39/EU (EC 2013). For microplastic (MP) particles several different sampling approaches exist. Mostly, sediments and the water body are sampled for evaluation of MP burden. Bivalves are filter feeders and therefore thought to work like passive samplers that accumulate MP. Together with the Bavarian Environment Agency we examine the uptake of MP by bivalves and evaluate their feasibility as samplers for MP.

Bivalves Exposed to PVC. First, the uptake of MP by the indigenous bivalve (Unio tumidus) under laboratory conditions was examined. Bivalves in fish tanks (see figure) were exposed to different well-defined amounts of PVC for different time spans including a PVC-free time after exposure. For the bivalves different digestion schemes were tested. The final filter samples were then analyzed by means of Raman microspectroscopy (RM). It was shown that bivalves take up PVC but can also get rid of it partially after an exposure free-time. PVC particles smaller than 50 µm are preferentially incorporated by bivalves and particles of this size are also preferentially found in the bivalves even after an exposure free-time. This hints to a possible translocation of MP <50 µm into the tissue of the bivalves. Further research, e. g. three dimensional RM may be helpful for better understanding of this mechanism.

Bivalves in a fish tank at LfU.

Bivalves Exposed to Sewage Treatment Plant Effluent Reveals low MP Burden. In a second approach indigenous bivalves (*Unio pictorium*) were exposed to the effluent of a sewage treatment plant. These bivalves were digested according to the scheme developed for the bivalves in the first experimental setup and analyzed only by means of RM. The exposure of bivalves to the sewage treatment plant effluent revealed a low contamination of the effluent with MP. This is in accordance with other studies that report MP retentions inside the sewage treatment plant of 90 % and more.

Philipp M. Anger, Alexandra C. Wiesheu, Natalia P. Ivleva

References:
N. P. Ivleva, A. C. Wiesheu, R. Niessner (2017) Microplastic in Aquatic Ecosystems, Angew. Chem. Int. Ed. 56, 1720-1739.

Funding:
Bavarian State Ministry of the Environment and Consumer Protection

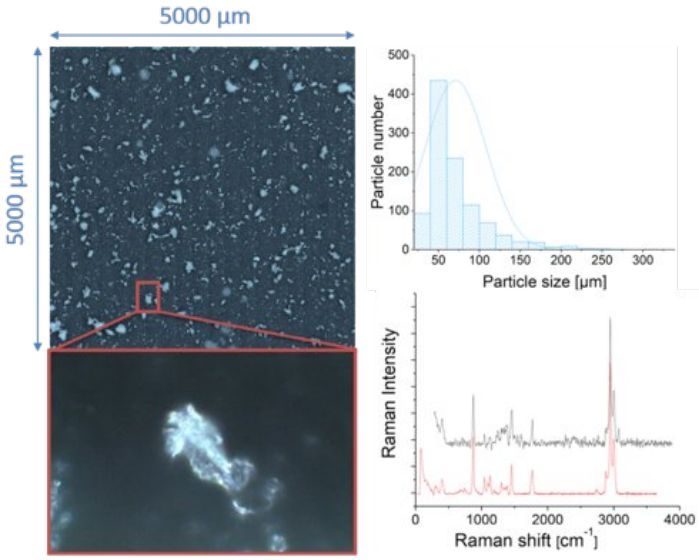
Cooperation:
Dr. J. Schwaiger, Dr. J. Domogalla-Urbansky, T. Geiger, Bavarian Environment Agency (Bayerisches Landesamt für Umwelt, LfU)

Automated Raman-Microspectroscopy of Biodegradable Polymer-Derived Microplastic

Are bioplastics a suitable alternative to conventional plastics regarding the microplastic problem? To answer this question, we develop Field-Flow-Fractionation and Raman-Microspectroscopy methods.

The microplastic problem.

Plastic is cheap, easy to manufacture and can be tailored to achieve desired properties, such as flexibility, durability, and color. This versatility makes plastics essential to modern life, especially in the packaging industry. Once plastic is exposed to UV-light or mechanical stress it slowly leaches additives or sheds microplastic (MP <5 mm). Thus microplastic can be found in the environment and has recently been shown in water from polyethylene terephthalate (PET) bottles. As food is often packaged in plastics and/or processed with plastic tools microplastic contamination is also possible. This leads to the question if biodegradable polymers are a prospective substitute for conventional polymers, as they have lower residence times in the environment and could be less potent contaminants as they are decomposed to water and carbon dioxide by bacteria, fungi or algae.



Raman analysis of PLA based microplastic.

Planned advances. Presently multiple procedures are available for the sampling, processing and analysis of MP samples. In this study enzymatic digestion, Field-Flow-Fractionation and automated Raman microspectroscopy will be developed and applied to MP and bio-MP in water, sediment and food samples.

MiPAq-Project. Our advances in MP characterization together with toxicological and interface interaction experiments by our partners will enable the comparison of the effects on the environment triggered by MP, bio-MP and naturally occurring particles. With this work, we hope to evaluate the environmental threat that MP poses and determine if bioplastics are a feasible solution for the microplastic problem.

Elisabeth von der Esch, Natalia P. Ivleva

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N. P. Ivleva, A. C. Wiesheu, R. Niessner (2017) Microplastic in Aquatic Ecosystems, Angew. Chem. Int. Ed. 56, 1720-1739.

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Bayer. Forschungsstiftung

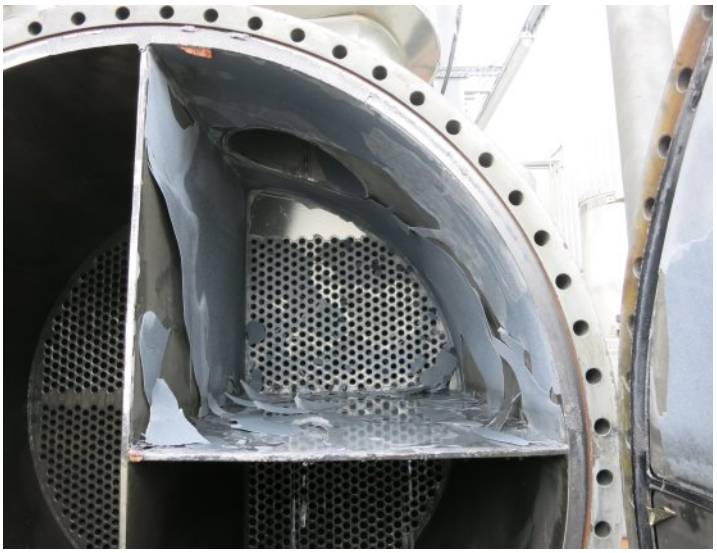
Cooperation:
Prof. Dr. J Geist, Dr. Beggel, Chair of Aquatic Systems Biology, TUM; Prof. Dr.-Ing. J.E. Drewes, Prof. Dr. T. Letzel, Chair of Urban Water Systems Engineering, TUM; Prof. Dr. H.C. Langowski, Chair of Food Packaging Technology, TUM; Prof. Dr. T. Hofmann, Dr. K. Glas, Chair of Food Chemistry and Molecular Sensory Science, TUM; Postnova Analytics GmbH; Münchner Stadtentwässerung; Qualitätsgemeinschaft Biomineralwasser e. V.; Neumarkter Lammsbräu Gebr. Ehrnsperger KG; Gehrig-Bunte Getränke Industrie GmbH & Co. KG; Bad Heilbrunner Naturheilmittel GmbH & Co. KG; Ludwig Stocker Hofpfisterei GmbH; HiPP-Werk Georg Hipp OHG; Huber SE; Huhtamaki Flexible Packaging Germany GmbH & Co. KG; Infiana GmbH & Co. KG; Allvac Folien GmbH

Scalings in Geothermal Facilities

Scalings are a widespread problem among geothermal plants which exploit the Malm Aquifer in the Bavarian Molasse Zone. They effect the technical and economic efficiency of geothermal plants.

Background. The majority of scalings observed at geothermal facilities exploring the Malm aquifer in the Bavarian Molasse Basin are carbonates. They are formed due to a disruption of the lime-carbonic-acid equilibrium during production caused by degassing of CO_2. These scalings are found in production pipes, at pumps and at filters and can nicely be described using hydrogeochemical models developed in previous projects.

Methods. In order to mitigate those scalings, the process of scaling formation and the underlying drivers have to be better understood. Therefore, scalings of all sections of geothermal facilities have been taken. So far, the database consists of scaling samples from 12 geothermal pumps, 5,000 m production pipe (sample interval 10-12 m), 11 evaporator revisions, 2 injection pipes and numerous filter elements. Samples were analysed by SEM-EDX, XRD and Raman spectroscopy and acid digestion to assess their chemical and mineralogical composition. Furthermore, the application of ultrasonic sensors for monitoring of the scaling thickness is tested. Parallel to that, a datalogger connected to a thermocouple and a cooler records the change of the thermal conductivity caused by the scalings. The monitoring should serve as an early warning of scaling formation at any section of the facility.



Precipitates at the inlet to a heat exchanger cause blocking and reduce the heat transfer.

Results. While $CaCO_3$ is the main component of the scalings, the initial scaling layer is often composed of iron sulfide or copper sulfide depending on the material, on which the scaling forms. The scaling thickness along the production pipes, together with operational data, allow to assess the average scaling rate for each depth, which is rising from bottom to top and lies in the order of 800 µm/10^6 m^3 for two independent facilities. The analysis of the crystal size and morphologies indicates different scaling processes along the production pipes. To determine the composition and mass of the scalings at the ground level facilities of 3 geothermal plants water samples were taken during the ground level cleaning processes. The cleaning was performed by pumping an inorganic acid through the ground level pipes. The hydrochemical composition of the reaction fluids reflects the general scaling composition. The mass balance showed that a total mass of 2.2 tons had accumulated in the ground level facilities for a produced water volume of 3.5 million m^3 . Although high, the observed scaling mass still represents only a fraction of the potential scaling mass which would form if a full equilibrium for $CaCO_3$ would establish.

Bernhard Köhl, Thomas Baumann

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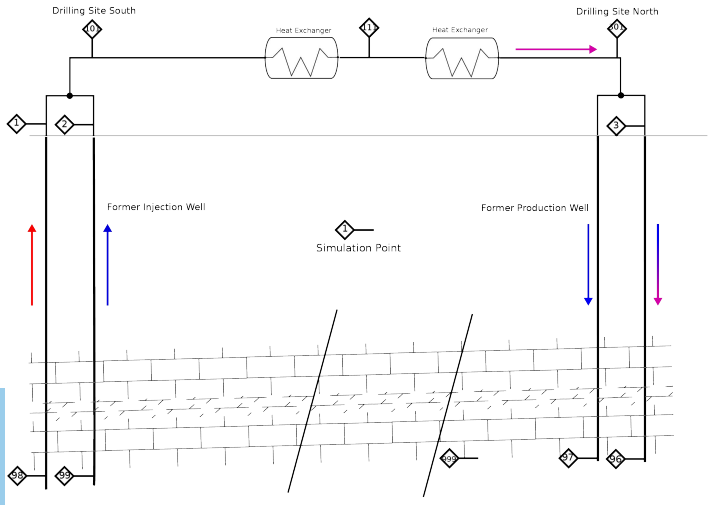
Operators of geothermal facilities in the Bavarian Molasse Basin; SWM Services GmbH

Large-Scale Geothermal Exploration of the Bavarian Molasse Basin

Coupling of geothermal facilities south of Munich (high temperatures, energy production) and north of Munich (lower temperatures, heat networks) seems to be a smart idea, but only if the operation does not cause disturbances on a regional scale

The Idea. The aim of the project is to use both bore holes of a geothermal site in the south to produce geothermal energy. Instead of injecting the water, which has now a temperature about 75 °C on site, the water is then pumped to the north and supplies heat to several district heating networks on the way. Finally the cool water in two injection wells of a former geothermal heat production site. This results in an increase in efficiency of about 70 %. However, the increased production and injection rates could also result in large-scale hydraulic changes and hydrochemical changes due to the mixing of different water compositions will affect the aquifer matrix.

The Model. Hydrogeochemical monitoring is vital to geothermal systems, since it is the most reliable source to assess the reactions in the reservoir. Monitoring data from two sites was used to establish a hydrogeochemical model for regional geothermal exploration. Using this PhreeqC based model, reactions in the aquifer can be predicted and quantified, which is crucial for plannning operations. The hydrochemical composition varies significantly between the southern and the northern sites, indicating a different lithostratigraphic setting.



Schematic of the large scale exploration with simulation breakpoints of the hydrogeochemical model.

Results. The hydrogeochemical model was validated with data from the Pullach facility and shows reliable results. As long as the bubble pressure is maintained while the produced water is still at reservoir temperatures precipitations in the facility can be maintained at a low level. Mixing of the two production wells with slightly different hydrochemical composition is further reducing the potential for precipitations. Producing water at a temperature of 130 °C in the south and cooling it to below 60 °C results in a strong undersaturation with respect to calcite (and dolomite). There is little potential for precipitations in the pipes, even if moderate degassing occurs. Injecting that water into the reservoir at the second site north of Munich will lead to a dissolution of more than 0.5 mmol/L calcite or araound 0.5 mmol/L dolomite until an equilibrium with the matrix is reached. Multiplied with volumetric flow rates exceeding 50 L/s this will result in dissolution rates on the order of cubic meters per week and a significant increase of the injectivity. These rates have been experimentally proven at the Pullach site, whereas the effects of increasing injectivity have been observed qualitatively at several other sites throughout the Molasse basin.

Martina Ueckert, Thomas Baumann

Funding:
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Cooperation:
Exorka GmbH; LIAG Hannover

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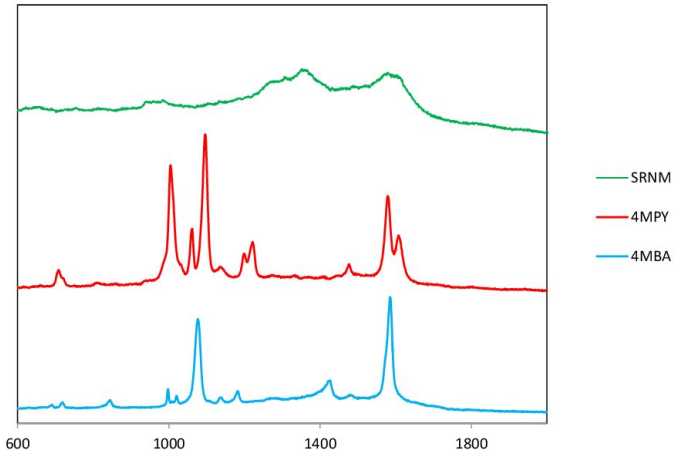
T. Baumann, Validation of hydrochemical analyses and gas concentrations of deep geothermal aquifers, In: , Proceedings, 41st workshop on geothermal reservoir engineering, 1269-1277, Stanford University, (2016).

Characterization of Coatings on Au@Ag Nanoparticles by Surface-Enhanced Raman Spectroscopy

The developments and innovations in nanotechnology and nanoscience have led to increasing use of engineered inorganic nanoparticles (EINP) in numerous fields which brings about the risk for their release into the environment.

Background. The fate of nanoparticles in the environment is dependent on their surface properties and also the stability of the nanoparticles in terms of dissolution and aggregation. For toxicity issues, it is important to study the chemical nature of nanoparticle clusters as well as their coatings. Coating of nanoparticles can alter the stability of the nanoparticles. Among different methods implemented to characterize the coating of nanoparticles, surface-enhanced Raman spectroscopy (SERS) has shown great capability for detection of coatings on noble metal nanoparticles. With developments and innovations in nanotechnology, core-shell nanoparticles have been observed to be more appropriate than pure metal nanoparticles. Au@Ag nanoparticles are similar to Ag nanoparticles but they show a higher SERS enhancement factor in comparison with Ag nanoparticles. Therefore, they can be more effective to gain more information regarding the coating process. We have studied the exchange and competition of different coating agents with different binding abilities to stimulate the release of nanoparticles into a water body with a number of potential coating agents.



Different coatings on Au@Ag nanoparticles as seen with SERS.

Results. Suwannee River Natural Organic Matter (SRNOM), 4-mercaptobenzoic acid (4-MBA) and 4-mercaptopyridine (4-MPY) were selected as sample molecules for the experiments. The results show that the 3 selected coating agents are successfully measured by SERS and coating takes place after 2 hours of shaking in an overhead shaker followed by two washing steps. In addition, it was observed that coating agents with higher binding ability can successfully compete with a coating agent which has a lower binding ability in cases where both coating agents are present in the media at the same time. When SRNOM and 4MBA were both present in the Au@Ag containing system, the spectrum showed the characteristic signals of 4-MBA demonstrating that 4-MBA has a higher affinity than SRNOM with nanoparticles. A similar result was observed for the mixture of 4-MPY and SRNOM and the spectrum showed the characteristics of 4-MPY. The competition between 4-MBA and 4-MPY showed that 4-MPY outcompeted 4-MBA and has a stronger bonding with the nanoparticles. The concentration of the coating agents plays also a role in this competition.

Sayed Amininejad, Natalia P. Ivleva, Thomas Baumann

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G. E. Schaumann, A. Philippe, M. Bundschuh, G. Metreveli, S. Klitzke, D. Rakcheeva, A. Grün, S. Kumahor, M. Kühn, T. Baumann, F. Lang, W. Manz, R. Schulz & H.-J. Vogel, Understanding biological effects of Ag- and TiO_2-nanoparticles in the environment: The quest for advanced analytics and interdisciplinary concepts, Sci. Tot. Environ. 535, doi:// http://dx.doi.org/10.1016/j.scitotenv.2014.10.035 (2015).

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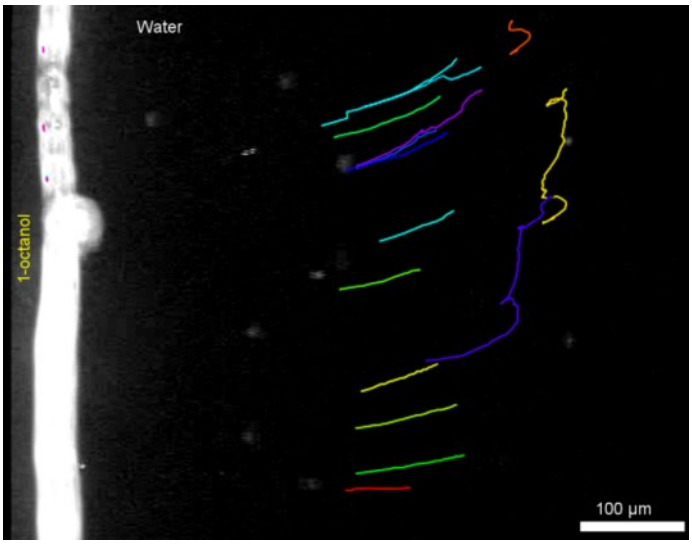
Cooperation:
Research Unit Internano

Mass Transfer at Interfaces to Nonaqueous Phases

Spontaneous interfacial convection currents have potential to affect local mass transfer rates at interfaces to nonaqueous phases and significantly contributes to mixing in the aqueous phase. In a combined experimental and numerical study, we aim at clarifying the hydrodynamics at fluid interfaces and quantifying the convective contribution on interfacial mass transfer processes.

State of the Art. Mass transfer at fluid interfaces is relevant in many environmental applications and provides the basis for numerous technically relevant processes of material separation and conversion. The mass transfer at fluid interfaces is associated with interface convection caused by local inhomogeneities at the interface. Hydrodynamic instabilities can generate a shear stress jump that results in spontaneous interfacial currents. These spontaneous convection currents can lead to an increased mass transfer and can have a significant influence on the efficiency of several process applications and on the subsurface transport of contaminants in groundwater.



Trajectories of single particles along an 1-octanol-water interface.

Tracking Fluid Motion With Particles. Using microfluidic systems and advanced experimental techniques it is possible to measure the fluid flow and mass transfer rates at these interfaces directly and to quantify the effect of the interfacial convection on the mass transfer rates at interfaces between a nonaqueous liquid and water with high temporal and spatial resolution. The use of fluorescent particles as well as the recording and analysis of their trajectories is intended to visualize interfacial processes and to quantify the mass transfer at fluid interfaces. Extended test series provide the experimental basis for quantifying and analyzing the impact of these extremely high flow velocities of the interfacial convection on the mass transfer rates at interfaces in subsurface aquatic environments.

Results. As a model for studying fluidic multiphase systems the combination of nonaqueous phase liquids (NAPL) – water – air is chosen. It was found that there is a fast-rotating convection current along an 1-octanol-water interface that shows a persistent movement in the form of a roll cell for min 99 h. We experimentally characterized the influence of physical and chemical parameters of the interfacial convection. The experimental results show that interfacial convections along fluid interfaces can be quantified and clarified by visualization combined with trajectory analyses and particle tracking methods. Due to the extremely high flow velocity, it can be postulated that the mass transfer along a fluid interface is not only diffusion limited and that the recorded interfacial convection has to be taken into account for further assessments of mass transfer rates in complex multiphase systems.

Carina Wismeth, Thomas Baumann

Funding:
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Cooperation:
Prof. Manhart, Chair of Hydromechanics, TUM

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Publications

Peer Reviewed Journals

S. Atashgahi, Y. Lu, Y. Zheng, E. Saccenti, M. Suarez-Diez, J. Ramiro-Garcia, H. Eisenmann, M. Elsner, A.J.M. Stams, D. Springael, W. Dejonghe H. Smidt, Geochemical and microbial community determinants of reductive dechlorination at a site biostimulated with glycerol, Environmental Microbiology 19 (2017), pp. 968–981, doi:10.1111/1462-2920.13531

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X. Dong, M.A. Jochmann, M. Elsner, A.H. Meyer, L.E. Bäcker, M. Rahmatullah, D. Schunk, G. Lens, R.U. Meckenstock, Monitoring microbial mineralization using reverse stable isotope labelling analysis by mid-infrared laser spectroscopy, Environ. Sci. Technol. 51 (2017), pp. 11876-11883, DOI: 10.1021/acs.est.7b02909

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S. Franke, Ch. Lihl, J. Renpenning, M. Elsner, I. Nijenhuis, Triple-element compound-specific stable isotope analysis of 1,2-dichloroethane for characterization of the underlying dehalogenation reaction in two Dehalococcoides mccartyi strains. FEMS Microbiology Ecology 93 (2017), 1 December, fix137, https://doi.org/10.1093/femsec/fix137

M. Gharasoo, M. Thullner, M. Elsner, Introduction of a new platform for parameter estimation of kinetically complex environmental systems, Environ. Modell. Softw. 98C (2017) pp. 12-20, DOI: 10.1016/j.envsoft.2017.09.005

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N. Ivleva, A. Wiesheu and R. Niessner; Microplastic Particles in Aquatic Ecosystems. Angewandte Chemie 56 (2017) 1720-1739

C. Kober, R. Niessner, M. Seidel. Quantification of viable and non-viable Legionella spp. by heterogeneous asymmetric recombinase polymerase amplification (haRPA) on a flowbased chemiluminescence microarray.Biosens. Bioelectron. 100 (2018) 49-55.

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A. Nistler, C. Hartmann, C. Rümenapp, M. Opel, B. Gleich, N. Ivleva, R, Niessner and M. Seidel; Production and Characterization of Long-term Stable Superparamagnetic Iron Oxide-shell Silica-core Nanocomposites. Journal of Magnetism and Magnetic Materials 442 (2017) 497-503

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J. Palau, R. Yu, S. Hatijah Mortan, O. Shouakar-Stash, M. Rosell, D. L. Freedman, C. Sbarbati, S. Fiorenza, R. Aravena, E. Marco-Urrea, M. Elsner, A. Soler, D. Hunkeler, Distinct Dual C–Cl Isotope Fractionation Patterns during Anaerobic Biodegradation of 1,2-Dichloroethane: Potential To Characterize Microbial Degradation in the Field, Environmental Science & Technology, 51 (2017), pp 2685–2694, http://dx.doi.org/10.1021/acs.est.6b04998

A. Rinkenburger, T. Toriyama, K. Yasuda and R. Niessner; The Catalytic Effect of Potassium Compounds in Soot Oxidation. ChemCatChem 9 (2017) 3513-3525

K. Thaler, R. Niessner and C. Haisch; Laboratory and Field Studies on a New Sensor for Dissolved HN2O. ABC 409 (2017) 4719-4727

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C. Torrentó, J. Palau, D. Rodríguez-Fernández, B. Heckel, A. Meyer, C. Domènech, M. Rosell, A. Soler, M. Elsner, D. Hunkeler, Carbon and Chlorine Isotope Fractionation Patterns Associated with Different Engineered Chloroform Transformation Reactions, Environ. Sci. Technol. 51 (2017), pp. 6174–6184, DOI: 10.1021/acs.est.7b00679

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Books

R. Niessner and Andreas Schäffer; Organic Trace Analysis. De Gruyter, Berlin, 357 pages

Conference Presentations

Oral Presentations

T. Baumann & M. Ueckert, Hydrogeochemical modelling of geothermal systems in the malm aquifer, EGU General Assembly, 23.-28.4.2017, Vienna.

T. Baumann & M. Ueckert, Hydrogeochemical modelling of deep geothermal systems in the Upper Jurassic aquifer, bavaria, Der Geothermie Kongress, 13.-14.9.2017, München.

T. Baumann, B. Köhl & M. Herbrich, Reasons for scalings in the geothermal cycle, Praxisforum Geothermie.Bayern, 12.9.2017, München.

J. Bemetz, A. Wegemann, R. Niessner, B. Gleich, M. Seidel, Folienmikroreaktor zur Synthese magnetischer Nanopartikeln gekoppelt mit einer NMR-basierten Methode zur online-Messung der Magnetisierbarkeit, ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

J. Bemetz, A. Wegemann, R. Niessner, B. Gleich, M. Seidel, In Situ T2-Relaxivitätsmessungen magnetischer Eisenoxid-Nanopartikel in kontinuierlichen Syntheseprozesse, 13. Dresdner Sensorsymposium, 4.-6.12.2017, Dresden, Germany.

J. Bemetz, C. Kober, R. Niessner, M. Seidel, A Low-Cost Minimal-Step Preparation Method for Mass Production of Antibody Microarrays from Polycarbonate, First European BioSensor Symposium 2017, 20.-23.3.2017, Potsdam, Germany

M. Elsner, Methodische Entwicklungen in Substanzspezifischer Isotopenanalytik: Neue Perspektiven zur Untersuchung von Reaktionen in komplexen Systemen, ANAKON 2017, Tübingen, Germany, 3-6 April 2017

M. Gharasoo, M. Elsner, M. Thullner, ReKinSim: A numerical platform for parameter estimation of kinetically complex environmental systems, 16th International Conference on Chemistry and the Environment (ICCE 2017), Oslo, Norway, 18-22 June 2017.

M. Gharasoo, M. Elsner, M. Thullner, How Porous Media Heterogeneities Influence Biodegradation of a Self-Inhibiting Substrate, Goldschmidt Conference, Paris, France, 13-18 August 2017.

B. Heckel, C. Lihl, K. McNeill, L. M. Douglas, S. Franke, A. Perez de Mora, A. H. Meyer, E. A. Edwards, I. Nijenhuis, B. Sherwood Lollar, M. Elsner, Which Mechanisms of Chlorinated Ethene Transformation Lie at the Heart of Reductive Dehalogenases?, Isotopes 2017, Ascona, Switzerland, 9-14 July 2017

C. Kober, J. Bemetz, A. Gründel, M. Petzold, C. Herr, C. Lück, R. Niessner, M. Seidel, Culture-independent serotyping of L. pneumophila in water and urine samples, 1st European & 10th German BioSensor Symposium, 20.-23.03.2017, Potsdam, Germany.

C. Kober, R. Niessner, M. Seidel, Rapid verification and risk assessment of Legionella by on-chip amplification and live / dead differentiation, ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

N. P Ivleva, P. Kubryk, R. Weiss, M. Seidel, R. Niessner, SERS in Combination with Stable Isotope Approach for Characterization of Bacteria at Single Cell Level, International Conference on Enhanced Spectroscopies (ICES), 4.-7.9.2017, Munich.

N. P. Ivleva, P. M. Anger, A. C. Wiesheu, R. Niessner, Raman Microspectroscopy for Analysis of Microplastic in Environmental Samples, 14th Confocal Raman Imaging Symposium, 25.-27.9. 2017, Ulm. Invited.

N. P. Ivleva, A. C. Wiesheu, R. Weiss, P. Kubryk, R. Brechja, M. Elsner, C. W. Müller, I. Kögel-Knabner, R. Niessner, On the Potential of Stable Isotope Raman Microspectroscopy (SIRM) for Nondestructive Spatially-resolved Analysis of Environmental Samples, ANAKON 2017, 3.-6.4.2017, Tübingen.

S. Marozava, K. Kundu, B. Ehrl, J. Mehrl-Pham, M. Elsner, Physiology of the atrazine degrader Arthrobacter aurescens TC1 under low dilution rates in chemostats, retentostats and at zero growth, The International Society for Subsurface Microbiology (ISSM) 2017 Conference, Rotorua, New Zealand, 6-10th of November, 2017

R. Niessner, A. Rinkenburger and K. Yasuda, The catalytic effect of potassium salts in Diesel soot oxidation, 36th American Association for Aerosol Research Conference (AAAR) 2017, 16.10.2017 - 20.10.2017, Raleigh, North Carolina, USA.

R. Niessner, Analytische Chemie - Quo vadis?, ANAKON 2017, 3.-6.4.2017, Tübingen.

R. Niessner, Diesel exhaust - analytically a hard nut to crack, EUROANALYSIS, 30.8.2017, Stockholm

A. Rinkenburger, T. Toriyama, K. Yasuda and R. Niessner, The Catalytic Effect of Potassium Compounds in Soot Oxidation, European Aerosol Conference (EAC) 2017, 27.08.2017 - 01.09.2017, Zürich, Switzerland.

M. Seidel, Bioanalytische Messmethoden zur schnellen Quantifizierung von pathogenen Bakterien und Viren, ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

M. Seidel, Rapid methods for the quantification of pathogenic bacteria and viruses in water, HELENA Seminar “Environmental Sciences”, 06.11.2017, Helmholtz Zentrum München, Neuherberg, Germany.

M. Seidel, Applications of novel methods for quantification of water-borne pathogens in water, METAWATER Workshop “Lessons learned for improving the safety of irrigation water in Europe”, 10.10.2017, Munich, Germany.

M. Seidel, Rapid concentration and microarray-based detection methods for pathogens in water and food, Batsheva de Rothschild Seminar on New Concepts in Biosensing, 12.-16.2.2017, Dead Sea, Israel.

M. Seidel, Chemiluminescence microarrays in analytical chemistry, AC@TUM Get Together Symposium,24.-25.4.2017, TUM Science and Study Center Raitenhaslach.

M. Seidel, Schnellmesstechnik zum Nachweis von Legionellen – Welche Methoden gibt es? VDI Wissensforum – 1. VDI Fachkonferenz: Legionellen aus Verdunstungskühlanlagen, 21.-22.11.2017, Düsseldorf, Germany

M. Ueckert & T. Baumann, Quantification of the reactions in heat storage systems in the malm aquifer, EGU General Assembly, 23.-28.4.2017, Vienna.

M. Ueckert & T. Baumann, Hochtemperaturaquiferspeicher im bayerischen Molassebecken, Der Geothermie Kongress, 13.-14.9.2017, München.

R. Weiss, P. Kubryk, M. Seidel, R, Niessner, M. Elsner, N. P. Ivleva, Applicability of SERS in Combination with Stable Isotope Approach for Characterization of Microorganisms at Single Cell Level, 11th Workshop “FT-IR Spectroscopy in Microbiological and Medical Diagnostics” 2017, 19.-20.10.2017, RKI, Berlin.

C. Wismeth & T. Baumann, Mass transfer ar interfaces between water and non-aqueous liquids: Marangoni and others, IMMENS Workshop 5.-6.10.2017, Centre of Integrated Petroleum Research (CIPR), Uni Research, Bergen, NO.

C. Wismeth, M. Manhart, R. Niessner & T. Baumann, Quantification of the mass transfer at fluid interfaces in microfluidic channels, EGU General Assembly, 23.-28.4.2017, Vienna.

Poster Presentations

P. M. Anger, C. C. Neumann, R. Niessner, N. P. Ivleva, Microplastic in Environmental Samples: Selective Analysis by means of Raman microspectroscopy, ANAKON 2017, 3.-6.4.2017, Tübingen.

P. M. Anger, C. C. Neumann, R. Niessner, N. P. Ivleva, Selective Microplastic Analysis by Means of Raman Microspectroscopy, WASSER 2017, 22.-24.5.2017, Donaueschingen.

P. M. Anger, R. Niessner, M. Elsner, N. P. Ivleva, Selective Analysis of Microplastic by Raman Microspectroscopy, Wissenschaftsforum Chemie – 150 Jahre GDCh, 10.-14-9.2017, Berlin.

P. M. Anger, R. Niessner, M. Elsner, N. P. Ivleva, Raman Microspectroscopy for Analysis of Microplastic, 14th Confocal Raman Imaging Symposium, 25.-27.9.2017, Ulm.

S. Amininejad, R. Niessner & T. Baumann, SERS investigation of coatings on thermal modified titanium dioxide nanoparticles, EGU General Assembly, 23.-28.4.2017, Vienna.

S. Amininejad, R. Niessner & T. Baumann, Observation of coating on titanium dioxide nanoparticles by surface-enhanced raman scattering, ANAKON, 3.-6.4.2017, Tübingen.

S. Amininejad, R. Niessner & T. Baumann, Observation of coating on tio2 nanoparticles by surface-enhanced raman scattering, NanoImpact Conference, 12.-17.3.2017, Monte Verita, Switzerland.

B. N. Ehrl, Kankana Kundu, Sviatlana Marozova, Martin Elsner, Substanzspezifische Isotopenanalytik zur Untersuchung von Membranprozessen bei dem Bioabbau von Pestiziden, ANAKON 2017, Tübingen, Germany, 3-6 April 2017

B. N. Ehrl, Kankana Kundu, Sviatlana Marozova, Martin Elsner, Nicht können oder nicht wollen? Wie Bioverfügbarkeitslimitierungen physiologische Veränderungen der Zelle auslösen und so den Abbau von Schadstoffen zum Erliegen bringen können, Wasser 2017, Donaueschingen, Germany, 22-24 May 2017

B. N. Ehrl, Kankana Kundu, Sviatlana Marozova, Martin Elsner, Decreased contaminant degradation rates caused by physiological adaptations and mass transfer limitations, Isotopes 2017, Ascona, Switzerland, 9-14 July 2017

C. Hartmann S. Pettinger, C. Massner, G. Westmeyer, R. Niessner, N.P. Ivleva, Non-destructive Chemical Analysis of Iron-containing Proteins Performed by Raman Microspectroscopy, ANAKON 2017, 3.-6.4.2017, Tübingen.

C. Hartmann S. Pettinger, C. Massner, M. Elsner, G. Westmeyer, R. Niessner, N.P. Ivleva, Raman Analysis of Iron-containing Proteins, 14th Confocal Raman Imaging Symposium, 25.-27.9.2017, Ulm.

C. Hartmann S. Pettinger, C. Massner, M. Elsner, G. Westmeyer, R. Niessner, N.P. Ivleva, Modified Protein Complexes for Non-invasive Molecular Control, 11th Workshop “FT-IR Spectroscopy in Microbiological and Medical Diagnostics”, 19.-20.10.2017, Berlin.

C. Kober, R. Niessner, M. Seidel, Microarray-based rapid verification and risk assessment of viable Legionella by on-chip amplification, The 9th International Conference on Legionella, 26.-30.09.2017, Rome, Italy.

C. Kober, A. Gründel, J. Bemetz, M. Petzold, C. Herr, C. Lück, R. Niessner, M. Seidel, Microarray-based serotyping of Legionella pneumophila for the risk assessment of Legionella expositions for water and urine samples, Wasser 2017, 22.-24.05.2017, Donaueschingen, Germany.

B. Köhl & T. Baumann, Scalings im geothermiekreislauf, Der Geothermie Kongress, 13.-14.9.2017, München.

B. Köhl, J. Grundy & T. Baumann, Ripple scalings in geothermal facilities, a key to understand the scaling process, EGU General Assembly, 23.-28.4.2017, Vienna.

G. Metreveli, S. Kurtz, A. Philippe, N. Tayyebi, F. Seitz, R. R. Rosenfeldt, A. Grün, S. K. Kumahor, T. Baumann, M. Bundschuh, F. Lang, S. Klitzke, W. Manz, R. Schulz, H.-J. Vogel & G. E. Schaumann, A floodplain mesocosm study: Distribution, mobility, aging, and functioning of engineered silver nanoparticles at the aquatic-terrestrial interface, EGU General Assembly, 23.-28.4.2017, Vienna.

A. Melsbach, V. Ponsin, C. Torrentó, R. Bakkour, C. Lihl, V. Prasuhn, T. B. Hofstetter, M. Elsner, D. Hunkeler, ð^{15}N Isotope Analysis to Investigate Desphenylchloridazon Degradation: Method Development, , Isotopes 2017, Ascona, Switzerland, 9-14 July 2017

V. K. Meyer, R. Niessner, M. Seidel, Monitoring der Verbreitungswege von veterinärmedizinisch eingesetzten Antibiotika mittels eines Multiplex-Chemilumineszenz-Mikroarrays. ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

O. Morgaienko, N. P. Ivleva, M. Elsner, Development of Bioorthogonal Noncanonical Amino Acid Tagging – Surface Enhanced Raman Scattering Approach to Visualize Bacteria Responsible for Degradation of Organic Micropollutants, 14th Confocal Raman Imaging Symposium, 25.-27.9.2017, Ulm.

O. Morgaienko, M. Elsner, N. P. Ivleva, Visualization of Pollutant Degrading Bacteria via Bioorthogonal Noncanonical Amino Acid Tagging Coupled to Surface-enhanced Raman Scattering, 11th Workshop “FT-IR Spectroscopy in Microbiological and Medical Diagnostics”, 19.-20.10.2017, RKI, Berlin.

A. Nistler, C. Rümenapp, M. Opel, B. Gleich, N. Ivleva, R. Niessner, M. Seidel, Evaluation of Long-Term Stability of Iron Oxide–Shell Silica-Core Nanocomposites by Raman Microspectroscopy and SQUID Magnetometry, ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

A. Rinkenburger and R. Niessner, The catalytic effect of K-compounds in soot oxidation - Is there a correlation between structure and reactivity?, Anakon 2017, 03.04.2017 - 06.04.2017, Tübingen, Germany.

S. Schäfer, G. Valenza, C. Calomfirescu, S. Huber, C. Höller, R. Niessner, M. Seidel, Development of an on-chip HDA-assay for the fast detection of ESBL-producing bacteria in irrigation water, ANAKON Conference, 03.-06.04.2017, Tübingen, Germany.

S. Schäfer, R. Niessner, M. Seidel, Pathogens in irrigation water? Harmonization of methods and protocols for analysis in Europe, Wasser 2017, 22.-24.05.2017, Donaueschingen, Germany.

K.Stutzer, Reinhard Niessner, Dietmar Knopp, Development and validation of an immunological screening method for the detection of toxicologically relevant pyrrolizidine alkaloids (PAs) in herbal tea and related matrices, ANAKON Conference, 03.-06.04.2017, Tübingen

M. Ueckert, C. Wismeth & T. Baumann, Crystallization of calcium carbonate in a large scale field study, EGU General Assembly, 23.-28.4.2017, Vienna.

M. Ueckert, C. Wismeth & T. Baumann, Crystallization of calcium carbonate in a large scale field study, Der Geothermie Kongress, 13.-14.9.2017, München.

R. Weiss, R. Niessner, M. Seidel, N. P. Ivleva, Raman Microspectroscopy for Non-invasive, Three-dimensional Analyses of Biofilms, ANAKON 2017, 3.-6.4.2017, Tübingen.

R. Weiss, R. Niessner, M. Seidel, N. P. Ivleva, Raman-Mikrospektroskopie für zerstörungsfreie, dreidimensionale Analysen von Biofilmen, WASSER 2017, 22.-24.5.2017, Donaueschingen.

R. Weiss, R. Niessner, M. Elsner, M. Seidel, N. P. Ivleva, Raman Microspectroscopy for Non-invasive, Three-dimensional Analyses of Biofilms, 11th Workshop "FT-IR Spectroscopy in Microbiological and Medical Diagnostics", 19.-20.10.2017, Berlin.

A. C. Wiesheu, P. M. Anger, J. Domogalla-Urbansky, T. Geiger, H. Ferling, J. Schwaiger, R. Nießner, N. P. Ivleva, Mikroplastik in Frischwasserorganismen – Raman-mikrospektroskopische Untersuchungen, ANAKON 2017, Tübingen, 03. – 06.04.2017 (best poster award).

A. C. Wiesheu, R. Brejcha, M. Elsner, R. Nießner, N. P. Ivleva, Organische Substanzen im Boden zur Erhöhung der Wasserrückhaltefähigkeit: Analyse mittels Stabilisotopen-Raman-Mikrospektroskopie WASSER 2017, 22.-24.5.2017, Donaueschingen.

C. Wismeth, M. Manhart, R. Niessner & T. Baumann, Quantification of the mass transfer at fluid interfaces in microfluidic systems and the Marangoni effect, ANAKON, 3.-6.4.2017, Tübingen.

Invited Lectures

T. Baumann & M. Ueckert, Hydrogeochemical Modelling of Geothermal Systems in Carbonates, Univ. Bergen, Dept. of Mathematics, 9.10.2017, Bergen, NO.

M. Elsner, Methodische Entwicklungen in Substanzspezifischer Isotopenanalytik: Neue Perspektiven zur Untersuchung von Reaktionen in komplexen Systemen, GDCh Kolloquium und Antrittsvorlesung, TU München, 25.7.2017, München

M. Elsner, Advancements in Compound-specific Isotope Analysis (CSIA): Perspectives for Studying Reaction Mechanisms in Complex Systems, University of Regensburg, GDCh Kolloquium, 4.12.2017, Regensburg

R. Niessner, Particles - A Challenge (Not Only) for Analysts, TU Wien, 29.4.2017, Wien

R. Niessner, Modern Spectroscopy as a Tool for Aerosol Characterization, Vienna Aerosol Summer School, Universität Wien,13.7.2017, Wien

R. Niessner, Grenzwertüberschreitungen durch Dieselabgas: Eindeutig messbar?, GDCh Wissenschaftsforum, 12.9.2017, Berlin

N. P. Ivleva, Microplastic in Environmental Samples: Focus on Raman Microspectroscopic Analysis, University of Vienna, Department of Environmental Geosciences, 26.6.2017, Vienna, Austria.

N. P. Ivleva, Raman Microspectroscopy for Nondestructive 2D and 3D Analysis of Environmental Samples, Department of Bioengineering and Electrical and Computer Engineering, Northeastern University, 9.5.2017, Boston, U.S.A.

Scientific Committees

T. Baumann, Fate and Transport of Biocolloids and Nanoparticles in Soil and Groundwater, EGU General Assembly, 23.-28.4.2017, Vienna (Convener)

M. Elsner, Isotopes 2017 - The Cross-Disciplinary Conference on Stable Isotope Sciences, Ascona, Switzerland, 9-14 July 2017

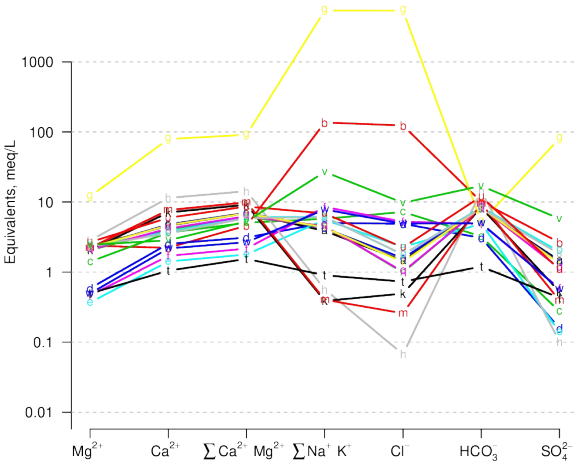
R. Niessner, 13. Dresdner Sensor Symposium, 4.-6..12.2017 (Programme committee)

Hydrochemical consulting

Mineralisation control analyses: Bad Abbach, Bad Aibling, Bad Birnbach, Bad Füssing, Bad Griesbach, Bad Gögging, Bad Wiessee, Bad Wimpfen, Bad Wörishofen, Bayreuth, Erding, Hölle, Kondrau, Neumarkt i. d. Opf., Sibyllenbad, Straubing, Weißenstadt

Hydrogeological and hydrochemical expertises (mineral water, spa water): Bad Endorf, Bad Rodach, Bad Steben, Bayreuth, Breitenbrunn, Siegsdorf

Deep Hydrogeothermal Energy Exploration: Aschheim, Freiham, Geretsried, Holzkirchen, Pullach, Sauerlach, Waldkraiburg



Schoeller diagram of the analyses performed in 2017

Theses

PhD Theses

Dipl. Phys. Christoph Berger: Photoakustische Spektroskopie zur Emissionsüberwachung

Dipl. Bio.-Ing. Dennis Elsäßer: Verbundverfahren zur schnellen Aufkonzentrierung von Bakterien und Viren für das Inline-Monitoring von Trink- und Rohwasser

MSc Chem. Benjamin Heckel: Investigating Mechanisms of Reductive Chlorinated Hydrocarbon Degradation with Compound-Specific Isotope Analysis

MSc Biol. Johannes Ho: Molecular biological live/dead differentiation for viruses and bacteria after disinfection

MSc Chem. Bettina Kiwull: Untersuchungen zu diffusiophoretischer Abscheidung, Dieselabgaspartikelzählung und Bioaerosolerzeugung

MSc Chem. Patrick Kubryk: Stabilisotopen-Raman-Mikrospektroskopie zur Untersuchungen von Mikroorganismen

Dipl. Biol. Michael Schmalenberg: Entwicklung fluoreszenzbasierter Immunoassays für den neuen Inflammationsmarker Chitinase 3-like 1 (YKL-40)

MSc Chem. Clemens Thaler: Anwendungen der photoakustischen Spektroskopie zur zeitaufgelösten Beobachtung der N_2O-Emission aus Kläranlagen und der Photokinetik in suspendierten Einzelnpartikeln

MSc Chem. Alexandra Wiesheu: Raman-Mikrosspektroskopie zur Analyse von organischen Bodensubstanzen und Mikroplastik

Exam. Lebensm. Chem. Anika Wunderlich: Antikörper Mikroarrays zur Analyse von Legionella Pneumophila in Wasser und anderen pathogenen Mikroorganismen im Lebensmittel

M.Sc. Theses

BSc Fabian Hagen: Experimental and Numerical Investigations on the Application of Ranque-Hilsch Vortex Tubes in Particle Technology

BSc Thorsten Hörbrand: Comparison of Hydrogeochemical Model Approaches for Problems in Deep Geothermal Energy

BSc Ryan Karongo: Biofunctionalization of Plasmonic Substrates Using Murine and Plant Based Antibodies for the Determination of Microcystin-LR and Diclofenac

BSc Constanze Neumann: Spektroskopische Analyse von Mikro- und Makroplastik (Sedimentproben aus Oberflächengewässern des Trinkwassereinzugsgebietes im Mangfalltal und im Trinkwasserbereich

BSc Selina Muffler: Hydrogeochemische Simulation eines Hochtemperatur-Aquiferspeichers im Malm-Aquifer

BSc Korbinian Sinzinger: Enzymatic Saccharification of Scenedesmus obtusiusculus Biomass using HT-PMP-UHPLC-UV-ESI-MS

B.Sc. Theses

Matthias Bauer: Mikrofluidische Synthese magnetischer Nanopartikel und Funktionalisierung zur detection von Mikroorganismen über NMR-T2-Relaxation

Christina Glaubitz: Examination of Dissolution Processes at Fluid Interfaces in Microfluidic Systems

Markus Heindl: Synthesis, characterization and immobilisation of Au@Ag nanoparticles for surface enhanced Raman scattering

Oliver Jacob: Infrarotspektroskopische Untersuchungen an verschiedenen Rußspezies

Aljoscha Körber: Raman Mikroskopie an suspendierten Partikeln

Ken Ong: Immobilization of Monoclonal Antibody MC10E7 against MC-LR on Epoxy-based Monolithic Column for Affinity Chromatography

Arun Payyalot: Monolithic Adsorption Filtration of MS2 Bacteriophage with Quantification Via Plaque Assay

Yasmin Selic: Metall-artige Flüssigkeitsfilme als innovative SERS (surface enhanced Raman scattering) Substrate

Mei Xi Tan: Optimization and Validation of a Functional Coating on Polycarbonate-Foil for the Application in Microarray Immunoassays

Christopher Wabnitz: Synthesis and Characterisation of Freestanding Metal Liquid-Like Films

Institute Colloquia

Dr. Torsten Frosch, Institute of Physical Chemistry, University Jena Raman Spectroscopy of Gases and Aqueous Solutions (23.3.2017)

Prof. Ji-Yen Cheng, Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan: Development of Microfluidic Devices and their Applications in Cell Culture with Controlled Microenvironment (8.5.2017)

Dr. Rani Bakkour, EAWAG, Department Environmental Chemistry, Switzerland: From Milli- to Micro-pollutants: Sample Preparation of Challenging Environmental Samples for Compound-specific Isotope Analysis (12.5.2017)

Prof. Dr. Mark Niedre, Northeastern University Boston, Department of Electrical and Computer Engineering and Bioengineering: Fluorescence Detection of Rare Circulating Cells In Vivo: Technology, Applications and Future Prospects (29.6.2017)

Gabriel Sigmund, Universität Wien, Department für Umweltgeowissenschaften: Biochar for the Remediation of Diffusely Contaminated Site (7.8.2017)

External Tasks and Memberships

T. Baumann

Bayer. Fachausschuss für Kurorte, Erholungsorte & Heilbrunnen	Deputy Member
VBEW Arbeitskreis Wasserschutzgebiete	Guest Member

M. Elsner

Bayer. Fachausschuss für Kurorte, Erholungsorte & Heilbrunnen	Member
Young Academy of Europe	Member
Isotopes in Environmental and Health Studies	Editorial Board
Fachausschuss "Chemikalien beim Hydrofracking zur Erdgasgewinnung" der Wasserchemischen Gesellschaft in der GDCh	Head

C. Haisch

Kommission Reinhaltung der Luft im VDI und DIN - Normen-ausschuss: Unterausschuss Messen von Partikeln in der Außenluft - Bestimmung der Partikelanzahl	Member

N. P. Ivleva

NA 054 DIN-Normenausschuss Kunststoffe (FNK); NA 054-01-06 AA Arbeitsausschuss Kunststoffe und Umweltaspekte. ISO/TC 61/SC 14/WG 4 „Microplastics“	Member
Fachgruppe für “Kunststoffe in aquatischen Ökosystemen (Mikroplastik)“ bei der Wasserchemischen Gesellschaft in der GDCh	Member

D. Knopp

International Journal of Environmental Research and Public Health	Editorial Board
Encyclopedia of Analytical Science Third Edition, Elsevier	Editorial Board
School of Chemical Engineering, National Technical University of Athens (NTUA), Greece. Election committee	Member

R. Niessner

Bayer. Fachausschuss für Kurorte, Erholungsorte & Heilbrunnen	Member
Heinrich-Emanuel-Merck Award	Jury Head
fms_ProcesNet-Gemeinschaftsausschuss Sensoren und Sensorsysteme (DECHEMA)	Member
German Council of Science and Humnities (WR)	Evaluation Working Group Member
European Research Council	Evaluation Panel Member
Analytical Chemistry	Associated Editor
Analytical & Bioanalytical Chemistry	Advisory Board Member
Analytical Sciences	Advisory Board Member
Fresenius' Environmental Bulletin	Advisory Board Member
International Journal of Environmental Analytical Chemistry	Advisory Board Member
Microchimica Acta	Advisory Board Member
Talanta	Advisory Board Member
Toxicological & Environmental Chemistry	Advisory Board Member

M. Seidel

Kommission Reinhaltung der Luft im VDI und DIN - Normen-ausschuss: Unterausschuss Messen und Bewerten von Legionellen	Member
Kommission Reinhaltung der Luft im VDI und DIN - Normen ausschuss: Arbeitsgruppe "Bioaerosole und biologische Agenzien – Luftgetragene Mikroorganismen und Viren"	Member
Spiegelgremium zur CEN/TC 264/WG 28 „Microorganisms in ambient air"	Member
Fachgruppe für „Viren und Parasiten“ bei der Wasserche-mischen Gesellschaft in der GDCh	Member

Teaching

GIST TUM-Asia

Industrial Chemistry (M.Sc.)

Bioengineering & Bioprocessing; Seidel
Hydrochemistry; Niessner

Chemical Engineering (B.Sc.)

Biochemical Process Engineering; Seidel

Chemistry (B.Sc./M.Sc.)

Hydrogeological, Hydrochemical and Environmental Analysis Seminar (Hydrogeologisches, Hydrochemisches und Umweltanalytisches Seminar); Elsner, Baumann, Haisch, Knopp
Graduate Course in Analytical Chemistry: Lecture in Organic Trace Analysis-Physical and Chemical Separation Methods (Nebenfach Analytische Chemie:Vorlesung Organische Spurenanalytik-Physikalisch-chemische Trennmethoden); Elsner
Graduate Course in Analytical Chemistry: Lecture in Organic Trace Analysis-Applications of Selective Receptors (Nebenfach Analytische Chemie: Vorlesung Organische Spurenanalytik-Nutzung selektiver Rezeptoren); Elsner, Seidel
Graduate Course in Analytical Chemistry: Lab in Organic Trace Analysis (Nebenfach Analytische Chemie: Kurspraktikum Organische Spurenanalytik); Elsner, Seidel
Graduate Course in Analytical Chemistry: Research Lab in Organic Trace Analysis (Nebenfach Analytische Chemie: Forschungspraktikum Organische Spurenanalytik); Elsner, Seidel
Trace Analysis Techniques (Spurenanalytische Techniken); Elsner, Seidel, Haisch

Biosciences (B.Sc./M.Sc.)

Analytical Chemistry - Separation Techniques, Chemical and Biochemical Sensors (Analytische Chemie - Trenntechniken, chemische und biochemische Sensoren); Knopp

Geosciences (B.Sc./M.Sc.)

Analytical Chemistry I: Instrumental Analysis for Geoscientists (Analytische Chemie I: Instrumentelle Analytik für Geowissenschaftler); Elsner
Analytical Chemistry II - Organic Trace Analysis for Geoscientists (Chemische Analytik II - Organische Spurenanalytik für Geowissenschaftler); Elsner
Contaminant Hydrogeology (Transport von Schadstoffen im Grundwasser); Baumann
Remediation Design (Erkundung und Sanierung von Grundwasser-schadensfällen); Baumann
Technical Hydrogeology (Technische Hydrogeologie); Baumann
Fluidflow in Porous Media Lab (Hydrogeologisches Laborpraktikum); Baumann, Haisch
Hydrogeochemical Modelling (Hydrogeologische Modellierung II); Baumann
Hydrogeological Field Lab (Hydrogeologische Feldmethoden); Baumann
Hydrogeological Mapping (Hydrogeologische Kartierung); Baumann
Hydrogeological and Hydrochemical Field Trips (Hydrogeologische und Hydrochemische Exkursion); Baumann
Water Chemistry I (Wasserchemie I); Elsner
Water Chemistry II - Hydrocolloids, Micellar Systems and Photochemical Transformations (Wasserchemie II - Hydrokolloide, micellare Systeme und photochemische Umsetzung); Elsner
Hydrochemical Lab (Hydrochemisches Praktikum); Haisch, Baumann

Equipment

Hydrogeology

Two pilot scale tanks with flow lengths of up to 10 m allow transport experiments in a controlled environment while preserving almost natural conditions. Apart from studies on the transport behaviour of contaminants and colloids, these facilities are used for testing sensor prototypes and serve as a test bed for numerical models

Großhadern Unsaturated Zone field laboratory (10 m deep)

1 Analytical Autoclave, Büchi Midiclave

Dioxin Laboratory

3 High security labs with locks, separate activated carbon filter and high-performance particle filter systems

Aerosol Research

1 Aerosol chamber (1 m^3)
1 Aerosol flow tube (10 L)
1 Ozone analyzer (UV absorption)
1 NO/NO_2 analyser (Chemiluminescence)
2 Aerodynamic particle sizers (0.5-25 µm)
1 Berner impactor (9 stages, 50 nm - 16 µm)
1 Electrical low-pressure impactor (12 stages, 30 nm - 10 µm)
2 Low-Volume filter samplers (PM 10, PM2.5)
1 High-Volume filter sampler (PM 2.5)
2 Differential mobility particle sizer systems (10-1000 nm)
2 Diffusion batteries (5-300 nm)
5 Condensation nucleus counters
3 Electrostatic classifiers (10-1000 nm)
2 Spark-discharge soot aerosol generators (polydisperse ultrafine carbon aerosol)
1 Berglund-Liu aerosol generator (monodisperse aerosols, 0.8-50 µm)
1 Floating bed aerosol generator (powder dispersion)
1 Rotating brush aerosol generator (powder dispersion)
1 Tube furnace
1 Cyclone Impinger (Coriolis µ, Berlin)
1 Micro soot sensor with dilution unit

Bioseparation

1 Crossflow-ultrafiltration unit (6 m^2-hollow fibre module, Inge-AG)
1 Munich Microorganism Concentrator (MMC 3)
1 Monolithic Affinity Filtration Unit

Molecular Biology

1 Biacore X100, General Electric
1 Real-time PCR (Light Cycler 480, Roche)

Microarray Technology

2 Chemiluminescence Microarray Reader (Immunomat, IWC)
4 Chemiluminescence Microarray Reader (MCR 3, GWK GmbH)
1 Ink-Jet Microdispenser (SciFlexarrayer 31, scienion)
2 Contact Microarrayer (BioOdyssee Caligrapher, BioRad)
1 Cutting Plotter (Graphtec CE6000-40)

Microbiology

1 Flow Cytometer (Cell Lab Quanta SC, Beckman Coulter)
1 Flow Cytometer (CyFlow Cube 6, Sysmex Partec GmbH)
1 Water Microbiology (Colilert-18 and Quanti-Tray 2000, IDEXX)
3 Clean benches
1 Microbiological Incubator (BD 53, Binder)
1 Autoclave (Century 2100, Prestige Medical)
1 Autoclave (SHP Steriltechnik)
1 Bio-2-Aerosol Chamber

Standard Lab Equipment

1 Lyophilizer (Alpha 1-4 LSC, Christ)
1 Washer Disinfector (DS 500 Lab, International Steel CO.SPA)
1 Ultrapure Water System (Direct-Q 3 UV, Millipore)
1 Refrigerated Centrifuge (Universal 320R, Hettich)
1 Centrifuge (Eppendorf 5804 R)
1 Climatic chamber (Memmert HCP 108)
2 Fluorescence reader systems, time-resolving
3 Photometric reader systems
1 384-channel washer, Biotek
1 Turbidometer (WTW GmbH)
1 Nanophotometer (Implen GmbH)

Chromatography and Particle Separation

3 GCs with FID, NPD, ECD, TEA, and AED
1 Orbitrap-based benchtop MS, Exactive/HCD-System, Thermo Fischer
1 GC/MS, VG Autospec
1 GC/MS, Shimadzu
1 Portable Micro-GC, MITEC
1 Asymmetrical Field-flow-fractionation system, Postnova
2 Concentrators for dynamic headspace analysis
4 HPLC, UV/VIS array detector, programmable fluorescence detector
1 Capillary electrophoresis system
1 Ion chromatograph, Dionex 4500 i
1 Ion chromatograph, Dionex BioLC (Photodiode Array Detector, Electrochemical Detector)
1 Ion chromatograph, Metrohm 881
1 LC system, ECONO
1 Preparative HPLC
1 Zetaphoremeter, SEPHY

Elemental Analysis

1 TXRF, Atomika EXTRA II a
1 Flame-Photometer, Eppendorf ELEX 6361
2 AAS systems with flame atomization, electrothermal atomization, hydrid system, Perkin-Elmer PE 3300, ELAN 4100
1 ICP-MS, Perkin-Elmer Nexion 350D

Laser

2 He/Ne-laser
5 Nd-YAG-laser, pulsed
1 Nd-YAG Laser 2 W cw, 532 nm narrow band
3 Nd-YAG-laser, cw
1 CO_2-laser
3 Dye-laser (tunable with frequency doubler)
5 N_2-laser
8 Diode-lasers (600-1670 nm; up to 2 W CW)
1 Laserdiode array with 10 diodes (0.8 µm - 1.8 µm)
1 Laserdiode with external resonator
2 Optical parameter oscillator (410 nm - 2.1 µm)

Optoelectronics/Spectrometer

1 Rowland spectrometer
2 Echelle spectrometer
1 ICCD spectrometer system
1 FTIR-Spectrometer, Thermo Scientific Nicolet 6700
1 Fluorescence spectrometer, Perkin Elmer LS-50
1 Fluorescence spectrometer, Shimadzu RF 540
1 Fluorescence spectrometer, Shimadzu RF 5301 PC
1 UV/VIS spectrometer, Beckman DU 650
1 UV/VIS spectrometer, analytic jena Specord 250 plus
1 UV/VIS spectrometer, analytik jena Spekol 1500
2 Boxcar integrator
4 Digital storage oscilloscopes (400 MHz, 500 MHz)
3 Optical multichannel analysators with monochromators, time-resolving
1 Wavemeter

SEM/Microscopy

1 SEM/EDX system, Zeiss Gemini
1 Polarisation microscope for phase analysis
1 Fluorescence microscope
1 Image analysis software for automated image processing
1 Inert gas glovebox
1 Laminar flow box

Raman-Microscopy

2 Laser Raman microscope, WITec alpha300R (532/633 nm)
1 Laser Raman microscope, Renishaw 2000 (514/633/785 nm)
1 Laser Raman microscope, Horiba LabRam HR (532/633/785 nm)
1 Temperature controlled stage (-196°C - 600°C, Linkam THMS 600)

Sum Parameters

2 Coulostat for C quantification, Coulomat 702
1 DOC analysator, UNOR 6 N
1 TOC analysator, TOCOR 2
1 AOX/TOX, Sigma

Staff 2017

Director of Institute and Full Professor
Univ.-Prof. Dr. Martin Elsner (4/17-)
Univ.-Prof. Dr. Reinhard Niessner (-3/17)

Senior Researchers
Dr. Rani Bakkour (12/17-)
PD Dr. Thomas Baumann
Prof. Dr. Christoph Haisch
Dr. Natalia Ivleva
Prof. Dr. Dietmar Knopp (-3/17)
PD Dr. Michael Seidel

Post Docs
Dr. Oleksii Morgaienko (6/17-)
Dr. Genny Pang
Dr. Klemens Thaler (7/17-)
Dr. Martina Ueckert
Dr. Noemi Utry (11/17-)

Dr. Kankana Kundu (Helmholtz Zentrum München)
Dr. Sviatlana Morazava (Helmholtz Zentrum München)
Dr. Mehdi Gharasoo (Helmholtz Zentrum München)

Technical & Administrative Staff
Birgit Apel
Christine Beese
Roland Hoppe
Mira Kolar (-3/17)
Joachim Langer
Susanne Mahler
Cornelia Popp
Hatice Poyraz
Christine Sternkopf
Sebastian Wiesemann

PhD Students
MSc Pharm. Bio. Manuela Adebar (-3/17)
MSc Wasserb. Sayed Amininejad
MSc Chem. Philipp Anger
MSc Chem. David Bauer
MSc Chem.-Ing. Jonas Bemetz
MSc Chem. Elisabeth von der Esch (11/17-)
MSc Geo. David Glöckler (7/17-)
MSc Umweltchem. Lisa Göpfert (5/17-)
Exam. Lebensm. Chem. Carolin Hartmann
MSc Chem. Stefan Heberle (-6/17)
MSc Chem. Catharina Kober
MSc Erdw. Bernhard Köhl
MSc Chem. Patrick Kubryk (-1/17)
Dipl.-Phys. Peter Menzenbach
MSc Chem. Verena Meyer
MSc Pharm. Angelika Nistler (-12/17)
MSc Chem. Li Qiu
MSc Chem. Alexander Rinkenburger
MSc Bio. Chem. Sandra Schäfer
MSc Chem. Christian Schwaferts (10/17-)
MSc MBT Katharina Stutzer
MSc Chem. Klemens Thaler (-5/17)
MSc Chem. Ruben Weiß
MSc Chem. Alexandra Wiesheu (-8/17)
MSc Chem. Carina Wismeth

External PhD Students
MSc Chem. Matthias Edelmann (TUM, Lebensmittelchem. u. molekulare Sensorik)
MSc Chem. Benno Ehrl (Helmholtz Zentrum München)
MSc Chem. Michael Göttel (ABF GmbH München)
MSc Chem. Benjamin Heckel (Helmholtz Zentrum München) (-12/17)
MSc Biol. Johannes Ho (DVGW-Technologiezentrum Wasser Karlsruhe) (-12/17)
MSc Toxikol. Anne Landmesser (ABF GmbH München)
MSc Bio. Christina Lihl (Helmholtz Zentrum München)
MSc Biochem. Stefanie Mak (Klin. r. d. Isar)
MSc Toxikologie Aileen Melsbach (Helmholtz Zentrum München)
Dpl. Biol. Michael Schmalenberg (Klin. r. d. Isar) (-9/17)
MSc Geol. Marina Spona-Friedl (Helmholtz Zentrum München)
MSc Hydrogeol. Fengchao Sun (Helmholtz Zentrum München)
MSc Biochem.Ruoyu Sun (Klin. r. d. Isar)

Master Students
BSc Chem. Jessica Beyerl (9.17-)
BSc Pharm. Lia Fucà (4/17-9/17)
BSc Chem.-Ing. Fabian Hagen (-5/17)
BSc Ind. Chem. Manjiang Hong (10/17-)
BSc UPIÖ Constanze Neumann (-5/17)
BSc Korbinian Sinzinger (TUM Asia) (2/17-7/17)

Bachelor Students
Nur Aisha Abdul Aziz (12/17-)
Matthias Bauer (4/17-7/17)
Rilette Bautista (12/17-)
Fabian Freire (11/17-12/17)
Christina Glaubitz (5/17-8/17)
Wei Yuan Goh (12/17-)
Markus Heindl (3/17-7/17)
Sharon Istvànffy (8/17-10/17)
Oliver Jakob (3/17-7/17)
Raphael Junk (3/17-4/17)
Aljoscha Körber (3/17-4/17)
Ken Ong (1/17-3/17)
Arun Payyalot (1/17-3/17)
Sabrina Schönberger (10/17-12/17)
Yasmin Selic (3/17-4/17)
Mei Xi Tan (-3/17)
Christopher Wabnitz (4/17-7/17)
Lilly Zacherl (10/17-11/17)

Guests
Laxalde Gwenole (1/17-3/17)
Dr. Na Liu (3/17-7/17)
Dr. Anna Cathrine Neumann PhD
Heidi Ramsower (6/17-8/17)
Christoph Sauerer (12/17-)
Aleksandr Sobolev (-3/17)
Bastian Striebel (-9/17)
Dr. Jan-Christoph Wolf
Dr. Klaus Wutz

Student Assistants
Jessica Beyerl (-3/17)
Markus Heindl (7/17-)
Leonhard Prechtl (8/17-)