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Poster

Background

There are several factors to make the organisers of this event hopeful, now is exactly the right time to consider future chemical water monitoring.

From the aquatic chemistry side, long-term trends in concentrations in many rivers in Central Europe are declining for most classical pollutants (e.g. metals, polycyclic aromatic hydrocarbons and nutrients), but there are a large number of organic trace substances (e.g. from the fields of pharmaceuticals, process chemicals or new generations of pesticides) as well as metals from new applications, which by their sheer numbers, variability and in some cases persistence pose a major challenge for monitoring activities.

On the technical side, advances in computing power, networking, self-learning systems (all part of the internet of things developments) and analytics give us hope that we will be able to take pioneering steps today, first for research-oriented monitoring and then for regulatory monitoring.

True to the utopia of "transporting data instead of samples" and in order to better meet the growing societal demands with regard to the protection of vital resources, this symposium offers to support the communication between university, public authority and industry, with the focal points:

> inline/ online/ atline techniques in surface water monitoring,
> close to real-time data verification, evaluation and provision,
> *in-situ* monitoring and observation interfaces,
> non-stationary, autonomous monitoring,
> automatization of sampling, enrichment and preservation,
> bridging the gap from the lab to monitoring stations,
> tracer-, speciation- and fate-modelling,
> close to real-time mass spectrometry based on multi-parameter analyses.

True to the motto of this event, we are pleased to welcome you online and translated this text from German into English by a self-learning system (DeepL, with minor modifications). We are grateful and excited to share with you a look at the current state of the art and a glimpse into our common future.

Julia Arndt
Lars Duester
Julia Kirchner
for the organising team

Keynotes and talks

Continuous measurements – a challenge for the future Water Quality Measuring Network in Hamburg (Keynote)

Werner Blohm

Chemical, chemical-physical and biological parameters are continuously measured in the Hamburg measuring stations. Sampling systems are available for additional examinations or questions. Additional data flow from measurements in the port of Hamburg and from the Sentinel-2 satellites of the EU program Copernicus.
The data are transferred to an innovative central data management system (ENMO®hydro) and is then immediately available to everyone. This system performs far more than data transmission. All relevant workflows (messages, maintenance, quality management, graphics and lists, evaluations, exports etc.) are integrated in this system and make daily work much easier.
The measuring programs of the measuring stations / measuring networks must always be adapted to the requirements. Everyone is talking about climate change. The (micro-) plastic poses special challenges. Solids (suspended matter) have long been a task, but there are still a number of open questions. These questions often result in requirements for the measuring stations that have to be met.
Many researches are concerned with the development of measurement systems for the current issues, unfortunately seldom with a view to the special requirements that automated measurement networks have.
A forum for the measurement network operators would have to be created to jointly formulate the requirements for automated systems. Support for research and development could thus be given in a more targeted manner.

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Setting up an online river monitoring station from scratch in 2020

Julia Arndt, Julia S. Kirchner, Alex Zavarsky, Anna-Lena Gerloff, Axel Schmidt, Jan G. Wiederhold, Michael P. Schlüsener, Arne Wick, Lars Duester

The river Rhine, one of the largest rivers in Europe, connects six nations from Switzerland to the Netherlands. Its catchment includes some of the most densely populated areas and it is one of the most important waterways in Germany. Therefore, several anthropogenic pressures and societal, economic, as well as ecological functions must be balanced e.g., discharge of treated waste water vs. drinking water production from bank filtrates. Thus, close to real-time monitoring is gaining more and more importance at the Rhine. As an example, for the International warning and alert plan Rhine, a cooperation of all six nations with warning stations, timely analyses by GC- and LC-MS are already undertaken with time intervals less than a day, in order to feed the Rhine warning system with data.
A next step activity initiated by the authors was to create a monitoring station by 2020, complementary to the regular Koblenz Rhine station (km 590), intended to go beyond current monitoring routine as far as possible by real-time monitoring. The setup follows the need for prototype real-world testing, without interfering the regular monitoring activities and the experimental platform delivers space for cooperation with science and industry. At the moment, online and atline techniques are compared like IC, sensors, and colorimetry for major anions including the nutrients nitrate, nitrite, and phosphate, total gamma activity is continuously measured online in a self-cleaning flow-through system, and atline analysis of trace elements and non-target analysis for organic compounds complete the automated monitoring concept.
The presentation describes the creation of the station from scratch and allows to sneak peek on ongoing developments and robustness testing.

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French Network of Riverlabs: A new way of management laboratory in real time and in network: Strengthens, weakness and next challenges

Paul Floury, Jérôme Gaillardet, Antoine Dolant, Ophélie Fovet, Béatrice Trinkler, Mikaël Faucheux, Yannick Hamon, Arnaud Blanchouin, Patrick Ansart, Romane Nespoulet, Laure Cordier, Marie-Claire Pierret, Colin Fourtet, Solenn Cotel, Sophie Gangloff

Launched in 2014, a scientific program called Critex aims to develop innovative instruments to explore and monitor the Earth's surface: Critical Zone, and in particular the quality of natural waters (rivers, aquifers, lakes, etc.). One of prototypes developed is a concept "lab in the field": Riverlab. The Riverlab project received € 1.4 million in grants are invested in a network of three stations of river water monitoring called Riverlab (Floury et al., 2017).
A Riverlab can perform measurements on all natural surface waters, regardless of their quality. Water analyzes can be loaded with a high concentration of suspended solids. High frequency time measurements: A complete measurement of 20 physicochemical parameters every 40 minutes (20 for major species), 36 per day and 1000 per month.
Since 2017 three stations are deployed in France and a network of collaboration have been emerged. This represents strengthens to share experience between all actors on Riverlabs in a new collaborative network. From field missions to scripts programs, how have we built this collaborative network? What improvements this represents to share experience on the quality and on the performance of the acquisition? This helps to leads us to manage one of dataset never ever build to the scientific community. From scientific program to the birth of a start up: comeback experiences on 5 years across France.

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Current systems and methods for the autonomous monitoring of inland waters (Keynote)

Christian Degel

Clean water is a fundamental requirement for a prosperous environment and a healthy diet of all living beings. An important obligation of our society is to preserve the nature and to improve the conditions of our surface and ground waters. Therefore, a steady monitoring of parameters in water bodies is necessary.
These parameters can be quite different depending on the water body of investigation and its characteristics, purpose, location or intended usage. In most cases, an autonomous and continuous monitoring is the best solution for the surveillance of a water body's condition. The monitoring systems need to be well adapted to this special task. A plurality of monitoring systems and sensor combinations are available today. Static buoys, floats, gliders, autonomously or remotely controlled vehicle systems below, on or above the surface of waters are the carrier systems for a wide range of sensors. These sensors can investigate physical, chemical, biological and other special parameters. Such systems and sensors can either be commercially available or especially developed for the usage in scientific projects. With this work, we give an overview on functions and possibilities of currently available monitoring systems for inland waters. Special solutions for the autonomous monitoring of chemical parameters will be highlighted. One example will be the autonomous monitoring platform "HydroCrawler", which was developed for high-resolution underwater measurements and can be equipped with a plurality of sensors and sampling systems.

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Two decades of mobile measuring stations – experiences with long term online-data collection in the field and its evaluation

Angelika M. Meyer, Horst P. Beck, Elisabeth Fuenfrocken

Over the past few years the importance of water quality has been paid ever increasing attention, reflected in corresponding jurisdiction setting forth Environmental Quality Standards and the planning of cost-effective measures to reduce pollution. However, for any management activities in a catchment it is of particular importance to know the sources and transport pathways of the various impacts in the catchment area very precisely. But especially in small and middle size rivers great temporal and spatial variability of inputs make comprehensive monitoring difficult.
To cope with this challenge 2 mobile measuring stations were designed by Saarland University on behalf of the Saarland State Ministry of Environment and Consumer Protection in 2002. Since 19 years these (and other) stations have been operated in the whole Saarland State to identify individual pollution sources and to weigh their relative importance in small and middle scale catchments. For this purpose a wide range of relevant parameters such as – phosphorous (TP and TRP), nitrate, ammonia, TOC, temperature, oxygen, pH, turbidity and EC - were recorded by suitable online monitoring equipment coupled in mobile water quality monitoring stations over a representative monitoring period of several months.
The recorded data were subjected to adapted interpretation together with other catchment-related factors. To retrieve maximum information from the online data sets the relationships of certain parameter pairs, such as total reactive to total phosphorous, TOC to particle bound phosphorous, ammonia to total reactive phosphorous and oxygen to temperature were also analysed for both storm events and low flow periods.
The holistic approach adopted in this study provides a comprehensive picture of the multidimensional pollution in small rivers and valuable information on input sources as basis for adopting cost-effective measures to reduce loads in small and middle scale river catchments and so to also meet the requirements of the WFD.

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Automated real-time monitoring of pharmaceuticals in treated wastewater with the transportable LC-HRMS platform MS2Field

Julian Bosshard, Michael A. Stravs, Philipp Longrée, Christian Stamm, Christoph Ort, Thomas Moehring, Guenter Boehm, Heinz Singer

Measuring at high temporal resolution is often crucial for an accurate assessment of organic micropollutants like pesticide peak concentrations in rivers. Similarly, point source emissions, such as discharges of active pharmaceutical ingredients (APIs) by industries, are expected to be highly intermittent. Therefore, the analysis of composite samples can lead to an underestimation of ecotoxicologically relevant peak concentrations. However, the time and effort required for traditional sampling and sample preparation presents a bottleneck to measuring with high temporal resolution over extended periods.
These issues are resolved by the MS2Field. The MS2Field is a transportable trailer with a fully automated LC-HRMS platform, which can autonomously measure datasets with high temporal resolution. A PAL RTC autosampler (CTC Analytics, Zwingen) was coupled to a Q Exactive HF mass spectrometer (Thermo Fisher, Bremen). Every 20 minutes, a sample is taken from a bypass stream, filtered and measured with online-SPE or large volume injection. The acquired data is automatically quantified and displayed on an online dashboard. Therefore, the measured concentrations can be viewed in close to real-time on a computer or smartphone. In summary, the MS2Field creates comprehensive datasets, minimizes time for degradation and delivers results quickly while saving time.
In the most recent campaign, we used the MS2Field to monitor the effluent of a WWTP for 1.5 months and investigate API emissions of a formulating pharmaceutical company. This serves as one of many examples how a fully-automated LC-HRMS platform can be used for autonomous on-site monitoring with high temporal resolution to reveal unknown micropollutant dynamics.

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Analytics 4.0: Online wastewater monitoring by GC and HPLC (Keynote)

Monika Wortberg, Joachim Kurz

Digitization is one of the main topics being discussed in society and industry. What do Industry 4.0 and the corresponding Analytics 4.0 mean for the future work in a laboratory? As an example of Analytics 4.0, we present an online wastewater monitoring laboratory at BASF's largest production site in Ludwigshafen, Germany. Multiple liquid and gas chromatographic analyzers coupled to mass spectrometric or UV detectors are employed in a mostly unstaffed laboratory, which operates 24/7 (WORTBERG & KURZ 2019, ZIEMER et al. 2010). Mixed samples of the influent of the wastewater treatment plant (WWTP) are collected at 20-min intervals and are subsequently analyzed. After automated chromatogram evaluation the quantitative results are transferred to the data base of the Environmental Monitoring Center's data base. If a compound exceeds a critical threshold an alert is generated, and measures are taken to protect the WWTP and the river Rhine.
A wide spectrum of chemically different compounds is quantitatively assessed, from volatile solvents to pesticides and organic complexing agents. The analytical instruments are commercial laboratory analyzers that are in part modified, and all are equipped with flexible, programmable autosamplers. All chromatography data systems are connected to special software routines which enable continuous operation and conversion of all data into a unified format.
By means of different software and visualization tools the laboratory personnel can remotely evaluate the status of all instruments and the sample preparation unit, assess the chromatographic performance and perform remote operations.
In total, about 10 million quantitative results are generated per annum – a multitude of what is possible in an offline-laboratory with the same number of employees.

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Online-analysis and direct assessment of illicit drugs and organic micro pollutants in wastewater treatment plant influent

Niklas Köke, Fernando Solano, Tobias Frömel, Micheal Pütz, Thomas P. Knepper

Wastewater monitoring of organic micro pollutants is generally following the principle of 24 h composite sampling, sample preparation, analysis utilizing hyphenated mass spectrometric techniques data evaluation and reporting (JIANG et al. 2013, AL AUKIDY et al. 2012, VAN NUIJS et al. 2011). Besides that sampling campaigns and sample preparation are time-consuming and expensive, there is an unavoidable time delay between offline analysis and assessment of results.
The method presented in this work was developed specifically to monitor wastewater treatment plant influent continuously following online-sampling. For this purpose, an automated wastewater filtration, sampling and online solid-phase extraction – high performance liquid chromatography – tandem mass spectrometry method was developed, which enables the analysis of illicit drugs and environmental pollutants in wastewater over a period of three days. The setup was configured in a way that a ten minute composite sample was analyzed every ten minutes. In order to minimize the time delay between analysis and evaluation, an R script was developed, which evaluated each measurement directly after its completion and enabled a direct assessment. The results were presented to the user in two different ways: i) exported in form of a table and diagram (concentration plotted against time) and ii) results of conspicuous substance(s) were sent promptly to the user via e-mail. A conspicuous substance means that a result has exceeded a predefined limit.
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Development of a fieldable, online solid-phase extraction, high performance liquid chromatography, electrospray ionization mass spectrometer (SPE-HPLC-ESI-MS) for continuous, near-real-time detection of munitions compounds in seawater

Aaron J. Beck, Mario Esposito, Eric P. Achterberg

Both environmental protection and offshore resource development are challenged by the presence of unexploded ordnance and relic munitions on the seafloor. In addition to the explosion and security risk, these munitions contain cytotoxic, genotoxic, and carcinogenic chemicals associated with conventional explosives, chemical warfare agents, and munition structural components (munition compounds, MC). There is a critical need to monitor leakage of these toxic chemicals into the marine environment, but existing laboratory-based methods are time- and labor-intensive. Within the framework of the EMFF-funded project ExPloTect ("Ex-situ, near-real-time exPlosive compound deTection in seawater"), we are developing a prototype system for shipboard, near-real-time detection of dissolved explosive compounds and chemical warfare agents in seawater. The underlying concept of ExPloTect is a flexible platform that is adaptable to explosive compounds such as TNT, as well as chemical warfare agents. The technology is based on an analytical methodology demonstrated extensively by GEOMAR in the Baltic Sea during the German science ministry (BMBF) funded UDEMM project ("Environmental monitoring for the delaboration of munitions in the sea"). This system will be the first to achieve high sensitivity and unequivocal identification of a suite of MC in seawater, and represents a major step change in field-deployable technology for chemical detection of munitions. Simultaneous sensing of chemical agents and MC has a wide range of benefits, including environmental monitoring of chemical release and ecological exposure, detection, localisation and potential classification of munitions objects on the seafloor, and providing safety for individuals who accidentally encounter underwater munitions..

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Development for a portable measuring device for the detection of pollutants in water based on nano-liquid chromatography and ion mobility spectrometry

Tobias Werres, Christian Thoben, Christian-Robert Raddatz, Ireneus Henning, Thorsten Teutenberg, Torsten C. Schmidt, Stefan Zimmermann

Within the research project *MiniLAB*, a portable measurement system is under development with the focus on industry and sewage treatment plants in case of accidents or disasters. The demonstrator to be developed will consist of a miniaturized system for enrichment and separation of target analytes in water by nano high performance liquid chromatography (nano-HPLC) (Institute of Energy and Environmental Technology) as well as a miniaturized detection system using electrospray ionization (ESI) ion mobility spectrometry (IMS) (Leibniz University Hannover). The 2D-separation achieved in this way is a promising approach, in particular since the analytes can be enriched and separated directly from the water phase using nano-HPLC columns (LEONHARDT et al. 2015). Usually, the ion detector, the amplifier and the data acquisition of the ESI-IMS are at ground potential, while the ion source is operated at high electrical potential. Coupling to HPLC is challenging in this configuration, so that the electrical potentials of the IMS have to be shifted (LIPPMANN et. al. 2020). Consequently, a low-noise, high-voltage isolated data acquisition is required, in which the amplifier and the analog-to-digital converter are set to high potential. In this work first results in the form of chromatograms are presented. Various pesticides and drugs, such as aclonifen, carbamazepine, dichlorvos and isoproturon are used as analytes.

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Monitoring of organic micropollutants in European wastewater treatment plant effluents

Saskia Finckh, Liza-Marie Beckers, Wibke Busch, Eric Carmona, Martin Krauss, Warich Leekitratanapisan, Tobias Schulze, Andreas Schüttler, Werner Brack

Water quality around Europe has immensely increased since the widespread installation and steady improvement of wastewater treatment plants (WWTPs). However, many organic micropollutants cannot yet be removed. Thus, WWTPs are still important point sources for emerging contaminants in the water cycle.
As part of an interdisciplinary case study, we analysed and evaluated the impact of organic micropollutants from wastewater discharge by assessing the chemical load of 56 European WWTP effluent samples. On-site large volume solid phase extraction (LVSPE) (SCHULZE et al. 2017) allowed a sample enrichment by a factor 1000. The samples were analysed in a wide-scope target screening of more than 500 compounds by liquid chromatography high resolution mass spectrometry (LC-HRMS). The raw LC-HRMS data was further processed based on the software MZmine (PLUSKAL et al. 2010) (peak picking, deconvolution, alignment, gap filling and peak annotation) and an in-house semi-automatic R-package (quantification of compounds). Three quarter of all analysed target compounds were detected in at least one sample. Approximately 100 of them were detected ubiquitously in >90% of the samples, while others were highly site-specific. For the risk assessment, concentrations were converted into toxic units (TUs) (SPRAGUE 1970) allowing a comparison with observed adverse mixture effects from another study (i.e. algae PSII inhibition).
This study looked at how future water quality monitoring can be improved by the applied high throughput methods, and how the latter could be further developed. Based on the combination of chemical concentrations and effect data, we received a more comprehensive picture of the impact of complex mixtures of organic micropollutants discharged by WWTPs.

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Monitoring strategies and process control in the drinking water treatment (Keynote)

Tobias Bader, Rudi Winzenbacher

The Landeswasserversorgung (LW) provides 100 million m³/a drinking water to three million people in southern Germany. In addition to groundwater, water from the Danube River is directly abstracted. A multi-stage process - comprising flocculation sedimentation, ozonation and activation carbon filtration - is applied for the drinking water production.
In contrast to groundwater, the surface water quality is subjected to larger temporal variations and thus requires more stringent monitoring concepts. Several online sensors (e.g. turbidity, spectral absorption coefficient) record data every few seconds and are used for real time process control by the operation crew. Some processes are controlled by machine learning algorithms, e.g. artificial neuronal networks are used to establish the most favourable coagulant/coagulant aid dosage during the flocculation sedimentation process.
To trace organic micropollutants, however, real time monitoring concepts are still missing. In recent years, special emphasis was given to screening methods such as non-target screening and effect-based methods to deal with the large variety of substances. Since 2017, raw and drinking water is screened at least twice per week. However, temporal dynamics of several mircopollutants have shown that even higher sampling frequencies would be necessary to adequately detect peak concentrations. Thus, high resolution mass spectrometers will be established at the raw water extraction point (pump station) in the near future and provide results before the raw water enters the waterworks (~ 2 h). This online monitoring would allow to initiate adaption measures such as the additional dosage of powdered activated carbon or a partial shut down of the surface water treatment.

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A database model for aggregating non-target-screening data

Kevin Jewell, Franziska Thron, Julia Kirchner, Michael Schlüsener, Kasjen Kramer, Thomas Scharrenbach, Ina Fettig, Jan Koschorreck, Christoph Schulte, Thomas Ternes, Arne Wick

The BfG and UBA are currently developing a novel database and analysis platform for non-target-screening (NTS) data of trace organic substances in rivers. The database is aimed at combining NTS results from different measurement stations and enabling aggregated re-analysis of the data, as well as real-time search to assist river monitoring. The project can be divided into three intermediate goals: 1) design of strategies to harmonize NTS results, 2) implementation of a central data repository, 3) development of prototype search and analysis tools. The first task to achieve these goals is to develop a unified data model as the basis for the harmonization strategies.
ElasticSearch was chosen for the implementation. ElasticSearch is an open-source, distributed document repository with an integrated search engine. Both asynchronous or real-time data upload is possible using built-in interfaces. Entries in ElasticSearch are based on documents in JSON format, where a document represents a non-target *feature* (peak) and contains various data types, including m/z, retention time, chromatographic peak area, sampling time and duration, geo-coordinates and substance name (if known). The structure allows searching or filtering by features using various criteria and provides a basis for the management of NTS data.
The database currently contains approximately 190,000 documents with annotated (with chemical name) non-target features from 14 measurement stations measured at one laboratory. Further collaboration with other environmental agencies is planned.
The presentation will present the data model and a draft online visualization dashboard which provides real-time search and displays time series data for selected compounds.

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Online sensing and machine learning for proactive protection of surface waters

Tomas Feseker, Wolfgang Kappler

Based in Aachen, Germany, ahu GmbH offers consulting and GeoIT-services concerning groundwater, surface water and soil. We are currently developing our own sensor network for monitoring projects. The network consists of low-cost controllers that can be attached to any kind of sensor and that transmit measurement data to a server over the Internet using standardized IoT/ Sensorthings protocols. Current monitoring applications focus on water quality in ponds and lakes and pollutants in shallow groundwater and include the acquisition of weather data. The data are automatically evaluated to detect sensor malfunctions and to identify outliers in nearer real-time. If required, the data can be compared to given thresholds and warning levels and measures can be initiated in response.
When deployed within an existing sensor infrastructure, online sensors improve both the spatial and temporal resolution of observations. Algorithms can be used to compare all available data in order to find similar stations or proxy parameters. Machine learning techniques will help to combine first-hand measurements with external data such as historical weather observations to predict mid- and long-term trends. Based on these automated predictions, we aim to establish early warning systems which facilitate proactive amelioration measures to water quality.
All measurement data can be visualized in real-time via responsive web applications providing expert dash boards or more general information for the public. As our server provides standardized interfaces, data can be accessed by all concerned stakeholders or forwarded to other software for further evaluation without delay.

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A graphical user interface for fast and accurate workflow for cleaning, calibration and validation of continuous datasets

Pali Felice Gelsomini, Tom Maris, Patrick Meire

Often water-quality monitoring programs contain high-frequency continuous datasets. Because of the high complexity of these datasets, they often require cleaning and manual validation for removing datanoise, which generally is time consuming and cumbersome when dealing with large datasets. Post calibration may also be necessary when sensors are miscalibrated or when variables of interest are not directly measured (e.g. chlorophyll-a florescence). We developed a graphical-user-interface computer application for visual, accurate and fast cleaning (e.g. spike removal, filtering), validation and post-calibration. The tool is an opensource, R based Shiny application with optimized code for very large datasets. The tool is generic and offers the user both the choice of visual guidance, in which no coding is required, and scripting. As a test case, we applied this application to a high-frequency, long-term chlorophyll-a florescence dataset measured in the Scheldt Estuary (Belgium) at three locations. The continuous florescence data at each site was linearly calibrated to chlorophyll-a concentrations using lab-tested point samples. Interestingly, each site calibration resulted in a significantly different linear relationship (slopes 0.82, 1.48, 2.84), stressing the importance of site-specific calibrations. The calibration was accurate ($R^2 > 0.9$) despite using multiple sensors of the same type at each location, showing that the calibration variability between sites is mainly environmentally driven.

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Testing the waters: Real-time mapping of water chemistry on the Rock River, Wisconsin, USA (Keynote)

Eric Compas

Citizen science initiatives are increasingly using new devices, smartphone apps, and interactive websites to improve data quality and collection procedures, better visualize trends and changes, and increase volunteer engagement and retention. This talk reports on the development and demonstration of a prototype water quality instrument array and website to modernize volunteer water quality sampling. Using open source software and off-the-shelf components, our device measures GPS location, dissolved oxygen, temperature, conductivity, and pH at a high sampling rate. Combined with a smartphone app and website, the system provides real-time maps and visualization of water quality data. We demonstrated the device on an 11-day public expedition called “Testing the Waters: A Paddle and Probe Adventure” down the Rock River in Wisconsin. The event was successful in collecting 30,000 GPS-tagged water samples across 324 km providing a unique profile of the river’s water, identifying potential water quality issues, and establishing a baseline for comparison. Through the project and additional volunteer feedback, we learned lessons about a broader-scale adoption including: 1) need to simplify setup and calibration; 2) need for further development of online tools to better communicate with a non-technical audience; and 3) need for a flexible device that works in a variety of situations, e.g., static deployment. The pilot demonstrated the potential of new technology and a low-cost device to expand the types and amount of water quality data collected by citizen monitors.

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Compact integrated multichannel probe for in situ autonomous monitoring of the potentially bioavailable fraction of a range of trace metals

Mary-Lou Tercier-Waeber, Fabio Confalonieri, Melina Abdou, Abra Penezic, Marianna Fighera, Eric Bakker, Jörg Schäfer

Trace elements are ubiquitous elements playing critical roles in aquatic ecosystem function. Some metals (e.g. Hg, Cd, Pb) and metalloids (e.g. As) have high toxicity even at very low concentrations, while others are either essential or toxic (e.g. Cu, Zn), depending on their concentrations and the nature of the organisms exposed. Trace metals are persistent and distributed under various chemical species (speciation). Only some specific metal species are potentially available for bio-uptake. Bioavailability is therefore of primary concern when considering if a trace metal serves as micronutrient or toxicant.
We present here a unique submersible compact integrated multichannel trace metal sensing probe (TracMetal). Innovative antifouling gel integrated microelectrode arrays (GIMEs) incorporated in this system enable *in situ* autonomous and simultaneous measurements of the dynamic (potentially bioavailable) fraction of a range of EU and US-EPA (priority) hazardous metals: Hg(II), As(III), As(V), Cd(II), Pb(II), Cu(II), Zn(II) with sensitivity at sub-nanomolar level. The TracMetal was successfully applied in the Arcachon Bay and the Gironde Estuary representative of the southwest European Atlantic Coast hosting major coastal protected areas and economic activities (seafood production areas). In parallel, master variables were monitored in situ, and water samples were collected for complementary analyses of particulate and total dissolved metal concentrations; water composition and proxies for primary production. Integration of all the data enabled to deeper understand the spatial and temporal behavior of the potentially bioavailable metal species and to identify abiotic and biotic processes that control their concentrations and cycling as it will be reported.

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Biogeochemical characterization of rust tubercles induced by microbial activity using a custom-made field microsensor system

Annika Fiskal, Lipi Raghunatha Reddy, Sven-Erik Wulf, Helmut Fischer, Jutta Meier

Microsensor systems are widely used to investigate environments characterized by strong spatial and/or temporal gradients. Due to live data acquisition and field applicability, microsensors offer great possibilities to collect on-site measurements.
Within the “RimiK” project (risk factors and indicators of microbially induced corrosion), we applied a field microsensor multimeter coupled to a micromanipulator (Unisense, DK) on corroding sheet piles in a lock (Obere Havel-Wasserstraße, Regow, Germany) and investigated rust tubercles formed by microbially induced corrosion. We constructed a custom-made motor and micromanipulator holder and attached the whole set-up to the sheet pile walls using neodymium magnets to measure horizontal profiles into two tubercles directly in the field. Thereby, we recorded profiles of different analytes (redox potential (E_h), O_2, H_2S and pH) with 500 µM spatial resolution.
The two tubercles show high similarities. O_2 concentrations decrease sharply from outside to inside, with a maximum penetration depth of 2 mm. One tubercle shows a small increase in O_2 concentration close to the surface, likely due to the presence of photosynthetic algae. No free H_2S was detected in both tubercles, presumably due to high Fe^{2+} concentrations sufficiently precipitating all free H_2S. In both tubercles, pH decreased to weak acidic conditions of ~5.5. Redox potential also decreases towards the core of the tubercles to values of -350 and -500 mV, indicating a strongly reducing environment.
Microorganisms strongly altered the chemical micro-environment within the rust tubercles. The microsensor system has proven to be a suitable tool to acquire real time data from this unique environment.

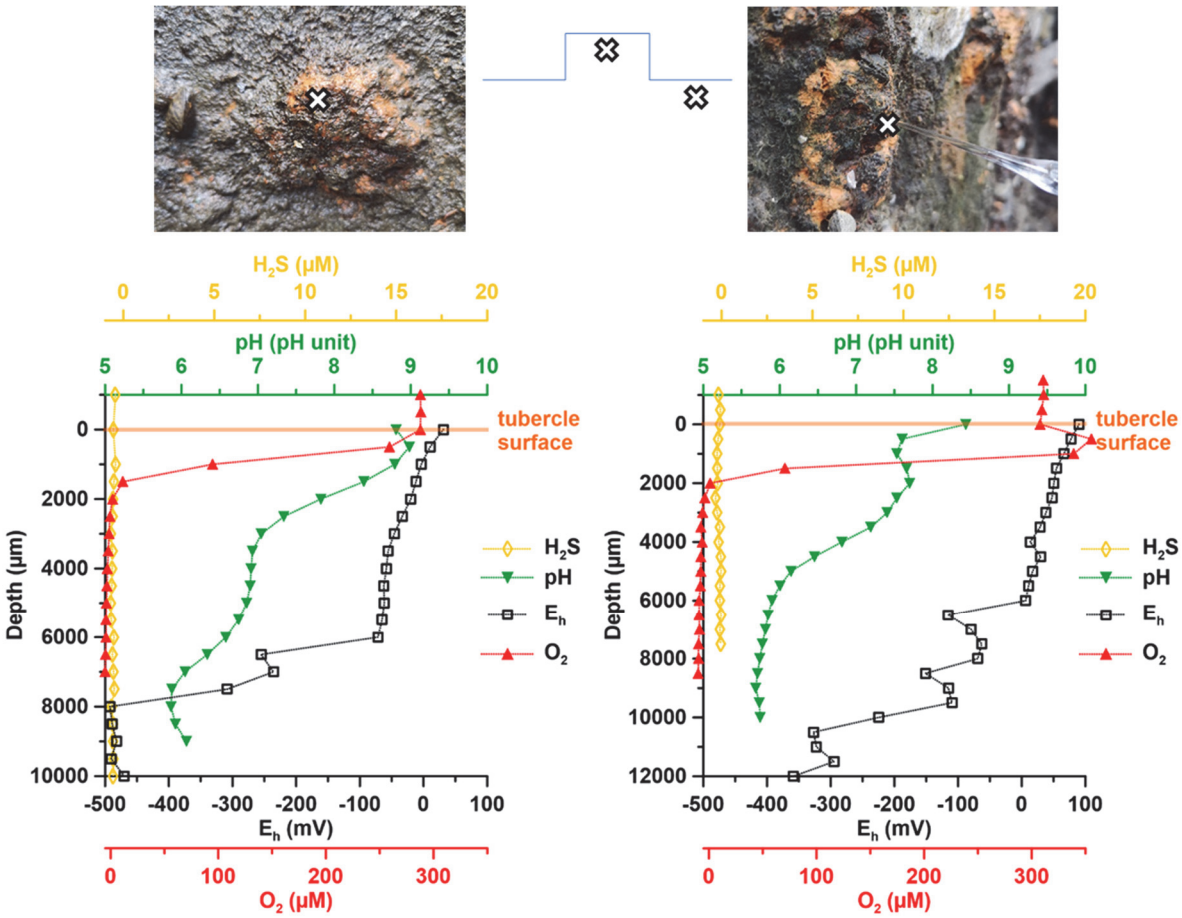

Figure 1: Microsensor profiles of two rust tubercles for H_2S, pH, redox potential (E_h) and oxygen (O_2) as well as pictures of the two tubercles and a schematic illustration of their location on the sheet pile.

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Chances and possibilities of soft sensors derived by online water quality data

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The advantages of online water quality motoring over grab sampling for constant surveillance and assessment of event dynamics are indisputable. However, sensors mounted in surface waters do not only record concentrations of a substance but also indirectly the impacts of driving processes and the boundary conditions in the waterbody on the analyte. In this abstract we want to demonstrate the possibilities of using such additional, high resolved temporal information in a soft sensors concept with water quality parameters easy to measure from our monitoring stations at Lockwitzbach, Dresden. According to SCHNEIDER et al. (2019) Schneider et al., 2019, soft sensors use the sensor signals together with a software that is designed to identify particular features in the monitored data in order to obtain a specific type of information. The nighttime slope method (HORNBERGER & KELLY 1975) (Hornberger and Kelly, 1975) was applied on recorded dissolved oxygen concentrations to determine rates for gross primary production, ecosystem respiration and reaeration of different subcatchments (urban/rural) and we were able to derive rates, which represented the different conditions of the two subcatchments. Whereas the oxygen reaeration showed similar results at both stations, the metabolism was significantly increased in the urban catchment, expressed by higher gross primary production and ecosystem respiration rates. A second example of soft sensor application is the evaluation of the lag time between the diurnal pH- and dissolved oxygen-maxima and the correlation with the buffer capacity of the stream water. Depending on this value, pH peaks were closer or further away from oxygen maxima. These examples are adding a striking argument for the importance of online monitoring for river basin management practices.

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Strengths and shortcomings of passive sampling for chemical monitoring of surface waters

Benjamin Becker, Christel Möhlenkamp, Christian Kochleus, Anna-Jorina Wicht, Julia Bachtin, Denise Spira, Georg Reifferscheid, Sabine Schäfer

Over the past decades great progress has been made in the field of passive sampling of organic chemicals in the aquatic environment. With such methods, a sorption phase is exposed in a medium (e.g., water, sediment) where it samples the target compounds at a rate that is proportional to the difference in chemical activity between sampler and medium, and where the uptake kinetics are controlled by passive processes (diffusion and ambient convection). Due to the enrichment of target chemicals in the sorption phase, passive sampling allows the quantification of very low contaminant concentrations which is particularly interesting for monitoring hydrophobic organic chemicals in the water phase. In water, time-integrated contaminant concentrations can, further, be determined that give a more representative picture of environmental contamination compared to the analysis of spot samples. In this regard, passive samplers can be an attractive and cheap alternative to the application of autonomous composite samplers, e.g. for monitoring of plant protection products in small water bodies, or the operation of measuring stations, e.g. for continuous chemical monitoring. Although passive sampling enables the measurement of freely dissolved contaminant concentrations (c_{free}) that are more relevant for ecotoxicological risks and bioaccumulation than total concentrations, this feature hampers the application of passive samplers for compliance monitoring since environmental quality standards are based on total contaminant concentrations. We will give examples for the potential application of passive sampling in water and sediment monitoring, discuss shortcomings of these approaches and point out research needs.

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Poster (authors alphabetically ordered)

Continuous monitoring of trace metal speciation in the Gironde Estuary: Successful application of innovative sensors

Melina Abdou, Mary-Lou Tercier-Waeber, Lionel Dutruch, Cécile Bossy, Eric Bakker, Jörg Schäfer

Trace metal biogeochemical processes in estuaries are very dynamic, and their comprehensive study requires an accurate high-resolution monitoring. We investigated the behavior of three EU (priority) hazardous contaminants i.e. cadmium (Cd), lead (Pb), and copper (Cu) in the Gironde Estuary during a primary production period (mid-June). Real-time measurements of the trace metal dynamic fraction, i.e. the potentially bioavailable fraction, were performed using an antifouling gel integrated microsensors arrays (GIME) incorporated in an innovative submersible multichannel voltammetric probe. We also quantified metal levels in the < 0.2µm and < 0.02µm dissolved phases, and the particulate phase including plankton material by ICP-MS. Master physicochemical parameters and indicators of primary production were also measured.
The unique profiles for dynamic fractions of Cd, Pb and Cu showed important variations in their concentrations and proportion to the dissolved fractions along the salinity gradient and over a diel cycle. High-resolution monitoring of the various fractions highlighted the importance of small colloids (< 0.02µm) on trace metal distribution. Furthermore, this dynamic fraction reflected the influence of primary producers on biogeochemical cycles of essential trace element such as Cu but also Cd, whereas Pb speciation was rather controlled by inorganic (mineral-oxide sorption) particle-water interactions. The successful in situ application of innovative GIME, coupled to master bio-physicochemical parameter measurements, highlighted the potentiality of a metal bioavailable-based tool acting as real-time sentinel to deeper understand the influence of site-specific conditions on the behavior and fate of the dynamic metal species and therefore enable more rigorous metal (eco)toxicity risk assessments.

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Identification of spatial-temporal emission patterns of micropollutants into receiving waters and associated (eco-)toxicological effects – the significance of temporary emissions arising from point sources

Stephan Beil, Sara Schubert, Christian Koch

Currently, monitoring of surface water and WWTP effluents is realized by grab sampling at large intervals by state authorities. Corresponding datasets are accordingly limited by capacities for manual sampling and subsequent analytics. Furthermore, the unmanageable variety of (un-)known micropollutants, metabolites and transformation products and their considerable toxic effects pushes options for target analytics to their limits. Therefore, in order to support state authorities in achieving good chemical and ecological surface water quality as demanded by EU-WFD, a flexible automated monitoring system is required, which also pays due respect to effect-based approaches.
Within several monitoring campaigns (project “MikroModell”) dedicated to point sources with different emission patterns we identified some aspects as particularly important for such a system: I) pronounced seasonal variations of micropollutants (e.g. pharmaceuticals) and ecotoxicological potentials in surface water, raw and treated wastewater of municipal WWTPs due to temporary emitters, II) a large impact of combined sewer overflow (CSO) events on surface water contamination and substantial differences between such events, III) very large differences between composite samples of industrial effluents based on 6 h and 24 h sampling intervals and of volume-proportional vs. time-proportional sampling, and IV) the high relevance of the time elapsed between sampling and measurement of sensitive micropollutants (e.g. hormones, antibiotics; estrogenic potential).
Based on those findings, we projected the construction of a flexible system for monitoring of point sources with temporally variable emission patterns. Primarily, we focus on CSO events and will implement several approaches for advanced automated sampling, subsequent sample preparation and on-site analysis.

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Biomonitoring of freshwater ecosystems in the area of the “Cilento Vallo di Diano e Alburni” National Park (Italy)

Alessandro Bellino, Daniela Baldantoni

The temporal and spatial variability in the chemical properties of freshwater ecosystems demand for novel approaches tackling the rapid changes induced by anthropogenic activities. The possible approaches can be divided into two classes: high resolution and integration strategies. The biomonitoring through accumulator organisms falls into the latter group and can be adopted in deriving time-integrated measures of environmental contamination and accurate spatial gradients. To accomplish these goals, the organisms should linearly accumulate pollutants in relation to the environmental concentrations, being able to live in the selected environments and be common, easily recognized and managed. In searching for better biomonitors matching these criteria, a large field biomonitoring study was performed in the area of two of the main freshwater ecosystems of the “Cilento Vallo di Diano e Alburni” National Park (Italy). Here a novel biomonitor of potentially toxic elements, the macrophytic alga *Chara gymnophylla*, was validated using a long-established biomonitor, the aquatic moss *Fontinalis antipyretica*, by exposing the species in purposely developed devices, enabling their floating at the water surface, for 21 days.
The experimental setting allowed not only validating *Ch. gymnophylla*, but also deriving spatial concentration gradients of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, V and Zn, measured trough ICP-OES, in an area of exceptional natural value. The latter achievement relies on the analysis of the joint responses of biomonitors through novel data analyses, defining a reference framework for the biomonitorg of freshwater ecosystems.

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I need to measure! Where, what, how and why?

Rana Bengül, Christoph Sommer, Timo Wolf

Every waterway or water body has its own challenges in regards to measurement sites and techniques. This talk/poster will show by means of a fictional water body how diverse the demands on monitoring station along different sections of this water body really are; which equipment is needed/available and fits best to these stations in terms of discharge and in situ water quality measurements.
The first section of the river will be the alpine part with high sediment loads and very dynamic discharge due to quick changes in flow velocities and water level. Further downstream monitoring options for (big) lakes will be analyzed. Issue of anti-fouling are paramount for longtime water quality measurements but also the topic of installation platforms is of importance. On its further way the water body changes to a big inland water way. At a (dynamic) monitoring sites like this the site conditions in regards to ship traffic and maintenance are of interest as well as real time data transfer and warning systems. Last but not least there is the river delta and the ocean and coastal area. Similar to the lake anti-fouling systems and data transfer are important as well as the right kind of buoy or platform is essential.
All this is shown from a unique perspective of companies that sell, install, support and even developed (some) of the equipment in question in Germany and all over the world.

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A State-of-the-Art Research Platform in the Elbe: Researching Land-River-Sea Interactions

Sina Bold, Jana Friedrich, Daniel Pröfrock, Holger Brix, Kirstin Dähnke, Helmuth Thomas, Jochen Horstmann, Rüdiger Röttgers, Yoana G. Voynova, Justus van Beusekom, Andreas Neumann, Marius Cysewski, Hajo Krasemann, Ulrike Kleeberg, Max Böcke, Tim Leefmann, Volker Dzaak

Estuaries, where riverine and marine influences interact, ultimately determine matter fluxes from land to sea. Thus, a floating research platform will be set up in Tesperhude at the Elbe about eight kilometres upstream of the weir in Geesthacht separating the Elbe River and its estuary. The research platform consists of a ponton with a container housing diverse state-of-the-art observation systems providing continuous, high resolution and near-real-time data. These include a FerryBox (e.g. temperature, chlorophyll, turbidity, pH, O_2), nutrient analysers (NH_4, NO_x, NO_3, PO_4, $Si(OH)_4$), gas analysers (N_2O, CO_2, CH_4, Rn), a mobile ICP-MS for element analysis, ADCPs for current measurements, as well as a weather station and a radiometer. In addition, the research platform contains an automated water sampler, a continuous flow centrifuge and a sedimentation box for suspended matter collection. In combination with data from a station in Cuxhaven, the data from the research platform in Tesperhude will allow e.g. to quantify carbon and nutrient budgets for the Elbe estuary.
The research platform is set-up in cooperation with the Helmholtz initiative MOSES ("Modular Observation Solutions for Earth Systems") and will be incorporated in the Elbe-North Sea Supersite of DANUBIUS-RI ("International Centre for Advanced Studies on River-Sea Systems"). Funding is provided by European Regional Development Funds, Schleswig-Holstein, the Helmholtz Association and the HZG. The research platform, planned to be operational in autumn 2021, is also open for users e.g. to develop and test new methods and technologies. Data will be made available through the "Helmholtz Coastal Data Centre" (HCDC).

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Water quality modelling in a small headwater catchment using stable-water-isotope-analysis for model calibration

Lukas Ditzel, Caroline Spill, Matthias Gassmann

Headwater catchments show quick discharge response times to precipitation events. Hence, temporal high resolution data is needed to describe chemical dynamics discharge. Our research headwater catchment is located in the low-mountain ranges of Nordhessen with a size of approximately 2.6 km². The landuse consists of more than 80% agriculture, about 10 % forest and a small settlement of farms and houses. A small wastewater treatment plant is also located in the research area. The aim of this study is to apply a physically-based water-quality model to assess the nitrate balance and the nitrate source dynamics in the catchment. For this purpose we will simulate discharge and nitrate fluxes aided by stable water isotope data for model calibration. Since the model runs at small timesteps, the sampling of data required for model calibration is challenging. Therefore we deploy a field monitoring setup, capable of collecting data with a high temporal resolution. The setup includes an optical nitrate probe (about 15 min resolution), discharge measurements based on water-level sensing (1 min), and stable water isotope analysis. Stable isotopes in precipitation will be collected via rain-gauges, stable isotopes in the stream via daily auto-sampling during base flow and hourly during event discharge. The isotope signature will be detected in our lab, using cavity-ring-down spectrometry. For the discharge measurements we are planning to construct a Thomson-Wehr downstream the waste-water-treatment-plant. We will also take discharge data from the wastewater-treatment-plant and climate data from an autonomous weather-station, located in the area, into account. The whole set up will be conducted for at least 3 years.

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Integrated setup of autonomous in-situ monitoring systems as an early warning system to predict the occurrence of algae mass developments in lakes and reservoirs

Kurt Friese, Burkhard Kuehn, Martin Schultze, Xiangzhen Kong, Marieke Frassl, Karsten Rinke, Thorsten Schmidt, Jürgen Plischke

Excessive nutrient input and the resulting eutrophication still represent the greatest problem for water quality of surface waters in Germany. In addition, climate-induced changes like droughts (as in 2018 and 2019) are also coming into focus, since they can intensify eutrophication and the development of harmful algae blooms (HAB).
Temperature is a critical factor regulating limnophysical and biogeochemical processes in lakes and reservoirs. One negative effect of warming is the extension of stratification duration. Longer stratification duration prolongs oxygen depletion and can induce anoxia and further related negative effects on water quality like nutrient release from the sediments. Such interactions can be highly relevant in lake and reservoir management especially for drinking-water reservoirs.
In order to create an early warning system for different water types, floating measuring buoys were installed on two reservoirs and one urban lake. These measuring buoys are equipped with a thermistor chain reaching down to the bottom and have additional oxygen loggers at different depths. A multi-parameter probe and a multi-channel fluorescence probe were both, integrated into the buoy systems and permanently suspended at 0.5 m depth for continuous monitoring of physiochemical properties at high frequency (sub-hourly for temperature, conductivity, pH, turbidity, oxygen, and chlorophyll-a concentration) and phytoplankton community dynamics in the surface water.
The resulting data of the different devices are transformed into a uniform data-protocol by individual data-converters and stored on the UFZ-database in real time. Thereby, the measuring buoys enables the authorities to react quickly to unfavorable changes in the water bodies and take countermeasures if necessary.

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Future environmental monitoring via supercritical fluid chromatography-mass spectrometry: A novel method for the revealing and tracking of small and polar organic water contaminants

Nadine Günther, Manoj Schulz, Michael P. Schlüsener, Julia S. Kirchner, Thomas A. Ternes, Arne Wick

The study of trace substances, threatening our water resources, requires novel analytical methods. Current monitoring routines are struggling with the diverse physicochemical characteristics of water contaminants. Particularly, small & polar organic compounds are challenging but of crucial importance. For instance, above 80 % of the analytes, detected in a wastewater treatment plant (WWTP) effluent own a negative log$D_{pH\ 7}$ value (BIEBER et al. 2017). Thus, new generic target methods that extend the current analytical window to highly polar contaminants need to be developed. The special properties of the eluent used for supercritical fluid chromatography (SFC), namely compressed carbon dioxide, enables a gradient with supercritical conditions in the beginning and liquid chromatographic conditions in the end allowing the simultaneous detection over a wide polarity range. The applicability of SFC-mass spectrometry (SFC-MS) was already shown for log$D_{pH\ 7}$ values from 5,42 down to -7,71 (BIEBER et al. 2017; SCHULZE et al. 2019). In this study we (1) optimise SFC-specific and classic liquid chromatographic parameters, (2) study SFC-associated difficulties, like the adjustment of the SFC-MS-interface, (3) test a simple as well as non-discriminatory sample enrichment procedure (despite the challenging physicochemical characteristics) and (4) investigate the matrix effects of various aqueous matrices. Therefore, a set of about 100 target compounds was chosen, among them rarely studied substances, their main transformation products, as well as human metabolites. The method is validated, its sensitivity and robustness are evaluated and finally the benefits and limitations are highlighted to show its applicability for future monitoring of environmental and WWTP samples.

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TriOS Water Quality Monitoring

Frank Meinhardt

TriOS' optical sensors have proven themselves as very reliable products of in-situ measurements of NO_3, NO_2, DOC, TSS, SAK254, turbidity as well as Chlorophyll, Phycocyanine, PAH, Colours and all electrochemical parameters over time.

- To get this technique optimised for future requirements, TriOS has introduced some important improvements:
- To get more accurate results, particularly for the spectral interpretation of sum-parameters (e.g. DOC, COD), the sensor calibration is continuously refined to allow a better analysis of individual water matrices, even for brackish water applications with changing salinity.
- In order to face new challenges in groundwater monitoring TriOS developed new independent multiparameter sensors for nitrate and SAC 254 nm with a diameter of 36 mm to enable measurements directly in a well (NICO SLIM line).
- To improve stationary sampling, TriOS and business partner MAXX developed an automatic sampler that provides the opportunity to take only samples that exceed limit values. The system provides a huge range of parameter combinations to save time and costs in monitoring projects (MEAS 100).
- A new water "Quality Tracking Portal" is currently under construction. TriOS and partners want to offer an open platform to combine data from various sources out of the monitoring world. TriOS has founded a team of five well-known German companies from the water business sector to build up an European server landscape to collect and process data. This data could be delivered from sensors or samplers as well as values from lab photometers. That system will allow cross-correlations between values as well as verification by a laboratory. If necessary, remote adjustments of a parameter scaling or settings will be possible. TriOS is looking for more members who are interested in such platform.

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Sediment cores as a tool to explore the historical deposition of the rare earth element in the Oualidia coastal lagoon-Morocco

Nezha Mejjad, Abdelmourhit Laissaouf, Azzouz Benkdad, Ouafa el Hammoumi, Ahmed Fekri, Hamid Amsil

Sediment cores are a useful tool to investigate the history of chemical element distribution which allows a better understanding of their origin. In the present study, we investigate the distribution of rare earth element concentrations in two sediment cores retrieved from the Oualidia coastal lagoon. The results revealed that the REEs concentrations are mainly related to human activities growth since the ’50s. The enrichment factor results indicated that the enrichment by REEs has become slightly significant in the last decades, suggesting that a new source fed the lagoon sediments by REEs and or changes in factors controlling their accumulation and distribution. These findings provided a clear picture of REEs evolution during the last decades and baseline information on the historical deposition of these elements in the Oualidia lagoon as well as useful guidance toward human-environmental interactions, allowing selection of coastal management actions for sustainable growth in the future of such ecosystem.

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What can we learn from online surface water monitoring with selective punctual in situ measurements in stratified water of Lake Scharmützelsee

Brigitte Nixdorf, Jacqueline Rücker, Ingo Henschke

Since 1993, dimictic Lake Scharmützelsee (lake type 13 acc. to WFD) has been monitored biweekly at four different sampling stations along the longitudinal axis of the glacial channel lake, representing the depth gradient of 7 – 30 m. A monitoring station was implemented in the littoral zone (0.3 m depth) in 2015 to record climatic conditions (air temperature, global radiation, wind…) and under water temperature, pH, redox potential, oxygen concentration and saturation, and conductivity. Whereas the temporal point measurements are valuable indicators for vertical and seasonal stratification or mixing of the lake, the high temporal resolution (registration every 15 min) of water parameters delivers relevant ecological information about the extent of their diurnal changes. In this study we compare

1. The differences in relevant high-resolution water parameters in the shallow part of Lake Scharmützelsee with deeper, stratified parts: How meaningful are littoral-measured parameters for the interpretation of vertical stratification patterns? How different is the trophic response in shallow and deep parts of stratified lakes?
2. The diurnal dimension of indicators for primary production: Oxygen concentration and pH reflect the photosynthetic intensity. In two measuring campaigns, we compared the diurnal changes of both parameters with directly measured in situ primary production using oxygen light and dark bottle and 14C measurements.

Results showed that diurnal changes in oxygen concentration and much better pH are suitable indicators for trophic responses primary producers.

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New insights into sources and attenuation of various emerging micropollutants along an impounded transboundary waterway by high-resolution longitudinal sampling

Sabrina Quanz, Simon Mischel, Michael Engel, Michael P. Schlüsener, Dirk Radny, Axel Schmidt, Arne Wick, Thomas A. Ternes

The objective of the presented study is to determine the status quo of trace organic compounds (TrOCs) along the impounded transboundary waterway Moselle and selected tributaries. The study is conducted within the frame of the research project *OGIMo* (Surface water-groundwater interactions along the Moselle). To get a first overview about the study site, a sampling campaign was performed in October 2020. Samples were collected along 240 km in 2 km intervals in the direction of flow at the German part of the river Moselle. Additionally, also the mouths of selected tributaries were sampled. The samples were analyzed for various parameters including pH, conductivity, temperature, dissolved organic carbon (DOC), an- and cations (including trace metals), tritium, radon and a broad spectrum of selected TrOCs. This multi-parametric approach enables a comprehensive evaluation of changes of the chemical status along the river stretch. Analysis of more than 150 different TrOCs including also several transformation products (TPs) was performed by LC-LRMS/MS. Subsequently, a cluster analysis was carried out, whereby individual substances with similar spatial concentration trends were grouped together. The results show that the Saar tributary has a relevant impact on the concentration of TrOCs in the Moselle river and that clusters can be explained by i) different consumption patterns in Germany and France as well as ii) differences in the degradability of individual compounds. Degradation of certain TrOCs such as valsartan was supported by increasing concentrations of their TPs.

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Annual loads of 12 selected organic micro-pollutants at the Rhine monitoring station RÜS between 2013 and 2019

Marie-Ève Randlett, Reto Dolf, Florian R. Storck

The Rhine monitoring station RÜS is equipped with a system allowing the continuous sampling of water at 5 points across the 100 meters river width. Water samples are analysed on a daily basis in the laboratory, for determining organic micro-pollutants concentrations. Automated sensors record water levels and water temperature, generating measurements every few minutes. Here, the annual loads of 12 selected organic micro-pollutants are determined between 2013 and 2019 at the station RÜS. Those 12 selected pollutants are mostly pharmaceuticals, which are efficiently degraded or removed in waste water treatment plants (WWTP) equipped with ozonation or activated carbon treatment. The overall load of these 12 substances slightly decreases from 16 to 12 tons between 2013 and 2019. The decrease is clearer for some substances (ex. Clarithromycin, Metoprolol). There is a clear increase for one substance (Candesartan). Those changes can be related to both WWTP removal efficiencies and pharmaceutical consumptions.

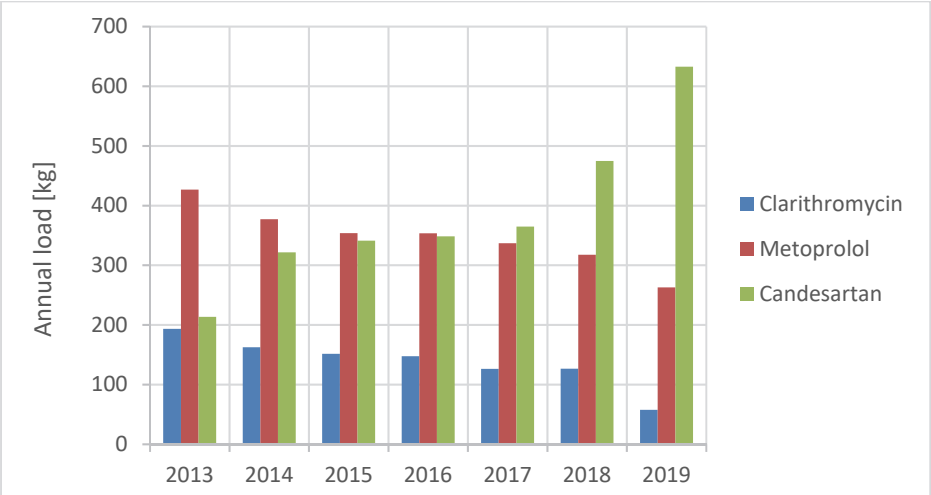

Figure 1: Annual load of Clarithromycin, Metoprolol and Candesartan between 2013 and 2019 at the RÜS station.

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Challenges of (near) real-time predictions of microbial water quality in rivers

Ilona Herrig, Julia Regnery, Wolfgang Seis, Georg Reifferscheid, Werner Manz

Emerging microbiological risks such as the frequent detection of antibiotic resistant bacteria in the aquatic environment or increasing numbers of *Vibrio vulnificus* infections in marine bathing waters and an increasing trend to use surface waters in multifunctional ways (e.g., for recreation, transport, water reuse) elicited the need to better monitor, predict, and manage microbial water quality to protect human health. Quantifying the spatiotemporal variability of microbial water quality and establishing relationships to various environmental factors for example is mandatory to successfully predict and manage microbial water quality. With regard to current modeling and management approaches, multidisciplinary efforts are required that link online chemical water quality monitoring with microbiological aspects. For (near) real-time predictions of microbial water quality in rivers, multiple linear regression models based on environmental parameters were established in a recent study. Environmental factors including hydro-meteorological or physico-chemical factors can explain a substantial proportion of the variation in microbial water quality indicators such as *Escherichia coli*, intestinal enterococci and somatic coliphages. Moreover, $bla_{\text{CTX-M}}$ genes were used as antibiotic resistance markers to complement data on fecal indicator organisms. *E. coli* could substantially explain variations in antibiotic resistance genes. However, model accuracy was limited by times of extraordinary weather conditions. Thus, to improve model accuracy, large databases covering a broad range of environmental conditions are required. Incorporating automated microbiological sampling techniques into surface water monitoring stations could be one way to generate reliable datasets needed for establishment and improvement of predictive microbial water quality models for surface waters.

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National Monitoring of Micropollutants in Switzerland

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The National Surface Water Quality Monitoring Programme (NAWA) aims to monitor the concentrations of pollutants and the ecological conditions in Swiss rivers for the national evaluation of their state. Since 2018, the monitoring program covers – besides nutrients – also micropollutants originating from diffusive sources, such as agriculture, and from waste water treatment plants. The 29 monitoring sites, which were studied during the first two years, are located mainly in the Central Plateau covering different regions, land use forms, and percentages of municipal waste water inputs.
Autonomous samplers are used to collect 14-days composite samples continuously through the year. At 13 sites, additional 3.5-days samples are collected during the pesticide application. At three sites in the main Swiss rivers, the subsamples are taken proportionally to the water discharge allowing the estimation of the pollutant loads.
All the composite samples are analyzed in the laboratory for more than 50 compounds, which can be quantified using a coupled liquid chromatography and mass spectrometry system (LC-MS). The prioritary compounds comprise mainly ecotoxically relevant plant protection products (e.g. Isoproturon, Propamocarb, Bentazone) and pharmaceuticals (e.g. Diclofenac, Carbamazepine, Sulfamethoxazole). At some monitoring sites further compounds, such as artificial sweeteners (e.g. Acesulfame) and complexing agents (e.g. EDTA), and compounds detectable using gas chromatography (GC-MS) are analyzed as well.
In this presentation, we give an overview of the concept and of the techniques used in the national monitoring of micropollutants in Switzerland. Furthermore, we present preliminary results from the two first years of monitoring.

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Application of online biomonitoring systems in wastewater treatment plants

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Wastewater treatment plants (WWTP) are a major source of micropollutants to surface waters. Currently, monitoring of treated wastewater effluent of WWTP this is realised by using grab or composite samples of the wastewater. However, especially in WWTP with industrial input, the wastewater composition can be highly variable and a continuous testing would be advantageous, but very labour and cost intensive. A promising concept is to monitor the wastewater by automated online-biomonitoring systems. Generally, they are applying living organisms to monitor water quality constantly and are designed to raise an alarm if the organism's responses exceed a harmful threshold. Currently online-biomonitoring systems are established for drinking water and surface water but only few experiences exist where wastewater comes in the focus. In this project, two biomonitors were selected to address this research gap. The DaphToxII, which is based on video tracking of the movement pattern of Daphnia magna and the SensaGuard, which is based on changes in the electromagnetic field with Gammarus pulex as a test species. The aim of this study is to see if the selected systems can be applied successfully in wastewater and to understand the behavioural changes of the test organisms exposed to changing wastewater compositions. To have a better understanding of a change in behaviour, the biomonitors were tested with a flow through of wastewater and spike concentrations of different micropollutants under controlled conditions as well as on a wastewater treatment plant in parallel to online chemical analysis. Results of these experiments will be presented. If successful, the online-biomonitoring systems could open up new possibilities to check the effectiveness of wastewater treatment.

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The Elmvale Groundwater Observatory: a facility dedicated to trace metals research

William Shotyk

A summary is presented of experience collecting groundwater from flowing artesian wells in the Elmvale area of southern Ontario, for the determination of trace elements. Emphasis is placed on potentially toxic “heavy metals” such as Ag, Cd, Pb, Sb and Tl which are of great contemporary environmental interest. Groundwater sampling from existing, galvanized steel pipes, often with brass valves, is inappropriate because of leaching of many chalcophile elements from both materials. Instead, dedicated groundwater sampling wells were designed and constructed in stainless steel, acid-cleaned high-density polyethylene (HDPE), and surgical (316) stainless steel. Although the HDPE well components had been leached in nitric acid, we found more leaching of V from this plastic than the stainless steel well. Surgical stainless steel is an excellent choice for these types of investigations and is readily available. Bottles made of low-density polyethylene (LDPE) proved problematic for a long list of trace elements and performed especially badly for Pb, the metal of greatest environmental concern. A number of cleaning procedures were evaluated, but none yielded satisfactory results using LDPE bottles to sample for Pb. In contrast, HDPE bottles provided excellent results for Pb, but leach V. Some part of the variability in the trace element concentration data could be due to ambient air, but metal-free, laminar flow, clean air cabinets eliminated this factor. Based on a comparison of LDPE, HDPE, polypropylene (PP) and FEP bottles, PP is recommended, providing excellent blank values for V, Pb and the other elements of interest. Cleaning the sampling bottles with soap, followed by leaching in HCl and then afterwards in sub-boiled HNO_3, with a final rinse in high purity water, all within a metal-free, clean lab environment is critical for this work.
Using surgical stainless steel wells sampled within laminar flow clean air cabinets using acid-cleaned PP bottles, we find concentrations at or below 1 ng/l for Ag, Bi, Cd, Pb, Sb, and Tl. These results document the natural filtration of water by soil, provide baseline values for comparison with groundwaters from other regions, but also can be used to estimate the human health exposure to trace elements by indigenous peoples inhabiting the region in the past.

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Sampling and chemical monitoring in Switzerland – an overview

Florian R. Storck, Marie-Ève Randlett, Päivi Rinta

Swiss Federal Office for the Environment FOEN runs more than 250 monitoring stations at lakes, rivers and creeks all over Switzerland. The basic parameter is water level or discharge. The latter is important to estimate the load of chemical water pollutants, nutrients, suspended solids, metals and nutrients. Temperature is monitored at more than 70 stations. A subset of stations is equipped for online analysis of physical water quality parameters and continuous water sampling. Sampling strategies comprise both time proportional and discharge proportional sampling. The state of physical water quality is available for the public via internet in real time.
Submerged or vacuum pumps continuously feed a basin in the stations with river water. Most online measurements and automated sampling are conducted in this basin. The advantage of this setting is a protected infrastructure, a large water volume available for sampling and a low impact on the water composition. However, the current methodology of automated sampling and the storage of samples has some restrictions for volatile compounds in several stations. An exception is the station in Weil/Rhine that uses advanced samplers, but is not representative for the federal monitoring network. Composite samples are taken over periods of 3.5 to 14 days, stored cool and shipped to laboratories for chemical analyses.
Federal monitoring is supplemented by cantonal stations and campaigns. Current questions deal with prioritisation of chemical parameters to be analysed, replacement of infrastructure and new developments like particulate matter, e.g. the potential for microplastic analysis.

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