Duester *et al. Environmental Sciences Europe* (2024) 36:44
https://doi.org/10.1186/s12302-024-00874-0

Environmental Sciences Europe

COMMENT

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Qualitative hydrology: a review of the last quarter century and a glimpse into the future from the perspective of the Division G of the Federal Institute of Hydrology

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Abstract

With the nationwide introduction of wastewater treatment the overall water quality improved significantly, but challenges remain, including diffuse pollution, historical sediment contamination and the presence of a multitude of anthropogenic chemical species. The implementation of several EU directives in the twenty-first century led to a stronger focus on improving water and sediment quality and the sustainable management of sediments at river basin scale. Hence, in the last 25 years, not only have the regulatory frameworks significantly changed, but also the scientific backbone of our products, delivered to Germany's federal ministries, practitioners from the German Waterways and Shipping Administration, German federal states and the public. In this respect, approaches such as non-target screening, multi-element analysis, effect-based methods, novel approaches in microplastic and nanoparticle analysis and the benefits from the increase in digitalization and automation are key methods and processes to face future challenges, especially those connected to the global climate crisis.

Keywords Water quality, Contaminants, (Suspended) sediments, Modelling, Ecotoxicology, Management, Aquatic chemistry, Biochemistry, Environmental radioactivity, Monitoring

Introduction

The authors take the 25th anniversary of German Language Branch of the Society of Environmental Toxicology and Chemistry (SETAC GLB) as an opportunity to illustrate their respective disciplines in the Division of Qualitative Hydrology at the Federal Institute of Hydrology during this time and to venture a brief look into the future. Today, the division is divided into four departments for these tasks. Department G1 addresses general water/sediment quality issues covering waterway management, transport modelling of inorganic and organic contaminants and groundwater quality. The aquatic chemistry department G2 focusses mainly on the development of analytical methods for the detection and quantification of inorganic and organic substances as well as on investigating their sources and environmental fate in the aquatic environment. How pollutants and their mixtures affect the aquatic environment is assessed in the department ecotoxicology and biochemistry (G3) and finally, environmental radioactivity and qualitative

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monitoring approaches are addressed by the department G4. A high proportion of the specialized tasks is carried out in cross-departmental areas within the division G and in cooperation with the divisions Ecology (U) and Quantitative Hydrology (M). Each of these task areas contains elements of consultation and assessment, research and development as well as aquatic data collections, data provision paths and projections.

Till the 1990s, severe river pollution was observed in many German river systems and elsewhere in Europe, mostly due to the history of emissions from chemical industry as well as a variety of diffuse pollution sources, e.g., from agriculture or mining. With the EU Water Framework Directive (WFD) and the EU Marine Strategy Framework Directive (MSFD), objectives were defined for surface waters, including marine waters, and groundwater bodies by the EU member states. The implementation of these directives in the beginning of the twenty-first century led to a stronger focus on the improvement of water and sediment quality and the overall status of water bodies (good chemical and environmental status) and therefore, among others, a sustainable management of sediments at river basin scale, although sediments are only briefly considered in the WFD. Hence, it was necessary to develop efficient ways to overcome existing deficiencies and to continue limiting pollution entering water and sediments. As examples, since the beginning of this progress our division significantly participated in the development of trend analysis and assessment criteria for contaminants in water and sediment in the International Council of the Exploration of the Sea (ICES) working groups.

The overall goals of our division are today as in the past to advise federal ministries responsible for transportation and, to a steadily growing extent, for the environment with regard to the variety of national and European regulations dealing with chemicals potentially entering aquatic environments and drinking water. Therefore, the division has developed, in the last 25 years, methodologies and models to predict, measure and assess water and sediment quality as well as the accumulation of contaminants in aquatic organisms based on the respective current state of the art. Using the developed methods and models, advice and support is delivered to the federal ministries and the practitioners from the German Waterways and Shipping Administration (WSV) as well as to the German Federal States.

This publication aims to provide a comprehensive overview of the broad field of qualitative hydrology from the authors' perspectives, covered by the division's core topics mentioned above, over the past 25 years, while at the same time using this knowledge of the past to venture a brief glimpse into the future.

General water quality issues—playground for scientific basic principles and practical applications

The implementation of the WFD (Directive 2000/60/EC), MSFD (Directive 2008/56/EC) and requirements from adjacent regulated areas (e.g., waste disposal, soil protection) was a game changer at its time and surely made water legislation as well as sediment management (with focus on dredged material assessment) a more complex task over time.

To better understand the various river systems from the source to the sea and to support the WSV in Germany in their operational work, efficient monitoring activities and in some cases impact forecasts (mostly in coastal areas) were implemented and conducted considering both WFD and MSFD. Based on our respective expertise and the available scientific knowledge within the last 25 years, we developed and adapted guidance values for contaminants in sediments and dredged materials on the national level for assessing potential environmental risks during management and maintenance of rivers.

Looking back, we were able to support the introduction of new national regulations (e.g., the regulation on the introduction of a "Substitute Construction Materials Ordinance, on the Revision of the Federal Soil Protection and Contaminated Sites Regulation" and on the "Amendment of the Landfill Ordinance and the Commercial Waste Ordinance" (https://www.bgbl.de/), as well as the "Arrangement for the Handling of Dredged Material in German Federal Freshwater Waterways" (https://izw.baw.de/publikationen/umwelt-handbuch/0/20180403_HABAB_WSV%202017.pdf) and "Joint Transitional Arrangements for the Handling of Dredged Material in German Federal Coastal Waterways" (https://www.bafg.de/Baggergut/DE/04_Richtlinien/guebag.pdf?__blob=publicationFile). At the international level, the revision guidelines of the Oslo and Paris Commission (OSPAR; www.ospar.org) and the Helsinki Convention (HELCOM: www.helcom.fi) on how to handle dredged materials in coastal areas in an environmentally responsible manner were milestones, to which we contributed.

Due to climate change, the management of dredged material has changed fundamentally in the last decade, inter alia. In the past the overall process focused on single cases and the respective challenges, and often only a single maintenance option, like dredging of sediments and their relocation in adjacent waterbodies or disposal on land, was given for harbours and waterways. During the last 5 years the adaptive management of dredged materials was introduced (Fig. 1).

To enable fact-based decision processes, actual concentrations of well-known micropollutants, new emerging contaminants and nutrients are monitored adaptively to assess the impact of anthropogenic inputs on sediment

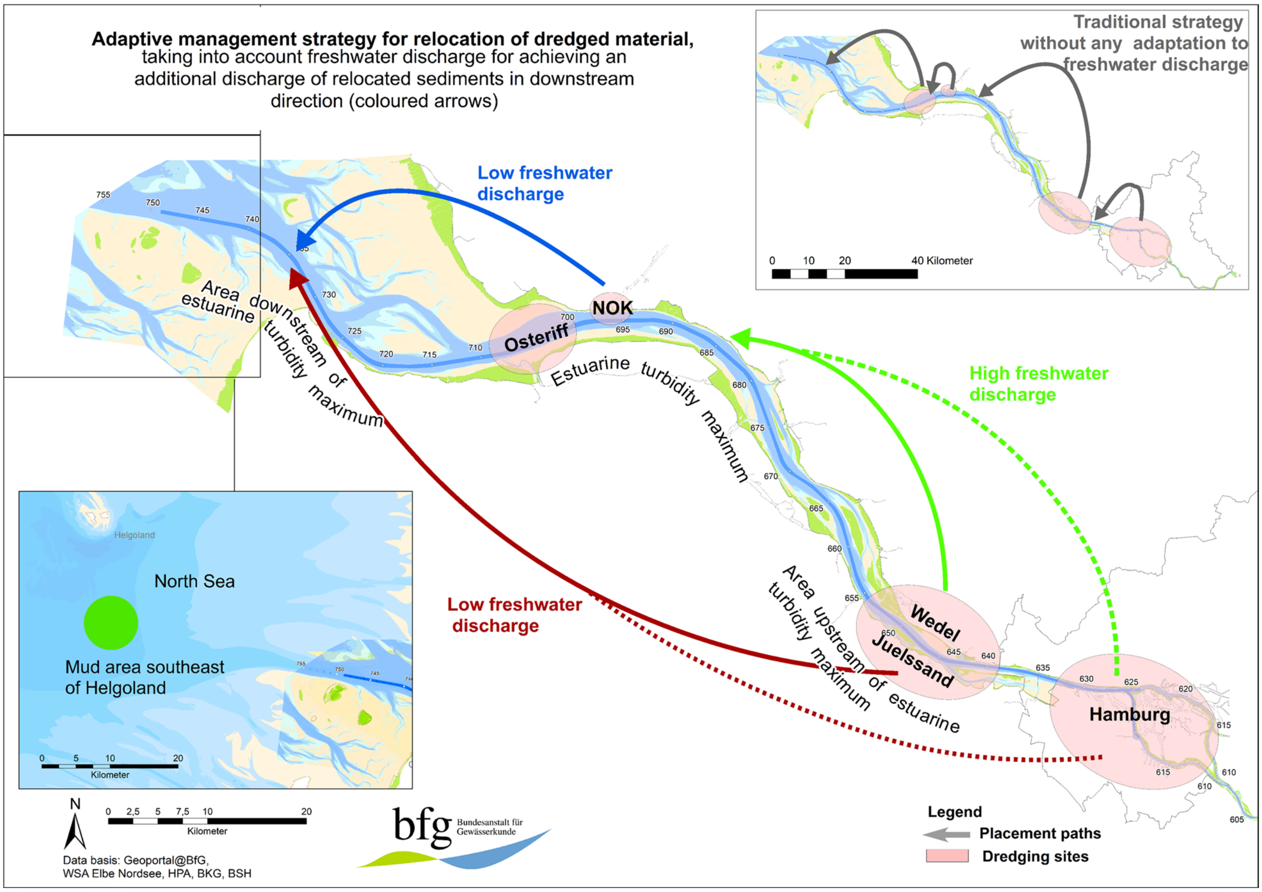

Fig. 1 Change of sediment management strategies in the past 5 years

quality and subsequently the surface water and groundwater quality. The monitoring data (also acquired during extreme hydrological situations, i.e. low flows or floods) were and are also used to validate numeric models which calculate the transport and the dispersion of individual pollutants in the river system (e.g., [1]). By implementing an increasing number of natural processes in these models within the last 25 years the prediction of water quality, also by interpolation between monitoring points in space and time, became more common and is today an indispensable tool in our daily work.

In terms of groundwater quality, the new emerging compounds lead to even more challenging requirements on sampling and analytical methods as concentrations in groundwater are usually significantly lower in comparison to sediment and surface water. Nonetheless, local authorities and water suppliers more frequently claim an increasing number of these new emerging substances to be part of monitoring schemes accompanying constructions along the federal waterways, which makes quality assurance measurements an even more crucial aspect.

With an improved system understanding on contaminants it was possible to support the design and implementation of international integrated sediment management plans in different river basins (e.g., [2]). From these plans, comprehensive management activities were successfully derived within the last decades (e.g., [3] or [4]). The activities of the European Sediment Network (SedNet) within the last 20 years helped additionally to raise awareness on the European level for the urgent need to better integrate sediments and suspended particulate matter (SPM) as key factors in our rivers in terms of the overall system health, of erosion and with this as a potential carrier of contaminants, sedimentation processes and the ecoresponsible management [5]. A milestone was reached with the introduction of sediment and SPM in the progress report of the Working Group ECOSTAT on the European level [6]. Managing of several million tons of dredged material each year by the WSV to ensure safe navigation has to fulfil a multitude of legal requirements and societal demands. In this respect the contamination of dredging material needs to be determined and assessed prior to relocation/disposal in order to prevent adverse effects on the aquatic organisms.

Costs, resource demands and time consumption for these investigations increased over time. However, the whole process is nowadays largely standardized according to quality criteria demands. The effort for the dredged material assessment can be minimized step by step solely with the help of IT management systems (e.g., by using form management systems for the administration of projects and business rule management systems for the assessment, Fig. 2). A management milestone was the introduction of the laboratory management system for the WSV [7] which provides functions for the project management, for the server-side processing of the dredged material assessment and for the reporting.

Improved data management and provision systems form the basis to expand our knowledge and experience in our consulting duties. We further develop environmental information systems (e.g., web services) for research purposes and continue to make environmental quality data available to the public in accordance with the Environmental Information Act in Germany (https://www.umweltbundesamt.de/en/access-to-environmental-information).

In the future, further simplifications and an increase in efficiency appear possible in the course of further digitalization of processes. For this purpose, it will continue to be necessary to maintain close cooperation between authorities, researchers and users.

Occurrence, fate and origin of contaminants in rivers and streams—from the investigation of selected pollutants to multi-element analysis, non-target screening and particle analysis

A major focus of the BfG is on the analysis of trace elements, trace organic compounds (TrOCs) and anthropogenic particles as well as the investigation of the environmental fate of pollutants including sorption, speciation of metals and metalloids, transformation of TrOCs and the leaching from construction materials applied in waterways.

The analysis of trace elements in water, SPM, soil and sediment samples has been subjected to a strong instrumental change within the last two decades. In particular, analytical methods for the determination of single elements have been replaced by high-resolution mass spectrometric multi-element analyses using triple quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) [8, 9]. At the same time, the research focus in the field of elemental analysis changed and is still changing from the traditional metals analysed (e.g., Cd, Pb or Zn) and arsenic to speciation and fractionation-based research questions. To a growing extent, trace elements are investigated using coupled separation systems and mass spectrometric detection techniques [10–12], for example, to investigate elemental chemical species in metal-based antifouling biocides [13]. Other examples of elements that found their way on the lists of analytes of interests within the last 25 years are the rare earth- and the platinum group elements [14] and more recently the technology-critical elements defined by the EU [15]. An element which continuously was and is a focal point of scientific and societal discussion is Hg. Especially its biogeochemical cycle including methylmercury is still from superior environmental interest. The reason at the moment is often the continued exceedance of the EU environmental quality standard for mercury in biota samples of almost all German (and elsewhere) surface waters, despite decreasing anthropogenic Hg releases into aquatic systems. The cause is assumed to be the bioaccumulation of mercury, mostly originating from industrial legacy sources, via the food chains of aquatic organisms, which is facilitated by the microbial methylation of mercury in the water column and sediments [16].

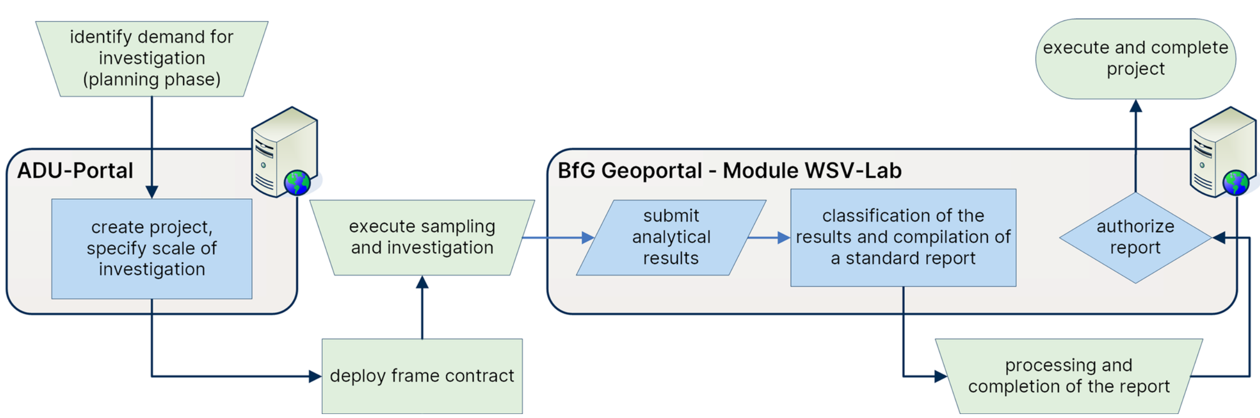

Fig. 2 Work flow for managing the process from investigation to the assessment of dredged material

Also, the gas chromatography with mass spectrometry (GC–MS) and with liquid chromatography tandem mass spectrometry (LC–MS/MS) analysis used for the quantification of TrOCs experienced considerable changes, especially regarding sensitivity and the spectrum and number of analytes. Until the early 2000s the analysis of TrOCs was mainly focused on more apolar and mainly particle-associated pollutants (e.g., PCBs, PAHs, HCHs, HCBs, chlorophenols) using GC coupled to electron-capture or mass spectrometric detection. While the presence of many of these compounds was mainly related to former applications and releases from contaminated sites, recent and ubiquitous emissions of so-called emerging contaminants experienced an increasing awareness. This was also fostered by the developments in the field of LC–MS/MS offering new possibilities for the analysis of polar TrOCs such as the majority of pharmaceuticals and biocides. In the beginning of the twenty-first century specialized LC–MS/MS methods for analysis of single groups (e.g., iodinated X-ray contrast media, acidic pharmaceuticals, antibiotics, psychoactive drugs) in environmental water samples were commonly based on high-volume solid phase extraction (SPE, up to 1 L, e.g., [17–19]). However, due to the continuously improving sensitivity in LC–MS/MS, the trend shifted towards the use of direct injection methods as for example that developed at the BfG by Hermes et al. which is still applied to analyse more than 150 TrOCs in groundwater, surface water and wastewater [20]. On the other hand, there is still a lack of analytical methods to monitor very small and polar TrOCs (e.g., [21, 22]) leading to the development of specialized LC–MS/MS methods based on hydrophilic interaction chromatography (HILIC, e.g., [23]) or coupling of ion-chromatography with mass spectrometry (e.g., [24]). During the last years also supercritical fluid chromatography (SFC), using supercritical CO_2 and an organic modifier on a polar stationary phase, was implemented for the development of sensitive multi-residue SFC–MS methods covering a broad polarity spectrum within one chromatographic run (e.g., [25]).

Since about the 2010s, non-target screening (NTS), based on LC coupled to high-resolution mass spectrometry (HRMS), has found its way into environmental analysis in order to tackle also the high number of unknown TrOCs, i.e. not included in our target methods. In the beginning, a validated LC–HRMS analysis method was established (e.g., [26]), functioning as a basis for continuing water and sediment analysis. Nowadays, a daily monitoring approach of Rhine water in Koblenz is already established since 2014. Today, the development and research need in NTS is not solely within the instrumental field, but to a high and still growing extent within the field of data-processing and workflows to make full use of the large datasets [27, 28]. This is required, mostly to obtain a high time resolution overview on chemical contamination and to gain insights into specific, possibly unknown, emissions from upstream sources. Therefore, the developments at BfG within the last years focused especially on workflows and methodologies for high-throughput automated processing [29, 30] and statistical analysis studies utilizing time series [31], spatial distributions [32] or specific chemical properties [33]. Based on these workflows NTS has found applications not only in regional monitoring projects supporting the Federal States, but was also established as an essential tool to investigate the environmental sustainability of construction materials in hydraulic engineering (see below) as well as to determine the efficiencies of processes such as the success of management tools applied in rivers or the removal of organic contaminants in wastewater treatment plants. In order to make NTS data accessible for users in governmental laboratories and agencies, recently a system for digital archiving, harmonizing and linking *pre-processed* NTS data from different laboratories as well as a frontend web-application (NTSPortal, Fig. 3) was created. This tool allows for the interactive searching, displaying of maps (spatial distributions) and time series of the detection of pollutants in rivers across Germany.

Taken together and as mentioned before it is important to emphasize that the current research is continuing in both the analytical and the data science area, including introducing new chromatographic methods to widen the scope of accessible chemicals and the aggregation of datasets and digital archiving to enable data mining.

In addition to soluble contaminants also particulates are of emerging concerns. After decades on studies on colloids in the environment (e.g., [34]), engineered nanoparticles (ENPs) gained a huge public and scientific awareness approximately within the first decade of the new century as a potential new class of emerging particulate contaminants, e.g., [35, 36]. Taking the number of publications on ENPs (search: analytical chemistry and environmental sciences) in the Web of Science™ as an indicator, rising numbers until 2015 are visible reaching a plateau with about 1500 publications per year by 2020. In contrast to many other emerging contaminants the wastewater treatment was found to alter the particle surfaces and to remove a substantial amount of the ENPs from the wastewater (e.g., [37] or [38]). A particle type that preserves its functionality, that causes after its aging highly significant ecotoxicological effects and which, at the same time, is emitted in high amounts, is luckily at present, to the best of the authors knowledge, still not visible. After the peak funding within the ENPs field, scientists often shifted to the following new hot topic, micro- and nanoplastics in the environment.

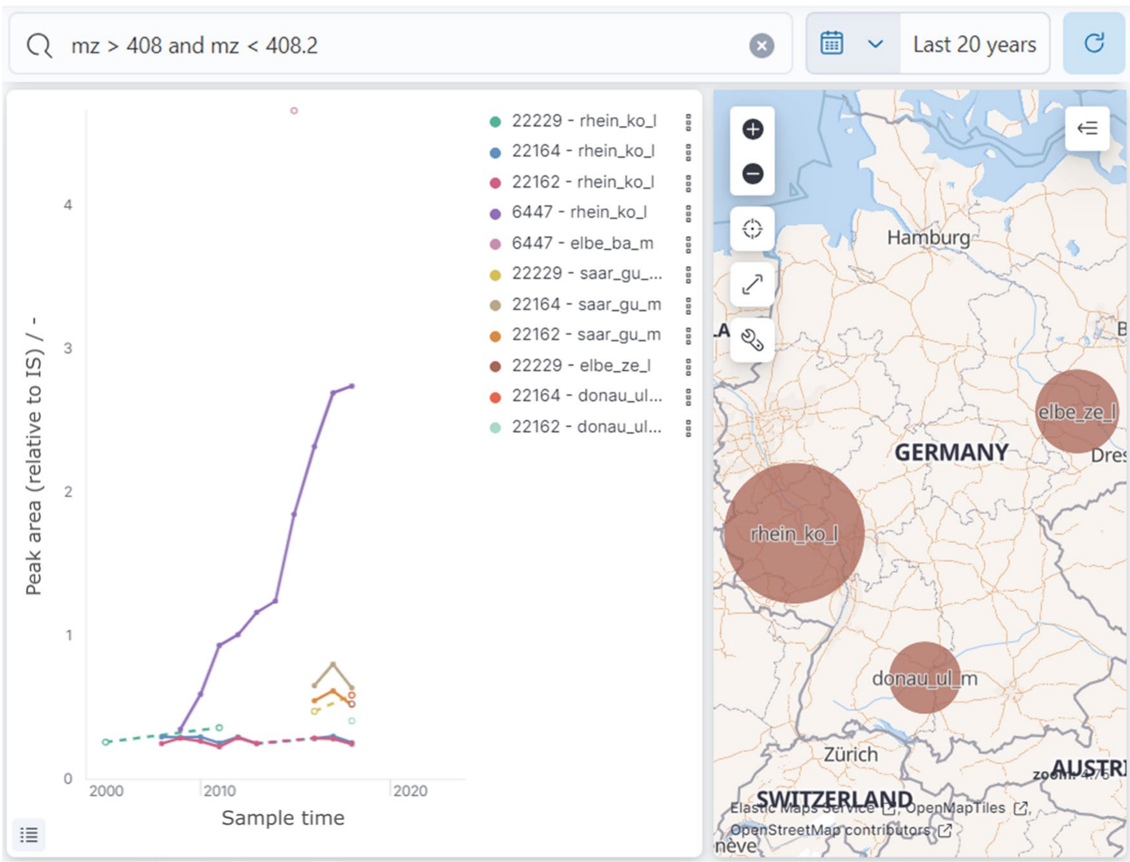

Fig. 3 Screenshot of the NTSPortal web interface showing the use of the search box to search and prioritize non-target-features of a specific mass range in SPM. The time series shows the change in peak area (relative to internal standard (IS)) from 2005 to 2018 at different measurement stations across Germany

Microplastics (MPs) are ubiquitously distributed in the environment. Here, properties of the materials as well as environmental and anthropogenic factors lead to heterogenous distributions of MPs [39]. For a better understanding of those factors including sources and pathways of environmental MPs, comprehensive and comparable data on the abundance are still needed. Studies show that riverine systems are not only pathways for plastics entering the sea, but also act as (temporary) sinks. Therefore, rivers are of particular interest in microplastic research (e.g., [40, 41]). Studies show that barrages hinder sediment and thus MPs to be transported further downstream and that rivers may act as a sink for plastics [42, 43].

In an international context, regional action plans on marine litter have been initiated by, e.g., HELCOM initiative [44]. Moreover, technical ISO committee 61 with the subcommittee 14 is working on a suggestion for standardization of analytical methods [45]. During the last 7 years these synthetic polymers (MPs 5 mm down to 1 µm and nanoplastics < 1 µm), received increasing attention as emerging particulate contaminants. For determination of bulk concentrations of the polymers, several methods were created in the last decade [46, 47] and the BfG developed a pyrolysis GC–MS method [48]. The method is based on indirect determination of the polymers by analysis of decomposition products formed during thermal degradation. Special research focus lay on matrix effects during pyrolysis and their influence on quantification results [49, 50] and on the capabilities of SPM samplers to sample MPs [51]. The analytical method allows for quantification of polyethylene (PE), polypropylene (PP) and polystyrene (PS) in complex environmental samples such as particular matter, sediment and soil. Since pyrolysis products of polyvinylchloride (PVC) are very unspecific, a separate combustion ion-chromatography method using hydrogen chloride as marker was developed [52]. The abundance and properties of MPs (e.g., size) imply interactions with a wide range of biological species. Feeding studies show that the interaction is material- (e.g., size, shape, polymer) and biological species- (e.g., feeding type, development) specific [53, 54].

The same holds true for the ecotoxicity of microplastic. Multiple properties of MPs have the potential to negatively affect biota (e.g., particulate and chemical factors), however, the outcome of an exposure to microplastic depends on the specific material and the biological species [43, 54]. As such, generally valid statements concerning the toxicity of MPs are difficult to derive, this particularly when complex environmental scenarios (e.g., aging) as well as the methodological challenges of particle testing are considered [55]. Overall, the BfG actively participates in the research needed in order to better understand the abundance, fate and effects of environmental MPs.

In addition to the development of analytical methods and monitoring of water contaminants, the environmental fate of trace elements and TrOCs was one key research topic during the last 25 years. In the 2000s research was mainly focused on assessing the sorption and primary degradation of TrOCs such as pharmaceuticals and hormones in lab experiments (e.g., [17]) and field studies (e.g., [56]). More and more the speciation and fractionation of metals and metalloids as well as the identification of transformation products (TPs) and the elucidation of whole transformation pathways became a major issue. First studies used a combination of mass spectrometric (GC–MS and LC–MS) and nuclear magnetic resonance spectroscopy (NMR) analyses for successful identification of TPs from TrOCs (e.g., [57]). A crucial step was the increasing availability of HRMS systems in the late 2000's which pushed TP identification and considerably improved our current mechanistic understanding of TrOC transformation (e.g., [58–60]). Moreover, nowadays relationships between the degradation potential, the environmental/operation conditions as well as microbial community composition and their functional potential are more and more addressed by combining chemical analysis with rapidly developing bioanalytical methods (omics approaches, e.g., [61–63]). This also includes the research on enzymes involved in TrOC degradation, for example, the use of cell-free biodegradation experiments with enzyme lysates shed light on the enzymatic activities likely involved in the biotransformation of TrOCs [64, 65]. Just recently enzyme fractionation of lysates and shot-gun proteomics was successfully applied to unravel the enzymatic transformation of the artificial sweetener acesulfame [66].

Another topic, which gained increasing attention during the last decades is the investigation of the release of TrOCs from construction materials and the involved (eco-) toxicological effects [67–70]. With an initial focus set on the potential release of metals and metalloids from armor stones [71–73] in view of maximum release limits provided for the German Technical Terms of Delivery for Armor Stones (2003 and 2022, https://izw.baw.de/publikationen/tr-w/0/Technische_Lieferbedingungen_Wasserbausteine_TLW_2022.pdf), research was successively extended to other construction materials. In collaboration with other federal authorities responsible for traffic infrastructure within the "BMDV Network of Experts" (Federal Waterways Engineering and Research Institute (BAW), the Federal Highway Research Institute (BASt), the German Centre for Rail Traffic Research (DZSF) and the Federal Maritime and Hydrographic Agency (BSH)) these comprise concrete, corrosion protection and geotextiles [74–76]. Especially due to the nature of the latter two, analytical techniques have been extended to TrOCs including non-target approaches in order to assess the release of potentially harmful substances from these materials [77].

Regarding the spectrum of contaminants as well as the sensitivity of the analytical methods a big step forward was made during the last 25 years. However, one lesson learned is that the analytical window still needs to be broadened especially with respect to very polar and ionic compounds. Moreover, we have to realize that data science including artificial intelligence approaches will be the next crucial step in exploiting the potential of advanced chemical analysis (e.g., anomaly analysis, standard-free quantification as well as chemical identification of unknown compounds and particles) and in predicting the environmental fate of contaminants. Advanced data science approaches will also be one of the keys for providing missing links between the chemical burden and the effects on organisms, populations and whole ecosystems (cf. next chapter) which is still a main obstacle for prioritization of chemical stressors and targeted measures for an effective protection of aquatic ecosystems.

From compounds to effects

Biological methods are key to capture, assess and understand harmful effects of pollutants. Thus, ecotoxicological methods are essential tools to complement data from chemical analysis. At the BfG such methods are well established for the quality assessment of dredged material (HABAB, https://izw.baw.de/publikationen/umwelt-handbuch/0/2201_2_5_habab_text.pdf) based on national and international standards. During the last 25 years the BfG has continuously contributed to the further development and standardization of methods and approaches to assess water and sediment quality based on effect data [78, 79]. The following sections focus on a number of developments in this research area at the interfaces between science, environmental management and regulation.

Analysing contaminant concentrations in biota is often applied for the assessment of water quality, e.g., for compliance checking according to the WFD. In comparison to measurements of biota, passive sampling suffers less from variability and may—in some cases—complement biota monitoring [80]. Passive sampling devices contain a sampling phase, usually a polymer that accumulates chemicals when exposed in the environment or to an environmental sample. Over the last decade, silicone-based passive samplers for quantifying hydrophobic organic chemicals in water bodies or in bioassays gained more and more attention, e.g., [81]. Due to the enrichment of target analytes in the sampling polymer, very low contaminant concentrations are quantified. The calibration of sampling rates further enables the determination of averaged concentrations over the exposure time of the samplers. For example, passive sampling in combination with sediment monitoring showed that in North Rhine Westphalia pit waters from coal mines contribute to contamination of surface waters with PCBs and PCB surrogates in the direct vicinity of the discharge sites only [82]. In addition, silicone-based passive samplers were also used in hazard and risk assessments as well as in the management of contaminated sediments to address bioavailable concentrations in sediment porewater. When applied as equilibrium samplers, freely dissolved concentrations of organic contaminants in the porewater of sediments can be measured that are considered to be responsible for exposure, bioaccumulation, and effects in aquatic biota [83]. As an example, samples from the river Elbe tested for PCBs showed a close link between bioaccumulation in fish and sediment contamination [84]. At present, passive samplers are applied—partly in combination with biota monitoring—to improve risk assessments and the management of dredging activities as well as of disposal sites in different waterways. EBMs address adverse effects elicited by mixtures of compounds in the environment rather than individual substances. In this sense EBMs are sum parameters that reflect the biological activity of an environmental sample. The use of in vivo-bioassays such as the acute test with *D. magna* or the growth inhibition test for the green algae have a long history in Germany for the assessment of dredged material (cf. HABAB) but is as well implemented in the German Waste Water Ordinance [85]. Besides the contribution to standardization efforts on the national and international level, the BfG (co-)developed sediment contact assays using in vivo-approaches [86–91] to better understand the bioavailability of particle-associated contaminants as a key factor for the assessment of sediment quality. As an important step towards an implementation of sediment contact assays for regulatory purposes a number of validation studies have been performed including the definition of toxicity threshold values for a number of sediment contact assays based [92, 93].

In addition to the use of in vivo-bioassays there are growing efforts to develop and implement mechanistic in vitro-bioassays for the assessment of water quality. First attempts to develop such methods were undertaken in environmental genotoxicity and mutagenicity and the regulatory use dates back to the early 1990s [94–100]. At the beginning of the 2000s, endocrine effects and later on dioxins like activity mediated effects by the aryl-hydrocarbon receptor received more attention [79, 101–104]. Such in vitro-bioassays allow for the quantification of the effect-strength in terms of a biological equivalence concentration (BEQ) that expresses the outcome of the bioassays as a concentration of a reference compound, e.g., as an estradiol equivalence concentration (E2-Eq) [105, 106]. Recently, an ISO-standard for the calculation of BEQ [107] was successfully published, surely a milestone in the last 25 years. This development opens the opportunity to define effect-based trigger (EBT) values that are used in analogy to the well-established compound-based environmental quality standards implemented in the WFD. The BfG was involved in a number of studies leading to proposals for EBT-values for the assessment of estrogenicity and other adverse effects [108, 109]. In addition to the use of EBMs for a water quality assessment, in vitro-bioassays are used in combination with a chromatographic separation of extracted environmental samples and LC/MS/MS for an effect directed analysis (EDA) to identify toxic drivers in the environment. As a consistent next step in the last years, a methodology to directly couple high performance thin-layer chromatography (HPTLC) and in vitro-bioassays were published, e.g., [101, 110]. Several in vitro-bioassays were successfully implemented already to detect, e.g., genotoxicity [111], inhibition of the photosystem II (PS II) [112], anti-androgenicity [113] and further yeast-based assays for the detection of hormonal effects [114]. The latter was used to identify bisphenol A as an UV-induced degradation product of epoxy-based anti-corrosion protection [115].

The combination of passive sampling and effect-based methods (EBMs) is a highly valuable approach to capture the presence of harmful contaminants in the environment [116]. A combination of passive sampling using a Chemcatcher for the enrichment of polar contaminations with the effect-based analysis of inhibitors of the photosystem II—such as the priority compounds atrazine and diuron—was used to investigate a small river system (Fig. 4).

The results show clearly the increasing contamination of the surface water with inhibitors of the PSII from the source of the river to its mouth. The obtained effect profiles might be used to pinpoint sources of emission using a sampling with a higher spatial resolution. Since the detection is effect-based a knowledge about the chemical

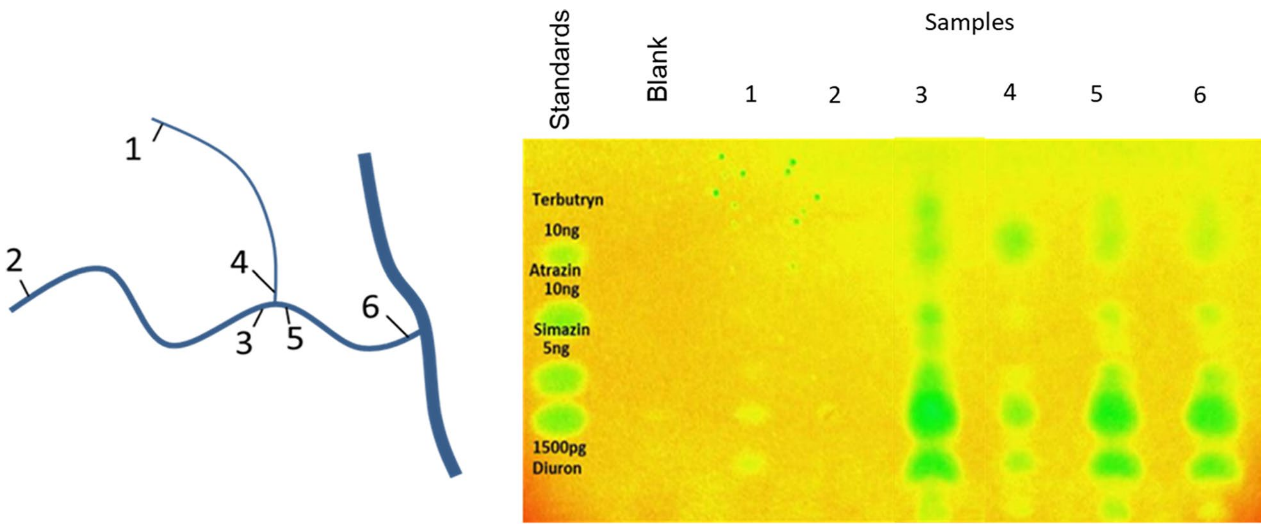

Fig. 4 Occurrence of PSII-inhibitors in surface water (modified from [116]). The surface water of a small river was sampled using Chemcatcher at different locations (sampling points 1–6) and subsequently analysed by a combination of HPTLC and an on-plate assay using fresh water algae for the detection of PSII-inhibition by measuring the quantum yield via imaging pulse-amplitude-modulation (IPAM) [117]

entity causing the effect is not required. Candidate compounds causing the observed effect can be easily falsified by the application of the respective standard in parallel to the environmental sample via the chromatographic behaviour. Signals that cannot be matched by a candidate compound can be identified by further in-depth effect directed analysis. In this respect, the BfG aims to develop a framework for effect directed analysis based on combinations of HPLC- and HPTLC-based separation techniques in direct combination with in vitro-bioassays.

Fine sediments are often hotspots of chemical pollution and meiobenthic organisms are usually more dominant in these sediments than macroinvertebrates. In addition, meiobenthic organisms are exclusively endobenthic and are thus more consistently exposed to sediment-bound pollutants. However, there is a lack of meiobenthos-based assessment tools (e.g., indices) to detect pollution-induced changes in these communities, which would help to assess sediment quality. Moreover, there is a general deficit of pollution-sensitive indices for assessments in the aquatic environment, including metrics as defined by the WFD [118]. Besides contributing to the development of a sediment-contact assay with *Caenorhabditis elegans* [86, 119] and evaluating the derivation of sediment quality guidelines based on nematodes, it was thus an important step forward in the last decades to initiate and take part in several projects for the development and validation of the NemaSPEAR[%]-index [120, 121]. This made it possible to consider one of the most abundant and species-rich meiobenthic taxa, the nematodes, to support risk assessment of pollutants in sediments by covering all major lines of evidence according to the sediment quality triad approach. An important task of the BfG is the assessment and management of sediments and dredged material and these lines of evidence allow for identifying and prioritizing management options and can be used to investigate cause–effect relationships in a multiple stressor scenario. The importance of the latter has been recently addressed in a CIS technical document of the European Union concerning integrated sediment management in the context of the WFD [122].

The general applicability of the NemaSPEAR[%]-index and its ability to complement metrics based on macroinvertebrates in environmental assessments by more specifically reflecting sediment pollution has been assessed (e.g., [123–127]. Furthermore, it was important to support first steps towards DNA-based molecular characterization of nematodes (barcoding and metabarcoding), in particular to enable the application of the index independent of morpho-taxonomic expertise. As an example, in the 4 year project NESTOR (2016–2020), sequence databases were expanded (especially for relevant NemaSPEAR[%] species) and methods were optimized and already successfully applied to natural samples for quality assessments using the NemaSPEAR[%]-index (e.g., [128–130]. It was shown that the DNA-based calculation of the index is also possible with semi-quantitative data (i.e. relative biomass-related abundances). In order to further improve the application of the NemaSPEAR[%]-index, new sequencing techniques (esp. long-read sequencing and PCR-free techniques) need to be evaluated to achieve a better taxonomic resolution and to facilitate quantitative species analysis.

A consequent next step to us is to develop frameworks which complement targeted chemical analytics of environmental samples with ecotoxicological effect prognoses. To achieve this, effect data from various databases, e.g., Toxcast [131, 132], ECOTOX [133] or ChEMBL [134] are integrated and consistent high-content effect profiles of chemicals are inferred using machine-learning methods. Additionally, refined mixture models are developed in order to enable the inference of overall effect profiles of chemical mixtures, measured in environmental samples. High-content effect profiles can be assessed for their potential in identifying and prioritizing hazardous substances in complex environmental mixtures, thus adding value to state-of-the-art chemical monitoring approaches at the BfG and elsewhere.

Closing the loop—from analyses, via data communication to data provision

Continuous monitoring of the aquatic environment for radioactive substances has been taking place by the BfG across Germany since 1958 [135–138]. The monitoring programs are based on the German Radiation Protection Act (StrlSchG) which was updated in 2017, the General Administrative Regulation on the Integrated Measuring and Information System for Monitoring Radioactivity in the Environment (AVV-IMIS, last updated in 2006 and currently in revision) and associated ordinances, regulations and guidelines. In the AVV-IMIS, the mandatory specifications for determining the specific activities or activity concentrations of radionuclides in environmental samples are specified. Connected to this, the international and national emergency plans required by the EU and the StrlSchG are being revised at the moment. The aim is to record (long-term) changes in radioactivity within federal waterways and to estimate possible effects on humans and the environment on the basis of the surveys. Looking at the last 25 years a very significant and long-lasting political impact was caused by the nuclear power plant disaster 2011 in Fukushima [139, 140] which fostered also the nuclear phaseout in Germany, even though no radioactive anomalies were monitored within the BfG monitoring and measuring network. Today, the monitoring network consists of 67 stations (supported by the WSV, the German Meteorological Service (DWD), the Federal Institute for Geosciences and Natural Resources (BGR) and some federal state offices), which include radiological warning stations, monthly samplers (river water and SPM) and precipitation collectors (Fig. 5) as well as two radiochemical laboratories.

In general, the monitoring systems for environmental radioactivity have undergone less pronounced changes than other areas in environmental analytics. Nonetheless, the concepts and operating systems for radioactive emergencies were constantly improved (e.g., [141]). However, for more than 25 years the basic concept for monitoring environmental radioactivity on federal waterways in Germany is based on two independently operating systems [135, 136]: in the monitoring stations for radioactive nuclides, the total gamma activity concentration of river water is online measured continuously with a scintillation detector (NaI) which is positioned within a lead-shielded flow-through cell. To avoid rising background levels from the deposition of SPM over time a self-designed measuring cell with an automatic rinsing function was developed. This provides an overall picture of the gamma activity from 40 stations in the German federal waterways, from where the data are retrieved online at 10-min intervals at the recently inaugurated control centre for environmental radioactivity in Koblenz. Supported by the innovations connected to the keyword "industry 4.0", the control room and the associated processes allow us the integration of an almost infinite number of parameters. Together with ongoing material and process standardization, it is possible today to manage and maintain nationwide monitoring networks far better than 25 years ago.

In parallel, river water, SPM and sediment samples are regularly collected, brought to the laboratories for environmental radioactivity in Koblenz, and analysed for natural and artificial radionuclides. The laboratory methods which are used in this monitoring program are standardized by published procedure manuals [142], but improvements of existing methods and the development of new methods are constantly taking place. In addition to the evaluation of new radioactive tracers in the water cycle such as S-35 [143], new opportunities for complementary radionuclide analyses are provided by triple quadrupole plasma mass spectrometry (ICP-QQQ-MS) which enables the detection of several relevant radionuclides (e.g., Sr-90) due to its efficient removal of interferences and the analysis in mass-shift mode after a reaction cell (e.g., [144–147]). Such approaches also offer new applications for environmental nuclear forensics [148] including in aquatic environments [149–152].

The nuclides measured via environmental monitoring (e.g., tritium) are also available to the scientific community [153] and are used for scientific research, e.g., surface water/groundwater interaction [154], or catchment travel times [155].

In addition, a new class of nuclides from medical applications are increasingly found in the environmental samples [156–158]. These mostly relatively short-lived nuclides with half-lives (HWZ) of a few days are used in large quantities for diagnostics and treatment in nuclear medicine (e.g., cancer therapy) and also enter

Fig. 5 Monitoring network of the BfG department G4 for environmental radioactivity and qualitative aquatic monitoring

surface waters through excretions of the treated patients via wastewater treatment plants [159]. While, e.g., iodine-131 (HWZ: 8 days) has been measured regularly in SPM of various German rivers for many years, the detection of lutetium-177 (HWZ: 6.6 days) has so far been rarer and limited to a few sites [157].

Accidental or discharge driven river pollution, not only with radioactive but with any soluble substance, was and is a substantial pathway for pollutants into the aquatic environment. In order to reduce the risk of sustained damage and create a basis for measures to protect the public, numerical transport models are used to predict the arrival time, duration and maximum concentration of any soluble and less often of particulate contaminants in flowing waterbodies. Within the large-scale monitoring concept of environmental radioactivity, our responsibility is, among other things, to stand by with effective models for federal waterways. In the past, Excel-based forecasts were used for this purpose, but were replaced by a one-dimensional water quality model [160]. With these developments it has since been possible to predict pollutant transport in real-time, considering the respective river morphology and changing hydrological boundary conditions. In order to calibrate the transport model, tracer experiments were and are necessary, which provide solid knowledge about the longitudinal dispersion coefficient and velocity of river waters within the respective river section [161, 162]. Within the last 25 years, this type of field experiments was conducted by making use of tritium that is routinely emitted from nuclear power plants and by tracing it along the flow path of the rivers. However, the shutdown of the German nuclear power plants is not only a step change in the energy supply of Germany but delivers also challenges for the transport modelling approaches. Tritium as a non-sorbing, low background, conservative tracer is no longer available, thus crucial information for the development and calibration of the transport models is missing. Next to fluorescent tracers, owing their own challenges [163, 164], the search for alternative tracers, like intended and unintendedly released anthropogenic substances, is one of the main goals in the last and the coming years. Further, with increasing scientific knowledge and threats like global warming, the demand on numerical models is also growing. Thus, the consideration of soluble and particulate transport in two or even three dimensions is certainly a reasonable step, which however, requires the availability of a new generation of tracers. Hence, it is foreseeable that our tracer experiments will undergo significant changes as before in the working field of metals and metalloids in the environment as already mentioned in the second chapter.

The focus of investigations on metals and metalloids in surface water systems has shifted over the last few decades from the determination of total concentrations for a limited number of metals and metalloids of particular concern (e.g., As, Pb, Cd, Zn, Cu, Ni) to a much larger number of elements, some of them only present at (ultra) trace levels, and the elucidation of their element species dynamics under different environmental conditions. This development and the additional knowledge gain were triggered by the availability of more sensitive and versatile analytical instruments such as ICP-QQQ-MS which are capable of measuring a multitude of major and trace elements simultaneously over a wide range of concentrations and reliably by removing interferences by a collision/reaction cell and the use of two independent mass filters [165]. A new method for the analysis of 68 elements in river water in a single analytical run was recently developed at BfG [9] representing an important step towards multi-element river monitoring and the possibility of using elemental fingerprints of a multitude of elements as tracer for natural/anthropogenic sources and biogeochemical cycling in surface waters. As already briefly mentioned before, a particular group of trace elements, which have only recently come into the focus of attention, are the so-called "technologically critical elements" with high supply risks and expected increasing demand in industry, but the understanding of their behaviour and fate in surface waters is often still limited and their distribution has only been studied in recent studies (e.g., [166]). Another example of an "emerging pollutant" is gadolinium, used in medical imaging and which is, together with other "rare earth elements", increasingly allocated to anthropogenic sources in natural waters (e.g., [167]). The understanding of metal and metalloid speciation in surface waters is still another research frontier in which important progress has been made over the last few decades. For example, the widespread occurrence of Mn(III) complexed to organic ligands in oxygenated waters has been recognized [168], while hyphenated techniques such as HPLC–ICP-MS offer further insights into metal speciation in environmental samples (e.g., [169]). Analytical advances have also made it possible to resolve small variations in the stable isotope ratios of metal and metalloid elements in environmental samples [170], providing a new tool for source and process tracing in environmental metal and metalloid cycling, including for example in contaminated stream environments (e.g., [171]). Considering all these changes, some things remained the same for good reasons. Examples are long-term monitoring programs in catchment management and even though the number of parameters grew significantly with our analytical skills for the monitoring program of the International Commission for the Protection of the Rhine (https://iksr.bafg.de), principle aims and concepts have remained the same for more than 60 years. Hence, working with water quality data from 25 years ago one might think nothing has significantly changed. Apart from sensor robustness, online measurement of parameters like pH, conductivity, temperature and oxygen indeed has not fundamentally changed at all since the 1990s and some of the original equipment is still capable of providing reliable data at a high time resolution. Metals and metalloids played and play an important role, but when looking at the last 25 years a changed balance between organic and inorganic compounds measured on a regular basis immediately catches the eye. In 1980, the German part of the Rhine database (FGG 2023, https://fgg-rhein.bafg.de) provided data for 23 inorganic compounds and two organic ones. In 1999, this increased to 25 inorganic and 69 organic substances. In 2023, 300 organic and 30 inorganic substances are listed in the monitoring program. This is closely connected to the previously mentioned changing analytical capabilities as well as to changing societal demands (e.g., [172]). The focus has shifted from inorganic to organic substances and today a much higher monitoring resolution in time and space is demanded [173], also to be better prepared for environmental disasters [9] and the direct and indirect effects of global warming. Therefore, within the last 25 years we have broadened our monitoring capabilities, together with analytical capabilities that have drastically changed. Starting from automation (samples are taken and analysed automatically [172]), this also includes multi-mode instruments (more compounds can be measured in a single instrument [9]) and non-target screening [33]. Of course, the instruments have to be maintained, the methods have to be developed and the costs and benefits of each additional measurement have to be weighted. Still each year more and more methods are standardized and handed over to regular monitoring programs and together with the evolvement of data science, these methods may be a building block to make us better capable of facing future challenges in our river systems. At the moment, we lay the basis for the future monitoring, building a sophisticated and up-to-date framework for data and knowledge provision for the public, the political consulting and the civil security.

If we take the last 25 years as a point of reference, we can clearly draw a positive, expectant and anticipatory picture for the areas addressed in this chapter. All areas are currently clearly development areas, so that it is to be expected that significant positive changes will happen within the next two decades spanning from data collection (temporal resolution and spatial coverage), via communication and data analysis (connection possibilities and speed, as well as machine-supported data analysis) to data provision (prompt free availability of the data including extended forecast possibilities). However, for our research objects, the major rivers of Germany, the outlook for the future is less positive. In particular, the change due to man-made climate change will already pose great challenges to those conducting research and the entire population in the next decades.

Conclusions

In order to remain able to deliver highest quality services to the BfG "clients" and deliver the best possible political consulting our challenges in future will remain the identification as well as quantification of emerging regional and global trends and thereby, the detection and elucidation of the huge number of substances discharged into the aquatic environment. Surely, via several primary and secondary effects, global warming will cause additional substantial pressure to our aquatic environments and significant conflicts of interest with respect to water utilization are already present (e.g., discharge constrains under low water conditions). The recent development of analytical multi-methods using mass spectrometry helps us to assess the occurrence of a multitude of inorganic elements as well as organic compounds in a variety of environmental matrices. However, we are aware that even multi-methods such as NTS using LC-RP-electrospray–HR MS are not able to detect "all" organic compounds discharged into rivers and coastal areas. Especially extremely polar and highly lipophilic compounds are hardly covered and thus, there is a need to develop NTS methods for these extremely polar compounds using, e.g., SFC and GC–HRMS for lipophilic compounds.

Furthermore, sensitive target methods are needed for extremely potent compounds such as estrogens or gestagens with no effect concentration values down to the sub sub-nanogram per litre range. In addition, the detection and occurrence of particles became recently a very important environmental topic. Currently the accurate detection and the fate of ENPs and MPs are a major challenge. Here a standardization and quality assessment would still be very crucial, to enable a comparison of monitoring results.

It is extremely important to link the occurrence date of chemicals with those obtained from effect studies of individual substances, mixtures of substances as well as from environmental samples. There is a need to further develop sensitive in vitro and in vivo test systems and to standardize them. However, it is still a challenge to explain the ecotoxicological effects measured in the water phase or in sediments and SPM by the occurrence of the complex mixture of substances detected in rivers and streams. To enable this, new approaches including quantitative structure–activity relationship models and EDA are very important.

Sediment management needs to consider potential dredging activities. Thus, it is essential that contamination hotspots in rivers and coastal areas will continue to be removed. Furthermore, new emerging contaminants and innovative biotests indicating a contamination of sediments and dredging material have to be integrated into current monitoring and assessments concepts allowing for a reliable relocation of dredging material into rivers or to apply alternative measures.

Finally, it is essential to avoid and to balance the discharge of all kinds of contaminants in the aquatic environment. Therefore, we need analytical and ecotoxicological methods which are able to accurately quantify their concentrations and effects in treated and untreated water as well to determine their removal in processes such as biological or oxidative wastewater treatment.

In order to successfully face future challenges, also connected to the global climate crisis, and to assess the discharge and occurrence of contaminants in aquatic environments and drinking water, a set of online and atline methodologies need to be combined in a few strep-stone monitoring stations. The BfG sees a significant potential to increase the data resolution in time and quantity (where needed). With such a step-stone structure of few automated stations within a catchment, the foreseeable benefits can be improved (artificial intelligence supported) highly adaptable forecasting and modelling capabilities as well as holistic catchment substance balances to better face extreme situations in the future. This may end in establishing an integrated international chemical data and prognosis centre enabling the surveillance of inland and coastal waters across borders. We must keep in mind that intelligent water management systems across borders to protect and share water resources, based on common interests and sharing data between countries, is a core piece of our future water diplomacy and will support the stability in Europe and elsewhere.

Abbreviations

G	Division Qualitative Hydrology
BfG	Federal Institute of hydrology
EU	European Union
SETAC GLB	German Language Branch of the Society of Environmental Toxicology and Chemistry
WFD	EU Water Framework Directive
MSFD	EU Marine Strategy Framework Directive
ICES	International Council of the Exploration of the Sea
WSV	German Waterways and Shipping Administration
OSPAR	Oslo and Paris Commission
HELCOM	Helsinki Convention
SedNet	European Sediment Network
SPM	Suspended particulate matter
TrOCs	Trace organic compounds
ICP-MS	Inductively coupled plasma mass spectrometry
GC–MS	Gas chromatography with mass spectrometry
LC-MS/MS	Liquid chromatography tandem mass spectrometry
SPE	Solid phase extraction
HILIC	Hydrophilic interaction chromatography
SFC	Supercritical fluid chromatography
NTS	Non-target screening
HRMS	High-resolution mass spectrometry
IS	Internal standard
ENPs	Engineered nanoparticles
MPs	Microplastics
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
TPs	Transformation products
NMR	Nuclear magnetic resonance spectroscopy
BAW	Federal Waterways Engineering and Research Institute
DZSF	German Centre for Rail Traffic Research
BSH	Federal Maritime and Hydrographic Agency
EBMs	Effect-based methods
BEQ	Biological equivalence concentration
E2-Eq	Estradiol equivalence concentration
EBT	Effect-based trigger
EDA	Effect directed analysis
HPTLC	High performance thin-layer chromatography
StrlSchG	German Radiation Protection Act
AVV-IMIS	Integrated measuring and information system for monitoring radioactivity in the environment
DWD	German Meteorological Service
BGR	German Federal Institute for Geosciences and Natural Resources
ICP-QQQ-MS	Triple quadrupole plasma mass spectrometry
HWZ	Half-lives

Acknowledgements
We thank the former and the current staff of Division G, our cooperation partners in the BfG, from federal states, from federal authorities and universities as well as the federal ministries involved.

Background
The authors celebrate the 25th anniversary of SETAC GLB by highlighting the tasks of the Division Qualitative Hydrology (G) at the Federal Institute of Hydrology (BfG) in Germany and their development over time. The division focuses on the occurrence, mobility and availability of hazardous substances incl. radionuclides as well as their effects on surface waters, sediments, and dredged materials. Within four departments, the authors address general water/sediment quality issues, aquatic chemistry, ecotoxicology and biochemistry, environmental radioactivity, and qualitative monitoring approaches.

Author contributions
All authors were involved in the writing process and quality assurance of the respective chapters. The entire text was revised by LD, TAT, AW and JGW. The idea and initiative go back to LD. The concept was created by VB, SB, LD, GR, AW and TAT.

Funding
The authors are financed by the German Federal Ministries for Digital and Transport and for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection.

Availability of data and materials
Not applicable.

Declarations

Ethical approval and consent to participate
Not applicable.

Competing interests
The authors declare no competing interests.

Received: 28 December 2023 Accepted: 20 February 2024
Published online: 01 March 2024

References

1. Hübner G, Schwandt D, Wyrwa J. (2023) Modellierung von Schwermetallen und Arsen in der Elbe bei extremem Niedrigwasser. In Ergebnisse der Jahrestagung 2022

2. Heininger P, Pelzer J, Claus E, Pfitzner S (2004) Results of long-term sediment quality studies on the river Elbe. Acta Hydrochim Hydrobiol 31(4–5):356–367
3. BfG: sedimentmanagement tideelbe—strategien und potenziale—systemstudie II.
4. The Sediment Management Concept of the ICPER [https://www.iksemkol.org/fileadmin/media/user_upload/E/06_Publikationen/01_Wasserrahmenrichtlinie/2015_ICPER-Infomation-Sheet_Sediment.pdf]
5. Brils J, Brauch HJ, Liska I, Miloradov M, Nachtnebel HP, Pirker O, Rast G, Almodovar M, Dias EB, Gomes FV et al (2007) Sediment management: an essential element of river basin management plans. J Soils Sediments 7(2):117–132
6. EU. (2022) Integrated sediment management Guidelines and good practices in the context of the Water Framework
7. Breitung V, Schwandt D, Hoffmann M, Stoffels M, Heininger P. (2015) WSV-Lab—ein Managementwerkzeug zur qualitativ-gewässerkundlichen Bearbeitung von Baggermaßnahmen der WSV. Koblenz.
8. Schroeder H, Duester L, Fabricius AL, Ecker D, Breitung V, Ternes TA (2020) Sediment water (interface) mobility of metal(loid)s and nutrients under undisturbed conditions and during resuspension. J Hazardous Mater. https://doi.org/10.1016/j.jhazmat.2020.122543
9. Belkouteb N, Schroeder H, Arndt J, Wiederhold JG, Ternes TA, Duester L (2023) Quantification of 68 elements in river water monitoring samples in single-run measurements. Chemosphere 320:10
10. Michalski R, Szopa S, Jabłońska M, Łyko A (2012) Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium. Sci World J. https://doi.org/10.1100/2012/902464
11. Au Mvd Schwinn M, Kuhlmeier K, Büchel C, Meermann B (2019) Development of an automated on-line purification HPLC single cell-ICP-MS approach for fast diatom analysis. Anal Chim Acta 1077(87):94
12. von der Au M, Karbach H, Bell AM, Bauer OB, Karst U, Meermann B (2021) Determination of metal uptake in single organisms, corophium volutator, via complementary electrothermal vaporization/inductively coupled plasma mass spectrometry and laser ablation/inductively coupled plasma mass spectrometry. Rapid Commun Mass Spectr: RCM 35(2):e8953
13. Faßbender S, Döring A-K, Meermann B (2019) Development of complementary CE-MS methods for speciation analysis of pyrithione-based antifouling agents. Anal Bioanal Chem 411(27):7261–7272
14. Balaram V (2019) Rare earth elements: a review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci Front 10(4):1285–1303
15. EU Commission. (2020) Critical Raw materials resilience: charting a path towards greater security and sustainability. (Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions
16. Regnell O, Watras CJ (2019) Microbial mercury methylation in aquatic environments: a critical review of published field and laboratory studies. Environ Sci Technol 53(1):4–19
17. Loffler D, Rombke J, Meller M, Ternes TA (2005) Environmental fate of pharmaceuticals in water/sediment systems. Environ Sci Technol 39(14):5209–5218
18. Richardson SD, Ternes TA (2011) Water analysis: emerging contaminants and current issues. Anal Chem 83(12):4614–4648
19. Magdeburg A, Stalter D, Schliusener M, Ternes T, Oehlmann J (2014) Evaluating the efficiency of advanced wastewater treatment: target analysis of organic contaminants and (geno-)toxicity assessment tell a different story. Water Res 50:35–47
20. Hermes N, Jewell KS, Wick A, Ternes TA (2018) Quantification of more than 150 micropollutants including transformation products in aqueous samples by liquid chromatography-tandem mass spectrometry using scheduled multiple reaction monitoring. J Chromatogr A 1531:64–73
21. Reemtsma T, Berger U, Arp HPH, Gallard H, Knepper TP, Neumann M, Quintana JB (2016) Voogt Pd: Mind the Gap: persistent and mobile organic compounds—water contaminants that slip through. Environ Sci Technol 50(19):10308–10315
22. Schmidt TC (2018) Recent trends in water analysis triggering future monitoring of organic micropollutants. Anal Bioanal Chem 410(17):3933–3941
23. Boulard L, Dierkes G, Ternes T (2018) Utilization of large volume zwitterionic hydrophilic interaction liquid chromatography for the analysis of polar pharmaceuticals in aqueous environmental samples: Benefits and limitations. J Chromatogr A 1535:27–43
24. Schorr J, Therampilly S, Jiao L, Longree P, Singer H, Hollender J (2023) Closing the gap: Ion chromatography coupled to high-resolution mass spectrometry to trace highly polar anionic substances in groundwater. Sci Total Environ 889:164170
25. Bieber S, Greco G, Grosse S, Letzel T (2017) RPLC-HILIC and SFC with mass spectrometry: polarity-extended organic molecule screening in environmental (water) samples. Anal Chem 89(15):7907–7914
26. Nurenberg G, Schulz M, Kunkel U, Ternes TA (2015) Development and validation of a generic nontarget method based on liquid chromatography—high resolution mass spectrometry analysis for the evaluation of different wastewater treatment options. J Chromatogr A 1426:77–90
27. Nikolopoulou V, Aalizadeh R, Nika M-C, Thomaidis NS (2022) TrendProbe: Time profile analysis of emerging contaminants by LC-HRMS non-target screening and deep learning convolutional neural network. J Hazard Mater 428:128194
28. Carpenter CMG, Wong LYJ, Johnson CA, Helbling DE (2019) Fall creek monitoring station: highly resolved temporal sampling to prioritize the identification of nontarget micropollutants in a small stream. Environ Sci Technol 53(1):77–87
29. Jewell KS, Kunkel U, Ehlig B, Thron F, Schlusener M, Dietrich C, Wick A, Ternes TA (2020) Comparing mass, retention time and tandem mass spectra as criteria for the automated screening of small molecules in aqueous environmental samples analyzed by liquid chromatography/quadrupole time-of-flight tandem mass spectrometry. Rapid Commun Mass Spectr. https://doi.org/10.1002/rcm.8541
30. Dietrich C, Wick A, Ternes TA (2022) Open-source feature detection for non-target LC-MS analytics. Rapid Commun Mass Spectr 36(2):36
31. Schlusener MP, Kunkel U, Ternes TA (2015) Quaternary triphenylphosphonium compounds: a new class of environmental pollutants. Environ Sci Technol 49(24):14282–14291
32. Koppe T, Jewell KS, Dietrich C, Wick A, Ternes TA (2020) Application of a non-target workflow for the identification of specific contaminants using the example of the Nidda river basin. Water Res 178:115703
33. Köppe T, Jewell KS, Ehlig B, Wick A, Koschorreck J, Ternes TA (2023) Identification and trend analysis of organic cationic contaminants via non-target screening in suspended particulate matter of the German rivers Rhine and Saar. Water Res 229:12
34. Guo LD, Santschi PH (1997) Composition and cycling of colloids in marine environments. Rev Geophys 35(1):17–40
35. Fabricius AL, Duester L, Meermann B, Ternes TA (2014) ICP-MS-based characterization of inorganic nanoparticles-sample preparation and off-line fractionation strategies. Anal Bioanal Chem 406(2):467–479
36. Duester L, Fabricius AL, Jakobtorweihen S, Philippe A, Weigl F, Wimmer A, Schuster M, Nazar MF (2016) Can cloud point-based enrichment, preservation, and detection methods help to bridge gaps in aquatic nanometrology? Anal Bioanal Chem 408(27):7551–7557
37. Surette MC, Nason JA, Kaegi R (2019) The influence of surface coating functionality on the aging of nanoparticles in wastewater. Environ Sci-Nano 6(8):2470–2483
38. Duester L, Burkhardt M, Gutleb AC, Kaegi R, Macken A, Meermann B, von der Kammer F (2014) Toward a comprehensive and realistic risk evaluation of engineered nanomaterials in the urban water system. Front Chem 2:39–39
39. Stock F, Kochleus C, Spira D, Brennholt N, Bansch-Baltruschat B, Demuth S, Reifferscheid G (2020) Plastics in aquatic environments—results of an international survey. Fundam Appl Limnol 194(1):67–76
40. Mani T, Hauk A, Walter U, Burkhardt-Holm P (2015) Microplastics profile along the Rhine River. Sci Rep 5(1):117988
41. Lebreton LCM, Van der Zwet J, Damsteeg JW, Slat B, Andrady A, Reisser J (2017) River plastic emissions to the worlds oceans. Nature Commun 8:15611
42. Laermanns H, Reifferscheid G, Kruse J, Foeldi C, Dierkes G, Schaefer D, Scherer C, Bogner C, Stock F (2021) Microplastic in water and sediments at the confluence of the Elbe and Mulde Rivers in Germany. Front Environ Sci 9:11
43. Scherer C, Weber A, Stock F, Vurusic S, Egerci H, Kochleus C, Arendt N, Foeldi C, Dierkes G, Wagner M et al (2020) Comparative assessment of

microplastics in water and sediment of a large European river. Sci Total Environ 738:139866
44. HELCOM (2021). HELCOM Recommendation 42–43/3 on the regional action plan on marine litter
45. ISO/CD24187: Principles for the development of standards for investigation procedures of plastics in environmental matrices and related materials. in prep.
46. Seeley ME, Lynch JM (2023) Previous successes and untapped potential of pyrolysis–GC/MS for the analysis of plastic pollution. Anal Bioanal Chem. https://doi.org/10.1007/s00216-023-04671-1
47. La Nasa J, Biale G, Fabbri D, Modugno F (2020) A review on challenges and developments of analytical pyrolysis and other thermoanalytical techniques for the quali-quantitative determination of microplastics. J Anal Appl Pyrol 149:104841
48. Dierkes G, Lauschke T, Becher S, Schumacher H, Földi C, Ternes T (2019) Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography. Anal Bioanal Chem 411(26):6959–6968
49. Lauschke T, Dierkes G, Schweyen P, Ternes TA (2021) Evaluation of poly(styrene-d5) and poly(4-fluorostyrene) as internal standards for microplastics quantification by thermoanalytical methods. J Anal Appl Pyrol 159:105310
50. Lauschke T, Dierkes G, Ternes TA (2023) Challenges in the quantification of poly(ethylene terephthalate) microplastics via thermoanalytical methods posed by inorganic matrix components. J Anal Appl Pyrol 174:106108
51. Harhash M, Schroeder H, Zavarsky A, Kamp J, Linkhorst A, Lauschke T, Dierkes G, Ternes TA, Duester L (2023) Efficiency of five samplers to trap suspended particulate matter and microplastic particles of different sizes. Chemosphere 338:139479
52. Kamp J, Dierkes G, Schweyen PN, Wick A, Ternes TA (2023) Quantification of poly(vinyl chloride) microplastics via pressurized liquid extraction and combustion ion chromatography. Environ Sci Technol 57(12):4806–4812
53. Scherer C, Weber A, Lambert S, Wagner M (2018) Interactions of microplastics with freshwater Biota. In: Wagner M, Lambert S (eds) Freshwater microplastics: emerging environmental contaminants? Springer International Publishing, Cham, pp 153–180
54. Scherer C, Brennholt N, Reifferscheid G, Wagner M (2017) Feeding type and development drive the ingestion of microplastics by freshwater invertebrates. Sci Rep 7(1):17006
55. Lambert S, Scherer C, Wagner M (2017) Ecotoxicity testing of microplastics: considering the heterogeneity of physicochemical properties. Integr Environ Assess Manag 13(3):470–475
56. Andersen H, Siegrist H, Halling-Sorensen B, Ternes TA (2003) Fate of estrogens in a municipal sewage treatment plant. Environ Sci Technol 37(18):4021–4026
57. Schulz M, Loffler D, Wagner M, Ternes TA (2008) Transformation of the X-ray contrast medium lopromide in soil and biological wastewater treatment. Environ Sci Technol 42(19):7207–7217
58. Weizel A, Schlusener MP, Dierkes G, Wick A, Ternes TA (2020) Analysis of the aerobic biodegradation of glucocorticoids: elucidation of the kinetics and transformation reactions. Water Res 174:115561
59. Wick A, Wagner M, Ternes TA (2011) Elucidation of the transformation pathway of the opium alkaloid codeine in biological wastewater treatment. Environ Sci Technol 45(8):3374–3385
60. Helbling DE, Hollender J, Kohler HPE, Fenner K (2010) Structure-based interpretation of biotransformation pathways of amide-containing compounds in sludge-seeded bioreactors. Environ Sci Technol 44(17):6628–6635
61. Fenner K, Elsner M, Lueders T, McLachlan MS, Wackett LP, Zimmermann M, Drewes JE (2021) Methodological advances to study contaminant biotransformation: new prospects for understanding and reducing environmental persistence? ACS ES&T water 1(7):1541–1554
62. Cao L, Wolff D, Liguori R, Wurzbacher C, Wick A (2022) Microbial biomass, composition, and functions are responsible for the differential removal of trace organic chemicals in biofiltration systems: a batch study. Front Water. https://doi.org/10.3389/frwa.2022.832297
63. Wolff D, Krah D, Dotsch A, Ghattas AK, Wick A, Ternes TA (2018) Insights into the variability of microbial community composition and micropollutant degradation in diverse biological wastewater treatment systems. Water Res 143:313–324
64. Gonzalez-Gil L, Krah D, Ghattas AK, Carballa M, Wick A, Helmholz L, Lema JM, Ternes TA (2019) Biotransformation of organic micropollutants by anaerobic sludge enzymes. Water Res 152:202–214
65. Krah D, Ghattas AK, Wick A, Broder K, Ternes TA (2016) Micropollutant degradation via extracted native enzymes from activated sludge. Water Res 95:348–360
66. Castronovo S, Helmholz L, Wolff D, Poulsen JS, Nielsen JL, Ternes TA, Schmidt TC, Wick A (2023) Protein fractionation and shotgun proteomics analysis of enriched bacterial cultures shed new light on the enzymatically catalyzed degradation of acesulfame. Water Res 230:119535
67. Wicke D, Tatis-Muvdi R, Rouault P, Zerball-van Baar P, Dünnbier U, Rohr M, Burkhardt M (2022) Emissions from building materials mdash a threat to the environment? Water 14(3):303
68. Stefan G, Ines H, Ute S, Nicole B, Burkhardt NM, Monika R, Outi I (2017) Recommendation for a test battery for the ecotoxicological evaluation of the environmental safety of construction products. Chemosphere 171:580–587
69. Bandow N, Gartiser S, Ilvonen O, Schoknecht U (2018) Evaluation of the impact of construction products on the environment by leaching of possibly hazardous substances. Environ Sci Eur 30(1):14
70. Ilvonen O (2013) Assessing release of hazardous substances from construction products—review of 10 years of experience with a horizontal approach in the European Union. Build Environ 69:194–205
71. Schmukat A, Duester L, Goryunova E, Ecker D, Heininger P, Ternes TA (2016) Influence of environmental parameters and of their interactions on the release of metal (loid)s from a construction material in hydraulic engineering. J Hazard Mater 304:58–65
72. Schmukat A, Duester L, Ecker D, Heininger P, Ternes TA (2013) Determination of the long-term release of metal (loid)s from construction materials using DGTs. J Hazard Mater 260:725–732
73. Schmukat A, Duester L, Ecker D, Schmid H, Heil C, Heininger P, Ternes TA (2012) Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength. J Hazard Mater 227:257–264
74. Bell AM, Keltsch N, Schweyen P, Reifferscheid G, Ternes T, Buchinger S (2021) UV aged epoxy coatings ecotoxicological effects and released compounds. Water Res 12:100105
75. Bell AM, Baier R, Kocher B, Reifferscheid G, Buchinger S, Ternes T (2020) Ecotoxicological characterization of emissions from steel coatings in contact with water. Water Res 173:115525
76. Brand S, Veith L, Baier R, Dietrich C, Schmid MJ, Ternes TA (2020) New methodical approaches for the investigation of weathered epoxy resins used for corrosion protection of steel constructions. J Hazardous Mater. https://doi.org/10.1016/j.jhazmat.2020.122289
77. Luft A, Broder K, Kunkel U, Schulz M, Dietrich C, Baier R, Heininger P, Ternes TA (2017) Nontarget analysis via LC-QTOF-MS to assess the release of organic substances from polyurethane coating. Environ Sci Technol 51(17):9979–9988
78. CIS-Report. (2021) Technical proposal for effect-based monitoring and assessment under the water framework directive, report to the common implementation strategy (CIS) working group chemicals on the outcome of the work performed in the subgroup on effect-based methods (EBM) MANDATE 2016–2018.
79. ISO19040–1:2018: Water quality—determination of the estrogenic potential of water and waste water—Part 1: Yeast estrogen screen (*Saccharomyces cerevisiae*).
80. Schäfer S, Buchmeier G, Claus E, Duester L, Heininger P, Körner A et al (2015) Bioaccumulation in aquatic systems: methodological approaches, monitoring and assessment. Environ Sci Eur 27:1–10
81. Fischer F, Böhm L, Höss S, Möhlenkamp C, Claus E, Düring R-A, Schäfer S (2016) Passive dosing in chronic toxicity tests with the Nematode *Caenorhabditis elegans*. Environ Sci Technol 50(17):9708–9716
82. Rahm H, Plantikow K, Spira D, Reifferscheid G, Schaefer S (2019) Neues Leben ohne Grubenwasser? Auswirkungen der Beendigung des Steinkohlebergbaus auf die Gewässerqualität in NRW. Mitt Umweltchem Ökotox 25:67–71
83. Witt G, Bachtin J, Schäfer S (2020) Equilibrium sampling of hydrophobic organic contaminants in sediments. In: Seiler TB, Brinkmann M (eds)

Toolbox for assessment of in situ bioavailability and toxicity of organic chemicals in aquatic systems. Springer Protocols, Berlin
84. Schäfer S, Antoni C, Möhlenkamp C, Claus E, Reifferscheid G, Heininger P, Mayer P (2015) Equilibrium sampling of polychlorinated biphenyls in River Elbe sediments—Linking bioaccumulation in fish to sediment contamination. Chemosphere 138:856–862
85. Abwasserverordnung in der Fassung der Bekanntmachung vom 17. (2022). Juni 2004 (BGBl. I S. 1108, 2625), die zuletzt durch Artikel 1 der Verordnung vom 20. Januar. (BGBl I S 87 2022)
86. ISO10872:2020: Water and soil quality—Determination of the toxic effect of sediment and soil samples on growth, fertility and reproduction of *Caenorhabditis elegans* (Nematoda).
87. ISO16191: (2013): Water quality—Determination of the toxic effect of sediment on the growth behaviour of Myriophyllum aquaticum.
88. Brinke A, Buchinger S, Reifferscheid G, Klein R, Feiler U (2015) Development of a sediment-contact test with rice for the assessment of sediment-bound pollutants. Environ Sci Pollut Res 22(16):12664–12675
89. Brinke A, Reifferscheid G, Klein R, Feiler U, Buchinger S (2018) Transcriptional changes measured in rice roots after exposure to arsenite-contaminated sediments. Environ Sci Pollut Res 25(3):2707–2717
90. Feiler U, Kirchesch I, Heininger P (2004) A new plant-based bioassay for aquatic sediments. J Soils Sediments 4:261–266
91. Feiler U, Höss S, Ahlf W, Gilberg D, Hammers-Wirtz M, Hollert H et al (2013) Sediment contact tests as a tool for the assessment of sediment quality in German waters. Environ Toxicol Chem 32(1):144–155
92. Feiler U, Ahlf W, Hoess S, Hollert H, Neumann-Hensel H, Meller M et al (2005) The SeKT joint research project: definition of reference conditions, control sediments and toxicity thresholds for limnic sediment contact tests (2 pp). Environ Sci Pollut Res 12:257–258
93. Höss S, Ahlf W, Fahnenstich C, Gilberg D, Hollert H, Melbye K et al (2010) Variability of sediment-contact tests in freshwater sediments with low-level anthropogenic contamination—determination of toxicity thresholds. Environ Pollut 158(9):2999–3010
94. ISO11350:201: Water quality—Determination of the genotoxicity of water and waste water—Salmonella/microsome fluctuation test (Ames fluctuation test).
95. ISO13829:2000: ISO 13829: (2000) Water quality—Determination of the genotoxicity of water and waste water using the umu-test.
96. ISO21427–2: (2006): Water quality—Evaluation of genotoxicity by measurement of the induction of micronuclei —part 2: mixed population method using the cell line V79.
97. Reifferscheid G, Heil J (1996) Validation of the SOS/umu test using test results of 486 chemicals and comparison with the Ames test and carcinogenicity data. Mutation Res/Genet Toxicol 369(3):129–145
98. Reifferscheid G, Heil J, Oda Y, Zahn RK (1991) A microplate version of the SOS/umu-test for rapid detection of genotoxins and genotoxic potentials of environmental samples. Mutation Res/Environ Mutagene Related Subject 253(3):215–222
99. Reifferscheid G, Maes HM, Allner B, Badurova J, Belkin S, Bluhm K, Brauer F, Bressling J, Domeneghetti S, Elad T et al (2012) International round-robin study on the Ames fluctuation test. Environ Mol Mutagen 53(3):185–197
100. Reifferscheid G, Ziemann C, Fieblinger D, Dill F, Gminski R, Grummt H-J, Hafner C, Hollert H, Kunz S, Rodrigo G et al (2008) Measurement of genotoxicity in wastewater samples with the in vitro micronucleus test—results of a round-robin study in the context of standardisation according to ISO. Mutation Res/Genet Toxicol Environ Mutagene 649(1):15–27
101. Buchinger S, Heininger P, Schlusener M, Reifferscheid G, Claus E (2013) Estrogenic effects along the river Saale. Environ Toxicol Chem 32(3):526–534
102. Eichbaum K, Brinkmann M, Buchinger S, Reifferscheid G, Hecker M, Giesy JP, Engwall M, van Bavel B, Hollert H (2014) In vitro bioassays for detecting dioxin-like activity—application potentials and limits of detection, a review. Sci Total Environ 487:37–48
103. Schiwy A, Brinkmann M, Thiem I, Guder G, Winkens K, Eichbaum K, Nüßer L, Thalmann B, Buchinger S, Reifferscheid G et al (2015) Determination of the CYP1A-inducing potential of single substances, mixtures and extracts of samples in the micro-EROD assay with H4IIE cells. Nat Protoc 10(11):1728–1741
104. Schmitt S, Reifferscheid G, Claus E, Schlüsener M, Buchinger S (2012) Effect directed analysis and mixture effects of estrogenic compounds in a sediment of the river Elbe. Environ Sci Pollut Res 19(8):3350–3361
105. Villeneuve DL, Blankenship AL, Giesy JP (2000) Derivation and application of relative potency estimates based on in vitro bioassay results. Environ Toxicol Chem Int J 19(11):2835–2843
106. Wagner M, Vermeirssen ELM, Buchinger S, Behr M, Magdeburg A, Oehlmann J (2013) Deriving bio-equivalents from in vitro bioassays: assessment of existing uncertainties and strategies to improve accuracy and reporting. Environ Toxicol Chem 32(8):1906–1917
107. ISO23196:2022: Water quality—Calculation of biological equivalence (BEQ) concentrations.
108. Brion F, De Gussem V, Buchinger S, Hollert H, Carere M, Porcher J-M, Piccini B, Féray C, Dulio V, Könemann S et al (2019) Monitoring estrogenic activities of waste and surface waters using a novel in vivo zebrafish embryonic (EASZY) assay: comparison with in vitro cell-based assays and determination of effect-based trigger values. Environ Int 130:104896
109. Escher BI, Aït-Aïssa S, Behnisch PA, Brack W, Brion F, Brouwer A, Buchinger S, Crawford SE, Du Pasquier D, Hamers T et al (2018) Effect-based trigger values for in vitro and in vivo bioassays performed on surface water extracts supporting the environmental quality standards (EQS) of the European water framework directive. Sci Total Environ 628–629:748–765
110. Schoenborn A, Schmid P, Bram S, Reifferscheid G, Ohlig M, Buchinger S (2017) Unprecedented sensitivity of the planar yeast estrogen screen by using a spray-on technology. J Chromatogr A 1530:185–191
111. Shakibai D, Riegraf C, Moscovici L, Reifferscheid G, Buchinger S, Belkin S (2019) Coupling high-performance thin-layer chromatography with bacterial genotoxicity bioreporters. Environ Sci Technol 53(11):6410–6419
112. Riegraf C, Reifferscheid G, Becker B, Belkin S, Hollert H, Feiler U, Buchinger S (2019) Detection and quantification of photosystem ii inhibitors using the freshwater alga desmodesmus subspicatus in combination with high-performance thin-layer chromatography. Environ Sci Technol 53(22):13458–13467
113. Riegraf C, Bell AM, Ohlig M, Reifferscheid G, Buchinger S (2022) Planar chromatography-bioassays for the parallel and sensitive detection of androgenicity, anti-androgenicity and cytotoxicity. J Chromatogr A 1684:463582
114. Riegraf C, Reifferscheid G, Moscovici L, Shakibai D, Hollert H, Belkin S, Buchinger S (2021) Coupling high-performance thin-layer chromatography with a battery of cell-based assays reveals bioactive components in wastewater and landfill leachates. Ecotoxicol Environ Saf 214:112092
115. Bell AM, Keltsch N, Schweyen P, Reifferscheid G, Ternes T, Buchinger S (2021) UV aged epoxy coatings—ecotoxicological effects and released compounds. Water Res X 12:100105
116. Schäfer S, Bachtin J, Becker C, Buchinger S, Kochleus C, Möhlenkamp C, Reifferscheid G, Spira D, Becker B: Kombinierte chemische und ökotoxikologische Überwachung von Schadstoffen in Gewässern. Abschlussbericht. UBA Texte 113/2021 98 S 2020.117.
117. Schreiber U, Quayle P, Schmidt S, Escher BI, Mueller JF (2007) Methodology and evaluation of a highly sensitive algae toxicity test based on multiwell chlorophyll fluorescence 608 imaging. Biosens Bioelectron 22(11):2554–2563
118. LAWA. (2021) Literaturstudie zu Auswirkungen von Spurenstoffen auf aquatische Organismen in Fließgewässern. Bund/Länder-Arbeitsgemeinschaft Wasser (LAWA).
119. Höss S, Ahlf W, Bergtold M, Bluebaum-Gronau E, Brinke M, Donnevert G, Menzel R, Möhlenkamp C, Ratte H-T, Traunspurger W et al (2012) Interlaboratory comparison of a standardized toxicity test using the nematode *Caenorhabditis elegans* (ISO 10872). Environ Toxicol Chem 31(7):1525–1535
120. Höss S, Claus E, Von der Ohe PC, Brinke M, Güde H, Heininger P, Traunspurger W (2011) Nematode species at risk —a metric to assess pollution in soft sediments of freshwaters. Environ Int 37(5):940–949
121. Höss S, Heininger P, Claus E, Möhlenkamp C, Brinke M, Traunspurger W (2017) Validating the NemaSPEAR[%]-index for assessing sediment quality regarding chemical-induced effects on benthic communities in rivers. Ecol Ind 73:52–60

122. European Commission. (2022) Integrated sediment management—Guidelines and good practices in the context of the Water Framework Directive. In: Common Implementation Strategy for the Water Framework Directive (2000/60/EC), European Commission. Brussels.
123. Lemaire GG, Jessen Rasmussen J, Höss S, Figari Kramer S, Schittich A-R, Zhou Y, Köppl CJ, Traunspurger W, Bjerg PL, McKnight US (2022) Land use contribution to spatiotemporal stream water and ecological quality: Implications for water resources management in peri-urban catchments. Ecol Ind 143:109360
124. Brüchner-Hüttemann H, Höss S, Ptatscheck C, Brinke M, Schenk J, Traunspurger W (2021) Added value of the NemaSPEAR[%]-index to routinely used macrofauna-based indices for assessing the quality of freshwater sediments. Ecol Ind 121:107015
125. Cordier T, Reo E, Cermáková K, Höss S, Pawlowski J, Weigand A. (2020). Metabarcoding of sediment communities. In: Edited by Liska I, Wagner F, Sengl M, Deutsch K, Slobodnik J, Paunovic M (eds). Joint Danube Survey 4 Scientific Report A Shared Analysis of the Danube River. International Commission for the Protection of the Danube River (ICPDR). Vienna.
126. Wolfram G, Höss S, Orendt C, Schmitt C, Adámek Z, Bandow N, Großschartner M, Kukkonen JVK, Leloup V, López Doval JC et al (2012) Assessing the impact of chemical pollution on benthic invertebrates from three different European rivers using a weight-of-evidence approach. Sci Total Environ 438:498–509
127. Sonne AT, Rasmussen JJ, Höss S, Traunspurger W, Bjerg PL, McKnight US (2018) Linking ecological health to co-occurring organic and inorganic chemical stressors in a groundwater-fed stream system. Sci Total Environ 642:1153–1162
128. Schenk J, Höss S, Brinke M, Kleinbölting N, Brüchner-Hüttemann H, Traunspurger W (2020) Nematodes as bioindicators of polluted sediments using metabarcoding and microscopic taxonomy. Environ Int 143:105922
129. Schenk J, Kleinbölting N, Traunspurger W (2020) Comparison of morphological, DNA barcoding, and metabarcoding characterizations of freshwater nematode communities. Ecol Evol 10(6):2885–2899
130. Schenk J, Höss S, Kleinbölting N, Traunspurger W (2022) Suitability of molecular taxonomy for assessing polluted sediments using the NemaSPEAR[%] index. Ecol Ind 137:108761
131. Tice Raymond R, Austin Christopher P, Kavlock Robert J, Bucher John R (2013) Improving the human hazard characterization of chemicals: a Tox21 update. Environ Health Perspect 121(7):756–765
132. Dix DJ, Houck KA, Martin MT, Richard AM, Setzer RW, Kavlock RJ (2007) The toxcast program for prioritizing toxicity testing of environmental chemicals. Toxicol Sci 95(1):5–12
133. Olker JH, Elonen CM, Pilli A, Anderson A, Kinziger B, Erickson S, Skopinski M, Pomplun A, LaLone CA, Russom CL et al (2022) The ECOTOXicology knowledgebase: a curated database of ecologically relevant toxicity tests to support environmental research and risk assessment. Environ Toxicol Chem 41(6):1520–1539
134. Mendez D, Gaulton A, Bento AP, Chambers J, De Veij M, Félix E, Magariños María P, Mosquera Juan F, Mutowo P, Nowotka M et al (2019) ChEMBL: towards direct deposition of bioassay data. Nucleic Acids Res 47(D1):D930–D940
135. Dersch G, Krause WJ (2004) Monitoring and prediction of the dispersion of radioactive substances in German Federal waterways—concepts and methods. Kerntechnik 69(5–6):214–222
136. Dersch G. (2017) Radioaktivitätsüberwachung und Monitoring an der BfG: Ein Rückblick. In: Radioaktivität in Forschung und Umwelt—60 Jahre Radiologie in der Bundesanstalt für Gewässerkunde. Koblenz, Bundesanstalt für Gewässerkunde (BfG). 11–21.
137. Mundschenk H (1996) Occurrence and behaviour of radionuclides in the Moselle River 1 entry of natural and artificial radionuclides. J Environ Radioact 30(3):199–213
138. Wiederhold JG, Schmidt A. (2022) Radioaktive Stoffe in Binnengewässern. In: Umweltradioaktivität in der Bundesrepublik Deutschland: Bericht der Leitstellen des Bundes und des Bundesamtes für Strahlenschutz; Stand 2021, Daten und Bewertung. Bundesministerium für Umwelt, Naturschutz, nukleare Sicherheit und Verbraucherschutz (BMUV). 52–60.
139. Steinhauser G, Brandl A, Johnson TE (2014) Comparison of the Chernobyl and Fukushima nuclear accidents: A review of the environmental impacts. Sci Total Environ 470:800–817
140. Jens Wolling J, Arlt D (2014) Fukushima und die Folgen—Medienberichterstattung, Öffentliche Meinung. Universitätsverlag Ilmenau, Politische Konsequenzen
141. Zähringer M, Gering F (2019) Nuclear emergency preparedness in Germany: Lessons learned from Fukushima and Chernobyl and their implementation. In: Steinhauser G, Koizumi A, Shozugawa K (eds) Nuclear Emergencies: a holistic approach to preparedness. Springer, Singapore, pp 229–236
142. Procedure Manuals ("Messanleitungen") [https://www.bmuv.de/en/themen/strahlenschutz/ionisierende-strahlung/ueberwachung-der-radioaktivitaet-in-der-umwelt/federal-offices-and-their-procedure-manuals/federal-coordinating-office-for-surface-water-suspended-particulate-matter-and-sediment-in-inland-waters]
143. Schubert M, Michelsen N, Schmidt A, Eichenauer L, Knoeller K, Arakelyan A, Harutyunyan L, Schuth C (2021) Age and origin of groundwater resources in the Ararat Valley, Armenia: a baseline study applying hydrogeochemistry and environmental tracers. Hydrogeol J 29(7):2517–2527
144. Lariviere D, Taylor VF, Evans RD, Cornett RJ (2006) Radionuclide determination in environmental samples by inductively coupled plasma mass spectrometry. Spectroc Acta Pt B-Atom Spectr 61(8):877–904
145. Croudace IW, Russell BC, Warwick PW (2017) Plasma source mass spectrometry for radioactive waste characterisation in support of nuclear decommissioning: a review. J Anal At Spectrom 32(3):494–526
146. Diez-Fernandez S, Isnard H, Nonell A, Bresson C, Chartier F (2020) Radionuclide analysis using collision-reaction cell ICP-MS technology: a review. J Anal At Spectrom 35(12):2793–2819
147. Russell BC, Warwick PE, Mohamud H, Pearson O, Yu Y, Thompkins H, Goddard SL, Croudace IW, Zacharauskas Z (2023) Development of a single method for direct measurement of multiple radionuclides using ICP-MS/MS. J Anal At Spectrom 38(1):97–110
148. Steinhauser G (2019) Environmental nuclear forensics: the need for a new scientific discipline. Environ Sci Pollut Res 26(17):16901–16903
149. Weller A, Ramaker T, Stager F, Blenke T, Raiwa M, Chyzhevskyi I, Kirieiev S, Dubchak S, Steinhauser G (2021) Detection of the fission product palladium-107 in a pond sediment sample from Chernobyl. Environ Sci Technol Lett 8(8):656–661
150. Magre A, Boulet B, de Vismes A, Evrard O, Pourcelot L (2023) Identification of the origin of radiocesium released into the environment in areas remote from nuclear accident and military test sites using the 135Cs/137Cs isotopic signature. Environ Pollut 329:121606
151. Ni YY, Bu WT, Ding XT, Xiong K, Wang HL, Yang CT, Hu S, Men W (2022) Automated method for concurrent determination of thorium (Th-230, Th-232) and uranium (U-234, U-235, U-238) isotopes in water matrices with ICP-MS/MS. J Anal At Spectrom 37(4):919–928
152. Zok D, Blenke T, Reinhard S, Sprott S, Kegler F, Syrbe L, Querfeld R, Takagai Y, Drozdov V, Chyzhevskyi I et al (2021) Determination of characteristic vs anomalous Cs-135/Cs-137 isotopic ratios in radioactively contaminated environmental samples. Environ Sci Technol 55(8):4984–4991
153. Schmidt A, Frank G, Stichler W, Duester L, Steinkopff T, Stumpp C (2020) Overview of tritium records from precipitation and surface waters in Germany. Hydrol Process 34:1489–1493
154. Schubert M, Siebert C, Knoeller K, Roediger T, Schmidt A, Gilfedder B (2020) Investigating groundwater discharge into a major river under low flow conditions based on a radon mass balance supported by Tritium data. Water 12:2838
155. Rodriguez NB, Pfister L, Zehe E, Klaus J (2021) A comparison of catchment travel times and storage deduced from deuterium and tritium tracers using StorAge Selection functions. Hydrol Earth Syst Sci 25(1):401–428
156. Fischer HW, Ulbrich S, Pittauerova D, Hettwig B (2009) Medical radioisotopes in the environment following the pathway from patient to river sediment. J Environ Radioact 100(12):1079–1085
157. Zehringer MR (2018) Fate of radiopharmaceuticals in the environment. IntechOpen, London
158. Martinez J, Baciu T, Penalver A, Aguilar C, Borrull F (2019) Occurrence of and radioanalytical methods used to determine medical radionuclides

in environmental and biological samples a review. J Environ Radioact 207:37–52
159. Hormann V, Fischer HW (2018) A simple compartment model for the dynamical behavior of medically derived I-131 in a municipal wastewater treatment plant. Environ Sci Technol 52(16):9235–9242
160. Kirchesch V, Schöl A (1999) Das Gewässergütemodell QSIM—Ein Instrument zur Simulation und Prognose des Stoffhaushalts und der Planktondynamik von Fließgewässern. Hydrol Wasserbewirtsch 43:302–309
161. Krause W, Rost W, Lüllwitz T (2009) Zur Bestimmung von Fließzeiten, Fließgeschwindigkeiten und longitudinaler Dispersion in der Mosel mit 3HHO als Leitstoff. Hydrol Wasserbewirtsch 53(6):360–379
162. Leibundgut C, Maloszewski P, Külls C (2009) Tracers in hydrology. Wiley-Blackwell Chichester, Chichester
163. Uba AK (1997) Human- und ökotoxikologische Bewertung von Markierungsmitteln in Gewässern. Grundwasser 2(97):61–64
164. Bork M, Lange J, Graf-Rosenfellner M, Lang F (2020) Controls of fluorescent tracer retention by soils and sediments. Hydrol Earth Syst Sci 24(2):977–989
165. Balcaen L, Bolea-Fernandez E, Resano M, Vanhaecke F (2015) Inductively coupled plasma - Tandem mass spectrometry (ICP-MS/MS): a powerful and universal tool for the interference-free determination of (ultra) trace elements—a tutorial review. Anal Chim Acta 894:7–19
166. Klein O, Zimmermann T, Hildebrandt L, Profrock D (2022) Technology-critical elements in Rhine sediments—a case study on occurrence and spatial distribution. Sci Total Environ 852:13
167. Kulaksiz S, Bau M (2013) Anthropogenic dissolved and colloid/nanoparticle-bound samarium, lanthanum and gadolinium in the Rhine River and the impending destruction of the natural rare earth element distribution in rivers. Earth Planet Sci Lett 362:43–50
168. Oldham VE, Mucci A, Tebo BM, Luther GW (2017) Soluble Mn(III)-L complexes are abundant in oxygenated waters and stabilized by humic ligands. Geochim Cosmochim Acta 199:238–246
169. Marcinkowska M, Baralkiewicz D (2016) Multielemental speciation analysis by advanced hyphenated technique—HPLC/ICP-MS: a review. Talanta 161:177–204
170. Wiederhold JG (2015) Metal stable isotope signatures as tracers in environmental geochemistry. Environ Sci Technol 49(5):2606–2624
171. Schwab L, Rothe FM, McLagan DS, Alten A, Kraemer SM, Biester H, Wiederhold JG (2022) Large extent of mercury stable isotope fractionation in contaminated stream sediments induced by changes of mercury binding forms. Front Environ Chem 3:1058890
172. Arndt J, Kirchner JS, Jewell KS, Schluesener MP, Wick A, Ternes TA, Duester L (2022) Making waves: Time for chemical surface water quality monitoring to catch up with its technical potential. Water Res 213:7
173. Bieroza M, Acharya S, Benisch J, ter Borg RN, Hallberg L, Negri C, Pruitt A, Pucher M, Saavedra F, Staniszewska K et al (2023) Advances in catchment science, hydrochemistry, and aquatic ecology enabled by high-frequency water quality measurements. Environ Sci Technol 57(12):4701–4719