Advancing Chemical Water Quality Monitoring in Small and Medium-Sized Rivers: The Critical Role of Real-Time Measurements for Detecting Pollution Sources and Evaluating Chemical Status

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μετὰ τοῦ αὐτοῦ ποταμοῦ οὐκ ἂν ἐμβαίης

Man kann nie zweimal in denselben Fluss steigen.

Heraklit von Ephesos (* um 520 v. Chr.; † um 460 v. Chr.)

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List of Abbreviations

BOD	Biochemical Oxygen Demand
BPA	Bisphenol A
(c)DOM	(Coloured) Dissolved Organic Matter
CSO	Combined Sewer Overflow
CSS	Combined Sewer System
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EDCs	Endocrine Disrupting Compounds
EEA	European Environment Agency
EPA	United States Environmental Protection Agency
ES	Ecosystem Services
ESs	Emerging Substances
FM	Floating Matter
FNU	Formazine Nephelometric Units
ISE	Ion-Selective Sensor
ISO	International Organization for Standardization
ISO	Ion-Selective Optod
MNPs	Micro- and Nano-Plastics
MUKMAV	Saarland State Ministry of Environment, Climate, Mobility, Agriculture and Consumer Protection (Ministerium für Umwelt, Klima, Mobilität, Agrar und Verbraucherschutz des Saarlandes)
NPOC	Nonpurgeable Organic Carbon.
NTU	Nephelometric Turbidity Units
OGewV	German Surface Water Ordinance (Oberflächengewässerverordnung)
PAH	Polycyclic Aromatic Hydrocarbons
PBT	Persistent, Bioaccumulative, Toxic
PCB	Polychlorinated Biphenyl
PCPs	Personal Care Products
PFAS	Per- and Polyfluoroalkyl Substances
PMT	Persistent, Mobile, Toxic
POC	Particulate Organic Carbon

SBR	Sequencing Batch Reactor
SS	Suspended Solids
SSS	Separate Sewer Systems
STP	Sewage Treatment Plant
TAN	Total Ammonia-N
TNb	Total Nitrogen Bound
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VOC	Volatile Organic Carbon
vPvM	Very Persistent, Very Mobile
WFD	EU Water Framework Directive

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Abstract

The European Water Framework Directive (WFD) mandates achieving 'good ecological and chemical status' in all EU surface waters. Small and medium-sized rivers, which constitute over 70% of the EU's river network, are critically important, yet extremely vulnerable to any pollution due to their low dilution capacity and rapid hydrological responsiveness. Consequently, conventional monitoring, based on monthly grab sampling, is fundamentally inadequate for these dynamic systems, leading to a chronic misclassification of their chemical and ecological status. The presented work underscores the power of real-time monitoring in small, dynamic rivers using in situ sensors directly in the water, as well as on-site sensors and wet-chemical analysers in mobile riverbank stations. The parallel recording of reliably measurable target parameters such as oxygen, temperature, pH, and nutrients makes it possible to capture the transient, event-driven pollution patterns characteristic of small rivers. This enables precise source identification, load determination, and a valid assessment of the chemical status of small and medium-sized rivers. This paradigm shift overcomes the limitations of traditional methods and is crucial for protecting these vital aquatic ecosystems, developing targeted mitigation measures, and ultimately achieving the environmental objectives of the WFD.

Zusammenfassung

Die Europäische Wasserrahmenrichtlinie (WRRL) schreibt vor, dass alle Oberflächengewässer in der EU einen „guten ökologischen und chemischen Zustand“ erreichen müssen. Kleine und mittlere Flüsse, die über 70 % des Flussnetzes der EU ausmachen, sind hierbei von entscheidender Bedeutung, aber aufgrund ihrer geringen Verdünnungskapazität und ihrer schnellen hydrologischen Reaktion äußerst anfällig für jede Art von Verschmutzung. Folglich ist die herkömmliche Überwachung auf Grundlage monatlicher Stichproben für diese dynamischen Systeme grundsätzlich unzureichend, was zu einer chronischen Fehlklassifizierung ihres chemischen und ökologischen Zustands führt. Die vorgestellte Arbeit unterstreicht die Leistungsfähigkeit der Echtzeit-Monitorings von kleinen, dynamischen Flüssen unter Verwendung von in situ-Sensoren direkt im Wasser sowie von at-site-Sensoren und nasschemischen Analysegeräten in Messstationen am Ufer. Die parallele Erfassung zuverlässig messbarer Parameter wie Sauerstoff, Temperatur, pH-Wert und Nährstoffen ermöglicht es, die für kleine Flüsse charakteristischen ereignisbedingt kurzfristigen Belastungsmuster zu erfassen. Dies ermöglicht eine präzise Identifikation der Herkunft der Belastung sowie auch eine zuverlässige Bewertung des chemischen Zustands kleiner und mittlerer Fließgewässer. Dieser Paradigmenwechsel überwindet die Grenzen traditioneller Methoden und ist entscheidend für den Schutz dieser lebenswichtigen aquatischen Ökosysteme, die Entwicklung gezielter Maßnahmen zur Schadensminderung und letztlich für die Erreichung der Umweltziele der WRRL.

1. General Part

1.1 Introduction

Water bodies around the world are subject to a wide variety of pressures. Interventions in the morphological state and impairment of the water quality inevitably lead to a deterioration in the chemical and ecological status. The numerous valuable ecosystem functions performed by water bodies are being permanently disrupted, which also has a direct negative impact on humans.

In order to halt or even reverse this highly negative development, the European Union established a framework for Community action in the field of water policy - the Water Framework Directive (WFD, 2000/60/EC) in 2000. The WFD establishes ambitious targets for water protection across all member states and represents a transformative legislative framework designed to achieve a “good ecological and chemical status” in all surface waters by 2027.

Although improvements in the chemical and ecological status of water bodies have been achieved in many parts of the EU, the European Environment Agency (EEA) concluded in 2024 that the very ambitious goal initially set by the WFD, to achieve a good status in European water bodies by 2015, had not been met and only limited progress has been made. In 2022, only 38% of Europe's surface water bodies achieved a good or high ecological status. 30% achieved a good chemical status (Fig. 1). “A large proportion of surface waters fail to meet good chemical status. This mainly owes to widespread pollution by mercury and brominated diphenyl ethers (flame retardants)” (WISE, 2024).

The deadline for achieving the overarching goal of good status for all waters in the EU has therefore been extended to 2027.

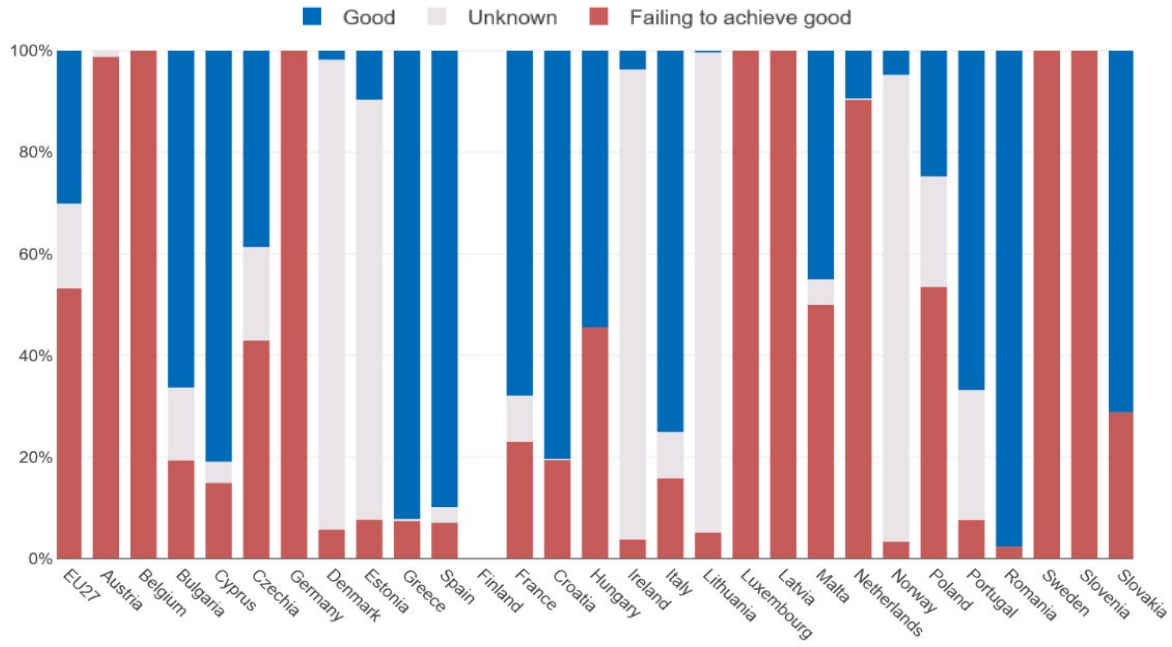


Fig. 1: Percentages of European surface water bodies in good, unknown and failing to achieve good chemical status (by number of water bodies) (WISE, 2024).

The EU member states cited the following aspects as major pressures on the surface waters: impacts via atmospheric deposition, changes to the physical features and natural flow, agricultural impacts and discharges via point sources such as from wastewater discharges and abstraction (Fig. 2).

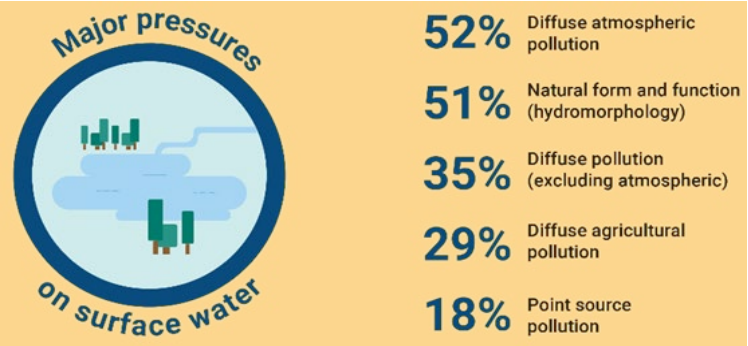


Fig. 2: Percentage of European surface waters suffering by the named major pressures (EEA, 2024).

In Annexe V of the WFD, biological, chemical and physico-chemical quality elements for the classification of ecological status of surface waters are defined. Biological elements are indicators of aquatic communities such as fish, benthic invertebrates and aquatic flora (composition and abundance of the organisms). Hydrological elements (water quantity and flow, groundwater connection) and morphological elements (depth, structure, substrate etc.) as well as chemical and physico-chemical elements are referred as supporting the biological elements. Physico-chemical and chemical elements thereby include general parameters such as thermal conditions, oxygen concentrations, salinity, acidification and nutrient conditions as well as pollution by priority substances and catchment-specific pollutants, which are discharges into a water body in significant quantities (e.g. metals, industrial chemicals or pesticides (EC, 2000).

In Germany, the criteria for evaluating the morphological, chemical and ecological status of water bodies are set in the German Surface Water Ordinance (OGewV). Compared to most other member states, Germany has defined very strict classification criteria in the OGewV. Therefore, only 9% of all surface waters in Germany can currently be classified as being in very good or good ecological status. Pollution from substance inputs occurs everywhere, and only 1% of German surface waters are considered to be unpolluted. Agriculture, industry, municipalities and households are cited as major pressures on German rivers. With the planned measures, 18% of water bodies could achieve the objectives of the Water Framework Directive by 2027. Such measures can include renaturation to improve habitats for animals and plants (planned in over 80% of catchment areas) as well as reduction of inputs from diffuse sources and point sources (planned in over 60% and 30% of catchment areas) (UBA, 2022).

Sophisticated monitoring is of fundamental importance for planning such measures and for the management of all water bodies in general; it is not just a matter of monitoring limit values and classifying water bodies. A targeted monitoring programme can help to locate pollution sources and to identify their transport pathways. The monitoring results also form the basis for planning targeted, cost-effective measures and can also be used for controlling the success of measures already implemented. Additionally, significant changes or trends that occur in water bodies over a certain time can be documented and provide information about the impact of all kinds of changes on the aquatic ecosystem, but also on other ecosystem functions of water bodies, and allow conclusions to be drawn about their vulnerability and resilience (DWA, 2017).

Traditional monitoring is based on random sampling, such as the monthly sampling required by the WFD guidelines (WFD, 2000). But as all watercourses are subject to more or less pronounced dynamics and conditions can therefore change very quickly, especially regarding the chemical status of the water, a paradigm shift towards real-time monitoring of chemical parameters is necessary.

This applies in particular to small and medium-sized rivers, which make up the vast majority (70 - 80%) of European rivers (Biggs et al., 2014; Lassaletta et al., 2010). These water bodies are extremely vulnerable. Their vulnerability stems from their intrinsic characteristics: they have a low dilution capacity overall and exhibit a flashy hydrology, i.e. they react quickly and intensively to precipitation events and other external influences. Small and medium-sized rivers are therefore subject to pronounced seasonal and daily fluctuations. Event-related pollution can lead to sudden deterioration in water quality, and chronic, continuous pollution also has a disproportionately large impact due to the limited amount of water. Continuous real-time measurement data can be used to capture the temporary impulses and short-term cycles that characterise small river systems. On the contrary, random samples can only provide a sporadic ‘snapshot’, causing an inevitable risk of misclassification of the chemical and ecological status of small and medium-sized rivers. Critical peak concentrations (e.g. maximum temperatures, minimum oxygen levels) and short-term pollution events may be missed, but they can just as easily be overestimated (Benisch et al., 2024; Meyer et al., 2021a, 2019b; Su et al., 2021).

Real-time monitoring involves the continuous, automated measurement of chemical and chemical-physical quality parameters with high temporal resolution (from seconds to minutes), thus providing a high-resolution, up-to-date picture of the river's condition at any time. Real-time systems can be used in situ, with the sensors placed directly in the water, or at-site, with the water pumped to an analyser on the riverbank. In both cases, a range of different technologies can be used: on the one hand, wet chemical analysers are deployed at-site, e.g. for total phosphorus (P_{tot}) and/or ortho-phosphate (PO_4^{3-}), ammonium (NH_4^-), total organic carbon (TOC) or various salts such as chloride (Cl-) or sulphate (SO_4^{2-}). On the other hand, in situ sensors can be operated directly in the water, including physical-chemical sensors for temperature, dissolved oxygen and electrical conductivity (EC), optical sensors (e.g. for nitrate (NO_3^-), nitrite (NO_2^-), dissolved organic matter (DOM), turbidity, chlorophyll) or ion-selective electrodes (ISE) (e.g for nitrate, ammonium, chloride) (Barjenbruch and Rettig, 2009; DWA, 2017; Meyer et al., 2021a, 2019b).

In order to create a spatially sufficient measurement network for real-time monitoring and to be able to operate it in a practical manner, cost-effective, low-maintenance and robust measuring devices are required, ideally for in situ use and with a self-sufficient power supply (battery, solar). However, only a few devices meet these criteria, in particular probes for physical-chemical parameters and optical sensors. More complex measuring devices, such as wet chemical analysers, are costly and maintenance-intensive and may require complex infrastructure.

This work examines the feasibility and practical application of a wide range of different technologies and strategies for real-time monitoring of small and medium-sized rivers. Detailed case studies describe the performance of different in situ and at-site systems in form of wet chemical analysers and electrochemical, optical sensors and ISEs under real conditions. Examples of the effects of substance inputs from point sources and diffuse sources as well as the correlation between various parameters are presented. In addition, the importance of substance loads for the identification of pollution sources is highlighted.

Given the need for simple measuring devices, another focus of this work is the evaluation of the applicability of ISEs for the analysis of small rivers. ISEs offer significant advantages as they can be installed on site, are insensitive to turbidity and colour of the water and, unlike analysers, do not require sample pre-treatment or reagents. They are usually miniaturised, energy self-sufficient (powered by batteries or solar energy) and offer extremely high temporal resolution and large measuring ranges. However, their use in the complex and variable matrix of natural river water poses considerable challenges, including sensitivity to temperature fluctuations, interference from other ions, sensor drifts and biofouling.

This work describes how real-time data obtained using the mentioned measuring systems can be interpreted in conjunction with data on runoff, precipitation and other parameters, and with the aid of additional information from the catchment area such as geogenic background, land use, point source discharges. The insights obtained serve as a sound basis for understanding the complex interaction of natural processes and anthropogenic pressures.

This detailed understanding is a fundamental prerequisite for the sustainable management and protection of water bodies and the development of targeted programmes of measures adapted to regional and local conditions, as required by the WFD.

1.2 Environmental Monitoring

The EEA defines environmental monitoring as “periodic and/or continued measuring, evaluating, and determining environmental parameters and/or pollution levels in order to prevent negative and damaging effects to the environment. Also include the forecasting of possible changes in ecosystem and/or the biosphere as a whole” (EEA, 2025). For practical implementation, this means that environmental information is gathered, assessed and reported on a basis of continuous or periodic sampling, observation and analysis of both natural variation or changes and anthropogenic pressures and their effects on humans and the environment (UN/ECE, 2003). In this context, both a systematic-repeated approach procedure and a sophisticated data evaluation and interpretation are of great importance. In general, the overall objective of an environmental monitoring is to assess environmental conditions and trends. The insights gained from such monitoring are indispensable foundations for policymakers but also for researchers and the general public. A monitoring programme can pursue various (even simultaneous) objectives, such as comparing measurement data with applicable environmental standards, ensuring public health, searching for polluters, assessing ecotoxicological effects, calibrating computer-aided (prediction) models, or is carried out for research or investigative purposes (DWA, 2017).

Monitoring requires planning and, as a sequence of related activities, is also an ongoing process. As such, monitoring can be schematically represented as a cycle (Fig. 3). The first step is to determine the objectives of the monitoring, what information is needed and, if necessary, how the information collected will be used. Basically, it is crucial for every monitoring that the programme is tailored to the information needed, not vice versa. The next step is to design the programme by specifying and/or developing the evaluation criteria and scheme, which leads to the technical organisation and the establishment of the monitoring programme. When doing so, it is important to consider all the key criteria such as determination of sampling sites and frequency, selection of the parameters and compartments to be investigated (e.g. dissolved substances, suspended matter, floating matter etc., see chapter 1.3.3). Also, the investigation methods and equipment, observation frequency, analytical quality assurance, have to be defined. Apart from that, functional data management system must be established. Once the monitoring programme has been launched, the actual data collection can start. The gathered data must be continuously checked, processed, and evaluated before it can be interpreted and used in reporting. In this context, relevant data from ongoing or completed monitoring programme s may also be taken into account. At this point, deficiencies in the monitoring programme may also be identified, which in turn must result in a change and/or expansion of the monitoring. The evaluation and use of this information can also lead to further questions and trigger a new monitoring cycle. In this way, the process of monitoring and evaluation is continuously improved (UN/ECE, 2003).

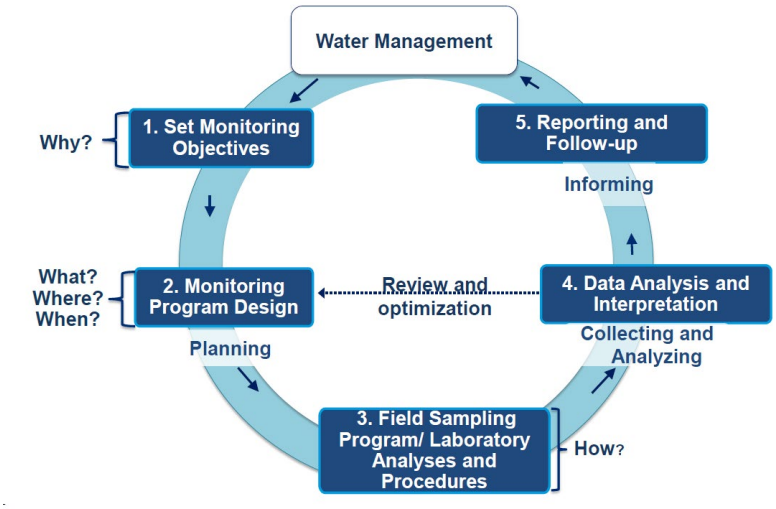


Fig. 3: Different steps of the monitoring cycle for water management (CCME, 2015).

Difference between Emission and Immission Monitoring

In the case of monitoring surface water quality, a distinction must be made between emission and immission monitoring. This differentiation refers to the processes of measuring and assessing the discharge of pollutants into a river (emission) and the resulting levels of pollution within a river (immission), respectively (DWA, 2017).

Emission monitoring focuses on the sources of pollution, such as wastewater discharges from industries, sewage treatment plants (STPs), or from agricultural or urban runoff. It aims to quantify the sources of pollution, to track their contribution to overall river pollution, and/or to control if emission limit values and/or significant reductions of emissions are achieved (e.g. according to EU-Directive 2024/3019). For pollution from point sources which are discharged at one single (waste)water effluent or pipe emission monitoring can simply by done by direct sampling. In contrast, emission monitoring of diffuse pollution it is proving much more difficult. Diffuse inputs that are transported into the rivers over a large area (also via atmospheric deposition) so it cannot be detected at a single point. For estimating diffuse pollution models can be involved based on process data and other factors.

In contrast, immission monitoring is carried out to measure the levels of pollutant concentrations and loads in the river itself and thus assess their impact on the water quality and aquatic ecosystem. It can also serve to track changes and trends in water quality over time. The measurements are conducted at representative sites in the river itself or the samples to be analysed are taken from the river. Of course, the information gathered by immission monitoring will always present the mixture of all impacts at the monitored site.

Monitoring under the WFD

The WFD stipulates three different monitoring types to assessing and managing water quality for the ecological and chemical status of surface waters:

- Surveillance monitoring is done by regular measurement of water quality parameters at representative locations to track overall ecological and chemical water status. Its aim is to provide a broad overview of water body status within a river (sub-)basin on a large-scale, to classify water bodies, to validate anthropogenic impact assessments, and to track long-term trends in water quality (Arle et al., 2016). In Germany, 290 measuring stations were registered for surveillance monitoring at rivers with the EU in 2010 (BMU, 2013). The stations must be representative of the assigned hydrological unit and permanent in time. Surveillance monitoring sites usually assess all ecological status, i.e., biological, hydromorphological, chemical and physico-chemical quality elements and, if relevant, the priority substances named in the WFD.

- Operational monitoring is the tool for assessing the status of those water bodies which are at risk of failing to meet environmental objectives and/or to control the effectiveness of implemented measures. In 2010, 7252 monitoring stations were registered at the EU for operational monitoring at rivers in Germany (BMU, 2013). At these stations, biological, chemical and/or physico-chemical quality elements indicating the presence of significant pollutants are determined.

- Investigative monitoring is conducted to identify the specific causes of failing to achieve the environmental objectives. (Arle et al., 2016). So, this is a reactive tool to understand and address specific problems as it is done e.g. by the monitoring of Saarland University (Meyer et al., 2021a, 2019b). In Germany, 375 measuring stations were registered for surveillance monitoring at rivers with the EU in 2010 (BMU, 2013).

“In surface waters, water is sampled regularly, animals and plants are collected, counted and identified; these data are analysed, and water course hydromorphology is mapped, covering thousands of kilometres. In recent years, the number of (all kinds of) monitoring sites has increased from 8500 (until 2009) to 16000 (2009 to 2016) and now, to more than 20000.” (UBA, 2022).

1.3 Basics for Planning and Performing a Purposeful Monitoring

In order to plan targeted monitoring, but also for interpretation of the collected data and for assessing the different impacts on the respective water body, it is important to understand the natural conditions of a rivers and its catchments including the general chemical, hydrological, hydromorphological and biological mechanisms and transport pathway as well as all the anthropogenic factors affecting a water body. The following chapter gives a short overview of the factors having significant influences on the chemical water quality. Hydromorphological, and biological aspects will not be discussed in detail here, although these factors also strongly impact on the chemical status of a river.

The first substances which must be considered are those originating from the natural environment in a river´s catchment forming the geochemical background. Apart from that the chemical status of a water body is also influenced by diffuse and point source inputs. While point source pollution can be fully recorded at a single point (e.g. at the end of a sewer pipe or at the outlet of a STP), diffuse pollution cannot be fully described by monitoring on the emission side. Indeed, diffuse pollution can only be completely recorded on the immission side (see above) but this means that it has to be detected as a mixture of all other impacts at the measuring site. The runoff components of the landscape water balance are used as an example of diffuse inputs, and the runoff components of urban drainage serve

as an example of point sources (DWA, 2017; EPA, 2004). Furthermore, when planning and performing a monitoring it must also be taken into account that the substances entering the water bodies can be transported in dissolved form or bound to solids. In addition, substances can also be deposited in the bed load, from where they can be re-mobilised under special circumstances. When establishing a monitoring strategy, information on the water compartments must therefore be provided, too.

1.3.1 Natural Conditions and Geogenic Background

Rivers reflect the natural conditions of their catchment areas. The concentrations, as well as the spatial and temporal distribution patterns of the natural chemical background values in a river, are influenced by geological conditions, climate and rock weathering, relief, soils, flora and fauna in the catchment as well as by the atmosphere. To distinguish between naturally occurring elements and anthropogenic contaminants, it is important to know the chemical background values (geogenic background) of a river or at least to be able to be able to estimate it as accurately as possible and thus to establish reference conditions. This process is critical for environmental management, pollution control, and ecological risk assessments.

The OGewV defines the term “natural background concentration” in §2.7 as “the concentration of a substance in a surface water body that is not, or is only very slightly, influenced by human activities.” However, it must be noted that natural conditions no longer exist in our cultural landscape. For numerous aspects, it is rarely possible to clearly distinguish between natural and anthropogenic influences. For example, headwater in forested catchments is often considered to be close to natural, even though anthropogenic influences from the atmosphere and forestry also affect the water bodies there. In many places, naturally occurring substances are only released and displaced in harmful concentrations as a result of human activity, e.g. increasing of metal concentration by rock weathering processes due to excessive warming of the weather and increased acid rain (Zhou et al., 2020).

Against the legal background any consideration of background concentrations is only necessary if a) a threshold value for an inorganic (naturally occurring) pollutant is exceeded and b) if detailed investigations into the emission situation prove that there are no significant anthropogenic sources of input and c) if it is known from the geochemical conditions in the catchment area concerned that a high natural background concentration could be responsible for this. In addition, background concentrations may also be significant in terms of research questions (LAWA, 2015).

There are various theoretical and practical approaches to determining the geogenic background in the river water. Ideally, these can also be combined with each other.

A purely theoretical approach is the classification of water bodies according to Briem (2003) for the Federal Republic of Germany is suitable for the consideration of natural background concentrations. According to this water classification, values for “very good ecological status and highest ecological potential” are specified in Annex 6 of the OGewV and can be used as theoretical background values (DWA, 2017). In the Geochemical Atlas of the Federal Republic of Germany the distribution of metals in waters and stream sediments can be found (Fauth, 1985).

In practice, the background concentrations can also be assessed by conducting water analyses in regions or water bodies of the catchment area, which are, regarding the substance concerned, less polluted, e.g. close to the source or in the groundwater. It must be ensured that the sampled (source) region or the groundwater body corresponds, particularly in geological terms, to what is representative of the water body section to be assessed. Even in small rivers, the geological subsoil can change along the course of the river, meaning that the background concentrations to be considered also change. This

means that a representative water sample must also be examined for this further river section. This can be done, for example, at an unpolluted tributary that rises in the same geological region nearby. Therefore, the lithological and pedological characteristics of the catchment area must always be included in the assessment of the natural background (LAWA, 2015).

The results of the sampling can also be processed mathematically, with which known correlations can be tested, e.g. correlation of zinc and cadmium often occurring in association (Bold, 2025). Additionally, statistical distribution clusters of different parameters can be created with the help of multivariate models, e.g. principal component analysis (PCA).

A detailed description of the parameters and parameter groups that make up the geogenic background in rivers can be found in chapter 1.3.4.

1.3.2 Water Balance and Substance Transport

The substances that make up the specific chemical composition of a river's water derive from different origins and enter the river via different pathways. Especially when discussing pollution sources and pathways in river catchments, the urban drainage from settlement areas must be highlighted as a special part of the entire landscape water balance in the watershed (chapter 1.3.2.2). While point sources are mostly found in urban areas, the transport from "natural" landscapes are mostly dominated by diffuse transport pathways (DWA, 2017).

1.3.2.1 Landscape Water Balance

According to UBA (2025), the term landscape water balance "refers to the natural processes of water distribution and storage within a landscape". Thus, it quantifies all water inputs, outputs, and changes in storage within a defined area, including "water moving through and stored in soils, plants, rivers, streams, lakes, and the atmosphere (…)".

The landscape water balance is kept in circulation by inputs via:

- precipitation: rain, snow, hail, or fog
- surface water inflow (also including river flow from upstream areas)
- groundwater inflow
- anthropogenic inputs (special case): irrigation or water transfers from other catchments.

and by outputs via:

- evapotranspiration as the sum of evaporation (from soils, water bodies and other surfaces) and transpiration (from plants): "Evapotranspiration is an important flow term in the water cycle and a key variable for understanding the complex interactions between climate, vegetation, and soil" (Silva-Júnior et al., 2021).
- anthropogenic withdrawals: water extracted for drinking water supply, irrigation or industrial use.

As water storing components soil moisture, groundwater bodies, snowpacks and ice as well as surface waters including lakes, reservoirs, wetlands, and ephemeral water bodies must be considered (UBA, 2025).

Shawul et al. (2019) define “evapotranspiration, lateral subsurface flow (interflow), groundwater flow, surface runoff, ponds, canopy storage, infiltration, redistribution, tributary channels, and return flow” as the main components in the hydrological cycle.

With regard to monitoring the chemical status of a river, the three primary runoff components sustaining the streamflow are to be considered due to their very different rules as transport pathways: baseflow, surface runoff, and interflow. Each component varies in pathway, timescale, and controlling factors, collectively shaping a catchment’s hydrological response. All the three components depend on the geological properties and soil texture, topography, vegetation, land use and sealed areas (impermeable surfaces) as well as climate conditions and human activities in the catchment, and they are subject to constant change due to weather, land use and due to changes in the water course itself. The distinction between the components and the significance of the special drivers leading to the generation and composition of the components are still not fully clarified and are the subject of numerous studies (Gu et al., 2018). Therefore, only a theoretical overview is provided here (Fig. 4 and Table 1).

- The baseflow (also groundwater runoff) is the sustained streamflow from groundwater seepage from discharging aquifers. More recent studies also distinguish between base flow and groundwater discharge (Gu et al., 2018).

- The surface runoff (also direct runoff or overland flow) is the water flowing overland when precipitation exceeds infiltration capacity or soils saturate. This also includes water that has already infiltrated (return flow) or infiltrates again along the further flow path. There are two types of surface runoff:
    - In ‘Horton’ surface water runoff (defined by Horton 1939) runoff occurs, when the precipitation intensity is higher than the infiltration rate into the soil.
    - In saturation, overland flow occurs when the water cannot be absorbed by the water-saturated soil.

- The interflow (also subsurface, intermediate or hypodermic flow) is the part of the water which laterally moves through the vadose zone (unsaturated soil), without reaching the groundwater

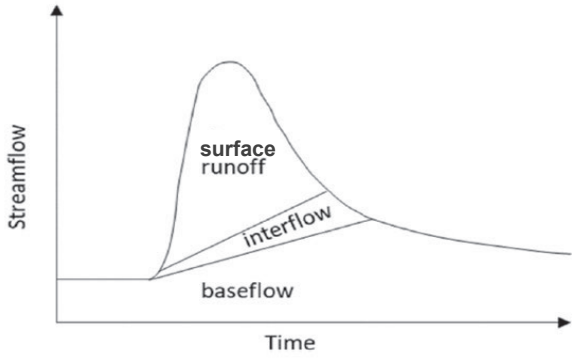


Fig. 4: Theoretical contribution of the runoff components to the rivers discharge after rainfall (Curtis et al., 2020).

Table 1: Comparison of runoff components (according to Curtis et al., 2020).

Component	Pathway	Timescale	Transport of	Primary Drivers
Baseflow	Groundwater	Months to decades	Dissolved substances	Aquifer properties, seasonal recharge
Surface runoff	Overland	Minutes to days	Suspended and particle-bound substances	Rainfall intensity, soil saturation
Interflow	Subsurface (vadose zone)	Days to months	Dissolved substances	Soil permeability, macropores

In the context of runoff component, also drainage systems must be mentioned as artificial part of the runoff in agricultural areas. Drains are systems for removing excess water from the soil surface and profile to prevent waterlogging. This aims to improve soil aeration, and allow for timely planting, harvesting, and the use of farm machinery or for reclaiming land for agricultural activities. For drainage, either surface methods, like ditches, or subsurface methods, such as perforated pipes, are used (DWA, 2017).

The interaction between water and dissolved substances or those bound to soil particles is crucial for the influence of runoff components on the material balance and material transport. This interaction is determined by the type of runoff component, the soil properties, the redox potential, the pH value, and the properties of the substance in question. Surface runoff has relatively little interaction with the soil matrix. However, surface runoff water usually transports large quantities of suspended solids and substances bound to soil particles (erosion). The other runoff components have a much lower suspended load than surface runoff. In contrast, interflow and baseflow show a much stronger interaction between the soil matrix and water and thus are to transport dissolved substances. An exception to this is drainage runoff in combination with macropores. In this case, the short flow paths can result in the macropores being permeable all the way to the drainage collector (DWA, 2017).

The different behaviour of substances in the landscape water balance must be considered when monitoring watercourses. This applies in particular to temporal resolution (Kirchner et al., 2004). For substances that are primarily introduced through surface runoff, a higher temporal resolution (event-related monitoring) should be selected than for substances that are more likely to be found in slower runoff components (e.g., delayed interflow runoff and groundwater runoff).

The significance of the individual runoff components for the various parameters and substance groups is explained in more detail in chapter 1.3.4.

1.3.2.2 Urban Drainage

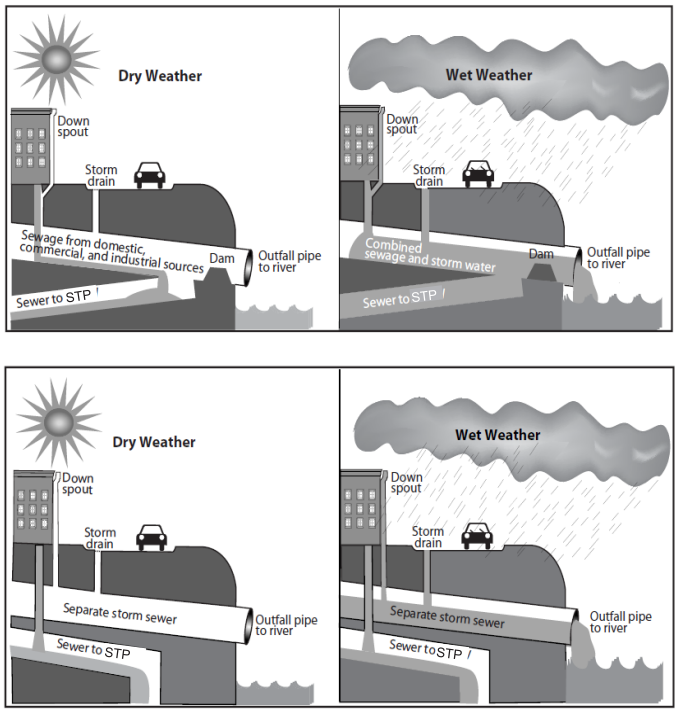
As mentioned previously, urban drainage from settlement areas must be discussed as a special part of the landscape water balance due to the abundance of paved and built surfaces and therefore, due to the lack of infiltration. They are designed to manage wastewater and stormwater in populated areas and form a rapid rate of runoff removing a large amount of surface water (Ao et al., 2018). In addition, it is usually heavily contaminated with a wide variety of substances while the composition of depends largely on the following factors urban structures: lifestyle habits (e.g. freshwater consumption), street furniture, traffic volume, indirect dischargers (industry and commerce) and the type of drainage

systems (DWA, 2017). The two primary types of urban drainage systems are combined sewer systems (CSS) and separate sewer systems (SSS).

- CSS are designed to discharge directly to surface waterbodies such as rivers, estuaries, and coastal waters during wet weather, when total flows exceed the capacity of the CSS or STP. In dry weather, CSS transport all flow to STPs for processing. However, during heavy rainfall or snowmelt, the volume of water can exceed the system's capacity, leading to combined sewer overflows (CSOs), where untreated sewage and stormwater are discharged directly into the rivers (outfall pipe to river, Fig. 5a). So, they introduce pollutants (e.g., nutrients, bacteria, metals, pharmaceuticals and other organic compounds as well as micro plastics) into the rivers, harming aquatic ecosystems and endangering water quality. In addition, the displaced water masses themselves, as well as the infiltration of pollution and the clogging of the interstitial space with sludge, pose a major threat to the aquatic ecosystem and water quality (Fig. 5b). These issues are addressed in the new EU-Directive concerning urban wastewater treatment with an increased focus on this topic (EC, 2024).

- SSS use two distinct pipe networks, one for sanitary sewage (blackwater and greywater) and another for stormwater (Fig. 5a). Sanitary sewage is transported to STPs for treatment, while stormwater is typically discharged directly into water bodies with little or no treatment. This separation prevents the contamination of stormwater with sewage-derived pollutants, reducing the risk of overflows during wet weather. In addition, only wastewater reaches the STP in the SSS, which leads to more effective wastewater treatment (EPA, 2004).

a)



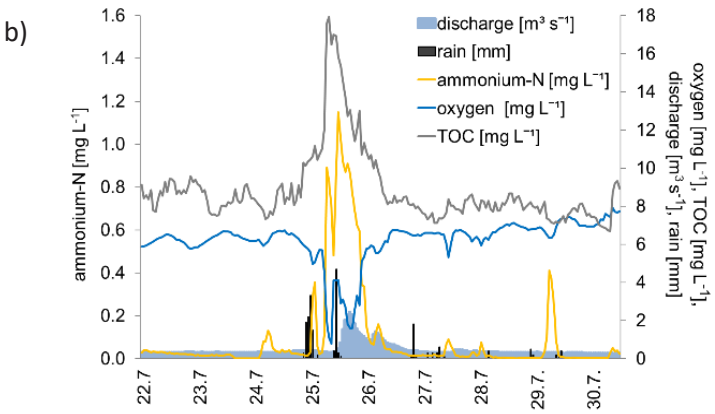


Fig. 5: a) Principle of drainage wastewater and stormwater in urban areas in CSS (above) and SSS (below) during dry weather and wet weather (EPA, 2004); b) impacts of a CSO due to rainfall (mean hourly values from 22. – 30.07.2015, Bist in *Wadgassen*) (Meyer et al., 2013a).

Apart from the discharges from CSOs as described above, other direct inputs in the water bodies have to be considered in urban areas:

- Discharges from municipal STPs: The dynamics of substance concentrations and the variability of discharge volumes from STPs depend on various factors. Large STPs may have better process technology (e.g. downstream flocculation filtration) and therefore have greater operational stability. The cleaning performance of STPs depends on the inflow volumes, which in turn depend on weather conditions in CSS. Depending on local conditions, the volume of water entering the STP and the pollutants it contains change over the course of a day. Depending on the structure of the settlements (commercial, industrial) whose wastewater is fed into the STP, the inflowing wastewater volumes may be greatest and the pollutant concentrations highest at certain times of the day (DWA, 2017). The efficiency of nitrification/denitrification is not the same for all STPs or at all times (seasonal effect: e.g. temperature dependence). In general, the emission level of municipal STP can be differentiated depending on the processing technology used, the size of the plant as well as seasonality and weather influence. The discharges of STPs can lead to pronounced diurnal cycles in the concentration levels of, for example, ammonium and phosphorus, particularly in small water bodies and at low water levels, due to the cycle of the wastewater produced (Fig. 6).

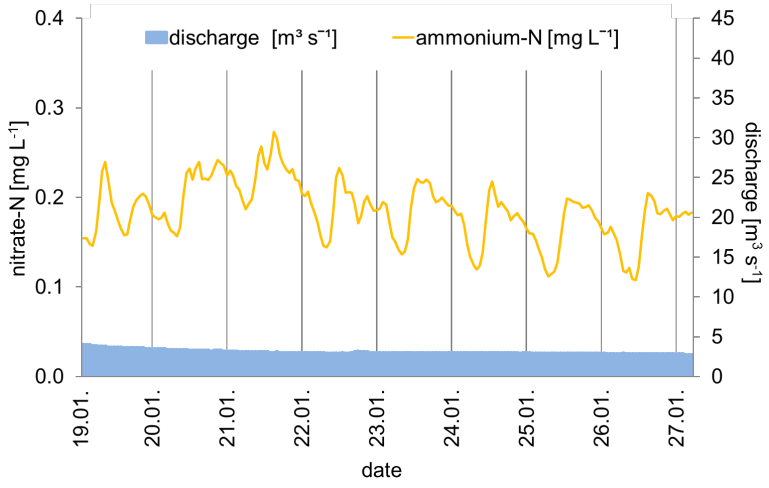


Fig. 6: Impacts from a STP causing diurnal cycles in the ammonium concentrations (mean hourly values from 19. to 27.01.2020, Blies in *Neunkirchen*) (Meyer et al., 2020).

- Industrial discharges: Industrial and commercial enterprises may, upon application, be assigned the obligation to dispose of wastewater. The enterprise thus assumes responsibility for the proper collection, conveyance, treatment and discharge of wastewater into water bodies. In contrast to indirect dischargers, they are therefore direct dischargers.

- Discharges from mixed STPs: The method of draining residential areas in a combined system is widely used in Germany. In this system, the wastewater produced during dry weather is collected together with the rainwater running off the paved surface in a sewer system and conveyed to the STP. The volume of wastewater collected in the CSS during precipitation that cannot be fed directly to the STP is temporarily stored in rainwater basins, usually CSO basins, and fed to the STP as soon as capacity becomes available in the sewer network. Relief structures are usually provided at the rainwater basins. If the amount of rainwater exceeds the retention capacity of the sewer network, the excess wastewater is roughly mechanically cleaned and discharged into the receiving water body via these relief structures. The adverse effects that can result from these mixed water discharges are sometimes considerable. This is particularly true for discharge events resulting from intense rainfall after long lasting dry weather periods (EPA, 2004).

- Discharges from rainwater treatment plants in the separation system: In the separation system, wastewater from residential areas is collected and discharged in separate channels according to its degree of contamination. Domestic wastewater and wastewater from industry and commerce that is not treated separately in a commercial STP is collected in sewer and fed into a municipal STP. In contrast, rainwater from unpolluted paved areas is collected separately in a rainwater sewer system. If additional retention basins are connected in between, the rainwater sewer system also can prevent hydraulic peak flows (EPA, 2004).

1.3.3 River Compartments

For designing and processing a monitoring, it is not only important to know about the sources and transport pathways, but it is equally important to know how the substances are transported in the river itself and thus to differentiate between dissolved substances and those bonded to solids (Fig. 7).

Dissolved Substances (for a detailed description of each see chapter 1.3.4)

In relation to water monitoring, dissolved substances are defined as substances that pass through a membrane filter with a pore size of 0.45 µm (ISO 5667-3:2018). This means that the exact distinction between ‘dissolved’ and ‘colloidal/dispersed’ can vary depending on the scientific context, with filterability with 0.45 µm filters representing the practical distinction. However, dissolved substances can be sampled from the free water column (without floating matter) (DWA, 2017).

- Dissolved ions: Due to their geologic background, most of the world's rivers water chemistry is dominated by the major ions dissolved in the water.

- Nutrients such as nitrogen (as nitrate, nitrite, and ammonium) and phosphorus naturally occur in very small concentration ranges and are essential for biological productivity.

- Trace elements like iron (Fe^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}), and copper (Cu^{2+}) occur naturally but can reach harmful levels due to further human impacts.

- Organic substances: Dissolved organic matter (DOM) like humic and fulvic acids from decaying terrestrial material, most of them causing a brown-yellow colour in the water, why the sum of these is also called cDOM (coloured DOM) or yellow substances.

- Dissolved gases: Further to this, gases are dissolved in the water. dissolved oxygen (DO) is critical for aquatic life, with concentrations depending on temperature, flow conditions, and biological activity, while carbon dioxide (CO_2) influences pH in the water.

Solids

Solids enter the water bodies due to rock weathering, erosion from natural and urban surfaces and - in case if very small grain sizes – via washout from the atmosphere. Solids strongly influence the aquatic ecosystem as a habitat and food source as nutrient source for microorganisms and thus have a strong impact on the aquatic ecosystem. Numerous pollutants can accumulate on these solids through adsorption, like metals (lead, mercury, cadmium, nickel, copper), pesticides, microplastics, pharmaceutical and cosmetic residues, other organic compounds (per- and polyfluorinated alkyl substances (PFAS), polycyclic aromatic hydrocarbons (PAH) (Tomei et al., 2026). The smaller the grain size, the higher the capacity for accumulation. Therefore, when providing information on the measured pollutant content in solids, it is essential to refer to the grain-size distribution examined. Depending on how the solids move in the flowing water, a distinction is made between floating matter and sediments (Vidmar et al., 2017; Wilcock et al., 2009).

- Floating matter (FM) floats on the water surface and consists of particulate matter of natural (e.g. wood, branches, leaves, seeds) and anthropogenic (e.g. plastic, human waste) origin as well as of floating organisms (Shumilova et al., 2019). River structure impairs the natural dynamics of FM through its removal at impoundments, changes in the discharge regime, and low morphological complexity, which can lead to a reduction in FM retention (Shumilova et al., 2019). This fact must be taken into consideration during the sampling process.

Based on the movement mechanism, sediments are separated into two classes: suspended matter and bed load. “In many streams, grains smaller than about 1/8 mm tend to always travel in suspension, grains coarser than about 8 mm tend to always travel as bed load, and grains in between these sizes travel as either bed load or suspended load, depending on the strength of the flow” (Wilcock et al., 2009). The distinction between suspended matter and bed load sediment can only apply to the current state of movement, as solids in flowing water can move from one compartment to another depending on the flow conditions. Pollutants can be remobilised with the sediment or detached from it and enter the aqueous phase in dissolved form. Substances can be deposited in the sediments at the bottom of the watercourse for long time periods, sediments are therefore referred to as ‘long-term memory’ of the watercourse (Vidmar et al., 2017).

Total suspended solids (TSS) and suspended solids consist of fine-grained solids inorganic (e.g. silt and clay) and organic (see below). These can come from e.g. sediments, sludge, sand, algae, bacteria, industrial waste and pollution. These particles can lead to increased water temperatures, reduced dissolved oxygen levels and decreased photosynthesis – resulting in the death of underwater vegetation and disruption of the food chain in the ecosystem. In addition, erosion and runoff can increase the amount of pollutants in a body of water. The biomass content, e.g. phytoplankton, diatoms, fungi bacteria, detritus, varies according to the season and discharge conditions (DWA, 2017). These inorganic and organic articles are held in the water column due to their density or are kept in suspension by turbulence and can be removed by a filter (usually 2 µm or finer) (Fan et al., 2023). While SS is the more general term for suspended solids, TSS is determined by filtration, drying and weighing (drying at approx. 103–105 °C) The grain fraction and amount of (T)SS depends on the flow velocity and the material´s density.

- Bed load are solid particles that sediment on the riverbed and remain there for a period. can consist of clay, silt, sand, gravel and stones and is moved downstream along the riverbed by rolling, sliding or salting. It should be noted that the composition and thickness of the sediments can change along the course of the water body. For example, smaller fractions of SM can settle especially in river sections with calm water currents. Under appropriate discharge conditions, the top layer of bed load is resuspended and transported with the flowing wave (Wilcock et al., 2009). The space between the sediments forms a very important habitat for fish and aquatic insects (especially space for mating and egg laying) (Khosrovyan, 2024).

- Clogging sediment (or fine sediment) is the accumulation of small particles like silt, clay, and fine sand (or organic compounds) that fill in the spaces between the larger solid particles on a riverbed. A clogged riverbed has severe consequences for the entire aquatic ecosystem (e.g. suffocating fish eggs and aquatic insects, see above) (EC, 2000).

The substrate is the layer of sediment that forms the stable bottom of the river.

It should be mentioned that real-time measuring methods refer to the dissolved water phase or suspended solids, either using optical methods, e.g. turbidity or chlorophyll a (non-specific), or by using upstream digestion to convert the particle-bound phase into a dissolved one and then measuring it as such (e.g. TOC or particle-bound phosphorus) (see chapter 1.3.4).

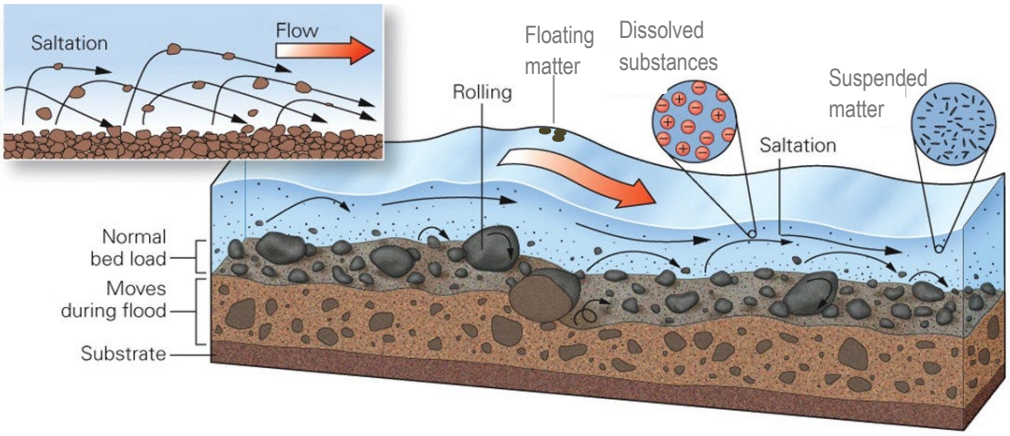


Fig. 7: River compartments: dissolved substances, floating matter, suspended matter, bed load and substrate in a river (Marshak, 2022) (Essentials of Geology, seventh edition by Stephen Marshak. Copyright © 2022, 2019, 2016, 2013, 2009, 2007, 2004 by W.W. Norton & Company, Inc., used by permission of W. W. Norton & Company, Inc.) (modified).

These aspects also play an important role in monitoring in terms of temporal representativeness, particularly for planning purposes. For the temporal representation of the monitoring changes of the target parameters over time must be considered. As soluble substances and the ones bound to SM are transported in the water column, their concentrations usually can change very quickly, especially in small and medium-sized rivers (Fig. 8). Changes in sediment-bound substances, on the other hand, tend to occur over longer periods of time. Biological components, in contrast, are suitable indicators of long-term changes (e.g. by accumulation of pollutants in organisms or through the presence or absence of species) (DWA, 2017).

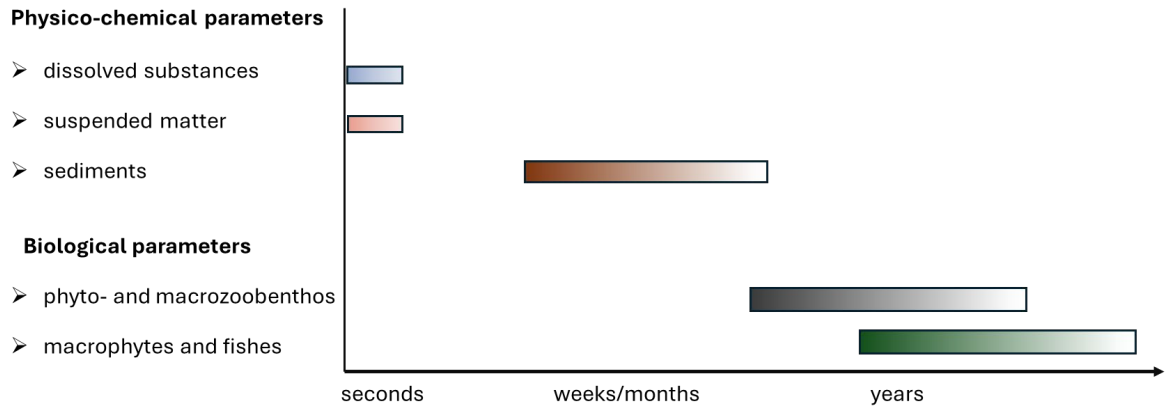


Fig. 8: Temporal representation of monitoring different river compartments.

1.3.4 Parameters and Substance Groups for Chemical Monitoring

The number of different substances found in river water is both immense and highly variable. On one hand it encompasses all natural compounds and their degradation products. All of them can also be introduced into water bodies through various anthropogenic activities (e.g. nitrates or chloride). In the description below, temperature, pH value, electrical conductivity (EC), turbidity and biological oxygen demand are mentioned with the natural parameters, as they are of particular importance for metabolic processes. But they can also be changed due to impacts and pollution immission in a river. Nevertheless, they are indispensable for assessing the river status and interpreting the monitoring data (DWA, 2017).

Apart from the naturally occurring substances, there is also the immense variety of synthetic chemicals and their degradation products from industry, agriculture, and urban runoff. These synthetical substances are often referred to as emerging substances.

Naturally occurring substances, temperature and turbidity

Naturally occurring substances vary significantly based on local geology, climate, and hydrology (chapter 1.3.1):

- Minerals and ions: Because of their geogenic background, most of the world's rivers water chemistry is dominated by the major ions dissolved in the water which are bicarbonate (HCO_3^-), calcium, sulphate, magnesium, sodium (Na^+), chloride and potassium (K^+) typically constitute the majority of dissolved substances (Fig. 9). “For example, global averages show bicarbonate accounts for approximately 58 mg L^{-1}, calcium 15 mg L^{-1}, and sulphate 11.2 mg L^{-1} in typical river water”) (Meybeck, 2003).

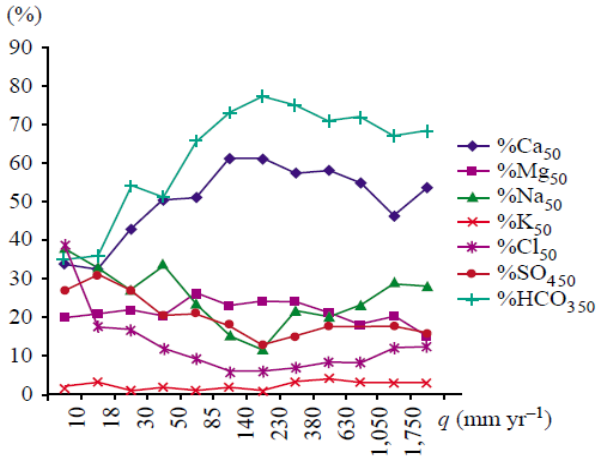


Fig. 9: Median proportions (in percent of cations or anions sum) in twelve classes of river runoff (q1 < 10mm per year, then 10 - 18, 18 - 30, 30 - 50, 50 - 85, 85 - 140, 140 - 230, 230 - 380, 380 - 630, 630 - 1050, 1050 - 1750 and q12 > 1750 mm per year; sample n = 1091) (used by permission of Elsevier from (Meybeck, 2003).

- Gases are dissolved in the water entering the water from the atmosphere and through biological processes. Dissolved oxygen is critical for aquatic life, with concentrations depending on temperature, flow conditions, and biological activity, while carbon dioxide (CO_2) influences pH in the water (Meyer et al., 2019a).

- Nutrients such as nitrogen (as nitrate, nitrite, and ammonium) and phosphorus (as phosphate) naturally occur in very small concentrations ranges and are essential for biological productivity.

- Trace elements such as iron, manganese, zinc, and copper also occur naturally in some regions due to geological formations.

- Water temperature plays an important role, particularly with regard to the solubility of oxygen. In addition, the speed of many metabolic and chemical processes depends on the water temperature. In addition to climatic and weather-related influences, it depends heavily on the type of water body and determines the characteristics of the fish community (LAWA, 2021). Discharges of cooling water, but also wastewater discharges, can influence the temperature regime of a water body.

- pH is defined as the negative decadic logarithm of the activity of H^+ ions in water (IUPAC, 2025). The pH value of surface waters depends on many factors. In addition to the geogenic background, biological processes also influence shifts in pH value. Apart from that, the photosynthetic activity of aquatic plants, which leads to a diurnal variation in pH, nitrification and denitrification processes in the water also cause a shift in pH. Domestic and industrial wastewater discharges, mining activities and other human influences can affect the pH value, too. Sulphur and nitrogen oxides in the atmosphere can lower the pH value of precipitation, which can contribute to the acidification of water bodies (UBA, 2024). The lower the buffer capacity of the water (e.g. in areas with low lime content), the more serious the impact of natural processes and anthropogenic inputs on the pH value. The pH value in rivers is differentiated according to eleven water types. For most types, the guideline value for good status is pH 6.5–8.5, and for organically dominated watercourses it is pH 5–8 (OGewV, 2016).

- The EC of water is a sum parameter for the content of dissolved salts in water. Naturally, EC depends on the geological subsoil. High conductivity can indicate anthropogenic inputs such as domestic and industrial wastewater (e.g. salt mining) but can also indicate natural influences (e.g.

tides). In urban areas, increased EC is measured in water bodies during snowmelt due to road salt. Rainwater itself generally has very low values (< 20 µS cm^{-1}) (UBA, 2024).

- Biochemical oxygen demand (BOD) measures organic pollution in water samples. It describes the content of biodegradable substances and is expressed in mg L^{-1} of oxygen consumed in a defined number of days. A consumption period of five days is common (BOD_5). It is defined as the amount of oxygen required by heterotrophic microorganisms in a consumption period in the dark at a temperature of 20°C to oxidatively degrade the water constituents (ISO 5815-1:2020-11).

- Turbidity in rivers is mainly caused by colloidal organic, inorganic or even living substances (such as plankton). A rapid increase in turbidity in water bodies can be the result of discharges from CSOs or erosion-related soil inputs, for example (Meyer et al., 2020, 2013a).

Anthropogenic pollutants

Anthropogenic pollutants, on the one hand, are synthetic substances, but on the other hand, they also include substances that occur naturally (see above) but are released into the environment in increased quantities as a result of human activity (non-synthetic pollutants).

The latter category includes:

- Nutrients are substances that are important for plant growth and promote an increase in plant biomass production in water bodies (especially phosphorus and nitrogen compounds). Anthropogenic (mostly organic) nitrogen inputs lead to an increase in biologically usable nitrogen, which – like phosphate – can cause overproduction of biomass (eutrophication). Nutrients deriving from agricultural fertilisers and wastewater.
  - Total nitrogen bound (TNb) is the sum of ammonium/ammonia nitrogen, nitrite nitrogen, nitrate nitrogen and organically bound nitrogen (proteins, amino acids, urea). The total load and the proportion of the individual nitrogen components vary depending on the different input pathways. In water bodies, the nitrogen components are largely oxidised to nitrate so that nitrate usually forms the main proportion of the total nitrogen in water (ISO 11905-1:1997).
  - Ammonium, like nitrite and nitrate, is an inorganic nitrogen compound. There is a natural balance between ammonium and non-ionised ammonia in the water. The formation of ammonia strongly depends on pH and water temperature. The chemical context is explained in detail in chapter 1.4.2.2. Due to its acute toxicity to fish, ammonia has a special relevance considering aquatic ecosystems.
  - Like ammonia, nitrite is toxic to fish. Nitrite is not stable in aqueous solution, as it is rapidly oxidised to nitrate in an aerobic environment or reduced to ammonium in an anaerobic environment. Nitrate, ammonium, nitrite and ammonia are generally present in dissolved form.
  - Phosphorus is usually measured as ortho-phosphate and total phosphorus. Ortho-phosphate (often reported as "soluble reactive phosphorus" or DRP) refers to the inorganic phosphate ions (e.g., PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$) that are immediately reactive and typically bioavailable in aquatic systems as it is the dissolved fraction (smaller than 0.45 µm) (EPA, 2026). It mainly originates from domestic and industrial wastewater discharges (component in urine, washing powders and detergents). The difference between ortho-phosphate and total phosphate is the particle-bound fraction indicating inputs from the landscape water balance (erosion) (Meyer et al., 2021a).
- Total organic carbon (TOC) is the sum parameter used to express the concentration of all organic substances (dissolved and bound to particles) in mg L^{-1} carbon. Water bodies contain a variety of organic carbon compounds of natural (e.g. algae, humic acids, etc.) or anthropogenic origin (organic wastewater). Since the measurements also include natural components of TOC, it is not possible to

interpret the data unambiguously. Nevertheless, the TOC content provides valuable information about organic pollution. As a sum parameter, TOC records various forms of organic carbon, which can be further differentiated by means of various preparative steps (Walker, 2003):

- dissolved organic carbon (DOC): the fraction not retained by a 0.45-µm filter
- particulate (POC): the fraction retained by a 0.45-µm filter
- purgeable or volatile (VOC): the fraction removed by gas stripping
- nonpurgeable (NPOC): the residue after gas stripping.

DOC is the most important component alongside TOC and is often used to compare different types of water.

- Salts such as chloride and sulphate are generally present in dissolved form:
  - Anthropogenic chloride inputs occur through domestic and industrial wastewater (e.g. mining), through the leaching of mineral fertilisers (especially potash fertilisers) or the runoff of road salt.
  - Sulphates enter water bodies via industrial wastewater from chemical industry and metal processing, mining and waste dumps, fertilisers, household cleaning products, water softening and in some regions due to acid rain (Oberhausen et al., 2023; Zak et al., 2021).

- Metals such as cadmium, copper, mercury, chromium, nickel, zinc, aluminium, lead and arsenic, have been used for centuries to manufacture everyday objects. Through this use, these substances enter domestic wastewater and thus indirectly via STPs or directly via rain (also from roofs, rain gutters, building installations, etc.) into water bodies. They are emitted with industrial wastewater, due to mining activities, soil erosion (including fertilisers containing metals) and atmospheric deposition. In rivers, the majority of these metals are chemically (complex) bound or physically bound to particles (DWA, 2017).

- Surface waters contain tens to hundreds of thousands of so-called emerging substances (ESs, also “upcoming”, “pollutants” or “contaminants”). But since ESs are not the subject of the present investigations and cannot be observed with real-time monitoring due to their low concentrations, they are only briefly described here. This substance group including pharmaceuticals, pesticides, personal care products (PCPs), per- and polyfluoroalkyl substances (PFAS), industrial chemicals like flame retardants (e.g., PBDEs), dioxins, nonylphenol, and their transformation products as well as micro- and nanoplastics (MNPs), (Brack et al., 2019; Kumar et al., 2022; Mishra et al., 2023). The Norman Experts Regularly Lists over 106000 of emerging substances and pollutants (NORMAN, 2025).

A key subgroup are endocrine-disrupting compounds (EDCs), which interfere with hormonal systems. This subgroup includes bisphenol A (BPA), dioxins, perchlorate, polychlorinated biphenyls (PCBs), and alkylphenols, found in certain plastics and resins, phthalates and certain pesticides (e.g. atrazine and DDT and synthetic hormones in oral contraceptives) (Li et al., 2024).

ESs originate mainly from households, industry, and agriculture and spread widely via wastewater, runoff, and atmospheric deposition, reaching even remote environments. Due to their persistence, mobility, bioaccumulation, and toxicity, they pose risks to ecosystems and human health, including endocrine disruption, antibiotic resistance, and biodiversity loss. Due to their mobility and thus widespread distribution, their persistence, bioaccumulative properties and toxicity (PMT/PBT) and/or high bioaccumulation (vPvM), they pose a risk to the environment and human health (Boahen et al., 2025; UBA, 2021). Although often present at low concentrations, their impacts can be amplified through biomagnification. Many ESs are not yet routinely monitored or fully regulated but are increasingly detected and assessed under frameworks such as the EU Water Framework Directive Watch List.

1.4 Water Quality Monitoring in Practice

The following chapter takes a closer look at the practical implementation of chemical and electrochemical parameters for river monitoring. The focus will be on real-time methods regarding their particular importance for the observation and assessment of small and medium-sized water bodies.

1.4.1 Technical Terms

When talking about river monitoring with help of continuously working systems, different terms are used in literature. The term “real-time monitoring” used in this work is also often used imprecisely in the context of environmental monitoring. What distinguishes it from conventional approaches is the improved speed of data availability, the increased measurement frequency, or a combination of both. Similar terms such as “online monitoring” are used synonymously. However, a distinction can be made: While “online monitoring” usually means that sampling and analysis take place in a bypass line outside the main stream, the terms “real-time” refers exclusively to the timeliness of the analysis and the availability of the data. In these cases, the analysis device may also be located directly in the main stream (Arndt et al., 2026). Apart from that, there are more terms describing different aspects of monitoring strategies and often overlapping but with distinct focuses:

- Real-time monitoring emphasizes immediate data delivery and analysis.
- Continuous monitoring focuses on non-interrupted observation.
- Online monitoring refers to monitoring using sensors external to the system being monitored.
- High-frequency monitoring tracks data at very short interval.
- High-resolution monitoring focuses on detailed data capture.

In this work, the term real-time monitoring is used to describe data which is collected in a very high temporal solution of a measuring frequency varying between several seconds to sub-hourly, depending on the measuring method. The monitoring is carried out continuously (over a longer period, from several months up to years). In practice, the raw data are delivered in real-time, nevertheless, these raw data must be crosschecked to detect potential faults, e.g. due to device errors.

1.4.2 In Situ and On-Site/At-Site Measurement

Depending on the location of a real-time measuring device, a distinction is made between two methods (Fig. 10) (DWA, 2017):

- In situ: The measuring device is located in the water body itself.
- On-site: The sampling point is located in the water body, meanwhile the measurement is carried out on the riverbank. At-site measurement is a subtype of the on-site measurement: the term on-site is broader and includes any field measurement (manual or automated), the term at-site often refers to dedicated monitoring stations that provide real-time data.

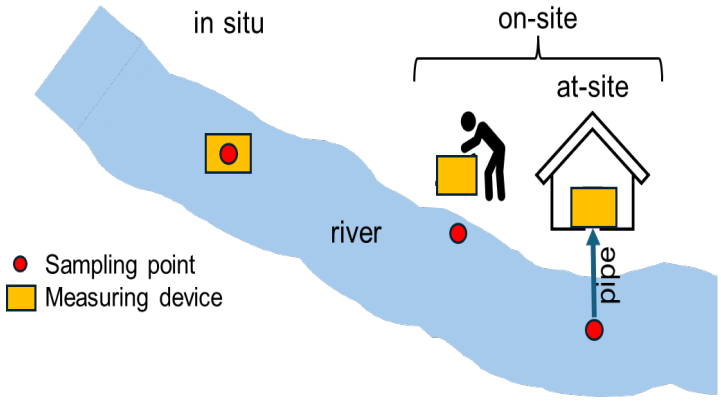


Fig. 10: Principle of in situ and on-site/at-site measurements.

In situ measuring devices are mostly sensors, which are continuously immersed in water. They can be fixed at anchored to riverbeds, buoys, or bridges. Since there can be no sample preparation in the form of filtering or digestion, they must be used for dissolved substances or such parameters which can be detected optically (e.g. turbidity, chlorophyll-a). At-site measuring devices are installed near the river (e.g., riverbank, boat) for immediate analysis. Since reagents can also be used and the samples can be treated accordingly before measurement, e.g. filtered, digested or diluted, there are more analytical possibilities. However, the effort in terms of maintenance, costs, etc. is significantly higher and the flexibility of use (power supply, location) is limited (DWA, 2017). The advantages and disadvantages of in situ and at-site measurements are listed in Table 2.

These two different approaches are decisive for the choice of measuring equipment, and therefore also for the choice of measurable parameters and, thus, for the overall design of the monitoring system.

Table 2: Advantages and disadvantages of in situ and at-site measurements (DWA, 2017).

	Advantages	Disadvantages	Example
In situ	○ Measurement in the river ○ Continuous measurement ○ No pumping costs ○ Small number of components (low maintenance) ○ Mobility in choice of location (e.g. critical pollution points can be sought out) ○ Low personnel costs ○ No reagent consumption ○ Self-sufficient operation ○ Out-of-sight operation	○ Limited parameter set ○ Unprotected against unauthorised access ○ Obstacle to waterway maintenance ○ Possible conflict with flood protection ○ Measurement accuracy may be limited ○ Measurement values may be distorted by floating debris/vegetation	Probes installed in the river

At-site	○ Sample preparation and processing possible (filtration, digestion, etc.) ○ Extended parameter set ○ Teal-time/quasi-real-time measurement ○ Protection from the weather ○ Protection against vandalism ○ Simplified operation and maintenance (accessibility of the measuring systems) ○ Laboratory workstation for comparative measurements or calibration possible	○ Possible contamination of the sample during transport (e.g. oxygen consumption) ○ High investment costs ○ High operating costs (e.g. energy for pump, air conditioning) ○ Large number of components (susceptibility to faults, maintenance) ○ Relocation is expensive ○ Location dependent on available infrastructure ○ High personnel costs ○ Reagent use and disposal may be necessary ○ Impact on the landscape· ○ Obstacle to water drainage and watercourse ○ Pump maintenance	Mobile measuring stations

The different approaches have various advantages and disadvantages depending on the issues at hand and the parameters to be measured. These challenges will be explained in more detail in the next chapter.

1.4.3 Technological Solutions for Real-Time Monitoring

Various technologies for numerous parameters are used to continuously record for real-time monitoring of water quality. However, the selection of substances and substance groups that can be continuously measured in the river is limited. On one hand, many substances, such as metals or organic compounds, occur in too small quantities in the river water and therefore cannot be reliably recorded by real-time measurements with automated probes or analysers. On the other hand, many methods, that are sufficiently sensitive in the laboratory, are interfered by numerous non-target substances or disturbed by physical influences (e.g. turbidity, temperature fluctuations). Sample preparation, as can be carried out in the laboratory, is also only possible to a limited extent in real-time measurements directly in or on the water.

The most common and reliable methods for real-time water monitoring are presented below. The methods and measuring instruments used in the studies presented in chapter 2 are explained as examples.

1.4.3.1 In Situ Sensors for Real-Time Monitoring

In situ sensors offer numerous advantages. They are relatively inexpensive, especially because no consumables (e.g. reagents) are needed. They offer large measurement ranges, very high sensitivity and exceptional temporal solution (seconds to minutes) as well as specificity for a range of parameters. In situ sensors usually have a self-sufficient energy supply (e.g. via rechargeable battery or solar power) and are therefore extremely flexible in their application. Many systems are also equipped with remote data transmission. Often, different sensors from one manufacture are installed together in a single sensor body, resulting in what are known as multi-parameter probes. Ideally, individual sensors can also be replaced by the users themselves, e.g. if a sensor is defective or another/additional parameter needs to be measured. All sensors must be calibrated, maintained and cleaned regularly, and replaced at regular intervals, meanwhile the frequencies depend on the measuring methods. Since the sensors are deployed directly in the water, they are susceptible to damage from dirt, sediments or vandalism. In addition, they are subject to biofouling processes and clogging and thus tend to drift (Meyer et al., 2025).

Physical sensors for real-time monitoring

Physical sensors are the simplest and most robust measurement methods and can be used for recording parameters like

- Temperature is measured by changes in electrical resistance with temperature.
- Dissolved oxygen (Clark electrode) is measured by reduction of oxygen molecules diffusing through a membrane, generating a current (ISO 5814-2012).
- pH is measured by the voltage difference between an ion-selective glass electrode and a reference electrode due to the hydrogen ion activity(ISO 10523:2008).
- EC is measured by the ability of ions in water to carry an alternating current (ISO 7888:1985).

Optical sensors for real-time monitoring

An optical sensor detects substances (or objects) by emitting light and measuring the change in that light (absorption, reflection, refraction or interruption) and converting it into an electrical signal. The basic functionality involves a light source (often an LED or laser) that directs light onto a target solution, a receiver (such as a photodiode) that detects the converted or reflected light, and evaluation electronics that convert the light intensity into a usable electrical signal (Lepore and Delfino, 2022). The primary interactions measured are:

- Absorbance, which is the amount of light a sample absorbs at a specific wavelength (related to concentration by the Lambert-Beer Law).
- Luminescence, which is the process of detecting light emitted by a sample, either through a chemical reaction (chemiluminescence) or through excitation with external light (fluorescence / phosphorescence) or electricity (electroluminescence).
- Scattering, which is the deflection of light by suspended particles (e.g., for turbidity).

Examples for optical sensors and how they work

Many dissolved substances can be measured using direct absorption. It should mentioned that the terms absorption and extinction are largely synonymous terms for the attenuation of light by a sample. While absorbance often focuses more on pure light absorption and is mostly used when speaking about measuring methods, extinction physically describes the total attenuation due to absorption and scattering (see also turbidity below) and is used in context with photometric results.

Lambert-Beer Law

Absorption measurements are basically carried out by sending a light beam of a specific wavelength through the sample onto a detector. The dissolved substance to be measured in the sample absorbs the light, so that a light beam with reduced intensity hits the detector. The difference between the emitted light and the light detected by the detector provides information about the concentration of the substance to be measured. The concentration calculation is based on Lambert-Beer Law, which is a fundamental concept in spectroscopy and will therefore be explained in more detail here.

The Lambert-Beer Law states that the amount of light absorbed (or extinguished) by a substance dissolved in a non-absorbing solvent is directly proportional to the concentration of the substance, the path length the light travels through the solution and to a substance specific extinction coefficient. The more concentrated a solution is, the more light it will absorb. The law is expressed in its logarithmic form (1) (IUPAC, 2026):

$$A = \log_{10}\left(\frac{P^0_\lambda}{P_\lambda}\right) = \varepsilon_\lambda * l * c \qquad (1)$$

A: absorbance

P^0_λ: intensity of the incident light at wavelength λ (entering the sample)

P_λ : intensity of the transmitted light at wavelength λ (exiting the sample)

ε_λ : molar (decadic) absorption coefficient (constant for a given substance at wavelength λ (nm) ($m^2\ mol^{-1}$)

l: optical path length (cm)

c: molar concentration of the absorbing substance (mol L^{-1}).

In general, concentrations up to 0.01 mol L^{-1} can be measured with this method. Optical interferences may occur due to other light reaching the detector or because of particles in the probe that scatter the light beam light.

Optical sensor for real-time measurement of nitrate by absorption

Nitrate can – among others - be measured using a simple optical sensor by direct absorption in the UV range with a wavelength between 210 and 230 nm (depending on the manufacturer) (Fig. 11). The sensor is immersed in the river so that the water can flow continuously through the sample chamber (Fig. 12). In addition to the measure light beam, many devices also record further absorptions, e.g. at 254 nm and 360 nm, in order to detect the influence of organic matter and turbidity. This range is calculated out so that the sensor is less sensitive to cross-influences in the water. The method is particularly effective for waters where high DOC concentration complicates UV-based nitrate quantification (Burkert, 2025). Dong et al. (2024) provide an overview of the influence of different DOC concentrations on the absorption maxima of a constant nitrate concentration (Fig. 11).

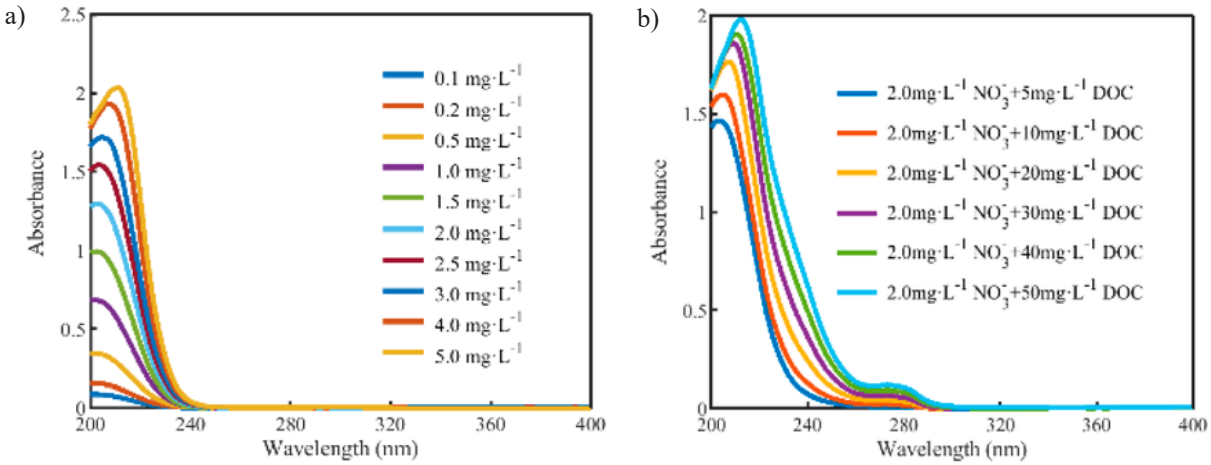


Fig. 11: (a) Absorption spectra of different concentrations of nitrate; b) absorption spectra of nitrate and DOC mixed solutions (take 2 mg L^{-1} nitrate as an example) solutions (Dong et al., 2024).

Fig. 12: Optical probe for nitrate (Hach, 2026a) (used by permission of Hach Company).

Optical sensor for real-time measurement of dissolved oxygen by luminescence

A reliable method for measuring the concentration of dissolved oxygen in solutions is based on the measurement of luminescence.

The sensor for dissolved oxygen (O_2) consists in a gas permeable polymer matrix which is coated with a luminescent material (Fig. 13a). Blue light from an LED hits the luminescent chemical on the sensor, which is immediately excited. When the excited chemical relaxes, it emits red light (luminescence) (Fig. 13b). Red light from a second LED is detected by a photodiode. The time it takes for the chemical to return to a relaxed state is measured. When oxygen meets the luminescent chemical, the intensity of the red light decreases (quenching), and the time required for the material to relax is reduced. The higher the oxygen concentration, the less red light is emitted by the sensor. So, the sensor measures the time required after excitation until the red light is emitted (the lifetime of the luminescence, but not its intensity). A second reference LED emits red light pulses with known characteristics onto the fluorescent spot, it´s signal detected by the photodiode serves as a reference signal. Luminescence sensors for oxygen measurement are designed for immediate and maintenance-free operation. They require no startup or polarization time nor special conditioning. preventing sensor poisoning (Hach, 2026b).

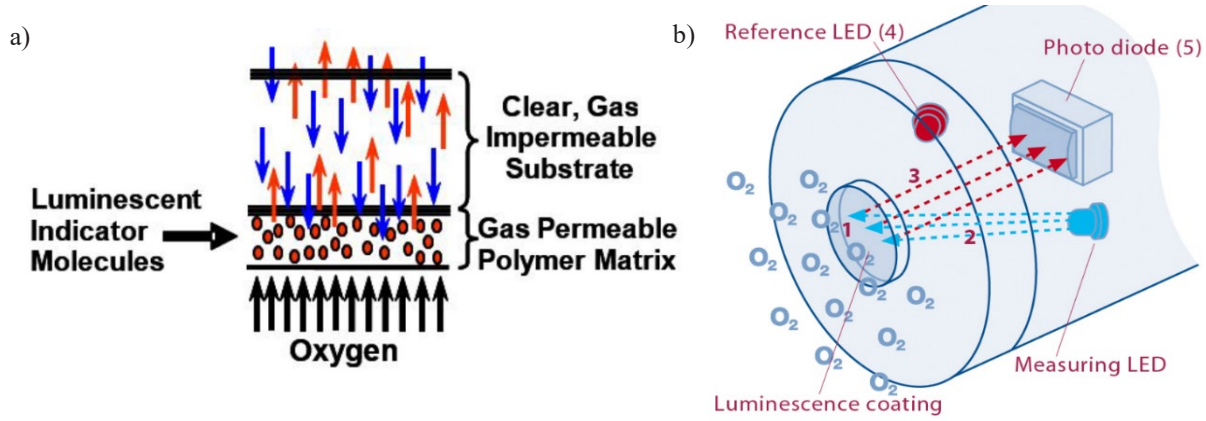


Fig. 13: a) Structure of the gas permeable matrix; b) scheme of a luminescence sensor for dissolved oxygen (Hach, 2026b) (used by permission of Hach Company).

Optical sensor for real-time measurement of turbidity by scattering light

Turbidity can be measured in two ways: by nephelometry or turbidimetry. In both methods, light (of known intensity) is passed through a medium and then detected and recorded. The two methods differ in terms of the position of the detector (Fig. 14).

The turbidimetric method determines the attenuation of light passing through the sample (transmission at an 180° angle). This method is suitable for samples with high particle concentration (high turbidity).

The nephelometric method measures the intensity of light scattered by particles at an angle such as 45° (backscatter) or 90° (sidescatter). As this method has a much higher sensitivity, it is suitable for low particle concentrations. The most common and standardized detector angle is 90°, as specified by the method 180.1 of the US Environmental Agency (EPA) and the International Organization for Standardization (ISO) 702-1:2016 (EPA 180.1-1, 1993; ISO 7027-1:2016, 2016).

Furthermore, two different light sources can be installed. On one hand, white light (400 to 600 nm) is used especially for detection of smaller particles. By using a 860 nm light source impact of colour can be eliminated, and the effects of stray light can be minimised (ISO 7027-1:2016).
In general, all results are given in nephelometric turbidity units (NTU) or formazin nephelometric units (FNU), meanwhile NTU mostly refers to white light measurement with at 90° angle (according to EPA) and FNU often refers to a measurement at 860 nm at 90° angle (according to ISO) (EPA 180.1-1, 1993; ISO 7027-1:2016, 2016).

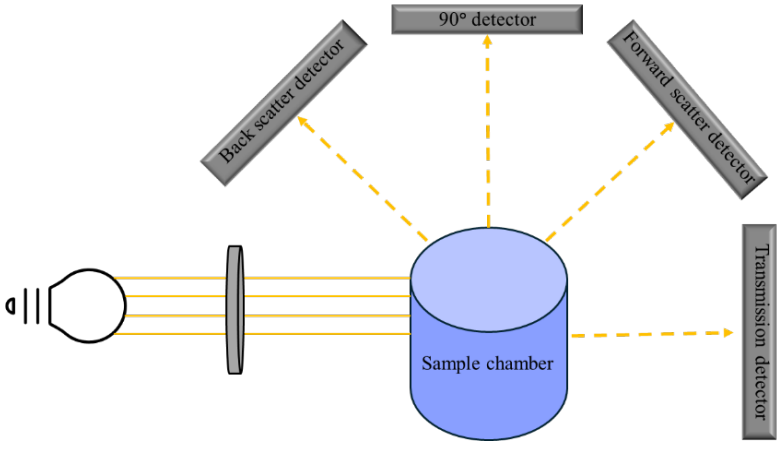


Fig. 14: Scheme of different scattering light measurement methods.

Ion-selective sensor for real-time monitoring

In ion-selective measurements, the ion activity of the ion to be measured is determined. This ion activity can be approximated by the ion concentration in the sample, if the concentrations are low enough (ideal for concentrations ≤ 0.001 mol·L^{-1}, very good approximation for concentrations between 0.001 and 0.01 mol·L^{-1}) (Harris, 2014).

In most cases, the measurement is done by converting the activity into an electrical potential (mV or V) (ion-selective electrodes, ISEs) or into an optical signal (ion-selective optodes, ISOs) (the sensor for dissolved oxygen presented above is also an optode as the oxygen ions are detected by converting ion binding events in special membranes into optical signals). At this point, the measuring principle will be explained using ISEs, i.e., potentiometric measurement.

An ISE consists of the actual ion-selective electrode and a reference electrode. The measured values are determined by measuring the potential difference between these two electrodes using a potentiometer (Fig. 15).

The reference electrode provides a stable, constant, and reproducible electrochemical potential. This means that any change in the measured cell voltage can be attributed exclusively to the change in the potential of the measuring electrode (the ISE), which is determined by the activity of the target ion to be measured (Bakker and Pretsch, 2007).

The reference electrode usually consists of a silver/silver chloride element (Ag/AgCl). The half-cell reaction is (2):

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq) \qquad (2)$$

The element is located in an internal filling solution (reference electrolyte, usually potassium chloride (KCl) in a high concentration), which keeps the potential stable, and a liquid connection (salt bridge, in the form of a diaphragm or similar), which establishes ion contact between the internal filling solution of the reference electrode and the sample to be measured via a capillary (Bakker and Pretsch, 2007).

The main component of the measuring electrode (ISE), on the other hand, is the membrane that is in contact with the sample to be measured. Embedded in this sensor membrane are so-called ionophores (ion carriers), molecular recognition elements that can selectively and reversibly bind the target ion to be measured. The selectivity results from the thermodynamic stability of the ionophore-ion complex, which is determined by the size, charge, and chemical affinity between the host molecule and the guest ion. There are two main classes of ionophores, neutral carriers (electrically neutral molecules) and charged carriers (lipophilic ions), which bind to target ions (Bakker et al., 1997).

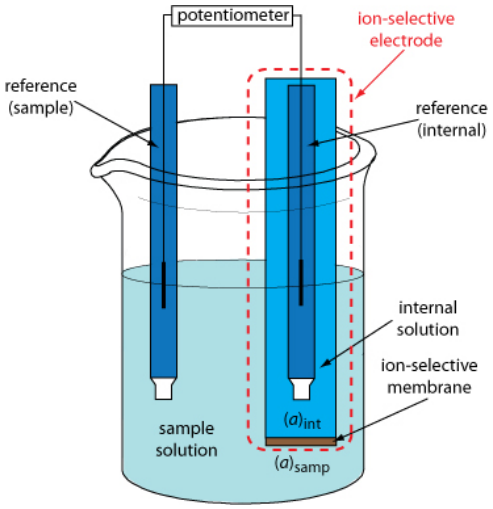


Fig. 15: Schematic diagram of a membrane electrode (in this case, an ion-selective membrane) (Harvey, 2013).

The binding between the host molecule and the guest ion generates a phase boundary potential, which is measured.

According to the Nernst equation (3) (Nernst, 1889), the electrical potential (E) depends on the activity of the target ion to be measured in the sample in a ln-linear relationship and is calculated as follows:

$$E(a_i) = E^0 + \frac{RT}{zF} \ln(a_i) \qquad (3)$$

$E(a_i)$: measured potential (mV)

a_i: activity of the analyte ion

E^0: the standard electrode potential (in mV)

R: the ideal gas constant (8.314 J mol^{-1} K^{-1})

T: the temperature (in K)

z: is the ionic charge (e)

F: the Faraday constant (96485 C mol^{-1}).

From equation (3), it can be seen that ISE measurements are highly temperature-dependent. Therefore, most ISEs available on the market feature temperature measurement so that this data can also be used to perform automatic temperature compensation when calculating concentration values.

In most cases, the measuring membranes are not absolutely specific to the target ion. Other ions dissolved in the sample with a similar charge density, similar ion size or due to forming hydrate shells of similar size can also bind to the membrane or penetrate it, which is referred to as interference or cross-sensitivity. This leads to a change in the membrane potential and simulates excessively high measured values, often described by the selectivity coefficient in the Nikolsky–Eisenmann equation as extension of the Nernst equation (4) K_{ij} for each target ion (Nikolsky et al., 1967):

$$E(a_i) = E^0 + \frac{RT}{zF} \ln \cdot \left[a_i + \sum K_{ij} a_j^{\frac{z_i}{z_j}} \right] \qquad (4)$$

z_i: ion charge of the analyte ion i

z_j: ion charge of the interfering ion j

a_i: ion activity of the analyte ion i

a_j: ion charge of the interfering ion j.

For lower ion concentrations, as they mostly occur in small and medium-sized rivers, the ion activity can be approximated by the ion concentration in the sample solution.

ISEs are used to measure pH and specific ions such as nitrate, ammonium, potassium, chloride, calcium, magnesium, and sodium. Technically, other ions can also be measured if their target concentrations in the water are high enough and the corresponding interfering ions do not occur in problematic concentrations (e.g., nitrite, copper, bromide, silver, fluoroborate, lithium, or perchlorate) (Libelium, 2025).

While the optical sensors mentioned above are more susceptible to interference from turbidity and water coloration, temperature changes, rapid concentration jumps in the matrix, and also in the target ion, compromise ISE measurements. In addition, they are susceptible to biofouling, clogging, and, in the case of liquid membranes, bleeding. All of this can lead to a drift in the measured values. Furthermore, a minimum level of background activity in the sample is required for an ISE measurement. This can be caused by target ions, but also by non-target ions. (Schönenberger, 2024) stated that "laboratory investigations led to the conclusion that a minimum EC of 300 - 400 µS cm^{-1} is required to enable reproducible and stable river measurements with the selected ISE sensor".

A detailed discussion of the use of ISEs for real-time monitoring of small watercourses and their advantages and disadvantages can be found in chapter 2.3.

Examples for ISEs and how they work

In the study presented in chapter 2.3, among other things, a combination probe for the simultaneous detection of ammonium and nitrate with integrated compensation measurement for potassium and chloride was used. This will therefore be explained in more detail here.

This ISE probe is a combination probe that has been specially developed for continuous real-time monitoring in water and wastewater (Fig. 16). It is inserted directly into the water and has a response time of less than three minutes. The combination probe contains four individual ISEs and a reference electrode with an integrated temperature sensor. It focuses on two target ions, which are measured simultaneously: ammonium and nitrate. Since ammonium ions are highly susceptible to interference from potassium ions and nitrate ions are highly susceptible to interference from chloride ions, two ISEs for potassium and chloride are also integrated into the probe. The controller, which processes the potential measured by the respective potentiometer (as an mV signal) on base of the Nernst equation, uses the simultaneously measured data of potassium, chloride, and water temperature to mathematically compensate for any interference in real time (Hach, 2026c).

Although ions such as nitrite (NO_2^-) can cause interference with nitrate ions and ions such as sodium (Na^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) can cause interference with ammonium ions, the concentration ranges in which these ions interfere with the measurement of the actual target ions are usually very high and therefore rarely play a role in practice.

According to the manufacturer's specifications, the reference electrode used for all four ions is an Ag/AgCl system (see above). The ISEs for ammonium, nitrate, and potassium each contain different solid-state polymer membranes with an organic ion exchanger, while the chloride ISE also has a solid-state membrane, namely a silver chloride/silver sulphide pellet ($AgCl/Ag_2S$). It consists of an inactive silver sulphide matrix material that stabilizes conductivity and silver chloride for chloride sensitivity.

All five electrodes are pre-assembled in a cartridge and factory calibrated as a single, replaceable cartridge. This means that the entire cartridge can be replaced on a probe body if necessary.

According to the manufacturer's specifications, the sensor operates in a range of 0 – 1000 mg L^{-1} for potassium and chloride, 0 – 780 mg $L^{-1}$for ammonium, and 0 – 225 mg L^{-1} for nitrate (Hach, 2026c).

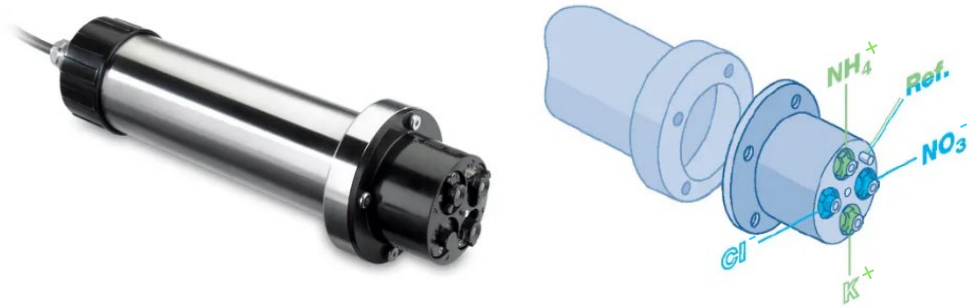


Fig. 16: Probe for simultaneous measurement of ammonium, nitrate, potassium and chloride (left) and scheme of measuring cartridge (right) (Hach, 2026c) (used by permission of Hach Company).

Sometimes, the above-described sensors are integrated into online analysers. In these cases, the sample is fed into an on-site device where it can be prepared under controlled conditions, e.g. by filtering, by temperature control or by adding reagents (adjusting the pH value, inducing a colour reaction) (e.g. sulphate, see chapter 1.4.3.2). This means that even measurement methods which, in theory, could be used directly in the water but are prone to interference in this matrix can be carried out under optimised conditions. Other methods, such as those requiring the use of reagents, can only be carried out within a closed system inside an analyser.

1.4.3.2 At-Site Measuring Devices for Real-Time Monitoring

The numerous measuring devices that collect sub hourly continuous data but cannot be operated directly in the water due to the methodology used. So, they must be installed at-site. The disadvantage of using analysers is that they are much more expensive to purchase, maintain and operate than pure probe measurements. In addition, a power supply is required, and the response time is significantly longer (sub hourly). On the other hand, they offer the advantage of being stable and are also able to detect even very low concentrations. Therefore, in some cases, these analysers represent the more reliable alternative for measurements in smaller concentration ranges(Meyer et al., 2019b).

Furthermore, the sample material must be transported to the measuring device. This can be done using suction pumps that are integrated into the device itself or using larger suction pumps (on land) or pressure pumps (in the water), which transport the sample to a storage basin from where the analyser extracts the required sample volume (again using an integrated pump).

In many cases, these methods use reagents that are automatically mixed with the sample to produce the desired reaction. Most of these analysers have an automatic calibration and cleaning function. Often, the methods used by these devices require sample treatment prior to analysis. For example, for analysers using a light source for measurement, interfering solids must be filtered out. If particle-bound

substances are to be measured, they must first be converted into the dissolved phase by means of digestion. Many systems also offer the option of choosing between different measuring ranges e.g. by changing the concentration of the reagents or by adding an automated dilution step to dilute the analyte if the initial concentrations are too high for analysis.

Online analysers generally work according to the following steps.

- A precisely measured quantity of the sample must be automatically supplied via a dosing pump.
- The required reagents must also be added in a controlled sequence and quantity (via dosing pumps), with the temperature being adjusted if necessary.
- The sample and reagents are combined in a reaction chamber and mixed if necessary.
- Often, a certain reaction time must then be waited for.
- The actual measurement is carried out.
- The integrated computer uses appropriate algorithms to determine the concentration from the resulting signals.

Many devices have an automated calibration mode. In this mode, a standard solution is processed instead of the sample at a specified time. If the measurement signals obtained in this way deviate from a certain value range, the device displays an error and, if necessary, stops the measurement operation. An automated cleaning cycle can often be programmed. In this case, a corresponding cleaning solution is pumped through the tubes in the device to remove contaminants.

Examples for online analysers and how they work

Analyser for photometric real-time measurement of phosphorus (molybdenum blue method)

The molybdenum blue method is a basic photometric method for measuring phosphate in water. It consists of a two-step chemical reaction that produces an intensely blue-coloured complex.

In the first step, soluble ortho-phosphate ions (PO_4^{3-}) react with molybdate ions (MoO_4^{2-}) under strongly acidic conditions (with sulphuric or hydrochloric acid) to phosphorus molybdate ($H_3PMo_{12}O_{40}$). The simplified reaction is (5):

$$PO_4^{3-} + 12\ MoO_4^{2-} + 27\ H^+ \rightarrow H_3Mo_{12}O_{40} + 12\ H_2O \qquad (5)$$

This intermediate complex is almost colourless or pale yellow.

In the second step, this acid is reduced. A reducing agent (usually ascorbic acid ($C_6H_8O_6$) with a catalyst) is added. This reduction converts some of the molybdenum atoms from oxidation state +VI to state +V, creating a mixed-valence compound. This electronic change leads to the formation of the intensely blue-coloured phosphor molybdenum blue complex, a representative formula for this reduced complex is $[H_4PMo^{VI}_8Mo^{V}_4O_{40}]^{3-}$. Since the complex has its absorption maximum in the near-infrared/red range, the extinction is measured at approximately 880 nm (see section 1.4.4.1) (Patella et al., 2023).

For real-time measurement using an analyser, the sample must either be filtered or the particles contained in the sample must be crushed and homogenised so as not to interfere with the measurement. This can be done using ultrasound, for example. If the sample is prepared in this way, the total phosphorus content can also be determined after subsequent high-temperature digestion using an oxidising agent (usually peroxydisulphate ($S_2O_8^{2-}$). During digestion, all particle-bound phosphorus fractions are transferred to the solution and oxidised so that they are all present as ortho-phosphate. Some equipment manufacturers offer analysers with alternating measurement of ortho-phosphate and total phosphorus.

In practice, for measuring ortho-phosphate and total phosphorus, a homogeniser first breaks down solid particles in the sample using ultrasonic (app. 2 minutes) to ensure a uniform mixture for accurate analysis (Fig. 18a).

For ortho-phosphate, an aliquot is injected directly into the reagent stream, total phosphorus, an aliquot is mixed with the digestion reagent (acidic peroxodisulphate) and heated (Fig. 18b). So, all phosphorus fractions are hydrolysed and oxidized to ortho-phosphate. Then the sample is cooled. The next steps are identical for measuring both ortho-phosphate and total phosphorus. The sample is mixed with ammonium molybdate reagent, then ascorbic acid reducer is added. The mixture passes through a reaction coil (at ~50°C) to allow the molybdenum blue complex to develop fully. In the flow-through spectrophotometer cell, extinction is measured at 880 nm. The concentration of phosphorus is calculated. With this approach, a measurement cycle takes 10 - 15 minutes (Hach, 2026d).

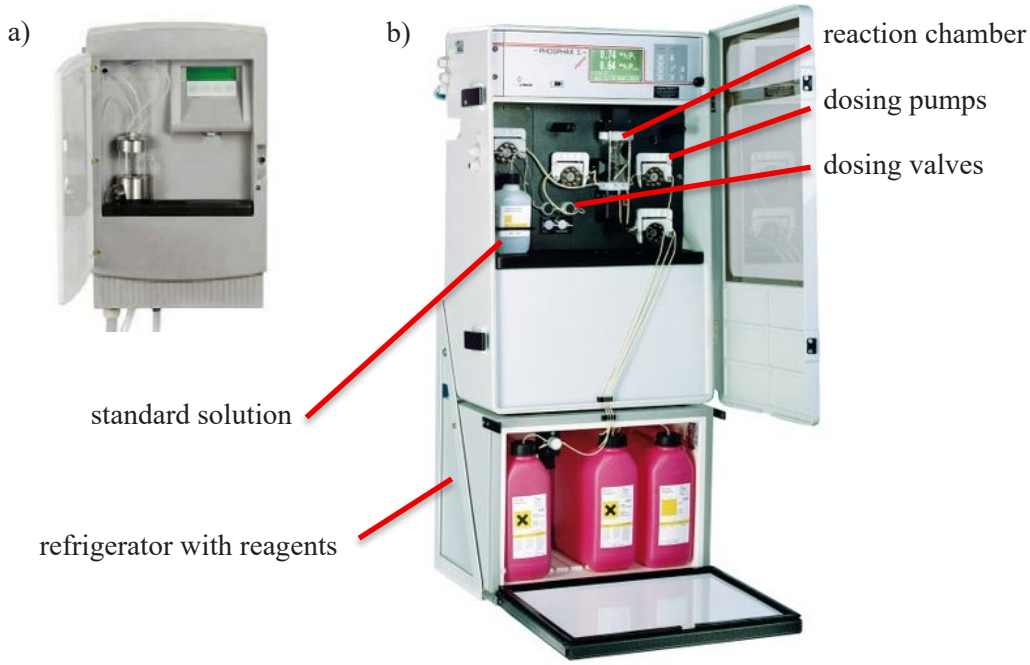


Fig. 17: a) Ultrasonic homogeniser (Hach, 2026e); b) analyser for photometric real-time measurement of ortho-phosphate and total phosphorus (Hach, 2026d) (both used by permission of Hach Company).

Analyser for photometric real-time measurement of ammonium (indophenol blue method)

Another photometric method is the indophenol blue method for measuring ammonium, in which ammonium ions produce a measurable blue colour.

In this method, the ammonium ions react with hypochlorite (OCl^-) under alkaline conditions (pH > 12). This produces monochloramine (NH_2Cl) (6)**:**

$$NH_4^+ + OH^- + OCl^- \rightarrow NH_2Cl + 2H_2O \qquad (6)$$

Under these conditions, most of the ammonium is present as ammonia, which is the actual reactive species (see also below). The monochloramine (NH_2Cl) thus formed reacts with salicylate ions ($C_7H_5O_3^-$) under still alkaline conditions. This reaction is catalysed by nitroprusside ($[Fe(CN)_5NO]^{2-}$) (7):

$$NH_2Cl + 2\,C_7H_5O_3^- + OH^- \xrightarrow{[Fe(CN)_5\,NO]^{2-}} C_{14}H_9NO_2 + Cl^- + 2H_2O \qquad (7)$$

The colour intensity of the resulting deep blue indophenol blue ($C_{12}H_9NO_2$) is proportional to the ammonium concentration and is measured at a wavelength of 630–660 nm (Hach, 2026c).

In an analyser for photometric real-time measurement of ammonium, the filtered water sample is brought together with all reagents in the mixing chamber and mixed using a stirrer (Fig. 18). After a short reaction time, the solution is pumped into the measuring chamber and measured there by help of the light beam. The analyser provides a measurement cycle of approximately 10 minutes.

Fig. 18: Analyser for photometric real-time measurement of ammonium (Hach, 2026f) (used by permission of Hach Company).

Analyser for gas-sensitive real-time measurement of ammonium

This measurement method is based on the natural ammonium-ammonia equilibrium in water, i.e. the relationship between ammonium ions and un-ionised ammonia gas in water, which can be seen in the following equation (8):

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \qquad (8)$$

The percentage of un-ionized ammonia (NH_3) in water is not fixed, it depends on the water's pH and temperature. The calculation uses the acid dissociation constant (pK_a) of ammonium ion, which varies with temperature (Fig. 19). The primary relationship for the fraction of total ammonia-N (TAN = NH_3-N + NH_4^+-N) present as NH_3-N is calculated as follows (9) (EPA, 2013):

$$NH_3 - N = \frac{NH_4 - N}{1 + 10^{pK_a - pH}} \qquad (9)$$

pK_a: acid dissociation constant for NH_4^+ at a specific temperature (see below).

pH: pH of the water sample.

The value for pK_a changes with temperature, it can be calculated using equation (10) (EPA, 2013):

$$pK_a = \frac{0.09018+2729.92}{T} \qquad (10)$$

T: absolute temperature in Kelvin (temperature of the water sample in °C + 273,15)

This results in the following equation (11):

$$NH_3 - N = \frac{NH_4-N}{1+10^{0.09018+\frac{2729.92}{T}-pH}} \qquad (11)$$

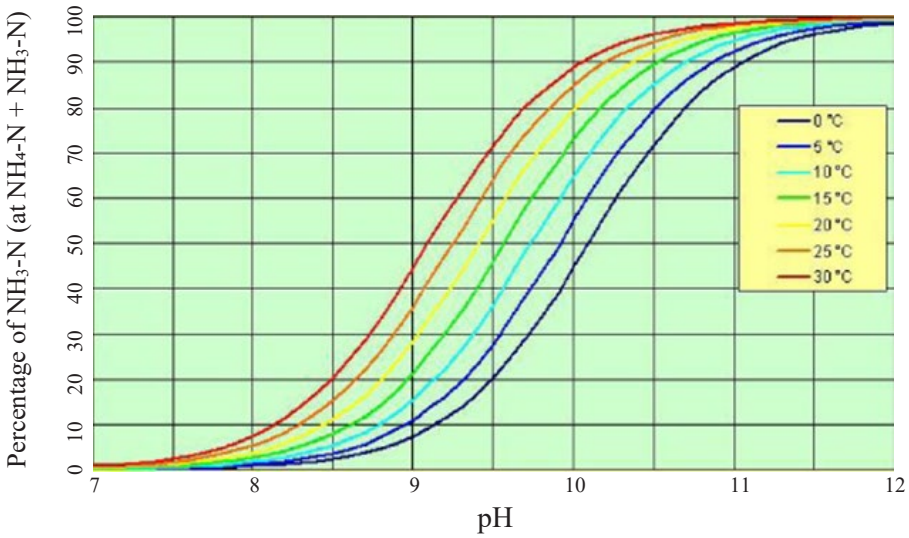


Fig. 19: Percentage distribution of ammonium/ammonia, depending on pH value at different temperatures (LUBW, 2015).

In the gas-sensitive analyser, ammonium is be detected by converting it into gaseous ammonia (Fig. 20). By the ammonia gas passing through a membrane, a precise, low-maintenance, and wide-range measurement (0.02 - 1000 mg L^{-1}) with rapid response (5 - 10 minutes) can be provided. The sample has to be filtered to remove suspended particles.

Since the reaction must take place at very high pH values (usually > 12), sodium hydroxide (NaOH) is added to the sample to raise the pH. This chemical reaction converts ammonium it into gaseous ammonia (equation 6) (Hach, 2026g).

To support the reaction, the solution may also be heated (see equation 7). The ammonia gas then diffuses through the hydrophobic, gas-permeable membrane into an electrolyte liquid (usually ammonium chloride) located between the membrane and the pH glass electrode. In the electrolyte, the ammonia gas reacts according to the equation (12):

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (12)$$

The formation of hydroxide ions causes the pH value in the electrolyte layer to rise. This pH shift is measured by the integrated pH electrode. The resulting electrical potential is logarithmically proportional to the concentration of ammonia in the sample (Hach, 2026g).

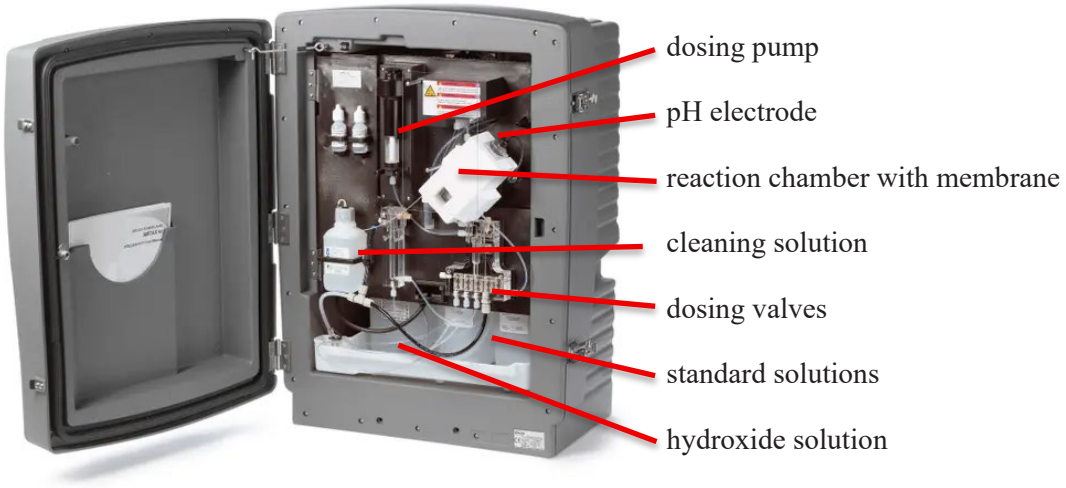


Fig. 20: Analyser for gas-sensitive real-time measurement of ammonium (Hach, 2026g) (used by permission of Hach Company).

Analyser for nephelometric real-time measurement of sulphate

The methods described above for measuring turbidity (turbidimetry and nephelometry) can be used in analysers if a chemical reaction causes the target substance to form a precipitate which then can be correlated with the concentration of this substance. The resulting precipitate (turbidity) is kept in suspension during the nephelometric or turbidity measurement with the aid of a stirrer (Hach, 2026h).

The determination of sulphate ions is based on nephelometric measurement by light scattering (90°angle). The sulphate is precipitated with barium chloride ($BaCl_2$) to form barium sulphate ($BaSO_4$).

For calcium sulfate ($CaSO_4$), e.g., the reaction can be represented as follows (13):

$$CaSO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow + CaCl_2 \qquad (13)$$

Before doing so, an acidic medium (hydrochloric acid, HCl) has to be created to prevent the precipitation of other ions like carbonate or phosphate. Additionally, a conditioning agent such as ethylenediaminetetraacetate (EDTA) is needed to stabilise the suspension during the measurement.

In the analyser, the filtered sample is therefore mixed with HCl, $BaCl_2$ and EDTA in the reaction chamber (Fig. 21). Insoluble $BaSO_4$ is formed (precipitation reaction). This suspension (turbidity) is then measured using the nephelometric method (see above). The light is scattered by the barium sulphate particles, the intensity of this scattered light is directly proportional to the particle density and thus to the sulphate concentration (Hach, 2026h).

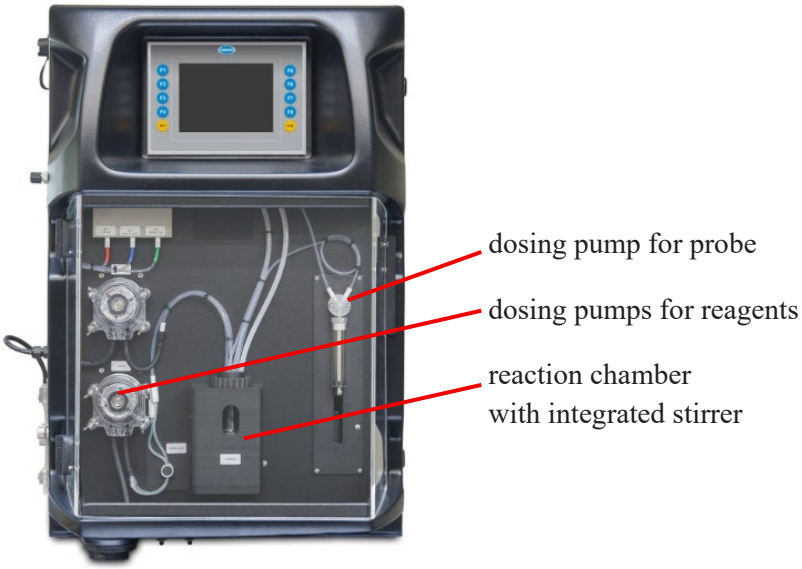


Fig. 21: Analyser for nephelometric real-time measurement of sulphate (Hach, 2026h) (used by permission of Hach Company).

1.4.3.3 Special Cases Automatic Samplers

While all of the methods described above ultimately refer to the measurement of grab samples - regardless of their temporal resolution, automatic sampling systems can generate grab samples and composite samples. A composite sample consists of the combination of grab samples taken at fixed intervals over a specific period.

Automatic samplers are often used for this purpose. With help of these devices, samples can automatically be taken proportionally to time, volume, flow rate, or be event-driven as the triggering signal (Fig. 22) (DWA, 2017). The selected volume of samples is filled into a specific bottle in accordance with the relevant procedure. The samples obtained in this way are then collected after a certain time and analysed in the laboratory for the parameters and substances to be considered. There are self-emptying devices that automatically empty the first bottles at the end of the programme me which are then available for the subsequent samples. In addition, some devices have a rinsing function for the suction pipe and bottles to prevent contamination from previously drawn samples. Some of the devices offer the option of cooling or even freezing the samples for preservation purposes. In addition, a specific amount of a suitable conservation liquid can be added to each bottle to be filled, e.g. acid to preserve samples for metal analysis. Particular care must be taken when selecting the materials for the pipes and bottles to ensure that they are inert to the substances to be measured. For example, bottles must be made of glass for the analysis of metals (DWA, 2017). While simple automatic samplers are relatively inexpensive to purchase and can be used flexibly in field thanks to battery or solar power, the more specific devices are much more expensive and require a more complex infrastructure such as accessibility and current power supply (Fig. 23).

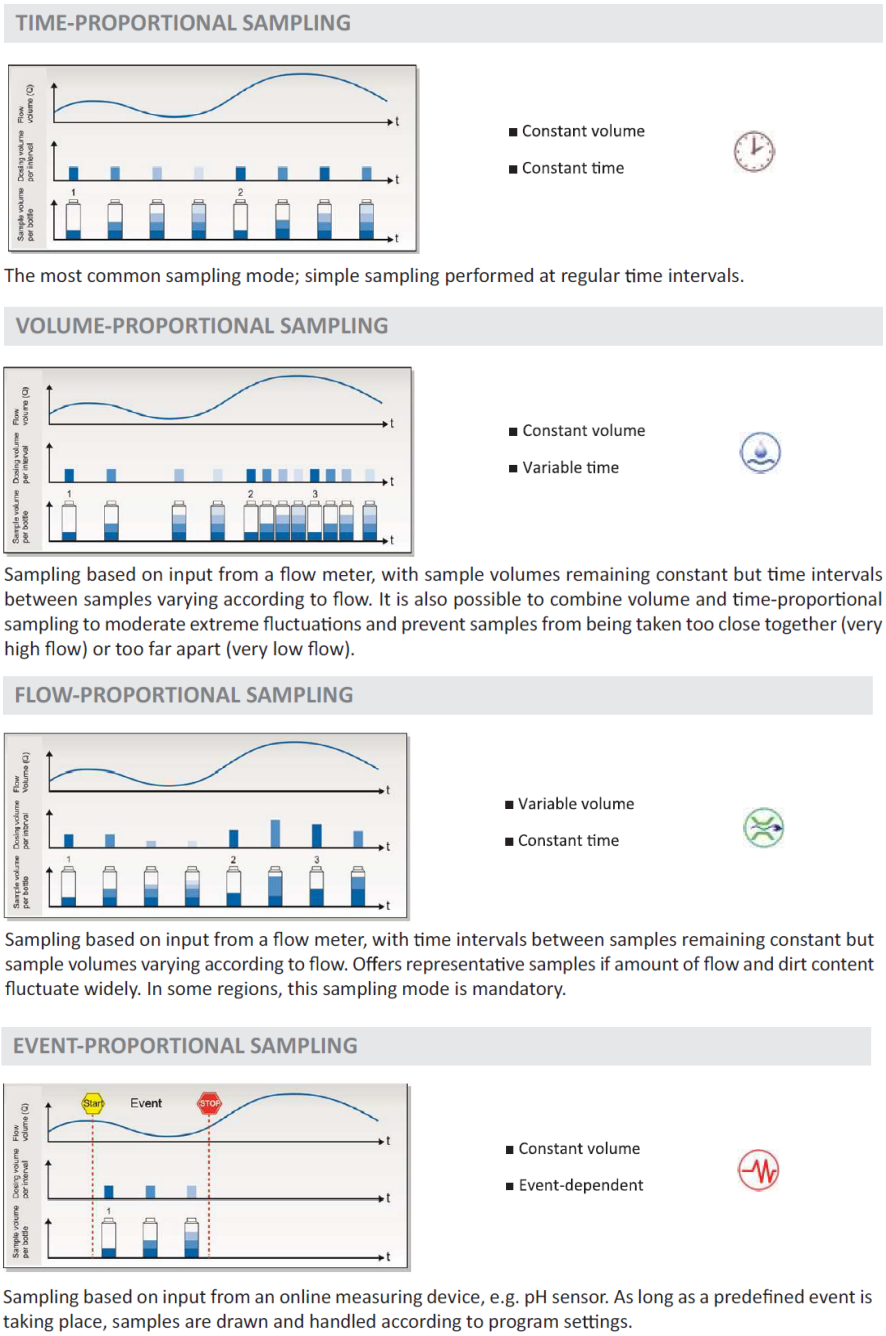


Fig. 22: Schematic overview of the different sampling strategies by an automatic sampler: time proportional, volume-proportional, flow-proportional and event-proportional sampling (Romanowski, 2015).

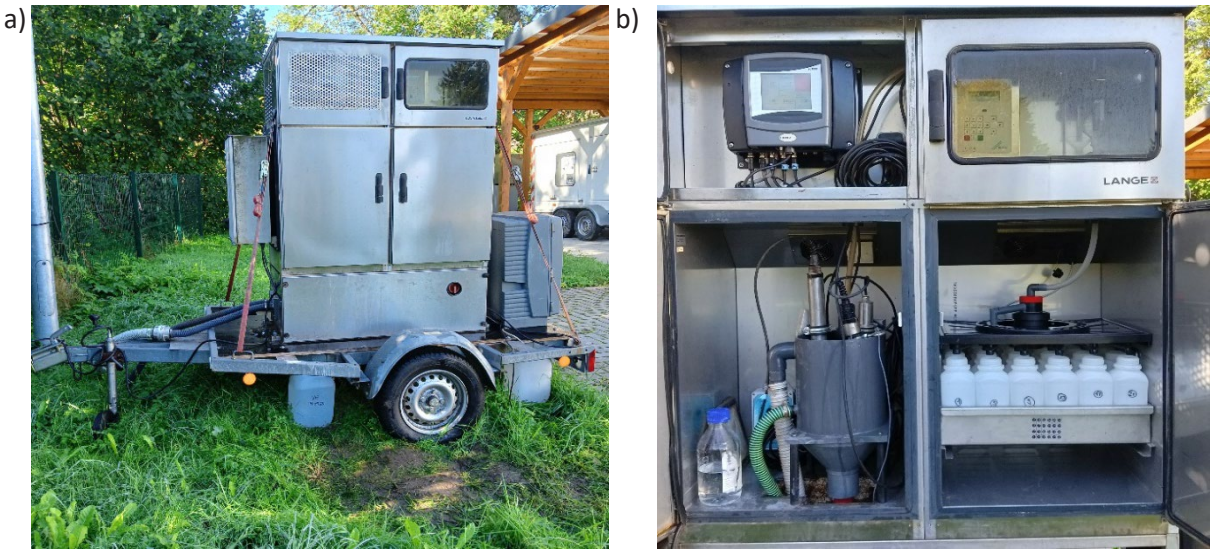


Fig. 23: Automatic sampler installed on a trailer: a) exterior view with pipes and power supply cable (left side) and stand alone analyser for ammonium (right side), b) interior view with small sample basin, probes (left side) and automatic sampling device (right side).

Composite samples also include samples taken continuously over a defined time period, such as those gained by so-called passive samplers. Passive samplers are monitoring devices that accumulate chemical pollutants from river water over time, providing time-weighted average concentrations rather than single-point measurements. Another example for passive sampling devices is a suspended matter (SM) collector. Since these were not used in the studies presented in chapter 2, they are only mentioned briefly here for the sake of completeness.

1.4.3.4 Combining Measuring Devices – Example of a Mobile Monitoring Station

Analysers offer additional advantages for real-time water monitoring, but they are expensive to purchase and maintain and require a great deal of maintenance. If such systems are to be used, many criteria must be taken into account, such as accessibility, power supply, protection against flooding and vandalism, and much more. But relying only on in situ sensors misses valuable data of other pollutants (e.g. phosphorus and TOC). For robust river monitoring, integrating both approaches is essential to overcome their individual limitations, especially in small and medium-sized rivers.

The mobile measuring stations in the studies presented in chapter 2 are an example for integration of both approaches (Fig. 24).

These measuring stations are designed as trailers and can therefore be used at a wide variety of locations (Fig. 24). At each location, a pump is installed in the river, which continuously pumps the river water through a pipe into the sample basin in the measuring station. The water can flow back into the river via the outlet at the other side of the basin. The sample basin thus serves as a bypass for the river.

Various measuring devices (probes and analysers) are combined in the station. Probes for measuring temperature, oxygen, pH value and EC as well as for nitrate and turbidity are located directly in the sample basin. In addition, analysers for measuring ammonium, ortho-phosphate and total phosphorus as well as TOC are available. They are supplied with treated sample water either via filters (ammonium) or an ultrasonic homogeniser. All measuring devices are connected to a data logger via

4 - 20 mA signals, through which the data is transmitted. The stations are designed to be adaptable, allowing additional probes (e.g. ISEs for measuring chloride), additional analysers (e.g. for measuring sulphate) or even an automatic sampler can be integrated.

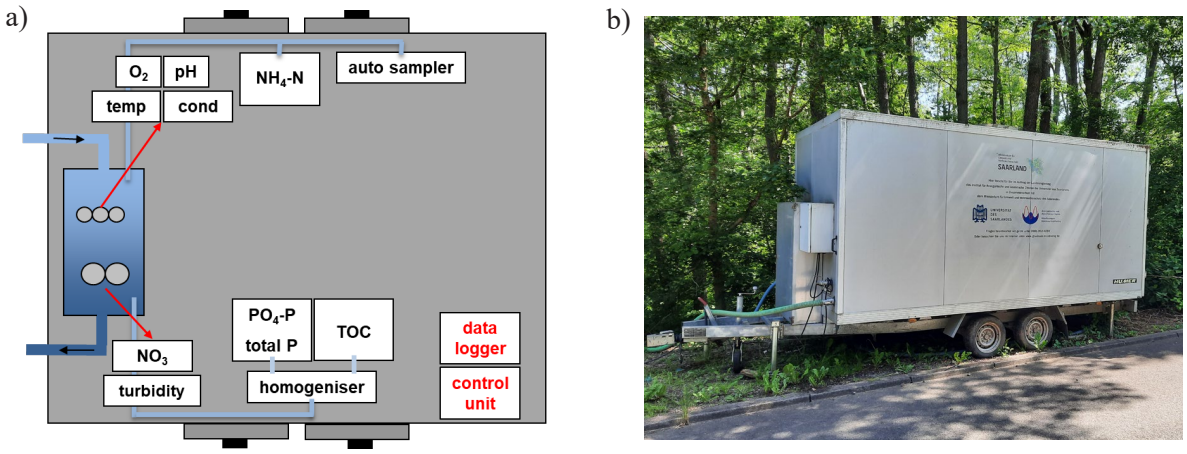


Fig. 24 a) Scheme of a mobile measuring station, b) mobile measuring station in *Fechingen*.

1.4.4 Limits to the Use of Real-Time-Methods

Although continuous water quality monitoring systems offer many advantages, they also have some limitations. One significant disadvantage is the high cost of purchase and maintenance. The need for special sensors, data loggers and telemetry equipment incurs considerable expense. Furthermore, regular maintenance and calibration work is essential to ensure the accuracy and reliability of the data. These financial hurdles make it difficult to implement such systems on a broad scale.

In addition, the analytical possibilities are limited: due to low concentrations or disruptive environmental influences, many important parameters can often only be determined after complex sample preparation in the laboratory.

Another disadvantage is the complex data management and analysis. Continuous monitoring generates large amounts of data, which are difficult to evaluate without the appropriate tools and expertise. Outliers, missing data or false alarms can hinder accurate interpretations. Qualified personnel and advanced analysis methods are therefore necessary for the effective use of the data obtained. Consequently, without appropriate training and resources, the potential benefits of continuous monitoring systems often remain untapped (Meyer et al., 2021a, 2019b).

1.4.5 Determination and Meaning of Loads

The calculation or estimation of registered substance loads serves to assess substance flows in water bodies and to balance the input into the higher-level river system or coastal waters. The substance load in water bodies is the mass of a substance that is transported through the flow cross-section of a water body within a period of time (e.g. year, day or even event). It is calculated as the product of the water volume (flow) and the measured substance concentration, which is assumed to be representative of the entire cross-section. A detailed description of various load calculation methods, as well as sampling strategies for the purpose of load calculation, can be found in LAWA (2003).

Especially in small and medium-sized rivers, which rarely exhibit pronounced laminar flow behaviour, the substance concentration measured at a water point can be assumed to be representative of the entire cross-section. However, substance concentration and flow can vary greatly in some cases and exhibit

characteristic patterns (daily, weekly, monthly, annual). Therefore, real-time measurements also provide the best possible results for determining loads, assuming the respective load from mixed samples or random samples inevitably leads to greater deviations from reality (Meyer et al., 2021a).

In addition, high-resolution loads allow the variability of substance transport to be better recorded, and further interpretation of this data enables conclusions to be drawn about the origin and transport routes of the substances under consideration, as well as about peak loads, e.g. during flood events. Furthermore, a comparison of the loads can provide information about the spatial origin of pollution, e.g. when the loads at two measuring locations in a catchment area are compared with each other (Fig. 25a). This comparison can then be used to determine in which part of the catchment area the largest proportion of the pollution occurs and which area in the catchment area is most effective for measures to reduce this pollution. A comparison of the loads at the same measuring site at different times is also useful to check whether measures implemented in the catchment area between the two measurement campaigns have led to a reduction in pollution and an improvement in the chemical status other (Fig. 25b) (Meyer et al., 2021a).

The loads are also of particular importance in relation to the question of the origin of the pollution and the proportion of the total pollution attributable to STPs, CSOs and agricultural inputs. First, a distinction must be made between the quantities of a substance transported at a measuring point in the base flow in a water body (base load) and the additional quantities introduced as a result of precipitation events (hereinafter referred to as precipitation load for the sake of simplicity). For this purpose, the respective median discharge is generally used to distinguish between base and “event discharge” (Moatar et al., 2017). The difference between the total load and the base load is then the precipitation load. Based on these values, a rough categorisation of the loads can be made, e.g. for nitrogen and phosphorus, into those originating from agriculture, STPs, CSOs and groundwater (Table 3). In this case, the sum of nitrate and ammonium is given as total nitrogen, since the proportion of nitrite and organic nitrogen compounds in the flowing water can be considered negligible. Regular measurements of nitrite confirm this theory. Nevertheless, it is clear that this results in inaccuracies, especially for the nitrogen fraction, since, for example, ammonium as an indicator of STP emissions (in groundwater runoff) and CSOs (in ‘precipitation runoff’), or because the distinction between nitrate inputs via groundwater and those from STPs cannot be easily made on the basis of the measurement data collected online alone. Such inaccuracies also exist for phosphorus, as sedimentation and resuspension processes cannot be taken into account in the balance. To verify this assessment more accurately, additional measurement data, e.g. emission data from STPs or data from groundwater measurements, can be used (Meyer et al., 2021a).

Table 3: Theoretical breakdown of nutrient loads into individual categories (proportions from STPs, CSOs, agriculture and groundwater).

Category	Agriculture	STPs	CSOs	Groundwater
nitrogen	Precipitation load Nitrate (inaccuracy due to the time lag between runoff and concentration)	Determined using the emission data from STPs	Precipitation load of ammonium	Base load of nitrate minus the proportion of STP emissions
phosphorous	Precipitation load of particle-bound phosphorus (the small amount of ortho-phosphate is negligible, see CSOs)	Base load of total phosphorus	Precipitation load of ortho-phosphate (small amounts of particle-bound phosphorus are neglected, see 'agriculture')	negligible

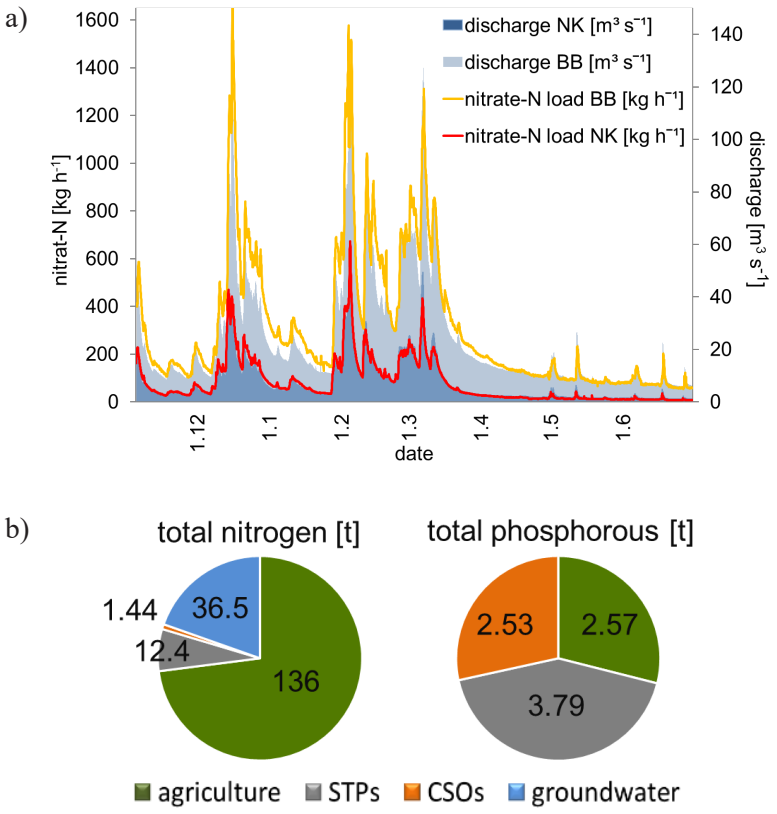


Fig. 25: Comparing loads for assessing the origin of pollution: a) spatial assessment: nitrate loads at two different measuring sites along river Blies (mean hourly values from 04.11.2019 to 30.06.2020, in *Neunkirchen* and in *Bierbach*) (Meyer et al., 2020);b) assessment according to the categories: loads of nitrogen and phosphorous from groundwater, agricultural impacts and discharges from STPs and CSOs (mean hourly values from 08.03. to 29.10.2022, Oster in *Wiebelskirchen*) (Meyer et al., 2023).

1.4.6 Data Management and Interpretation

Effective data management is crucial for converting the raw data collected through monitoring activities into usable insights into the status of a water body. It encompasses IT-supported data collection, transmission, storage, processing and management, as well as automated reporting and the organisation, documentation and quality assurance of the entire monitoring process. Each of these steps is subject to data security. Data management is particularly important in the field of real-time monitoring, mainly because real-time measurements usually generate very large amounts of data.

For the above-mentioned sub-steps, there are numerous technical solutions that are either commercially available or internally customized. Therefore, only the conceptual approaches to data management will be discussed here.

Data acquisition

The measured data is collected by a heterogeneous mix of sensors and instruments, which often have different formats, communication protocols and temporal resolutions. An important step - and also a major challenge - is the normalisation and integration of this data into a centralised platform in order to create a uniform view and to be able to further process, evaluate and interpret the data accordingly. The data collection system must also be designed to be adaptable when network requirements change, e.g. due to an expansion of the device pool or the use of newer measurement technology (Bumberger et al., 2025).

Data transmission

Data is often transmitted wirelessly (via Wi-Fi, GSM or encrypted networks) to cloud platforms or data centres for processing. Various technologies are used for efficient, scalable real-time data streaming. It is important that data transmission is not susceptible to interference and functions reliably at all times (DWA, 2017).

Data storage and management

Centralised, secure and scalable data storage solutions (e.g. cloud-based platforms) are essential for processing large amounts of data. For management in the database, the structure of the measurement data and its metadata must be standardised. The data stored in the database must be searchable for overview or detailed evaluations. It should be possible to retrieve the data according to the requirements of specific evaluation programme (statistics/time series visualisation/spatial analysis/modelling) (DWA, 2017).

While the first three points refer to the raw data itself, the following points refer to the conversion of the raw data into validated data and the resulting information, including in the form of alarms, graphics and reports.

Data processing, internal visualisation, evaluation and interpretation:

- Standardisation of data and conversion into the required uniform format: in this step, the collected data is normalised and merged. Measurement data from other external programme s (e.g. the results of grab sampling, third-party data (weather data, data from STP effluents, discharge measurements) or even measurements from other locations can also be integrated into this process.

- Data aggregation: for recurring evaluations, it makes sense to aggregate high-resolution data according to uniform criteria to data at the next higher time level, e.g. hourly values to daily values, which are stored as derived data series. The aggregation rules must be based on a specified minimum number of original values (DWA, 2017).

- Real-time processing: this procedure enables the output of warning messages and notifications when parameters exceed predefined thresholds (e.g. via email or SMS).

- Advanced analyses: special tools can be used, for example, to eliminate outliers or technical errors (e.g. due to device failure), identify trends or enable forecasts.

- Automated reporting and visualisation: a user-friendly, powerful tool for graphically displaying raw data and adjusted measurements, as well as any additional data, alarms, trends and forecasts is essential for internal visualisation the final evaluation and interpretation of the data. Additional creation of customised reports is crucial for e.g. ensuring the data to be formatted to comply with legal standards, where applicable, streamlines work processes and reduces manual errors. External visualisation of the measurement data can be done via web-based dashboards and portals by are user-friendly interfaces for authorities and citizens to access graphics and reports (DWA, 2017).

- General documentation: when documenting monitoring data, all framework conditions (location including coordinates, date and time, sampling method, equipment, sample preparation, analysis method and devices) must be recorded. These must also be stored in the data management system (DWA, 2017).

- Quality control: ensuring continuous data accuracy requires proactive quality control of the raw data. An important element of quality control is analytical quality assurance. This involves comparative measurements to check the functionality of the analytical equipment. The data must be systematically checked for transmission errors (actuality and completeness of the data). Further plausibility checks can be carried out by comparing identical parameters at nearby measuring locations or interdependent parameters at the same measuring point. Calibration data and maintenance information should also be documented within this process. Systematic data checking can be significantly supported by predefined database queries and programme med test routines. Values that are implausible, have been corrected retrospectively or are influenced by special measurement conditions should be marked and, if necessary, commented on so that they can be specifically excluded or included in later evaluations. The preliminary end product is quality-assured water quality data, the collection and analysis of which is fully documented and thus traceable (Bumberger et al., 2025).

- Data security: data security is of particular importance for the entire data management process. This includes ensuring data integrity, implementing backups and protecting sensitive information through robust security measures. When presenting data externally, a balance must be struck between security and accessibility (DWA, 2017).

- Data interpretation: the interpretation of data obtained by real-time monitoring should always take into account all available gathered data. Comparing simultaneously measured values of different parameters provides insights into the input patterns and, thus, to the origin of the pollution. In addition, if possible, the discharge data from the same or at least a nearby gauging station and the weather conditions representative of the location (precipitation, air temperature, air pressure and global radiation, if applicable) should also be included in the interpretation. Ideally, this information should also be available as high-resolution data. In addition, data such as discharge values from STPs or industrial dischargers located in the catchment of the measuring point as well as groundwater data can also be considered, e.g. for estimating continuous pollution from point sources or for assessing the matrix of the geogenic background (Meyer et al., 2021a, 2019b).

1.5 Significance of Small and Medium-Sized Rivers and their Monitoring

Sophisticated targeted, and spatiotemporal high-resolution monitoring is of utmost importance, especially for small and medium-sized rivers. In the WFD, such rivers with a catchment area of less than 100 km² are defined as small, while those with a catchment area of 100 to 1000 km² are defined as medium-sized rivers. The figures for the proportion of small and medium-sized rivers in the total number of water bodies in the EU vary between 70% (Lassaletta et al., 2010) and 80% (Biggs et al., 2014). Nevertheless, there is no doubt that most European rivers fall into this category.

1.5.1 Ecosystem Services of Small and Medium-Sized Rivers

Almost everywhere, rivers of all sizes have been significantly changed by human influences in morphology, hydrology, chemical and biological aspects. The anthropogenic pressure on the rivers is caused by e.g. damming and channelising of rivers to gather for water for any human use, the sealing of surfaces in the catchments changing the hydrological conditions, as well as by discharges of domestic and industrial wastewater, the runoff from agricultural and urban areas substantially influencing the chemical status and thus the biological status of the water bodies. This leads to the reduction of aquatic biodiversity by destroying habitats, and compromising ecological integrity, and inevitably to negatively impacting the rivers´ ecosystem services (Khosrovyan, 2024). For example, Su et al. (2021), state that "more than half of the river basins (52.8%) representing 40.2% of the world continental surface and 37.3% of the world river length (…), revealing deep and spatially distributed anthropogenic impacts on fish biodiversity".

Nevertheless, all water bodies fulfil many different ecosystem services (ES). The ES concept was formalized by the Millennium Ecosystem Assessment (2005) and is defined to be all direct and indirect contributions of ecosystems to human well-being and societal development. The ES are usually subdivided into provisioning, regulating, supporting and cultural services (Rodríguez et al., 2006). This subdivision can also be applied to the river´s ES. The main services of rivers for these categories are listed below, with special regard to the small and medium-sized rivers including also intermittent and ephemeral streams.

- **Provisioning services refer to all products obtained from nature:**
  - Water supply: Rivers serve as primary sources for drinking water but also for irrigation, and industrial use through surface flows, groundwater recharge as well as in lakes and freshwater reservoirs.
  - Food production: Rivers support fish populations or other (wild-harvested) foods (Khosrovyan, 2024) as well as biomass production in their riparian areas.

- **Regulating services are natural processes regulating environmental conditions:**
  - Flood mitigation: Particularly uninfluenced or only slightly influenced rivers absorb and slow stormwater runoff, also via riparian vegetation and floodplains, reducing downstream flooding. E.g. studies show intact small rivers can lower flood damage (Sousa et al., 2025).
  - Water purification: Healthy rivers have a high (self)cleaning ability, pollutants can be broken down or filtered due to (micro)biological activity, hydraulic and hydrological factors (Bui et al., 2024).
  - Sediment regulation: Especially small and medium-sized rivers contribute to stabilizing banks and reducing erosion, and thus to maintaining downstream channel integrity (Shaad et al., 2022).
  - Groundwater recharge: Rivers replenish aquifers, securing baseflows during droughts (Datry et al., 2018).
  - Climate resilience: Rivers are crucial for moderating local microclimates, wetlands and riparian forests can even sequester carbon (Sousa et al., 2025).

- **Supporting services summarize all foundational processes enabling all other services:**
  - Biodiversity hotspots: all rivers (can) provide immensely important habitats for countless animals and plant species. Small (headwater) rivers in particular host unique and sometimes even endemic species and provide critical spawning, nursery, and refuge habitats. Meyer et al. (2007) e.g. exemplified this diversity by identifying over 290 taxa in three unmapped headwaters.
  - Trophic support: Small (headwater) rivers supply the food chains in downstream rivers with organic material (e.g. phyto- and zooplankton) or nutrients.
  - Ecological connectivity: Rivers serve as wildlife corridors and stepping stones linking terrestrial and aquatic ecosystems.

- **Cultural services describe all non-material benefits**
  - Recreation and tourism: Rivers enable recreation and nature experiences like fishing, kayaking, swimming, and others. Urban river studies highlight their role in mental health and community well-being (Sousa et al., 2025).
  - Cultural heritage: Rivers can also serve as sacred sites and for traditional practices (e.g., ritual bathing, folklore) (Shaad et al., 2022).
  - Aesthetic and educational value: Rivers serve as living laboratories for environmental education and citizen science (Sousa et al., 2025).

The importance of the rivers' ecosystem services is also recognised by the United Nation (UN) in their Sustainable Development Goal Target 6, particularly in 6.3 to "improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally", as well as in 6.5 to "implement integrated water resources management at all levels, including through transboundary cooperation as appropriate" and in 6.6 to "protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes" (UN, 2025).

1.5.2 Special Conditions in Small and Medium-Sized Rivers

Although fulfilling the same ecosystem services as the large rivers, small and medium-sized rivers exhibit heightened vulnerability because of their flashy hydrology, their low dilution capacities and their proximity to diffuse pollution sources.

Due to these initial conditions, in small and medium-sized rivers the following situations or events occur more often and/or much more pronounced that in larger rivers (Meyer et al., 2021a, 2019b).

Seasonal changes and weather conditions

Heavy rainfalls as well as spring snowmelt create a pronounced runoff situation, causing a sharp increase in water volume and flow velocity. This leads to erosion of riverbanks, to channel change and to an increased transport of sediment and woody debris downstream. Further to this, sediment from the surrounding areas and dissolved terrestrial substances (e.g. nutrients) flush into the river. For example, in many rivers in autumn, after the growing season has ended and the fields have been harvested, large quantities of nitrate are washed into the water with the first rains. The nitrogen, which is bound in the soil during the growing season, is released, oxidised to nitrate and then washed out by the rain, leading to a pronounced raise of nitrate concentrations in the rivers (Fig. 26a). On the other hand, summer drought may cause low flow conditions, so with less water diluting them, concentrations of pollutants increase (Meyer et al., 2019a).

In contrast, during dry periods, discharges from technical facilities such as STPs, which discharge almost constant amounts of wastewater into the water body, are particularly pronounced due to low runoff. This effect is illustrated in Fig. 26b. Due to the declining water volume, the relative proportion of discharges from the STP is steadily increasing and the concentration of discharged ortho-phosphate (and total phosphorous) continuously rises (Meyer et al., 2019a).

Due to their low water volume, small bodies of water react immediately to temperature influences from the atmosphere and heat up or cool down faster than larger bodies of water. Additionally, during low flow conditions in summertime in combination with high air temperatures and intensive solar radiation water temperatures rise quickly, especially in shallow and slow-moving water. This also affects the solubility of gases such as oxygen and carbon dioxide in the water: the lower the temperature, the higher the solubility of gases in water. Temperature effect as well as their impacts (see below) emerge as seasonal trends but are much more pronounced in spring and summer becoming visible in short-time daily fluctuations (see below) (Fig. 26c) (Meyer et al., 2019a).

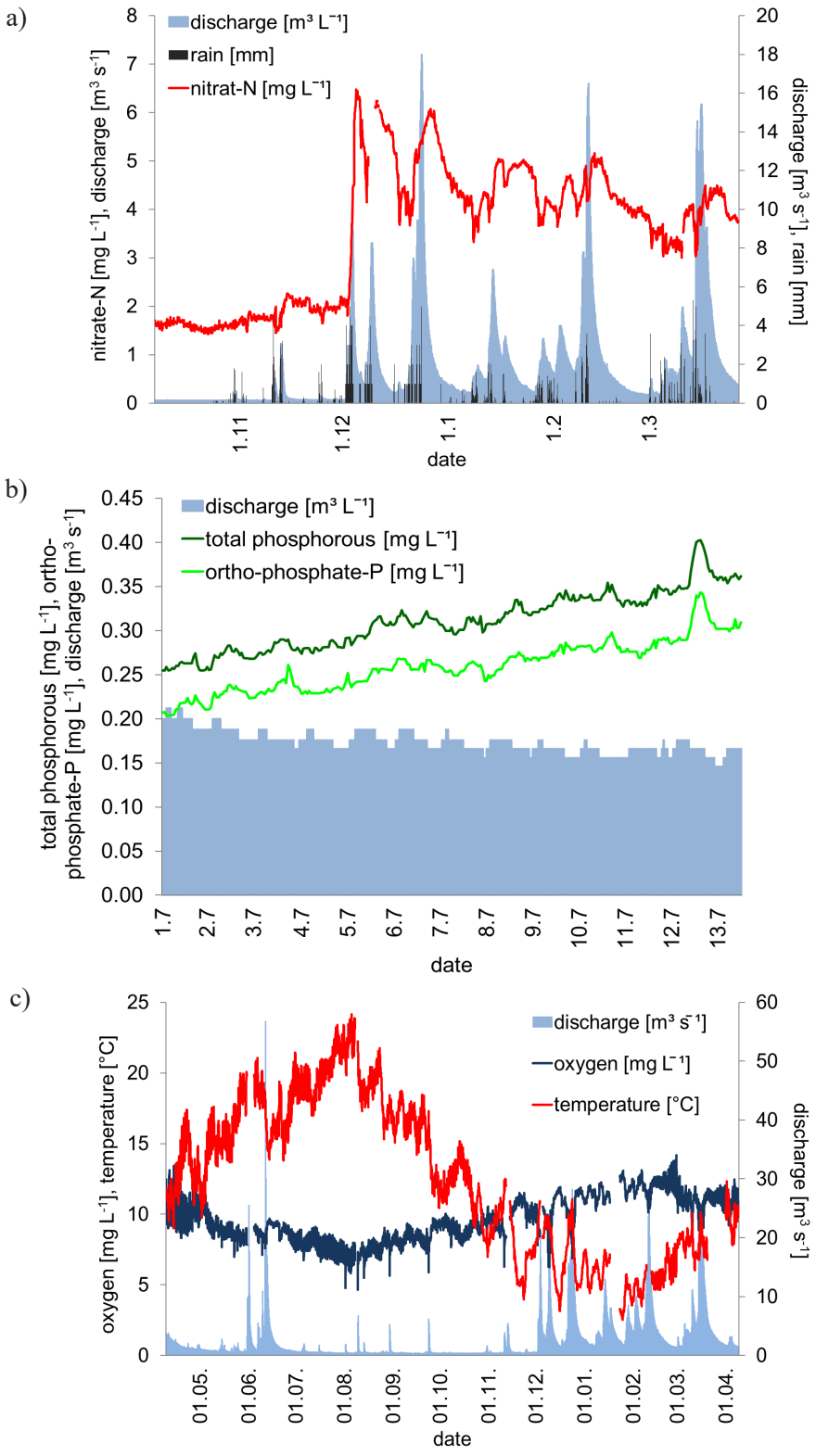


Fig. 26: Examples for seasonal changes in small rivers: a) difference of nitrate concentrations during summer (nitrogen consumption) and wintertime (washout of nitrate) (mean hourly values from 07.10.2018 to 26.03.2019, Ill in *Eppelborn*; in 2018, the "summer season" with dry and hot weather lasted until the end of November); b) rise of ortho-phosphate-P and total phosphorous by inputs from a STP during a dry weather period (mean hourly values from 1. to 13.07.2018, Ill in *Eppelborn*,); c) annual fluctuations of temperature, oxygen and discharge with rising trends for temperature in spring and summer and for oxygen in autumn and winter (mean hourly values from 13.04.2018 to 07.04.2019, Theel in *Knorscheid*) (all: (Meyer et al., 2019a).

Diurnal fluctuations

Due to lower water flow and the resulting direct connection to the atmosphere, changes in air and varying levels of solar radiation temperature throughout the day have a direct impact on the river. In small rivers, sunlight can often penetrate to the river bottom triggering photosynthesis if there is a sufficient number of green plants and algae in the water. This results in additional oxygen being produced during the day (primary production) and additional carbon dioxide being released at night (respiration). This can be seen from the fact that the temperature and oxygen contents run parallel to each other throughout the day and not, as in the case of a purely physical effect of solubility, in opposite directions (Fig. 27a). In small bodies of water, depending on the degree of eutrophication, this can lead to high oversaturation of the water with oxygen during the day and pronounced undersaturation at night (Fig. 27b). Carbon dioxide influences the pH value, especially in poorly buffered water: it lowers the pH value by forming carbonic acid dissolved in water, which releases H^+ ions. Conversely, the removal of carbon dioxide leads to an increase in the pH value. Since this also occurs during photosynthesis, as with oxygen, there is often a diurnal cycle in the pH value with an increase during the day when green plants and algae remove carbon dioxide from the system, and a decrease overnight when carbon dioxide is released (Meyer et al., 2019a).

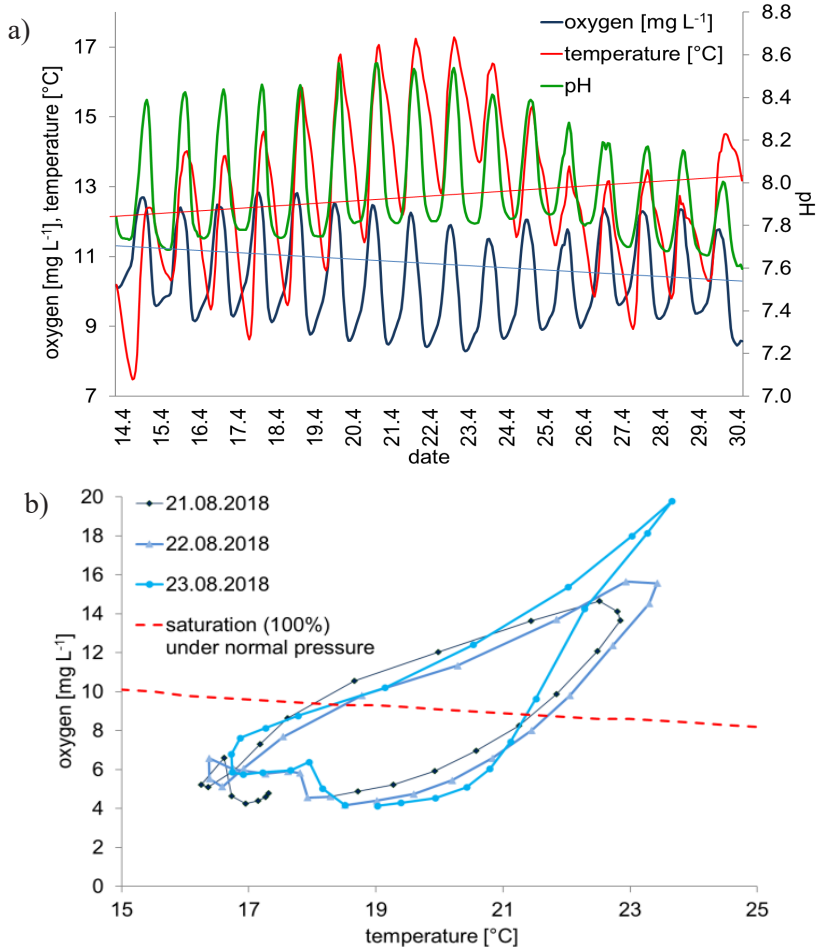


Fig. 27: Examples for diurnal fluctuations: a) temperature, oxygen and pH showing almost parallel diurnal cycles and overall trends (blue line for decreasing oxygen trend, red line for increasing temperature trend) (mean hourly values from 14.04. to 30.04.2018); b) oxygen vs. temperature at three days in summer with oversaturation at day and undersaturation at night (mean hourly values from 21.08. to 23.08.2018); (both Alsbach in *Marpingen*) (Meyer et al., 2019a).

Event-driven pollution

Spontaneous event-driven pollution also has a very strong impact on small water bodies due to their low water volume. Such events can occur due to diffuse leaching (e.g. fertilisers from agricultural land) (Fig. 28a), and run-off from point sources (e.g. CSOs) (Fig. 28b), but also because of discharges as a result of accidents or even unauthorised disposals. They usually cause an acute deterioration in water quality and acute stress on the aquatic ecosystem and are often accompanied by very high hydraulic stress for plants and animals (Benisch et al., 2024; Meyer et al., 2021a, 2019b).

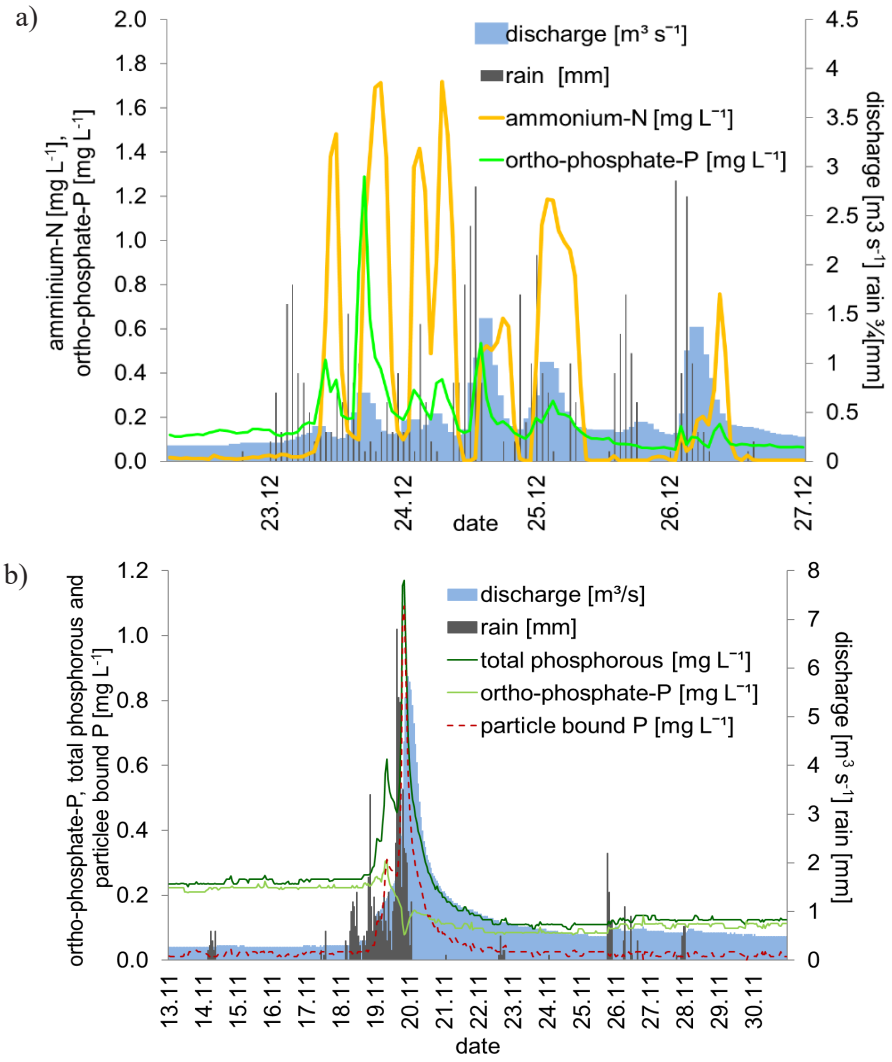


Fig. 28: Examples for event driven pollution: a) impacts from a CSO: discharges of (diluted) domestic wastewater leading to concentrations peaks of ammonium (mean hourly values from 22. to 27.12.2020, Erbach in *Homburg*) (Meyer et al., 2021b); b) impacts from arable land: erosion events leading to concentration peaks of particle bound phosphorous (mean hourly values from 13. to 30.11.2024, Mandelbach in *Habkirchen*) (Meyer et al., 2024).

Continuous pollution

Continuous inputs of contaminants, such as STPs effluents, or discharges from mine dumps also have a significantly greater impact on small and medium-sized rivers than on larger ones due to the reduced dilution potential (Fig. 29). In contrast to event-driven pollution, continuous contamination has a chronic effect on the aquatic ecosystem. Due to the prolonged stress, individual organisms or even the species composition can change (EPA, 2004; Kumar et al., 2022).

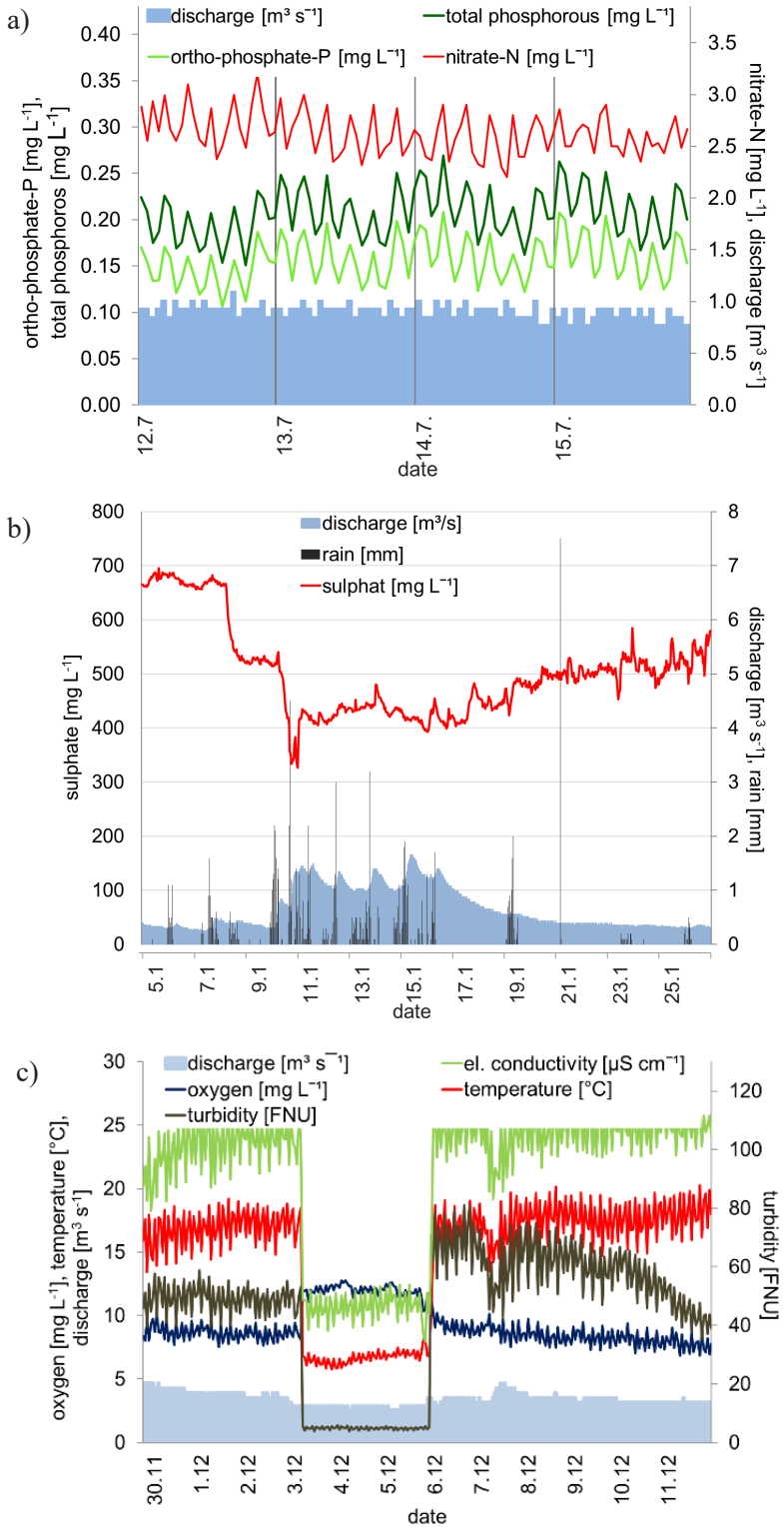


Fig. 29: Examples for continuous pollution: a) Diurnal cycles caused by discharges from a STP: six daily peaks due to the three sequence batch reactors of the STP (mean hourly values from 12. to 15.07.2013, Losheimer Bach in *Losheim*) (Meyer et al., 2013b); b) impacts of sulphate from a mine dump (mean hourly values from 01. to 31.01.2023, Trenkelbach in *Quierschied*) (Oberhausen et al., 2023); c) discharges of mine drainage water leading to high EC, temperature and turbidity as well as to oxygen deficits (mean hourly values from 30.11. to 1.12.2013, Fischbach in *Quierschied*) (Meyer et al., 2014).

Due to these special characteristics of small and medium-sized rivers, real-time monitoring is essential for assessing the chemical status of these water bodies. Spatiotemporal resolution of grab sampling, e.g. according to Annex V of the WFD, generally fail to capture the dynamic pollution characteristic of small and medium-sized rivers (Benisch et al., 2024; Brack et al., 2017; Meyer et al., 2025, 2021a, 2019b).

When grab samples are taken in periods with intensive diurnal fluctuations, the measurement results highly depend on the time of day and therefore provide little information about the overall condition of the water body (Benisch et al., 2024).

Especially in situations caused by extreme rainfall, the results of grab sampling very often do not represent the chemical status of a river. While some substances (e.g. geogenic salts or substances continuously introduced from STPs such as phosphate) are diluted by rainwater, the concentrations of other substances increase directly with the runoff (particle-bound substances such as TOC or total phosphorus). Easily soluble substances (e.g. nitrate from fertilisers) that are transported via interflow only reach the water body with a certain time lag to the runoff wave. Data obtained from grab samples during such situations are therefore not very representative and their interpretation remains difficult (Meyer et al., 2021a, 2019b).

As spontaneous event-driven pollution occurs unpredictably, it is almost impossible to detect it by grab sampling. On the other hand, if such an event is detected by chance, it is very difficult to interpret. In some circumstances, it may be assumed that the measurement or sampling is faulty because the measured values differ greatly from those of other measurement campaigns, and the results are discarded.

Continuous discharges (e.g. from STPs) also exhibit fluctuations in composition, concentrations and discharged water volumes, which inevitably lead to fluctuating levels of the discharged substances on the receiving side, i.e. in the water body and thus cannot be by grab sampling adequately. However, in small water bodies, these background levels are greatly overshadowed by weather-induced changes or event-driven inputs and may no longer be clearly described based on grab sampling. Depending on the quantity of substances discharged, this background pollution is much more evident in terms of concentration in a small river than a comparable quantity in a large water body.

Grab sampling of small and medium-sized rivers inevitable leads to:

- misclassification of the (chemical) status: For some parameters, the absolute values (maxima, e.g., for temperature, or minima, e.g., for oxygen) are decisive for classifying and evaluating the status. These values will not be recorded by grab sampling (Babitsch and Sundermann, 2020).

- high statistical uncertainty: Grab sampling introduces significant statistical variability and systematic bias due to the flow-dependent concentration changes or also due to artifacts from sampling handling (Babitsch and Sundermann, 2020).

- misjudgement of the portion of different impacts on the total chemical status (Meyer et al., 2021a, 2019b)

- misjudgement of the pollution sources and misunderstanding of the significance of the different transport pathways (Meyer et al., 2021a, 2019b)

- diagnostic uncertainties: Especially during event-driven contamination events can rarely be captured by monthly grab sampling, e.g. Cassidy and Jordan (2011) stated an average underestimation of load of total phosphorous of up to 60% by grab sampling compared to real-time monitoring data from different events in three small rivers.

- misjudgement of long-term trends due to insufficient data (Babitsch and Sundermann, 2020)

- ecological misclassification: The above-mentioned misjudgements inevitably lead also to misclassification of the ecological status. E.g. Benisch et al. (2024) reported, that grab sampling misclassified dissolved oxygen status in 40% of small rivers by failing to capture nocturnal minima.

Small and medium-sized rivers in particular demand monitoring strategies that reflect their rapid response to anthropogenic pressures and other external influences. Whenever and wherever it is possible, episodic "snapshots" must be replaced with continuous water quality trajectories that capture diurnal, event-driven, and seasonal dynamics. This provides a sophisticated data base for the accurate assessment of the chemical and thus ecological status of a water body and the relevant trends (Fig. 30).

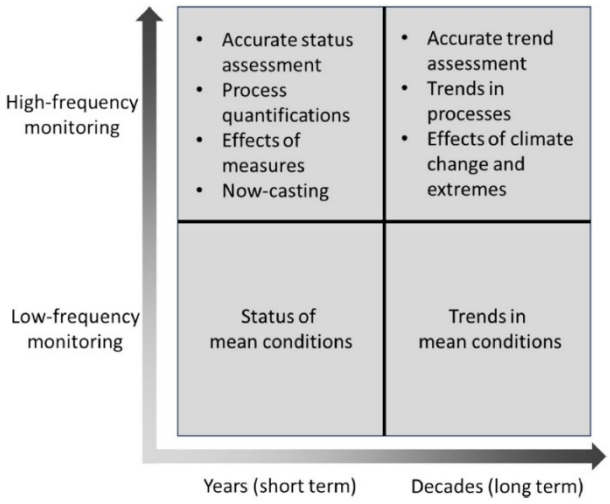


Fig. 30: Overview of the added values of utilising high-frequency sensors compared to traditional low frequency grab sampling for short- and long-term applications (Rozemeijer et al., 2025).

1.5.3 Measures to Improve Rivers Quality and their Overall Significance in Small and Medium-Sized Catchments

Sophisticated monitoring and appropriate interpretation of the measured values can also help to estimate the origin and transport routes of pollutants in a body of water more accurately. This is essential for planning targeted but also cost-effective measures to improve the chemical and ecological status of water bodies (Meyer et al., 2021a, 2019b).

Similar to emission and immission-related monitoring (see chapter 1.4), measures to improve water bodies can also be considered from the immission and emission side. The aim of the emission-based approach is to prevent pollution and to control the pollutant sources of critical substances entering the environment and thus the water bodies. In addition to infrastructural arrangements (urban) drainage systems, STPs, etc.) this can be achieved, for example, by banning sales, changing consumer behaviour or by reducing or eliminating the use of fertilizers and chemical herbicides/pesticides. Additionally, the retention or degradation of pollutants nutrients and toxic compounds into river systems can be improved, e.g. by improved wastewater treatment in an industrial STP or retrofitting a municipal STP with the so-called quaternary treatment to optimise the retention of microplastics and the degradation of pharmaceuticals and other organic pollutants (EC, 2024).

Emissions-based approaches can take place from a global down to a local scale and tend to improve the chemical, and thus the ecological status of the rivers. However, improvements also affecting the morphology of rivers can also be achieved on the immission side, i.e. through measures taken in the water bodies themselves and their riparian zones. Most of these measures fall under the umbrella term of restoration (or rehabilitation). These multi-discipline method of river restoration encompasses

ecological, physical, spatial, and management measures aimed at restoring the natural state and functioning of river systems. These efforts support multiple benefits including biodiversity conservation, enhanced recreational opportunities, improved flood management, and sustainable landscape development (Corday, 2024). Feio et al. (2021) state that "the largest percentage of rehabilitation works (worldwide) have aimed to recover water quality, facilitate fish migration, or restore flows or riparian vegetation. In fewer cases, rehabilitation has targeted channel naturalization or wetland ecosystem functioning and flooding cycles. Thus, the overall aim is to maintain or re-establish the rivers' ES (see chapter 1.5.1).

Basically, two different method groups of restoration activities can be distinguished: the processed based restoration (PBR) and the form-based restoration (FBR). While form-based methods (e.g., in-stream structures) often provide immediate structural and habitat changes (e.g., stable channel form, habitat features), the focus of process-based methods is to re-establish natural processes (e.g., sediment transport, floodplain connectivity nutrient cycling) is a long-term resilience by reinstating natural processes (Corday, 2024). Measures for PBR include e.g. sediment transport restoration for re-establishing natural sediment dynamics and improving channel morphology, flow regime management for maintaining channel processes and supporting aquatic life and barrier removal (dams, weirs) for re-connecting river subsets and enabling fish migration (ECRR, 2025). FBR Methods are e.g. channel reconfiguration by installing wooden or rock structures installed at the bank toe to create varied flow conditions and habitat diversity, or by building shaped structures (boulders/logs) to reduce bank erosion and improve aquatic habitat, bank stabilization to prevent erosion, floodplain modifications, riparian vegetation restoration (native species along banks), etc. (ECRR, 2025; Feio et al., 2021).

These measures shall lead to an overall improvement in the aquatic ecosystem. The combination of morphological-physical and biological improvements can also support the retention and improved degradation of pollutants in the water, as the self-cleaning capacity of the water is increased.

Many of these measures are very space-intensive, which means that they are more likely to be implemented in small and medium-sized rivers and upper cat catchments, as these areas tend to have a lower population density. Improving these water bodies, with all the associated benefits, also brings relief and improvements to the lower reaches of rivers and larger watercourses. Ultimately, this also has a positive effect on the seas into which the affected rivers flow. This is particularly true if it is possible to reduce pollutant loads from the respective catchment areas, i.e. if the measures contribute to improving the chemical status of the water bodies (Carvalho et al., 2019).

1.5.4 Situation in Saarland

Saarland is the smallest Federal State in Germany (apart from the city-states) located in the southwest. The Saarland's landscape is classified as low mountain range. In low-mountain regions the topographical conditions and the associated relief energy lead to the formation of many small rivers with steeper slopes and thus, high flow velocities and turbulence. These steep gradients also cause high sediment transport capacity. The rivers show a strong variability between peak and base flows (flash floods during storms and reduced dry-season flow). They are vulnerable to weather and climate changes as well as to human impacts and to land use changes (e.g., deforestation, urbanization). These water bodies play a critical role in downstream water (Meyer et al., 2019b).

The rivers relevant for management in Saarland have a total length of approx. 1030 km and cover 1 % of the total surface (MUKMAV, 2021). All rivers except three (Saar, Blies and Nied) belong to the category of small and medium-sized water bodies. According to LAWA (2021) these rivers are categorised as river types 5, 5.1, 6, 7, 9, 9.1 (silicate or carbonate, coarse or fine material-rich) and 19 (small lowland watercourses in river and stream valleys).

All these rivers suffer from various pressures such as:

- discharges of domestic wastewater: Saarland has the second highest population density in Germany (excluding the city-states) (386 habitants per km²) and 136 municipal STPs (EVS, 2025).
- discharges from CSOs: In Saarland, sealed surfaces account for more than 20% of the total area Saarland thus has one of the highest proportions of settlement and transport areas among the German federal states (Hoffmann, 2021). Further to this, in Saarland, approx. 2900 CSOs endanger water quality
- discharge of industrial wastewater and cooling water
- agricultural runoff from arable land, which covers 40 % of the total surface
- mine drainage water (in total 19 Mio. m³ per year) (RAG, 2014)
- extraction for irrigation and cooling water.

The above figures exclude illegal discharges or those resulting from accidents. Additionally, rivers in the western part of Saarland are strongly influenced by similar stressors from the French part of their catchments. Thus, for management purposes, international co-operation is required.

In almost all the rivers in Saarland, several of these stressors affect water quality and the aquatic ecosystem (MUKMAV, 2021). As the water bodies are small and medium-sized rivers with little dilution capacity, they are severely affected by those various pressures. For these reasons, monitoring using real-time measurement technologies is highly worthwhile. Based on the specific input patterns of the data obtained by this measurement technologies, valid conclusions can be drawn about the origin of the pollution, their respective relative proportion of the total pollution and the transport routes.

In the following section selected results from small and medium-sized rivers in the Saarland region are presented that have been published in three peer-reviewed publications.

2. Results and Discussion

2.1 Real-Time Monitoring of Water Quality to Identify Pollution Pathways in Small and Middle Scale Rivers

Extended Abstract

Increasingly stringent quality standards for surface waters pose new challenges for water policy and river basin management, particularly in the catchments of small and medium-sized rivers. These are characterised by pronounced temporal and spatial variability driven by hydrological dynamics, seasonal patterns, and diverse anthropogenic pressures. In such environments, precise identification of pollution sources and transport pathways is essential for the effective planning, implementation, and evaluation of mitigation measures. Conventional grab sampling strategies frequently fail to capture the highly dynamic and non-linear behaviour of water quality parameters of these rivers, resulting in significant information gaps. High-resolution real-time monitoring has therefore been repeatedly called for as a more appropriate approach to characterise riverine processes and pollution impacts.

This study presents a comprehensive real-time monitoring approach based on mobile measuring stations that integrate commercially available in situ sensors and wet chemical analysers. The system enables automated, high-frequency measurements (5 – 10 minutes intervals) of a wide range of physicochemical parameters, including oxygen, temperature, pH, EC, turbidity, nitrate, ammonium, total phosphorous, ortho-phosphate, and TOC. By combining continuous concentration data with discharge data, the approach allows for detailed analysis of both concentrations and loads, facilitating the identification of point and diffuse pollution sources as well as their dominant transport pathways.

The mobile stations have been deployed at 35 monitoring sites across 25 heterogeneous small and medium-sized rivers in Saarland, Germany – a region characterised by high population density, intensive agriculture, and industrial activity. The catchments is subject of substantial environmental pressure from discharges from STPs, CSOs, industrial plants, urban runoff and diffuse agricultural inputs. Despite the diversity of catchment characteristics, real-time monitoring consistently provided fundamental insights into the processes that influence chemical and ecological river status.

The results demonstrate that diffuse pollution, particularly from agricultural areas, can be reliably identified through characteristic parameter responses during rainfall events. Surface runoff events are marked by sharp increases in turbidity and total phosphorus concentrations, with particle-bound phosphorus constituting the dominant fraction, while ortho-phosphate often remains constant or becomes diluted. In contrast, nitrate transport via interflow produces delayed concentration maxima relative to discharge peaks, reflecting subsurface lateral transport processes. Such time-lagged responses would be difficult or impossible to detect using conventional sampling programmes.

Point source pollution was also clearly identifiable through real-time data. During dry weather conditions, diurnal concentration patterns of total phosphorous, ortho-phosphate, and ammonium revealed continuous inputs from STPs, including distinct signatures related to sequencing batch reactor (SBR) operation. Load calculations during low-flow periods further allowed quantification of constant baseline emissions attributable to technical installations. In addition, short-term and episodic pollution events from CSOs were detected with high confidence, including sudden increases in ammonium and TOC followed by delayed but prolonged oxygen depletion. The data further revealed CSO malfunctions during dry weather periods, which caused severe and persistent pollution in small rivers—events that would likely have gone unnoticed without continuous monitoring.

Beyond individual parameters, the combined interpretation of multiple parameters and their correlations proved essential for understanding pollution pathways. Strong correlations between total phosphorus and ortho-phosphate during dry weather conditions indicated dominance of dissolved phosphorus from point sources, whereas weak correlations during storm events reflected the influence of particle-bound phosphorus transported by erosion. Similarly, significant correlations between total phosphorus and TOC during rainfall events demonstrated shared transport via surface runoff. These multi-parameter analyses enabled the development of site- and catchment-specific “fingerprints” describing dominant pollution sources, pathways, and processes.

Load-based analyses provided additional critical insights. High-frequency data allowed accurate estimation of nutrient loads, revealing that a substantial proportion of annual pollutant transport occurs during a limited number of high-flow events. Comparisons between upstream and downstream stations further enabled attribution of loads to specific sub-catchments, thereby supporting targeted management measures. Such findings underline the limitations of surrogate parameters and trigger-based monitoring strategies, which risk missing both critical events and chronic low-flow impacts.

Overall, the study demonstrates that real-time monitoring using combined sensor and wet chemical analyser systems provides an exceptionally detailed and reliable representation of river water quality dynamics. While the approach entails high investment, operational, and maintenance costs and requires skilled personnel, its benefits for integrated catchment management are substantial. The generated data support regulatory authorities, water managers, and stakeholders in identifying pollution sources, evaluating compliance with environmental objectives, and designing effective mitigation strategies. Moreover, the findings contribute to the ongoing discussion on revising assessment frameworks under the EU Water Framework Directive, which currently rely largely on annual median values and may inadequately reflect ecological risks in dynamic river systems.

In conclusion, although the application of such complex monitoring systems is necessarily limited to selected investigations, real-time high-resolution monitoring represents a powerful and indispensable tool for advancing water quality assessment and management in small and medium-sized catchments.

These results have been published in Science of the Total Environment.

Angelika M. Meyer, Christina Klein, Elisabeth Fünfrocken, Ralf Kautenburger, Horst P. Beck (2019)

Sci. Total Environ., 651 (2019) 2323–2333.

https://doi.org/10.1016/j.scitotenv.2018.10.069

Table 4: Author contribution roles for the publication "Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers" in form of the CRediT standard.

Contributor roles	**Author(s)**
Conceptualisation	Angelika Meyer, Christina Klein, Ralf Kautenburger, Horst P. Beck
Methodology	Angelika Meyer, Christina Klein
Formal analysis	Angelika Meyer, Christina Klein
Writing – original draft	Angelika Meyer
Writing – review and editing	Ralf Kautenburger, Horst P. Beck
Visualisation	Elisabeth Fünfrocken
Data curation	Elisabeth Fünfrocken

Science of the Total Environment 651 (2019) 2323–2333

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Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers☆

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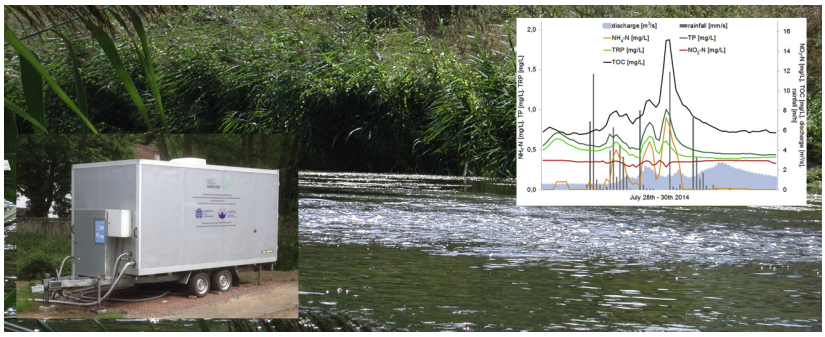
HIGHLIGHTS

- Real-time monitoring provides a perfect representation of the catchment processes.
- Impacts from point sources and from diffuse sources can be distinguished.
- Pollutions sources and transport pathways can be identified.
- Not only during rainfalls but also during dry periods crucial insights can be gained.

GRAPHICAL ABSTRACT



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ABSTRACT

The quality standards for surface waters increase steadily bearing new challenges for water policy. Precise knowledge of the sources and transport pathway of various impacts in a catchment area is of particular importance for any management activities. Online measurements with high temporal resolution are particularly suited for this purpose especially in small and middle scale catchments. In this paper we present an approach applying mobile measuring stations in which commercial available sensors and wet chemical analysers are combined in a new set to enable real-time monitoring of various parameters. The resulting data and the interpretation of their relationships allow the identification of diverse pollution situations in a river.
In this paper some examples of impacts from diffuse and point sources are given to illustrate the high information density obtained through the use of this system.

1. Introduction

Rivers in general are subject to high dynamics undergoing changes in time and space. Apart from natural diurnal and seasonal variations (Wade et al., 2012; Worrall et al., 2015) they are influenced by changing discharge regimes and very often by different kinds of pollution impacts. Mostly such pollutions are the more harmful to the ecological

☆ Part 1: On the meaning of real time data and their interpretation for surface water management.

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and chemical status the smaller the river is. Moreover, it must be kept in mind that the sum of the pollutants coming from small effluents accounts for most of the pollution in big streams.

In Europe, the status of small and middle scale rivers was put into focus as a consequence of the demands of the EU-Water Framework Directive (WFD) (European Commission, 2000). In order to assess different impacts on a river - and thus its status - it is very useful to evaluate different pollution sources and transport pathways in a combined approach (Behmel et al., 2016; Bieroza and Heathwaite, 2016; Leone et al., 2008; Outram et al., 2014). Pollutant sources and pathways must be identified precisely to enable a sophisticated planning and purposeful realisation of measures to improve the chemical and ecological status of surface water bodies. Due to the high dynamics of small rivers and the non-linear behaviour in time and space mentioned above grab sampling programmes very often fail to provide the necessary information density.

This paper emphasises the importance of real-time monitoring with an extended data set from online measurements for identification of pollution sources and pathways in small and middle scale rivers. Real-time monitoring by the help of automated measurements with high temporal resolution providing data with a frequency of a few minutes enables high resolution monitoring (HRM) which has often been called for (Blaen et al., 2016). Due to the high time resolution of such online measurements harmful impacts and their effects become apparent immediately and distinctively especially in smaller catchments and in rivers with particularly extreme hydrology. These measurements depict the real quality status of a river and enable to detect both short-term events as well as long-term changes. Moreover, they allow for distinction of different pollution pathways and sources.

Up to now, numerous kinds of real-time monitoring systems have been realised. Most of them were designed for special issues such as e.g. the estimation of nutrient fluxes (Jordan et al., 2007; Mellander et al., 2012; Shore et al., 2017), assessment of the ecological river status (Desmet et al., 2011; Bowes et al., 2016; Bowes et al., 2012) or detection of domestic wastewater impacts (Boënne et al., 2014; Even et al., 2007; Weyrauch et al., 2010). The majority of these studies is based on the use of in-situ sensors (Glasgow et al., 2004; Jiang et al., 2009; O'Flynn et al., 2010; Ungureanu et al., 2010). However, more elaborated devices like wet chemical analysers are rarely used due to high investment and maintenance costs. These kinds of analysers are e.g. applied to determine the fluxes of total phosphorus (TP) (Bieroza and Heathwaite, 2015; Bowes et al., 2003; Cassidy and Jordan, 2011; Lloyd et al., 2016; Ockenden et al., 2016; Outram et al., 2014) mostly in rural catchments. Nevertheless, ammonium (NH_4-N) and total organic carbon (TOC) also bear significant relevance to the chemical and the ecological status of the rivers as well as to the identification of transport pathways.

Thus, the scientific novelty of the presented approach consists of the measuring and the interpretation of an extended data set we focus not only on one kind of pollution but try to characterise and classify the whole spectrum of pollution sources.

In Saarland (Germany) mobile measuring stations equipped with both, sensors and wet chemical analysers have been operated since many years. In this context, specific parameter combinations in high time resolution turned out to be a very useful tool for the identification and the quantification of impacts in small and middle scale rivers.

The purpose of this paper is to present the potential of real-time monitoring for water quality assessment. In order to illustrate this approach in a first overview examples of impacts from point sources and from diffuse (or non-point) sources are presented and the correlation between concentrations and loads of different parameters are demonstrated. A second part to be published will deal with a thorough statistical multivariate analysis of the data sets acquired in such measuring campaigns.

2. Materials and methods

2.1. Study area-

Saarland is the smallest German Federal State (apart from the so called city-states) located at the French and Luxembourgian border in the West (see Fig.1). Because of its situation in a low mountain range area there are numerous small and middle scale rivers. Saarland has a very high population density (387 people per km^2), and the region is characterised by intensive agricultural and industrial activities which generally create a high environmental pressure. So a number of conflicting interests exist regarding the usage of surface waters concerning different aspects such as drinking water supply, wastewater impacts, agricultural irrigation, transport, fishery, recreation, tourism and many more.

During the last years numerous small and middle scale rivers were investigated by means of the presented system. Though all these rivers differ regarding catchment conditions and anthropogenic pressure real-time monitoring could always give fundamental insights into crucial processes affecting the chemical status as well as the ecological situation.

2.2. Conception and functioning of the mobile measuring system

When planning and performing a measuring station numerous aspects must be considered depending on monitoring objectives, financial resources and availability of skilled personnel (Jornet-Martínez et al., 2017). So designing and choosing the appropriate equipment always requires an intensive planning phase. In our case technical innovation was not the issue. On the contrary we especially searched for commercial and well-established, robust and reliable measuring devices whose reliability has long been proven by their operation in the surveillance of technical plants and which have been designed for a long service life in accurate continuous operation.

As mentioned above, wet chemical analysers for TP/TRP detection and electrochemical sensors for water temperature, dissolved oxygen (O_2), pH value and conductivity as well as optical UV-spectroscopy for the detection of nitrate (NO_3-N) and/or dissolved organic carbon (DOC) were also utilised in numerous studies. However, other nutrients like NH_4-N or TOC were rarely measured online in the context of river monitoring. There still exist different methods for online measurements of these parameters. NH_4-N (as well as nitrate and TRP for instance) can also be determined using Ion-Sensitive Electrodes (ISE). But these electrodes are sensitive to temperature changes and subject to ion interferences and drifting, so they lack practicality for this special purpose (Boënne et al., 2014; de Marco et al., 2007; Khalid et al., 2016; Wade et al., 2012). Measurements of TOC, however, are often replaced by optical methods (e.g. SAC (Spectral Absorption Coefficient) at 254 nm wavelength). These techniques also turned out to be less suitable for river monitoring because of the interferences of the optical sensors caused by high turbidity rates. TOC is mostly bound to particles and thus concentrations rise especially during storm events with high turbidity, so these concentration maxima can hardly be detected unbiased. To counteract these negative aspects, we implemented wet chemical analysers for the determination of NH_4-N and TOC in the stations. These analysers were proven to be very robust and reliable but, of course, they are very intensive in cost and maintenance.

Our mobile measuring stations were developed as mobile trailers (length: 6.1 m, width: 2.1 m, height: 2.8 m). These trailers can be installed on-site nearby the river. A pump submerged into the river transports the water via a tube into a sample basin (with a capacity of app. 200 L) within the station from where the overflow is drained back into the river by an outlet on the opposite side (see Fig. 2). To avoid algae growth and a warming of the water in summertime the tube from the pump to the station is of bright but non-transparent material and it is kept as short as possible. The integrity of the sample

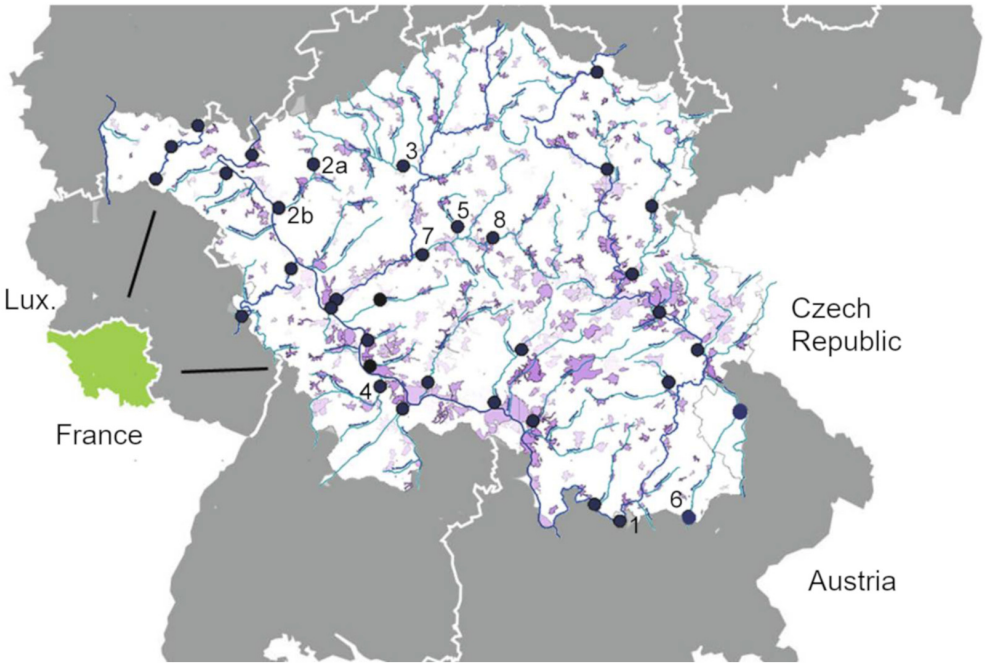

Fig. 1. study area: situation of Saarland in Germany and measuring sites (the numbers refer to the sites described in chapter 3).

transported is proven (see chapter 2.3). Measuring devices for O_2, temperature, pH value, conductivity, turbidity and nitrate (NO_3-N) - in fact total oxidised nitrogen (NO_{2+3}-N, which includes NO_3—N and nitrite (NO_2—N, which is mostly negligible) - are immerged into this basin. In addition, three wet chemical analysers (self-calibrating online-photometers) are installed in the station to measure the concentrations of NH_4-N, TOC and phosphorus measured as both TP (unfiltered and acidic hydrolysed) and total reactive phosphorous (TRP, unfiltered and un-hydrolysed). For the determination of NH_4-N, the water is drawn through a filter (0.45 µm PFT membrane). Before the measurement of TOC and TP/TRP the sample passes an ultrasonic homogenisation unit. The waste produced by the wet chemical analysers is stored in plastic canisters and disposed in accordance with the actual guidelines at the university's laboratory.

The system enables the automated analysis of the actual water quality with a frequency of one measurement each 5 to 10 min. The collected data are stored in a data logger from where they are transferred in a chosen time sequence to a central computer via GSM and stored in a database.

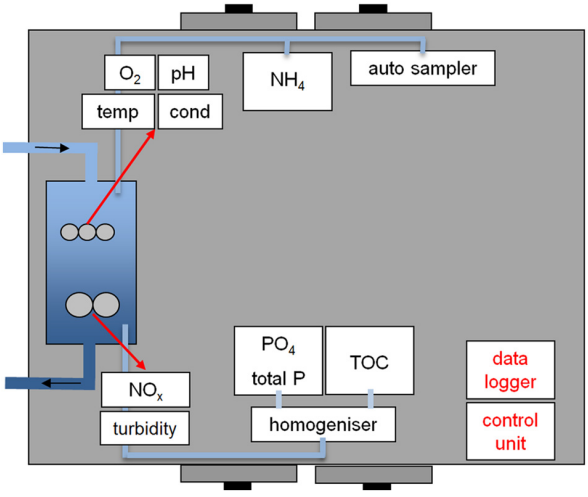

Fig. 2. Scheme of a measuring station with sensors in the sample basin (left side) and wet chemical analysers for NH_4-N, TOC, TRP and TP.

All analysers and sensors are from Hach GmbH (Berlin, Germany), the data logging and transferring system is from Ott Hydromet GmbH (Kempten, Germany). Fig. 2 shows a scheme of a measuring station, Table 1 gives an overview of the measuring ranges and methods used.

The stations are air-conditioned to counteract unwanted temperature effects on the measurements (Bieroza and Heathwaite, 2016). Up to now we have run three large stations and two smaller ones (without wet chemical analysers), one of them with a solar power supply (Khalid et al., 2016). The stations are very flexible considering territorial as well as methodological aspects and can easily be adapted to different requirements and applied to various investigation issues. The rivers which are to be monitored as well as the measuring sites and time periods are decided on in intensive discussion with the Ministry of Environment and Consumer Protection of Saarland State and the agencies in charge. Any site chosen has to be accessible by car. For operation of the station a power supply (1 × 400 V or 2 × 220 V) is required. Depending on investigation issues and significance of the water body one measuring period will last between 6 months and 1.5 years (see Conclusions).

2.3. Maintenance and quality assurance

Quality assurance (QA) is essential for any kind of analytical analysis. In the case of online measurements it is of crucial importance that all devices run reliably without a high calibration frequency or are self-calibrating because fouling processes, instrumental drifts and changing environmental conditions endanger the quality of the data collected (Jornet-Martínez et al., 2017).

For this purpose we have chosen wet chemical analysers providing an auto-cleaning facility and self-calibrating function. Once a day all tubes in the analysers are cleaned automatically with an appropriate cleaning solution. After that a two point calibration is carried out using certified standards from Hach GmbH. As soon as these results exceed the defined acceptable limits, the analyser turns into an error status. This information then appears in the transferred data.

Table 1
Parameters, measuring ranges and methods applied in the stations and references for the measuring methods.

Parameter	Meas. range	Method	Reference
Temperature	0–50 °C		
Oxygen dissolved (O_2)	0,05–20 mg/L	Optical (luminescence)	ISO 17289:2014
pH value	2–14	Electrochemical	ISO 10523:2008
Conductivity	0–4000 μS/cm	Conductometric	ISO 7888:1985
Turbidity	0–100 FNU	Nephelometric (two channel 90° scattered light)	ISO 7027-1:2016
Nitrate (NO_3-N/NO_{2+3}-N)	0.1–100 mg/L	UV absorption	
Ammonium (NH_4-N)	0.02–2 mg/L or 0.1–20 mg/L	Colorimetrical (indophenol blue method after filtration at 0.45 μm)	ISO 11732:2005
Total phosphorus (TP) and total reactive phosphorus (TRP)	0.02–5 mg/L	Colorimetrical (phosphomolybdenum blue complexation after ultrasonic pre-treatment and (only for TP) digestion with acid persulfate at 140 °C)	ISO 6878:2004
Total organic carbon (TOC)	0.1–100 mg/L	Combustion reaction: removing the inorganic carbon by acidifying, oxidation of organic carbon by high-temperature digestion to carbon dioxide (CO_2) and detection of CO_2 by infrared	ISO 1484:1997

The sensors for nitrate and turbidity are equipped with an automated wiper system to prevent soiling and biofouling of the measuring devices. When cleaned once a week the other sensors without wipers also turned out to be robust against drifts caused by biofilm growth.

Additionally, an adequate maintenance routine has to be established to guarantee the full function of the whole system. So once a week (in periods of extreme weather conditions also more often) the pump and all measuring devices are controlled, cleaned, maintained and calibrated, and the reagents in the analysers replaced if necessary. To ensure the quality of the monitoring data a sample from the river and one from the basin are measured using a portable multi meter for temperature, O_2, pH and conductivity and the results are compared to the data measured by the online devices. Furthermore, control samples are taken from the river and from the sample basin and analysed immediately for NO_3-N, NH_4-N, NO_2-N and TRP in the stations by use of so called cuvette tests with pre-dosed reagents in photometric evaluation. TOC and TP are to be analysed in the home lab, where additionally total N and TIC are determined as well. Malfunctions like drifts or offsets of the measuring devices can thereby be detected immediately and eliminated in time in most of the cases. During the last 5 years the maximum deviation between the online data and the control analysis were as follows (subsumed for all measuring devices in the different stations for each parameter): temperature: ±3%, O_2: ±9%, pH value: ±8%, conductivity: ±7%, turbidity: ±5%, NO_3–N: ±10%, NH_4-N: ±11%, TP: ±11%, TRP: ±10%, TOC: ±11%.

Every six months a full maintenance of the sensors and analysers is carried out by the service of the suppliers. Repeated checks of the transferred data also help to promptly identify malfunctions. Thereby regarding short time intervals serve to detect e.g. shutdown and calibration errors whereas longer time intervals are useful to discover instrumental drifts. The inspection of the development of different parameters in time will also help the skilled personnel to ensure the plausibility of the measured values with the help of typical correlations.

2.4. Evaluation and interpretation of the online data

All gathered data are controlled daily in order to recognise any kind of technical problem or system failures as soon as possible. When evaluating the data special focus is to be placed on eliminating all outliers and negative values caused by malfunctions or during maintenance phases. Apart from that possible drifts must be identified and the corresponding data must be rejected. Data missing due to such corrections are never replaced. The evaluated 5-min values are then aggregated to hourly mean values to both reduce the instrumental noise of the data and to be able to compare it to the hourly values of discharge, precipitation, air temperature etc. furnished by the Agency for Environmental Protection and Customers Safety of Saarland State. For further plausibility control the data is then examined again in view of the corresponding data of water quantity and climatic events.

However, it is a matter of considerable importance for the interpretation of the online data to gather all information available about the catchment. For this purpose we collect grab samples every two months at certain sites along the longitude of the river and from several important effluents. Apart from that, climatic data and river discharge data as well as knowledge of geological and hydrogeological characteristics of the catchment are imperative for data interpretation, especially for assessing natural phenomena and geological backgrounds. Furthermore, land use, domestic and industrial wastewater impacts, data of other monitoring programmes (e.g. by the state office or by local water companies) should be taken into consideration, too.

Thus regarding different parameter combinations and their relationship over various time periods and considering the mentioned additional data allows us to draw conclusions about the pollution's sources and intensity.

The following chapter is to highlight a few examples of the phenomena observed during the last years.

3. Results and discussion

3.1. Diffuse pollution

One of the most important demands of the WFD is the so called “combined approach for point and diffuse sources” set out in Article 10 (European Commission, 2000). According to this article all EU-Member States are requested to ensure the control of all discharges emitted in the rivers based on best available techniques. This claim can often not be realised by simple grab sampling.

According to the European Environment Agency (EEA, 2017) “agriculture is a key source of diffuse pollution” and its control can only be realised by help of continuous measurements on a high frequency. In agricultural catchments NO_3-N, TOC and P are the relevant parameters which can actually be detected online. The knowledge of quantity and pathways of the diffuse impacts of these three substances will also point to other potential contaminants like for pesticides (Cruzeiro et al., 2016).

3.1.1. Impacts via surface runoff

Diffuse pollution triggered by rainfalls on agricultural areas is very often dominated by erosion effects leading also to increasing turbidity values. Different substances such as P brought out in synthetic and natural fertilisers are bound to these turbidity causing particles which are transported via surface runoff. Depending on the soil characteristics the portion of P being dissolved or adsorbed on particles can differ.

Fig. 3 shows an example of several consecutive erosion events at the river Blies in Reinheim in the Saarland (№ 1 in Fig. 1) in spring season. One can see that with every increase of turbidity (filled grey line) the concentration of TP (dark green line) rises accordingly. Thus particle bound P (dotted red line) (which is calculated as the difference between dissolved TRP and TP) makes up most of the TP amount. The course of the TRP line (light-green) shows that the first flush contains much more particle bound P (TRP is even diluted), and it clearly indicates that this turbidity event is due to a run-off from soil where fertilisers

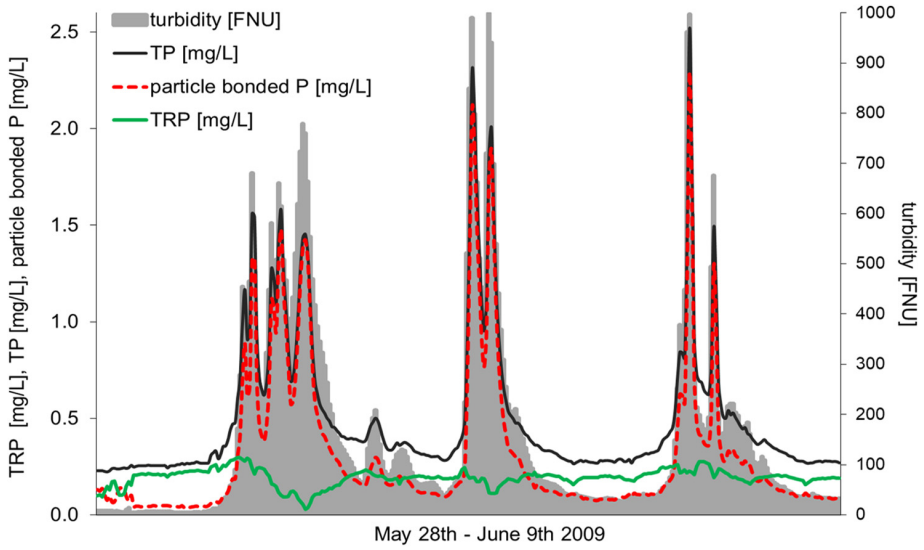

Fig. 3. Increase of turbidity and impacts of particle bonded P caused by surface runoff (erosion) in river Blies (Reinheim) (May 28th – June 9th 2009) (5-min-values).

has been brought out before May. It should be mentioned that the quality standard for TP is 0.1 mg/L in Germany for this type of surface water body.

In most cases such phenomena occur during the autumn season after harvesting. In numerous agricultural catchments we could define such TP-impacts during stormflow events as the most important source for P pressures. Shore et al. (2017) pointed out that even in rural catchment despite of the concentrations the TRP loads transported during stormflow events accounts for a major proportion of the annual TRP.

3.1.2. Diffuse pollution - impacts via interflow

In most agricultural catchments diffuse sources are the main impact sources for NO_3-N. When surplus NO_3-N from fertilisers applied on the fields is dissolved in rain water and the water then infiltrates the near stream unsaturated soil zone, dissolved NO_3-N can laterally transported through the soil before it again exfiltrates into the surface water. This transportation process (interflow) results in a time lag between the maximum of river discharge and the maximum of NO_3-N concentration. Fig. 4 illustrates an example of several interflow events in the agricultural catchment of the river Seffersbach in the Saarland. In this catchment two measuring stations were installed: one in the upstream area of the river (station 1 in Bachem) and the other one close to the mouth into the river Saar (station 2 in Merzig) (№ 2a and № 2b in Fig. 1). In both stations basic concentrations of NO_3-N were about 3.5 mg/L, and they were diluted during rainfalls. With decreasing river discharge the NO_3-N contents in the upstream area of the river (yellow line) immediately returned to the background level, whereas NO_3-N contents in the downstream area (red line) reached very high maximum values. There are obvious time lags between the river discharge maxima and the concentration maxima at station 2 caused by the interflow transport of NO_3-N in the area between the stations. We have found many similar events in other measuring campaigns, depending on the catchment properties. These events always occurred during fall or early winter also illustrating the process of bacterial oxidation of

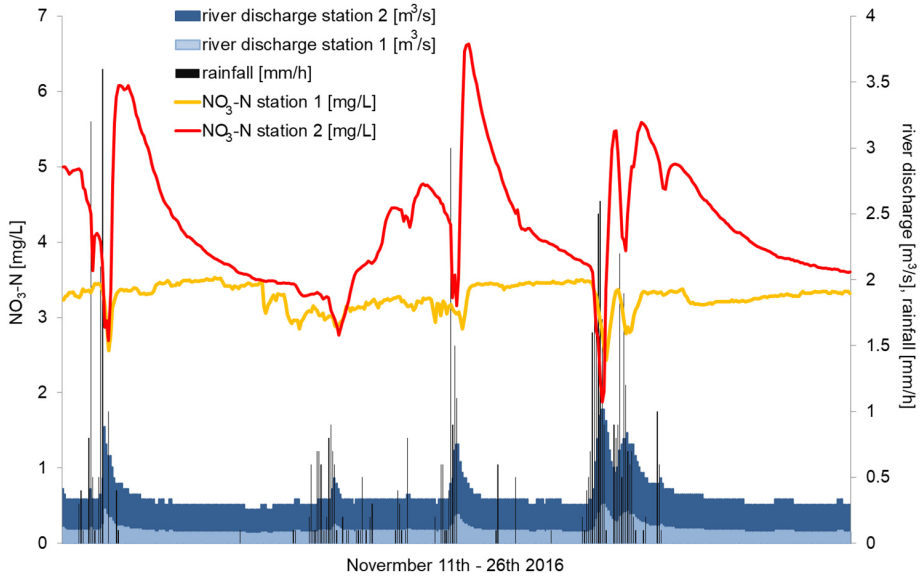

Fig. 4. Dilution of NO_3-N concentration, impacts of NO_3-N via interflow and river discharges in two measuring stations at river Seffersbach (Bachem – station 1, Merzig – station 2) (November 11th – 26th 2016) (hourly mean values).

nitrogen containing organic matter when it is exposed to air after harvesting or ploughing. Nitrogen transport via interflow is also described by many other authors (Ferrant et al., 2013; Rode et al., 2009).

3.2. Point source pollution

Continuous measurements also serve to identify point source pollution. Short time events can reliably be detected by them, but medium term observations can also help to identify different impacts and their pathways.

3.2.1. Point source pollution - impacts from wastewater treatment plants (WWTPs)

Impacts coming from technical plants such as waste water treatment plants (WWTPs) or industrial pollution can be observed during dry weather times. On one hand river discharges are small so dilution rates of pollution are reduced in these periods. On the other hand, these phenomena are then not covered by rainfall-driven impacts.

In Fig. 5 concentrations of TRP and TP are shown during a dry weather period with stagnating discharge into the river Losheimer Bach in Nunkirchen (№ 3 in Fig. 1). In this period the concentrations of both TRP (red line) and TP (grey line) change periodically within one day. Having a closer look at these concentration changes one can see 6 maxima and minima occurring each day at the same time. This is clearly not a matter of noise since the accuracy of the instrument is better by at least one dimension. So periodic changes obviously are caused by discharges from a technical plant which - in this case - is a WWTP working with 3 sequence batch reactors (SBR) each of them discharging twice a day. Additionally, the long term results of the groundwater samplings carried out by the authorities in this catchment area were considered. As the groundwater contents of TP and TRP were almost negligible it can be concluded that this basic P-contamination of app. 1.5 mg/L TRP and 0.2 mg/L TP is emitted by the treatment plant into this catchment.

3.2.2. Point source pollution - impacts from CSOs

One of the most pressing problems in many urban or settlement areas are incidents caused by combined sewer overflows (CSOs). During rainfalls these impacts can occur very suddenly when surface flows exceed the capacities of channels and treatment plants. Even though these events normally only last a few hours, they cause harmful pollution impacts and hydraulic stress. Since grab sampling is unsuitable to detect and especially to qualify such incidents, numerous strategies have been tested by using different aspects of continuous measurements (Boënne et al., 2014; Even et al., 2007; Khalid et al., 2016).

The effects of CSO's impacts are shown in Fig. 6 giving an example of two events in the river Bist in Wadgassen (№ 4 in Fig. 1). During the first incident NH_4-N concentrations (yellow line) increases up to 1.97 mg/L and TOC concentrations (black dotted line) to 14.6 mg/L. Since the decomposition of these organic substances flushed into the river requires a large amount of O_2 this leads to a 56 h lasting depression in dissolved O_2 (<7 mg/L) (blue line) in the river. The smaller events do not affect the O_2 content so much.

It must be kept in mind that any O_2 depressions caused by CSO impacts can often not be detected immediately after the event and close to the site of input. It has to be taken into account that the metabolic O_2 consuming processes takes some time, so the effects of the impacts will become evident only at a certain distance from the impact point. Hence, additional studies are planned to be able to describe the correlation of the impact's distance to the intensity of the O_2 depression in a small river.

Such online measurements can thereby help to detect impact duration, discharge frequency and loads of each CSO. Similar observations are also reported by Fu and Butler (2012) and Boënne et al. (2014).

Very often discharges from CSOs could be also detected during low water periods apart from impacts from CSOs caused by storm water events. These phenomena can be attributed to malfunctions of the CSOs when - mostly after a flash - throttles are blocked by flotsam or garbage. The channel thus cannot be closed and when a bypass from the channel to the river comes into being a part of the wastewater discharges into the river almost continuously. Above all such technical problems create devastating situations in a small river as shown in Fig. 7 where the online-measurements of NH_4-N, TP and TRP are plotted in such a critical situation lasting one month in summertime in the river Saubach in Lebach (№ 5 in Fig. 1). At the beginning the diurnal cycles with two peaks which are characteristic for wastewater (Wade et al., 2012) can be recognised in the NH_4-N (yellow line) and the TRP concentration curves (light green line). Then the nutrient's concentrations rise according to the declining water level so that the maxima of the NH_4-N concentrations exceed the detection range of the instrument (see also Table 1). On July 7th the damage was repaired and concentrations immediately returned to basic levels.

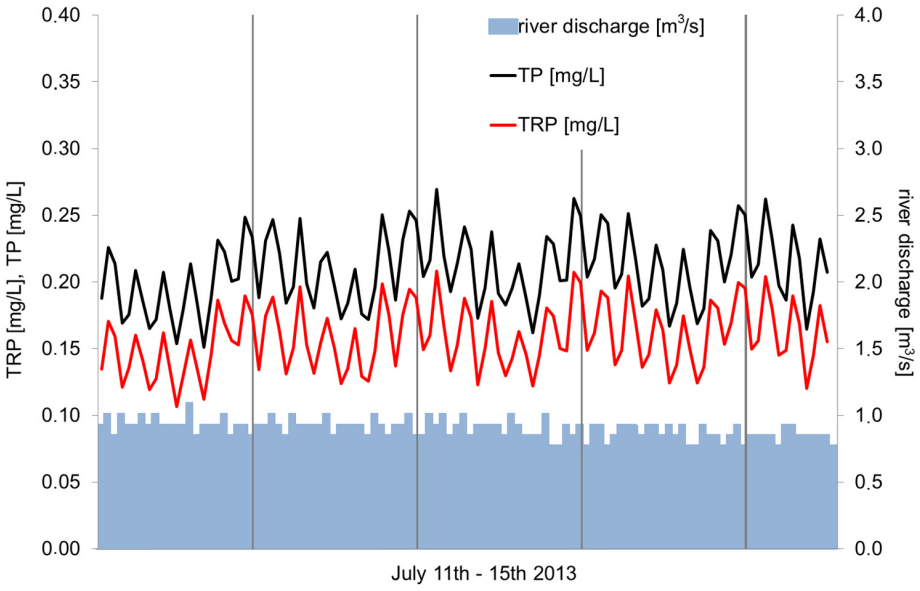

Fig. 5. Diurnal concentration changes of TP and TRP and river discharges during a dry weather period in river Losheimer Bach (Nunkirchen). (July 11th - 15th 2013) (hourly mean values).

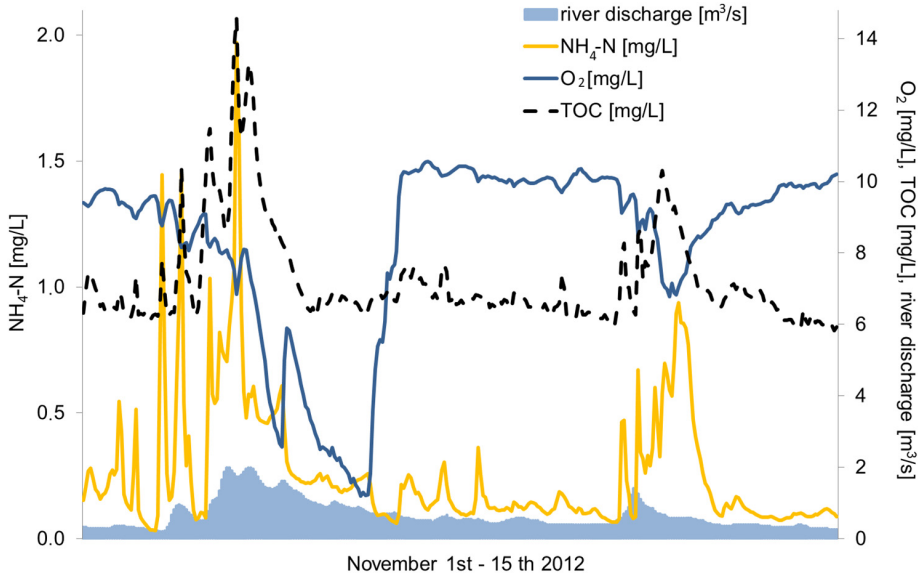

Fig. 6. Rising concentrations of NH_4-N and TOC and reduction of O_2 caused by impacts from a CSO in the river Bist (Wadgassen) (November 1st - 15th 2012) (hourly mean values).

This demonstrates clearly that it is of particular importance not to miss the dry weather periods if an assessment of all pollution factors at a measuring site is required. Any reduction of the measuring frequency, e.g. by applying a trigger parameter like precipitation or discharge, will inevitably lead to a serious loss of information (Blaen et al., 2016).

3.3. Parameter correlations

As shown above it is essential for the interpretation of continuous measurements to consider various combinations of different parameters at the same time in order to identify sources and pathways of pollution (Angulo et al., 2012). Such an approach should be applied for short term events as well as for mid-term or even long term periods. Especially a closer look at the correlation between different parameters can help to better understand the situation in the river.

To explain this approach two different time segments at one measuring site at river Bickenalb in Peppenkum (№ 6 in Fig. 1) are compared in the following. The first data set was recorded during a dry weather period (October 8th to November 8th 2017, see Fig. 8a) with very low water discharge rates. Considering the concentrations of TP and TRP three different aspects can be brought out. On one hand, there is almost virtually no difference between the two P fractions meaning that the P consists mainly in dissolved TRP (light green line) which is characteristic for pollution from domestic wastewater (see also Fig. 5 and Wade et al., 2012) and which becomes apparent especially during low flow situations (Ockenden et al., 2016). On the other hand, an increasing trend of rising concentrations can be observed while the water discharge is declining. This means that neither TP (dark green line) nor TRP is added by rain water input during this period. There is a continuous discharge all the time, and the concentration increase because the amount of water decreases to take up the load. Furthermore, after a small phase of decline every rain event causes a dilution of both TP

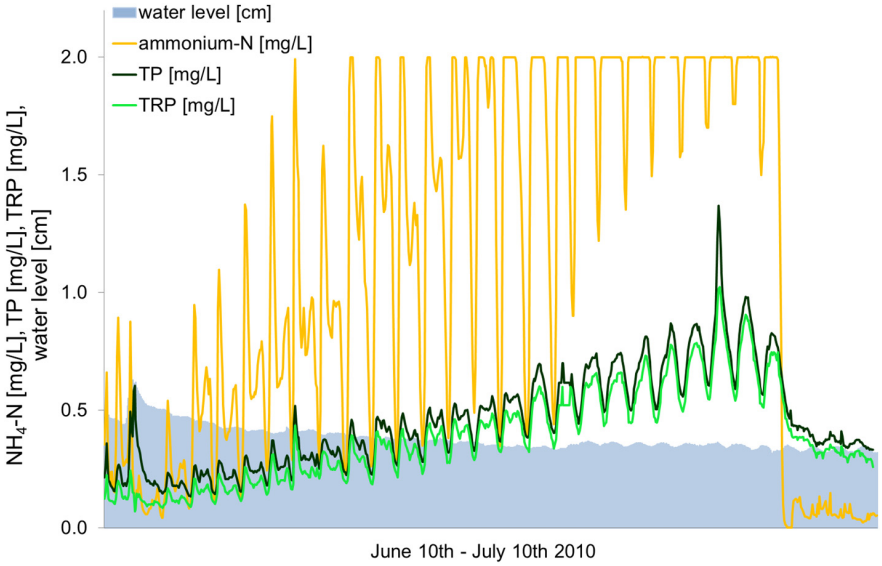

Fig. 7. Rising concentrations of NH_4-N, TP and TRP caused by a malfunction of a CSO in the river Saubach (Lebach) during a dry weather period (June 10th – July 10th 2010) (hourly mean values).

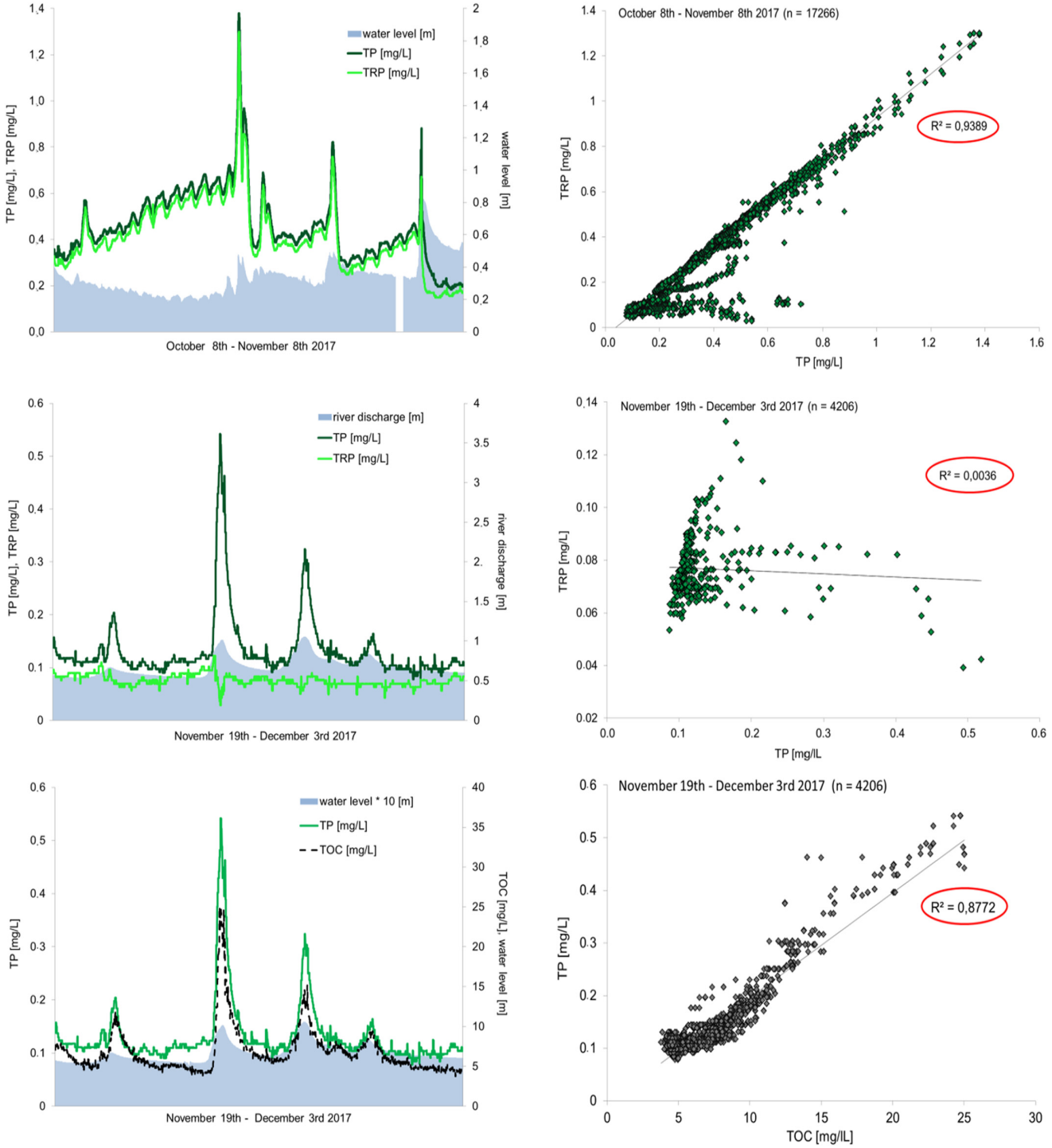

Fig. 8. Time courses and correlations between different parameters: a) time course of TP and TRP during dry weather times; b) correlation between TP and TRP during dry weather times; c) time course of TP and TRP during rainy weather; d) correlations of TP and TRP during rainy weather; e) time course of TP and TOC during rainy weather; f) correlation between TP and TOC during rainy weather; all registered at the river Bickenalb (Peppenkum) (October 8th - November 8th (8a and 8b) or November 19th – December 3rd 2017 (8c–8f)) (5-min-values).

and TRP, concentrations then return to basic level. These three phenomena give unambiguous proof for the pollution coming neither from groundwater (basic flow) nor from erosion (surface runoff) but surely from some technical plant, and this is authenticated by the diurnal cycle of the values.

The parallel progress of the TP and TRP concentration is reflected in a significant correlation (Pearson's correlation coefficient $R^2 = 0.9389$) between the two P fractions as shown in the scatter plots (see Fig. 8b) for which we used regression analysis by least squares. In contrast the concentration curves drift very much apart during rainy days a few weeks later (November 19th to December 3rd 2017, see Fig. 8c). At that time, water discharge was >5 times higher than before and impacts from the WWTP were strongly diluted, so the basic P-concentrations were very low. During this time period some impacts via surface runoff occurred leading to large concentration differences between TP and TRP and thus to a very weak

correlation factor ($R^2 = 0.0036$) (Fig. 8d). Similar observations could also be made by Lloyd et al. (2016).

On comparing the TP with the TOC concentrations (grey line) a very similar development of concentration can again be observed (see Fig. 8e). TOC can - among other pathways – get into a river by erosion of organic material (partly bound to particles and partly dissolved) via surface runoff. The significant correlation factor of 0.8772 between TP and TOC (see Fig. 8f) proves that these substances are transported via the same pathway.

Similar observations for TP and TRP could be made in different studies (Viviano et al., 2014) although without detection of the TOC contents. Bowes et al. (2003), Jordan et al. (2007) and other authors highlighted that in rural catchments the better part of the annual TP load is mainly transported by a few single events. Lloyd et al. (2016) call them “key transport events”.

3.4. Water discharge and loads

Supplementary information can also be collected from the loads of the nutrients and their short time changes. The loads of different substances, i.e. the total amount of transported matter, can be calculated from their concentrations and the total water discharges. They give very important clues to the sources and the pathways of pollution, and this is especially important for planning and implementation of purposeful measures to be carried out in the catchment to improve its ecological status. Many studies revealed the importance of real-time monitoring for the assessment of pollutant loads in small catchments.

It was pointed out by Cassidy and Jordan (2011) that - especially in small agricultural catchments - a false load estimation of TP can only be avoided by help of sub-hourly determination. In Fig. 9 the loads of NO_3-N of two different stations - one at the river Theel in Lebach (station 2, blue line) (№ 7 in Fig. 1) and a second one at its effluent river Ill in Eppelborn (station 1, dotted red line) (№ 8 in Fig. 1) - are plotted for one summer season. Comparing the loads, thus the total amount of NO_3-N which was transported in both rivers, it can clearly be seen that the large majority of the NO_3-N in fact comes from the catchment of the smaller river Ill and is transported later on through the river Theel.

So any measures to reduce NO_3-N pollution in the river Theel should be carried out in the catchment of river Ill. Nevertheless, during high water situations a certain amount of NO_3-N is also washed out in the catchment of the river Theel as can be seen at the beginning of the measuring campaign in March.

But also regarding the loads during low discharges can give valuable hints to understand pollutant sources and pathways. For instance, comparing the constantly increasing concentrations of TP and TRP during the decreasing discharge illustrated in Fig. 8a above with their loads (not given here) we see that the latter remain at a constant level. It can thereby be concluded that these loads represent the basic amounts emitted by the WWTP.

4. Conclusions

To this day the mobile measuring stations presented in this paper have been operated at 35 sites all over the Saarland monitoring 25 heterogeneous small and middle scale rivers. Though all these rivers differ very much regarding catchment conditions and anthropogenic pressure the real-time monitoring could always bring out fundamental insights and understanding of crucial processes affecting the chemical status as well as the ecological situation in each river.

The real-time measurements provide a perfect representation of the variation of both concentrations and loads and thus give a clear picture of the situation at all times. Due to the combination of sensors and wet chemical analysers a large number of different parameters can be detected reliably. A detailed study of these data together with their diverse correlations over various time scales allows us to draw very general conclusions, both catchment- and site-specific ones. The final goal of such studies is to characterise a catchment by a sort of fingerprint and to explain parameter changes and correlations in a coherent model. Thereby the entire number of impacts, their sources and emission pathways into the river as well as the geological background and other natural characteristics can be identified and described.

It has often been mentioned that surrogate parameters and grab sampling could be used to reduce time, effort and costs. However, grab sampling mostly misses crucial events and use of surrogate parameters is somehow misleading, e.g. turbidity for TP or SAC for TOC. Only a combined inspection of several parameters in time can bring out the duration, the intensity and the origin of most pollution impacts. Furthermore, online monitoring data can give precious hints on the representability of grab sample results as they point out the influences of time, season, hydrologic conditions etc. on the measured data.

Such “complex systems can provide multiple and accurate data and can do real time continuous monitoring”, but “they need highly skilled

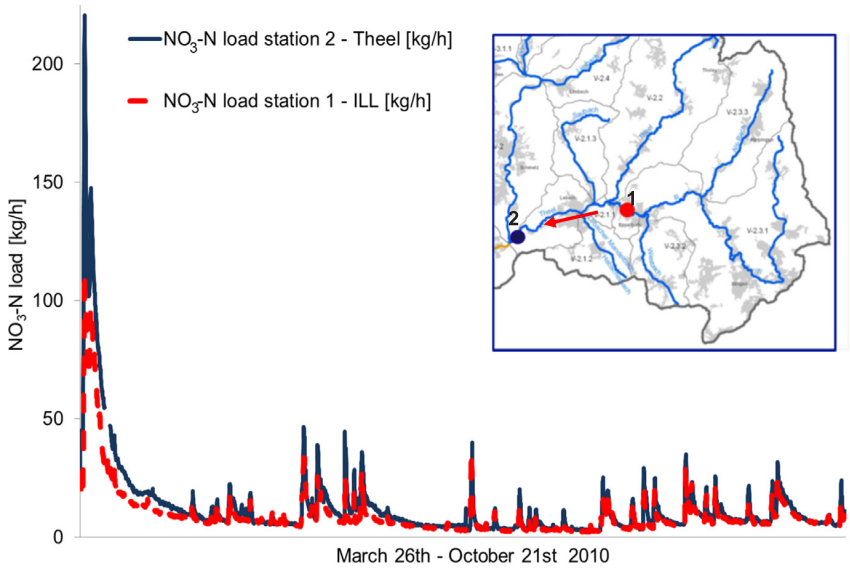

Fig. 9. Comparison of NO_3-N loads in the river Theel (station 2) and in its effluent river Ill (station 1) (March 26th– October 21st 2010) (hourly mean values).

personnel and expensive instruments and a high maintenance" (Jornet-Martínez et al., 2017). Beyond that, the spatial flexibility is of course limited due to infrastructural demands. As a consequence, the time for a measuring campaign will not only vary depending on season and weather changes but also on the operating expense.

Nevertheless it has to be underlined that the real-time monitoring of water quality presented here turned out to be a very useful tool to provide relevant information for all stakeholders involved in integrated catchment management and for planning and implementation of purposeful measures as well as for their evaluation. Thus the results can support all authorities in controlling the implementation of the WFD and other demands of water management, especially in small and middle scale catchments. Several authors (Blaen et al., 2016; Halliday et al., 2015; Wade et al., 2012), however, have highlighted the meaning of real-time monitoring for classifying the chemical status of rivers as defined in general in the WFD. It was proposed to consult real-time monitoring as a better means to revise the limits of the WFD which are still based on annual median values. So an improvement of the strategies of the WFD may also be part of the justification of the higher efforts and costs of such an approach.

Furthermore, the investigation results also provide arguments for the responsible parties and other stakeholders (operators of WWTP or industrial plants, agricultural associations, water suppliers, etc.) to generally discuss thresholds and quality standards of different parameters and to reduce the emissions of certain WTTPs or industrial plants and also to implement new regulations to intensify the so called good agricultural practice or to plan specific measures such as restoring projects.

In summary, the herein presented real time monitoring system provides extremely valuable data of a catchment. However, high costs of material, consumption and maintenance limit its use to very selected investigations.

Acknowledgments

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References

Angulo, C., Cabestany, J., Rodríguez, P., Batlle, M., González, A., de Campos, S., 2012. Fuzzy expert system for the detection of episodes of poor water quality through continuous measurement. Expert Syst. Appl. 39, 1011–1020. https://doi.org/10.1016/j.eswa.2011.07.102.

Behmel, S., Damour, M., Ludwig, R., Rodriguez, M., 2016. Water quality monitoring strategies - a review and future perspectives. Sci. Total Environ. 571, 1312–1329. https://doi.org/10.1016/j.scitotenv.2016.06.235.

Bieroza, M., Heathwaite, A., 2015. Seasonal variation in phosphorus concentration–discharge hysteresis inferred from high-frequency in situ monitoring. J. Hydrol. 524, 333–347. https://doi.org/10.1016/j.jhydrol.2015.02.036.

Bieroza, M.Z., Heathwaite, A.L., 2016. Unravelling organic matter and nutrient biogeochemistry in groundwater-fed rivers under baseflow conditions: uncertainty in in situ high-frequency analysis. Sci. Total Environ. 572, 1520–1533. https://doi.org/10.1016/j.scitotenv.2016.02.046.

Blaen, P.J., Khamis, K., Lloyd, C.E.M., Bradles, C., Hannah, D., Krause, S., 2016. Real-time monitoring of nutrients and dissolved organic matter in rivers. Sci. Total Environ. 569–570, 647–660. https://doi.org/10.1016/j.scitotenv.2016.06.116.

Bowes, M.J., House, W.A., Hodgkinson, R.A., 2003. Phosphorus dynamics along a river continuum. Sci. Total Environ. 313 (1–3), 199–212. https://doi.org/10.1016/s0048-9697(03)00260-2.

Bowes, M.J., Palmer-Felgate, E.J., Jarvie, H.P., Loewenthal, M., Wickham, H.D., Harmana, S.A., Carra, E., 2012. High-frequency phosphorus monitoring of the River Kennet, UK: are ecological problems due to intermittent sewage treatment works failures? J. Environ. Monit. 14 (12), 3137–3145. https://doi.org/10.1039/c2em30705g.

Bowes, M.J., Loewenthal, M., Read, D.S., Hutchins, M.G., Prudhomme, C., Armstrong, L.K., Harman, S.A., Wickham, H.D., Gozzard, E., Carvalho, L., 2016. Identifying multiple stressor controls on phytoplankton dynamics in the River Thames (UK) using high-frequency water quality data. Sci. Total Environ. 569–570, 1489–1499. https://doi.org/10.1016/j.scitotenv.2016.06.239.

Boënne, W., Desmet, N., Van Looya, S., Seuntjens, P., 2014. Use of online water quality monitoring for assessing the effects of WWTP overflows in rivers. Environ. Sci.: Processes Impacts 16, 1510–1518. https://doi.org/10.1039/C3EM00449J.

Cassidy, R., Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: comparison with near-continuous phosphorus time-series data. J. Hydrol. 405 (1), 182–193. https://doi.org/10.1016/j.jhydrol.2011.05.020.

Cruzeiro, C., Rocha, E., Pardal, M.A., Rocha, M.J., 2016. Seasonal-spatial survey of pesticides in the most significant estuary of the Iberian Peninsula - the Tagus River estuary. J. Clean. Prod. 126, 419–427. https://doi.org/10.1016/j.jclepro.2016.03.005.

De Marco, R., Clarke, G., Pejcic, B., 2007. Ion-selective electrode potentiometry in environmental analysis. Electroanalysis 19 (19–20), 1987–2001. https://doi.org/10.1002/elan.200703916.

Desmet, N.J.S., Van Belleghem, S., Seuntjens, P., Bouma, T.J., Buis, K., Meire, P., 2011. Quantification of the impact of macrophytes on oxygen dynamics and nitrogen retention in a vegetated lowland river. Phys. Chem. Earth 36, 479–489. https://doi.org/10.1016/j.pce.2008.06.002.

European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off. J. Eur. Communities L327, 1 22.12.2000.

European Environment Agency, 2017. Diffuse Sources. https://www.eea.europa.eu/themes/water/water-pollution/diffuse-sources (accessed 12 May 2017).

Even, S., Mouchel, J.-M., Servais, P., Flipo, N., Poulin, M., Blanc, S., Chabanel, M., Paffoni, C., 2007. Modelling the impacts of combined sewer overflows on the river Seine water quality. Sci. Total Environ. 375 (1–3), 140–151. https://doi.org/10.1016/j.scitotenv.2006.12.007.

Ferrant, S., Laplanche, C., Durbe, G., Probst, A., Dugast, P., Durand, P., Sanchez-Perez, M., Probst, J.L., 2013. Continuous measurement of nitrate concentration in a highly event-responsive agricultural catchment in south-west of France: is the gain of information useful? Hydrocarb. Process. 27 (12). https://doi.org/10.1002/hyp.9324.

Fu, G., Butler, D., 2012. Frequency analysis of river water quality using integrated urban wastewater models. Water Sci. Technol. 65 (12), 2112–2117. https://doi.org/10.2166/wst.2012.127.

Glasgow, H.B., Burkholder, J.M., Reed, R.E., Lewitus, A.J., Kleinman, J.E., 2004. Real-time remote monitoring of water quality: a review of current applications, and advancements in sensor, telemetry, and computing technologies. J. Exp. Mar. Biol. Ecol. 300, 409–448. https://doi.org/10.1016/j.jembe.2004.02.022.

Halliday, S.J., Skeffington, R.A., Wade, A.J., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J., Jarvie, H.P., 2015. High-frequency water quality monitoring in an urban catchment: hydrochemical dynamics, primary production and implications for the Water Framework Directive. Hydrol. Process. 29 (15), 3388–3407. https://doi.org/10.1002/hyp.10453.

Jiang, P., Xia, H., He, Z., Wang, Z., 2009. Design of a water environment monitoring system based on Wireless Sensor Networks. Sensors 9, 6411–6434. https://doi.org/10.3390/s90806411.

Jordan, P., Arnscheidt, A., McGrogan, H., McCormick, S., 2007. Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. Hydrol. Earth Syst. Sci. 11 (1), 372–381. https://doi.org/10.5194/hess-11-372-2007.

Jornet-Martínez, N., Moliner-Martínez, Y., Molins-Legua, C., Campíns-Falcó, P., 2017. Trends for the development of in situ analysis devices. In: Meyers, R.A., Valcarel, M. (Eds.), Encyclopedia of Analytical Chemistry. Wiley Online Library https://doi.org/10.1002/9780470027318.a9593 (online). (first published 25 March 2017, accessed 04 September 2018).

Khalid, R.R., Meyer, A.M., Meiers, J., Beck, H.P., Frey, G., 2016. Predictive power management for a solar-powered off-grid surface water quality monitoring system. 11th IEEE Conference on Industrial Electronics and Applications (ICIEA 2016) Hefei, China https://doi.org/10.1109/ICIEA.2016.7603614.

Leone, A., Ripa, M.N., Boccia, L., Lo Porto, A., 2008. Phosphorus export from agricultural land: a simple approach. Biosyst. Eng. 101, 270–280. https://doi.org/10.1016/j.biosystemseng.2008.07.005.

Lloyd, C.E.M., Freer, J.E., Johnes, P.J., Coxon, G., Collins, A.L., 2016. Discharge and nutrient uncertainty: implications for nutrient flux estimation in small streams. Hydrol. Process. 30 (1), 135–152. https://doi.org/10.1002/hyp.10574.

Mellander, P.-E., Melland, A.R., Jordan, P., Wall, D.P., Murphy, P.N.C., Shortle, G., 2012. Quantifying nutrient transfer pathways in agricultural catchments using high temporal resolution data. Environ Sci Policy 24, 44–57. https://doi.org/10.1016/j.envsci.2012.06.004.

Ockenden, M., Deasy, C.E., Benskin, C., Beven, K.J., Burke, S., Collins, A.L., Hiscock, K.M., 2016. Changing climate and nutrient transfers: evidence from high temporal resolution concentration-flow dynamics in headwater catchments. Sci. Total Environ. 548, 325–339. https://doi.org/10.1016/j.scitotenv.2015.12.086.

O'Flynn, B., Regan, F., Lawlor, A., Wallace, J., Torres, J., O'Mathuna, C., 2010. Experiences and recommendations in deploying a real-time, water quality monitoring system. Meas. Sci. Technol. 21, 124004 (10pp). https://doi.org/10.1088/0957-0233/21/12/124004.

Outram, F., Lloyd, C., Jonczyk, J., Benskin, C.M., Grant, F., Perks, M., Freer, J., 2014. High-frequency monitoring of nitrogen and phosphorus response in three rural catchments to the end of the 2011–2012 drought in England. Hydrol. Earth Syst. Sci. 18 (9), 3429–3448. https://doi.org/10.5194/hess-18-3429-2014.

Rode, M., Thiel, E., Franko, U., Wenk, G., Hesser, F., 2009. Impact of selected agricultural management options on the reduction of nitrogen loads in three representative meso scale catchments in Central Germany. Sci. Total Environ. 407 (11), 3459–3472. https://doi.org/10.1016/j.scitotenv.2009.01.053.

Shore, M., Murphy, S., Mellander, P.-E., Shortle, G., Melland, A.R., Crockford, L., O'Flaherty, V., Williams, L., Morgan, G., Jordan, P., 2017. Influence of stormflow and baseflow phosphorus pressures on stream ecology in agricultural catchments. Sci. Total Environ. 590-591, 469–483. https://doi.org/10.1016/j.scitotenv.2017.02.100.

Ungureanu, F., Lupu, R.G., Stan, A., Craciun, I., Teodosiu, C., 2010. Towards real time monitoring of water quality in river basins. Environ. Eng. Manag. J. 9 (9), 1267–1274.

Viviano, G., Salerno, F., Manfredi, E.C., Polesello, S., Valsecchi, S., Tartari, G., 2014. Surrogate measures for providing high frequency estimates of total phosphorus concentrations in urban watersheds. Water Res. 64, 265–277. https://doi.org/10.1016/j.watres.2014.07.009.

Wade, A.J., Palmer-Felgate, E.J., Halliday, S.J., Skeffington, R.A., Loewenthal, M., Jarvie, H.P., Bowes, M.J., Greenway, G.M., Haswell, S.J., Bell, I.M., Joly, E., Fallatah, A., Neal, C., Williams, R.J., Gozzard, E., Newman, J.R., 2012. Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring. Hydrol. Earth Syst. Sci. 16, 4323–4342. https://doi.org/10.5194/hess-16-4323-2012, www.hydrol-earth-syst-sci.net/16/4323/2012/.

Weyrauch, P., Matzinger, A., Pawlowsky-Reusing, E., Plume, S., von Seggern, D., Heinzmann, B., Schroeder, K., Rouault, P., 2010. Contribution of combined sewer overflows to trace contaminant loads in urban streams. Water Res. 44 (15), 4451–4462. https://doi.org/10.1016/j.watres.2010.06.011.

Worrall, F., Howden, N., Burt, T., 2015. Understanding the diurnal cycle in fluvial dissolved organic carbon – the interplay of in-stream residence time, day length and organic matter turnover. J. Hydrol. 523, 830–838. https://doi.org/10.1016/j.jhydrol.2015.01.075.

2.2 Detecting Pollutant Sources and Pathways: High-Frequency Automated Online Monitoring in a Small Rural French/German Transborder Catchment

Extended Abstract

Small and medium-sized rivers are characterised by pronounced spatial and temporal variability of nutrient and pollutant inputs, which makes comprehensive assessment of water quality particularly challenging. This limitation is exacerbated in transboundary catchments, where differing national monitoring strategies, regulatory frameworks, and environmental quality standards (EQS) may lead to inconsistent assessments and management priorities. In the context of the EU Water Framework Directive (WFD), reliable identification of dominant stressors and their origins is, however, essential for the design of cost-effective measures to improve ecological status. This study demonstrates how high-frequency, multi-parameter online monitoring can be used to disentangle diffuse and point-source pollution, quantify loads, and identify spatial heterogeneities in a small transboundary river catchment.

The presented research was conducted in the rural Bickenalb catchment (79 km²), which spans north-eastern France (Grand Est region) and south-western Germany (Saarland and Rhineland-Palatinate). Land use is dominated by intensive agriculture and low population density. In the catchment, two contrasting wastewater management approaches have been realised: in the French subcatchment, there is one centralised STP with CSOs, whereas in the German part there are several decentralised small-scale STWs. Previous River Basin Management Plans classified the ecological status of river Bickenalb as moderate to poor, with persistent deficits in nutrient concentrations and oxygen balance.

To capture the high variability of inputs, two mobile online water quality monitoring stations were installed at strategically selected locations: one near the French–German border (Peppenkum) to record inputs from the French subcatchment, and one further downstream (Hornbach) integrating nearly the entire catchment. Parameters were recorded synchronously at sub-hourly to minute-scale resolution over several months and included total phosphorus, ortho-phosphate, ammonium, nitrate, TOC (total organic carbon), temperature, dissolved oxygen, pH, turbidity, and electrical conductivity. Additional stand-alone oxygen sensors were deployed along the river, and automatic samplers were used to assess effluents from decentralised STWs in the German subcatchment.

Data analysis followed a holistic approach, evaluating not only individual concentration time series but also parameter relationships and concentration–discharge (C–Q) dynamics during both storm events and low-flow conditions. Particular emphasis was placed on analysing parameter pairs such as total phosphorus/ortho-phosphate, TOC/particle-bound phosphorus, ammonium/ortho-phosphate, and oxygen/temperature, as these relationships provide diagnostic information on pollution sources and in-stream processes that cannot be derived from single parameter data sets.

High-frequency monitoring revealed that diffuse agricultural sources dominate nutrient and carbon inputs during storm events. Particle-bound phosphorus and TOC exhibited strong correlations with discharge and turbidity, indicating erosion-driven transport from arable land, particularly during late autumn and winter due to harvested fields. In contrast, nitrate showed delayed concentration peaks relative to discharge maxima, consistent with interflow-driven transport through soils. This time lag, ranging from several hours upstream to more than a day downstream, highlights that nitrate loads cannot be reliably captured by low-frequency or flow-proportional sampling alone.

Superimposed on diffuse inputs, pronounced point-source signals from urban wastewater were detected, especially in the French subcatchment. CSO events were characterised by abrupt increases in ammonium, ortho-phosphate, and TOC concentrations, often accompanied by marked oxygen depletion.

Ammonium proved to be a particularly sensitive tracer for identifying CSO discharges and distinguishing them from agricultural runoff during rainfall events. During low-flow conditions, parallel total phosphorous and ortho-phosphate dynamics with a high proportion of dissolved phosphorus (>90%) clearly indicated continuous inputs from the French STW. Diurnal cycles in total phosphorous and ortho-phosphate, and ammonium further corroborated the influence of the STW.

Assessment of the oxygen regime showed that despite generally favourable morphological conditions, the river frequently exhibited oxygen undersaturation, especially upstream near the border. High-resolution oxygen/temperature and oxygen/pH relationships revealed strong diurnal fluctuations linked to photosynthesis, indicating eutrophication driven by elevated nutrient loads. Events of organic and ammonium-rich inputs caused additional oxygen consumption, occasionally leading to prolonged suboptimal conditions for aquatic biota.

Calculation of nutrient loads based on continuous time series demonstrated that the majority of phosphorus, nitrogen, and TOC loads were already present at the border-crossing point, confirming that dominant inputs originate in the French subcatchment. During the comparable monitoring period, approximately two-thirds of the total nutrient loads measured downstream could be attributed to upstream sources. Storm events accounted for the majority of transported loads, particularly for particle-bound phosphorus, TOC, and nitrate. By contrast, targeted sampling of decentralised STWs in the German subcatchment showed negligible contributions, underscoring the effectiveness of decentralised wastewater treatment in this rural context.

Comparison with German environmental quality standards (EQS) revealed frequent exceedances for total phosphorus, ortho-phosphate, ammonium, and derived ammonia concentrations, particularly at the upstream site. Oxygen deficits also occurred repeatedly. The application of differing national EQS would, however, lead to divergent assessments of ecological status on either side of the border, illustrating a key challenge for transboundary river basin management.

Overall, this study demonstrates that high-frequency, multi-parameter online monitoring is indispensable for understanding pollutant sources, transport pathways, and in-stream processes in small rivers. Analysing parameter relationships and load dynamics provides critical insights beyond those obtainable from conventional low-frequency sampling. While the operational costs of mobile monitoring stations limit their deployment to selected sites, their use is particularly justified in small, vulnerable catchments and in transboundary settings. The findings provide a robust scientific basis for prioritising mitigation measures and highlight the urgent need for cross-border harmonisation of monitoring strategies, parameters, and EQS to effectively implement the objectives of the EU Water Framework Directive.

These results have been published in Journal of Environmental Management:

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Table 5: Author contribution roles for the publication "Detecting pollutant sources and pathways: high frequency automated online monitoring in a small and rural Frech/German transborder catchment " in form of the CRediT standard.

Contributor roles	**Author(s)**
Conceptualisation	Angelika Meyer, Horst P. Beck
Methodology	Angelika Meyer, Christina Klein
Validation	Horst P. Beck
Formal analysis	Angelika Meyer, Christina Klein
Writing – original draft	Angelika Meyer
Writing – review and editing	Ralf Kautenburger, Horst P. Beck
Visualisation	Elisabeth Fünfrocken, Ralf Kautenburger
Data curation	Elisabeth Fünfrocken, Alban Cairault

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Research article

Detecting pollutant sources and pathways: High-frequency automated online monitoring in a small rural French/German transborder catchment

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ABSTRACT

Great temporal and spatial variability of inputs make comprehensive monitoring in small and middle sized rivers difficult. In this study, relevant inputs in a small river were recorded with suitable online monitoring equipment coupled in mobile water quality monitoring stations, the study area being a transborder catchment with French and German (Saarland federal state) subcatchments. In addition to a pronounced spatial variability necessitating a denser net of measuring points this catchment has also to be assessed in the light of different national regulations. To identify individual pollution sources and weigh their relative importance, relevant parameters were recorded over a representative monitoring period of several months: phosphorus (P) as total phosphorus (TP) and total reactive P phosphorus (TRP), nitrate (NO_3–N), ammonium (NH_4–N), total organic carbon (TOC), temperature, oxygen (O_2), pH, turbidity, and electrical conductivity (EC). The recorded data were subjected to adapted interpretation together with other catchment-related factors. In order to retrieve maximum information from the online data sets the relationships among certain parameter pairs were also analysed for both storm events and low flow periods.

Comparison of loads at the different monitoring sites could reliably verify the majority of nutrient inputs originating in the French subcatchment. Additional sampling of output channels from sewage treatment works (STWs) in the Saarland subcatchment revealed that inputs from several decentralised STWs do not result in significant loads, as opposed to inputs from one STW in France. Our holistic approach provides a basis for adopting cost-effective measures to reduce loads in small river catchments as well as cross-border harmonisation of environmental policies.

1. Introduction

In the context of complying with a great number of applicable legal provisions to secure good water quality, in particular the EU's Water Framework Directive (WFD) (European Commission, 2000), it is of fundamental importance to detect the causes and the origins of the main stressors in water bodies. Although in many cases the general problems are already known, there is still a lack of high-frequency monitoring data for many catchments that hinders definitive utilisable conclusions. This applies in particular to small and medium-sized rivers, which are typically characterised by very high spatial and temporal input variability (Abbott et al., 2017). In many cases, where temporal resolution of sampling is insufficient, the origin of stressors can usually only be estimated by modelling (Crockford et al., 2017; Daniels et al., 2018). The notorious discrepancy between interpolated and recorded data has however already been pointed out by different authors (e.g. Liu et al., 2018).

Many authors have therefore engaged in collecting high-frequency data sets with autosamplers, online sensors and bank side analysers. Most studies focus on characterising certain input pathways such as fluxes in rural watersheds (Kralisch et al., 2003; Drolc et al., 2007; Ribbe et al., 2008; Ferrant et al., 2013; Crockford et al., 2017; Bieroza et al., 2018). In many cases, however, only single parameters or parameter sets, such as P (Campbell et al., 2015; Chen et al., 2015) or nitrogen (N) (Ribbe et al., 2008; Chen et al., 2012), or only transport mechanisms during storm events are investigated (Chen et al., 2012; Lloyd et al.,

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2016; Paule-Mercado et al., 2018).

Rivers in most catchments are subject to multiple stressors consisting of within-river and anthropogenic pressures (Grizzetti et al., 2017; Elosegi et al., 2017). Type and quantity of pressures depend on countless human activities and natural conditions in the respective catchment (Comber et al., 2019). Due to the multidimensional pollution from both point and diffuse (or nonpoint) source inputs, it is important to detect those input sources responsible for the most damage to the aquatic ecosystem.

Many authors emphasise that monitoring should more relate to within-river dynamics, and they point to the benefits of online monitoring with automated sample collection and analysis equipment for assessing catchment system functions and vulnerability of the respective aquatic ecosystem (Bieroza and Heathwaite, 2015; Halliday et al., 2015; Rinaldi et al., 2017). Another problem is that, specifically in small catchments, the results from random low-frequency sampling strongly depend on the time when the samples are taken (time of day, day of the week, season) (Harmel et al., 2009; Crockford et al., 2017; Comber et al., 2019).

In addition, concentrations of transported substances may vary steeply at the same site, due to the complex processes influenced by concentration-flow relationships (Martin et al., 1992; Harmel et al., 2010; Ferrant et al., 2013; Gao et al., 2014; Lloyd et al., 2016; Kozak et al., 2019). Consequently, also loads should not be assessed from random sampling but recorded as continuous time series (Metadier and Bertrand-Krajewski, 2012; Ockenden et al., 2017). Numerous authors have established concentration-flow relationships (C-Q curves) for various parameters. These allow – even for large data sets – a description of the processes responsible for storing, remobilisation and transport in the catchment (Bieroza et al., 2018). This applies to correlation functions (e.g. in Jarvie et al., 2006; Herndon et al., 2015; Moatar et al., 2017) as well as to the interpretation of hysteresis loops (Chen et al., 2012, 2015; Ferrant et al., 2013; Bieroza and Heathwaite, 2015; Bowes et al., 2015; Lloyd et al., 2016).

All these aspects show that properly adapted monitoring is indispensable – in particular with respect to the purpose of implementing cost-effective measures to achieve a higher water quality status. This specifically applies with respect to implementing relevant legal provisions. However, such regulations are rarely based on extensive real-time monitoring campaigns and they are unfortunately different to divergent when comparing national legislations.

In a previous article (Meyer et al., 2018) we have described the instrumental methods incorporated in our measuring stations in which relevant parameters reliably measurable in a sub-hourly time series were synchronously monitored. While P and/or NO_3–N concentrations are already widely monitored, NH_4–N and TOC concentrations are commonly not. However, NH_4–N concentration monitoring can be essential for detecting domestic effluent inputs. We discussed this in several case studies and demonstrated how a careful evaluation of extensive data sets helps to characterize specific types of events in dry or stormy weather situations. We could show that analyses do not only aim at describing singular events but also at identifying all stressor sources and pathways as well as their effects, e.g. on the O_2 budget, and thus allow to draw a comprehensive picture of the total water pollution.

In the present article, we venture to show how simultaneous real-time monitoring at different locations allows mapping of subcatchment heterogeneities using the example of a small watercourse crossing rural areas both in France (Grand Est Region) and Germany (federal states of Saarland and Rhineland-Palatinate, with only the Saarland portion being investigated) with mobile monitoring stations. In the case of rivers crossing national borders this may also mirror differences in legislations pertaining to the classification of the ecologic status and to measures to be taken to improve this status.

2. Materials and methods

2.1. Study area

The River Bickenalb rises in Lorraine (north-east France) and crosses, after about 9 km of flow, the German border (federal states of Saarland and Rhineland-Palatinate). Flow distance totals about 20 km, the catchment covering a total of 79 km^2, with a 28.6 km^2 portion belonging to France and a 34.3 km^2 portion to Saarland (Fig. 1).

The catchment is dominated by lower and middle shell limestone and is exclusively rural. Intensive agriculture is practised on both French and German sides, with only a few villages (population density 70 p km^{-2}). Arable land covers 42% of the catchment, 40% is covered by pastures and grassland, 14% by forests, and only 4% are residential areas.

A sewage treatment work (STW) with a 4250 population equivalent (PE) and two Combined Sewer Overflows (CSO) are operated in Erching in the French sub-catchment near the national border. By contrast, wastewater disposal in Germany (Saarland) is decentralised: there are 8 small municipal STWs with between 70 and 650 PE designed as ventilated ponds or constructed wetlands.

On both the German and the French side, the ecological status of the River Bickenalb was classified as ‘moderate’ in the 1st River Basin Management Plan (RBMP) in 2009 due to morphological and biological deficits as well as to chemical loads and deficits in the O_2 budget. Until the 2nd RBMP was launched in 2015, previously planned measures to achieve improved ecological status in Germany (Saarland) were implemented. However, the same deficits were still detected thereafter, so that the status had to be derated to ‘unsatisfactory’ in Germany and to ‘very bad’ in France.

Further information of the catchment can also be found in Fig. S-1a and S-1b.

2.2. Monitoring system

Several mobile online water quality monitoring stations have already been in use for years on behalf of the Saarland Federal State Government to comprehensively map water pollution and to identify the origin of pressures in the examined water bodies.

Two of these mobile monitoring stations were installed at

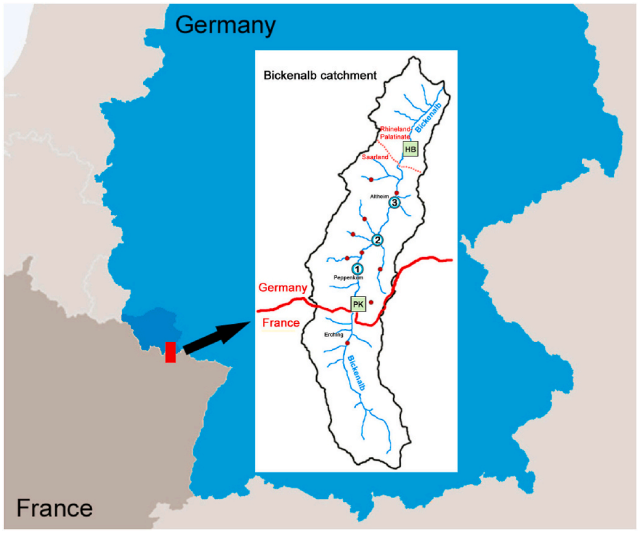

Fig. 1. Study area – Map of the River Bickenalb catchment, showing Peppenkum (PK) and Hornbach (HB) monitoring sites, additional O_2 Monitoring Points (1–3) and STWs in the catchment (red dots). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

representative sites for a certain period of time. A detailed description of the monitoring stations' layout, instruments and workflow is given in Meyer et al. (2018), so only a brief overview will be presented here. A submersible pump continuously pumps river water into the monitoring station's sample tank; a separate pipe system redirects the overflow from the sample tank into the river. Sensors for monitoring O_2, temperature, pH, EC, turbidity and oxidised nitrogen – NO_3–N with traces of nitrite (NO_2–N) – are installed in the sample tank. In addition, three wet chemical analysers (self-calibrating online photometers) monitor concentrations of NH_4–N, TOC and P, measured as both TP (unfiltered and acidic hydrolysed) and TRP (unfiltered and un-hydrolysed). NH_4–N concentration is measured after filtering the water through a 0.45 µm PTFE membrane. TOC and TP/TRP is measured after the water has passed an ultrasonic homogenisation unit (Fig. S-2).

This setup allows – depending on the method – very short measuring intervals of between a few seconds and ten (NH_4–N, TP/TRP) to twenty (TOC) minutes.

Further information on monitored parameters, methods, limits of detection, on monitoring station maintenance and quality management, as well as on online data evaluation and interpretation is also given in Meyer et al. (2018).

To continuously monitor water quality in the River Bickenalb one online monitoring station was installed in the river's headwaters in Peppenkum near the French border to record the situation in the French part and another one was installed in Hornbach near the Saarland border with Rhineland-Palatinate, which should show additional inputs from the Saarland part (Fig. 1).

The Peppenkum monitoring station (R374654 H5442744) was in operation from October 4, 2017 to June 27, 2018 and recorded all French inputs from the 28.6 km^2 catchment. The Hornbach station (R377649 H5451211) was in operation from October 20, 2017 to March 26, 2018, and also recorded the inputs from the Saarland subcatchment (70 km^2, approximately 90% of the total River Bickenalb catchment). In addition to the two mobile online monitoring stations, three stand-alone HOBO U26-001 sensors were deployed for temperature and O_2 monitoring at Monitoring Points 1, 2 and 3 (Fig. 1). O_2 concentrations were measured using the luminescent dissolved O_2 (LDO) method. The sensors are equipped with an antifouling cap and battery operated, hence self-sufficient.

Furthermore, a battery-powered automatic sampler was deployed in the Saarland subcatchment at the small tributaries of the River Bickenalb below the STWs' discharge points (red dots in Fig. 1). The sampler was timed to collect mixed samples, i.e. a volume of 100 ml was taken in hourly intervals and 8 consecutive samples mixed in one bottle, resulting in 3 mixed samples per day. The samples were subsequently laboratory analysed for nutrients.

Data for interpretation purposes (flow data, climate data, groundwater quality data) were provided by the Saarland Agency of Environmental Protection.

3. Results and discussion

3.1. Inputs from diffuse sources

In particular, diffuse source pollution via both erosion and interflow is extremely difficult to detect without recording high-frequency data sets (e.g. Moatar et al., 2017). This will be illustrated in the following examples from the study area, as there is a vast array of inputs from agricultural sources as could be expected from the intensive agriculture in the Bickenalb catchment.

As illustrated by the example from 19 November to 3 December for the near-border Peppenkum monitoring station, TP and TRP concentrations resulting from such inputs often do not parallel (Fig. 2): Despite TP levels increasing, TRP levels stagnate or even decrease, so that the portion of particle-bound phosphorus (PP) – being TP minus dissolved TRP – increases (see also Bowes et al., 2015). This P fraction mainly

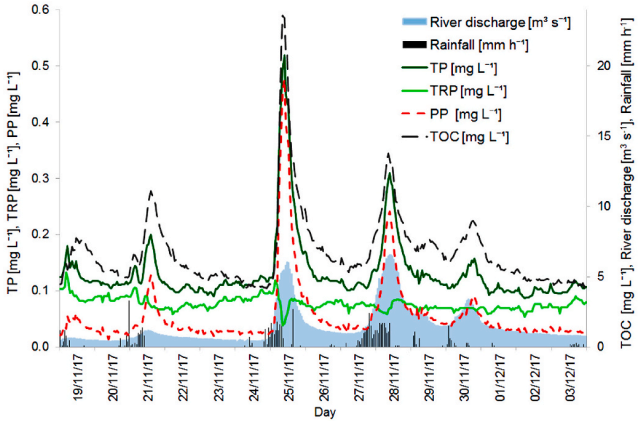

Fig. 2. Hourly average TRP, TP, PP and TOC concentrations, river discharge (Peppenkum monitoring station) and rainfall (Assweiler weather station) from 19 November to December 3, 2017.

originates from applied fertilisers, as P accumulates on soil particles and is transported into the river by erosion in rainfall events. Similar observations have been made by other authors (e.g. Chen et al., 2015). However, remobilisation of soluble reactive phosphorus (SRP) as described by Jarvie et al. (2006) could not be observed in this catchment. In general, remobilised P can hardly be differentiated from recent P inputs, even with high-frequency monitoring. To differentiate P inputs from erosion and those from CSOs, which also occur in storm events, additional NH_4–N monitoring is of crucial importance.

In addition to PP, erosion also releases dissolved and particulate carbonaceous substances into the river, such as carbon (C) from natural and synthetic fertilisers, from humic and fulvic acids and plant residues, all recorded as TOC. PP and TOC concentration curves in rural catchments therefore are often very similar (Meyer et al., 2018). For the time period shown in Fig. 2, a very strong correlation (given as Pearson's Correlation Coefficient $R^2 = 0.924$) suggests that PP and TOC result from the same input sources. In addition to river discharge, erosion processes naturally also increase turbidity, so that close correlations between all erosion-triggered parameters (river discharge, turbidity, PP, TP and TOC) could be mapped at all storm events, which is also mostly typical for rural catchments. By contrast, no correlation between TP and TRP ($R^2 < 0.01$) could be observed for the corresponding discharge event. These observations could be made at both monitoring stations at the near-border Peppenkum site and at the Hornbach site further downstream.

The impact of agricultural diffuse sources is also obvious in NO_3–N concentrations. In contrast to PP and TOC inputs, a very different transport mechanism for NO_3–N shows up in many rural locations: NO_3–N inputs from interflow could be recorded at both monitoring sites. The interflow as lateral part of the subsurface runoff transports dissolved NO_3–N through the soil so that it enters the river with a certain time lapse. Therefore, in a given event, the recorded NO_3–N concentration may increase several or many hours after the discharge maximum. At Peppenkum, for example, this time lapse was between 8 and 15 h (Fig. 3a) and at Hornbach it was between 12 and 41 h (Fig. 3b). Often, with river discharge increasing, NO_3–N is even diluted temporarily. Similar correlations were observed by other authors in rural watersheds (e.g. Kralisch et al., 2003; Ferrant et al., 2013; Wang et al., 2015; Bieroza et al., 2018). NO_3–N concentrations recorded at the Peppenkum site show sharp peaks (Fig. 3a) following rainfall maxima, so it can be assumed that the related inputs occur in the monitoring station's vicinity. In Hornbach, NO_3–N concentrations recorded are as high as upstream or even higher and decrease over a longer time period (Fig. 3b). The differing concentration gradients can be explained by the Hornbach station being sited much further downstream, i.e. a much larger part of

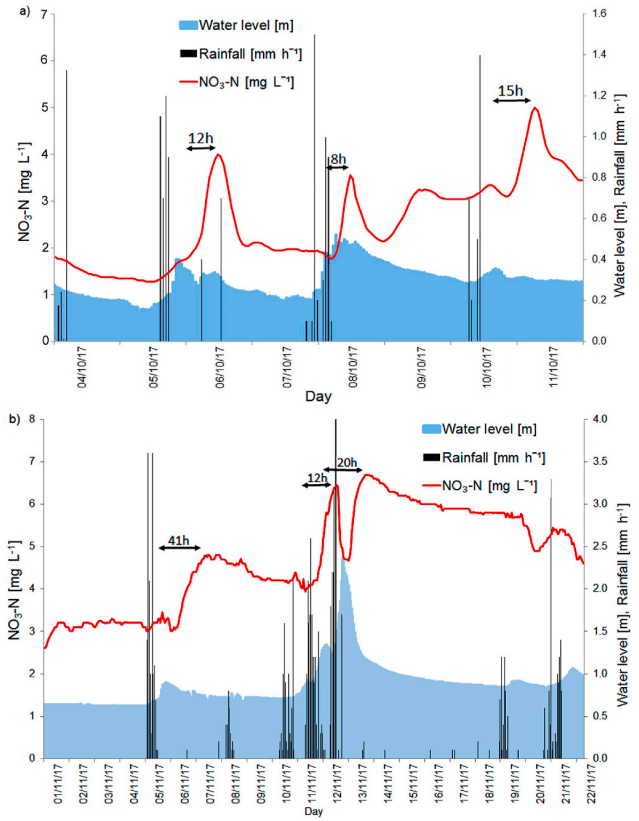

Fig. 3. Hourly NO_3–N means with peaks resulting from interflow inputs: a) Peppenkum monitoring station from 4 to October 11, 2017; b) Hornbach monitoring station from 1 to November 22, 2017.

the catchment is covered there. The NO_3–N peak is wider, as there are several NO_3–N input points with varying flow times to the monitoring site. This is already a sure indication of NO_3–N inputs from agricultural sources also in the Saarland subcatchment.

It should be expressly underlined that NO_3–N from interflow cannot, or not properly, be recorded by flow-controlled automatic sampling, as sampling frequency decreases with river discharge so that the actual NO_3–N peak is not captured. However, many authors observed NO_3–N inputs originating mainly from baseflow in other catchments (e.g. Moraetis et al., 2010; Gao et al., 2014; Bowes et al., 2015).

TOC and PP erosion as well as NO_3–N leaching from agricultural sources in the Bickenalb catchment occur mainly in late autumn and winter, when the fields are harvested and the absence of crops accelerates erosion. Hardly any such leaching processes were recorded over the following months, as NO_3–N is usually diluted with increasing water levels. Similar seasonal fluctuations in NO_3–N and P leaching have also been reported by other authors for comparable climatic zones (e.g. Rozemeijer et al., 2010; Saadat et al., 2018). Bowes et al. (2015) for example, detected an anticlockwise pattern in the hysteresis loops of the NO_3–N concentration-flow relationship during rainfall events from November to January, which is typical for interflow inputs.

We could, however, not observe NH_4–N inputs in this context, whereas e.g. Wang et al. (2015) found that the NH_4–N proportion in both mineral and organic fertilisers rapidly decreases after application, while the NO_3–N proportion increases. Notable P inputs via interflow or groundwater can be excluded, as the Bickenalb catchment is geologically dominated by lime, so P applied in fertilisers is easily bound as calcium phosphate and hence becomes insoluble (see also 3.1).

3.2. CSO inputs

Inputs from municipal CSOs pose major risks to aquatic ecosystems not only in densely populated areas. They were repeatedly recorded during rainfall events even in the sparsely populated Bickenalb catchment and are usually characterised by steep increases of dissolved TRP, TOC and, in particular, NH_4–N concentrations, which were observed at both monitoring sites. The examples in Fig. 4a and b shows that NH_4–N concentration in Peppenkum on 22 October increased from levels below detection limit (0.02 mg L^{-1}) to almost 1.2 mg L^{-1}, and to 1.3 mg L^{-1} shortly afterwards. NH_4–N levels recorded in Hornbach a few hours later even exceeded the measurement range of 2 mg L^{-1}. Such steep increases in NH_4–N levels from CSO inputs pose a high ecological risk particularly to small rivers, the more so as the hydraulic stress on the ecosystem is accompanied by heavy organic pollution causing serious O_2 depressions.

CSO inputs are another example illustrating how pressures, especially on small rivers, tend to be underestimated if monitoring is only done by random sampling. Over the monitoring periods shown in Fig. 4 the average NH_4–N concentration at Peppenkum was 0.167 ± 0.247 mg L^{-1}, whereas the maximum amounted to 1.33 mg L^{-1}; at Hornbach, average NH_4–N concentration was 0.141 ± 0.231 mg L^{-1}, the maximum even exceeding 2 mg L^{-1} NH_4–N. Due to the rapid changes in concentration, such representative data can hardly be produced by manual sampling.

At Peppenkum site, in total 19 CSO input events and 12 erosion input events with widely varying intensities were recorded over the monitoring period from October 4, 2017 to June 27, 2018, with some events occasionally overlapping. At Hornbach, 13 CSO input events and 6 erosion input events were recorded over the shorter monitoring period

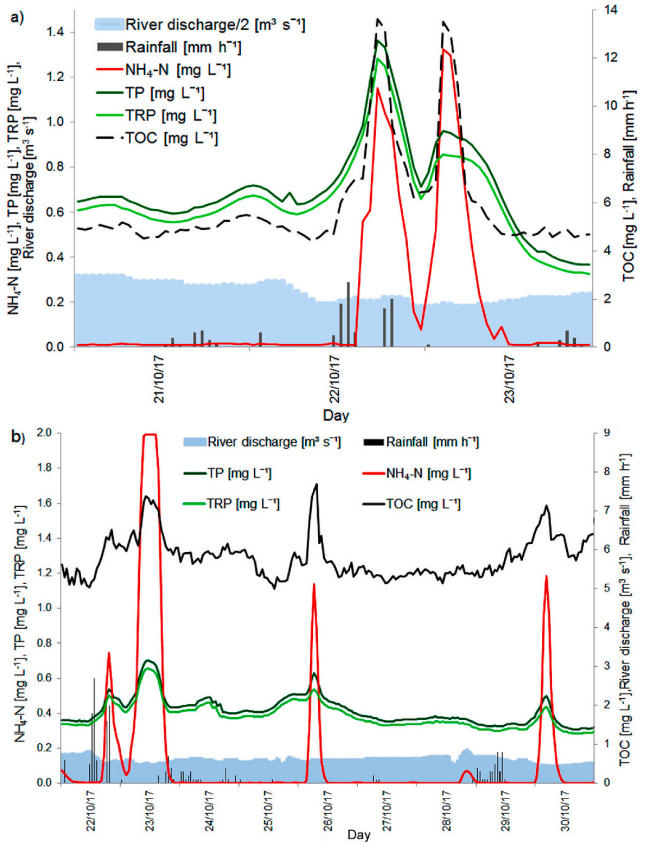

Fig. 4. Abrupt rises of TP, TRP, NH_4–N and TOC concentrations caused by CSO input events: a) Peppenkum monitoring station from 21 to October 23, 2017; b) Hornbach monitoring station from 22 to October 30, 2017.

from October 20, 2017 to March 26, 2018.

3.3. Influences of the STWs

Some specific weather conditions are well suited for observing imputs from diffuse sources or CSOs as described above. In contrast, inputs from municipal or industrial STWs can be better recorded during low flows. At the beginning of the monitoring period in early October (as also in summer 2018) low flow conditions prevailed, so that inputs from the Erching STW in France, located about 2 km upstream Peppenkum monitoring site, were clearly detectable.

At extremely low flows (Fig. 5a and b), TP and TRP concentrations were exactly parallel, the difference between the two being very small, so P inputs consisted almost completely of dissolved TRP (average TRP proportion > 92%). This ratio is an indicator for wastewater inputs from municipal STWs. As shown in Fig. 5a below, a strong correlation between the two P fractions is evident for the time period from 10 to October 21, 2017 ($R^2 = 0.939$).

P concentrations tend to increase with decreasing river discharge, hence the P load is relatively constant. On 11 October, rainfall resulted in additional inputs from CSOs, causing P concentrations to steeply increase. Between such low flows the phenomena described above became immediately manifest again. The exactly correlating time curves and the sharpness of the peaks are clear indications that these inputs occurred in the monitoring station's immediate vicinity, so that the Erching STW is likely the major source.

Halliday et al. (2015) also observed two-peak regular diurnal dynamics of TP concentrations with daily TP concentration changes of 0.18 mg P L^{-1} in low flow studies. Bowes et al. (2015) recorded an increase of TRP concentrations from 0.2 to almost 0.7 mg L^{-1} in comparable weather conditions. Both studies attribute these inputs to STWs. Jarvie et al. (2006) point out that even in rural areas, where the main portion of P loads often originates from diffuse sources, P from point sources pose a high risk for the aquatic ecosystem – particularly during periods of ecological sensitivity such as low flows in summer and spring time.

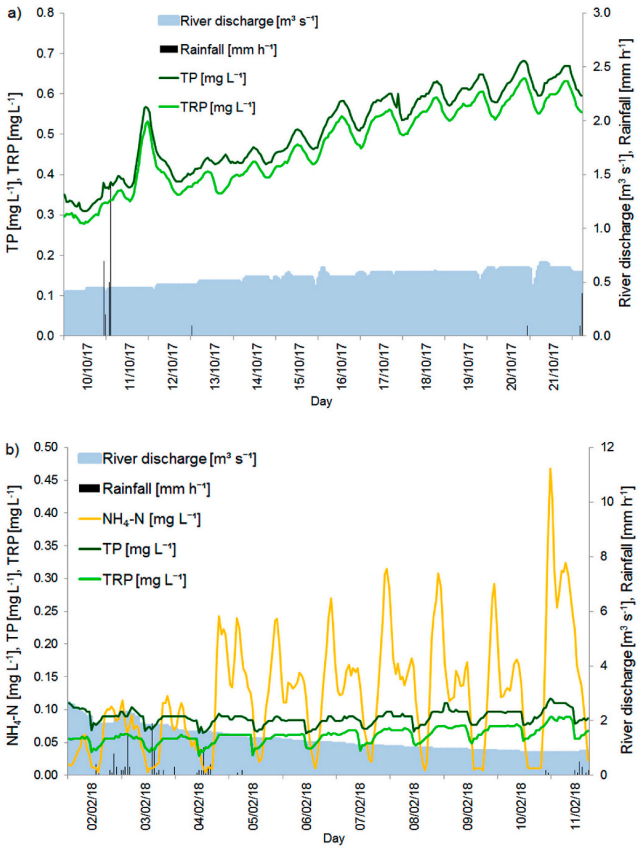

Fig. 5. Effects of STW effluent inputs at Peppenkum: a) diurnal fluctuations and daily increase of TRP and TP concentrations from 10 to October 21, 2017; b) TRP/TP diurnal cycles and corresponding NH_4–N concentrations from 2 to February 11, 2018.

Fig. 5b shows, in addition to TP/TRP diurnal cycles, also those of NH_4–N featuring the double peaks typical for inputs from a smaller STW, which is a result of more household wastewater being discharged in the morning and evening. For example, NH_4–N concentration increased to 0.467 mg L^{-1} at 19:00 h on 9 February and dropped to 0.255 mg L^{-1} at 21:00 h, returning to 0.324 mg L^{-1} at 3:00 h on the following day (Fig. 5b).

Due to a faster nitrification, baseline NH_4–N concentrations are much higher in winter than in summer. In Peppenkum the average NH_4–N concentrations measured at air temperatures below 10 °C were 0.109 mg L^{-1}, and 0.057 mg L^{-1} above 10 °C. However, this also highlights the negative impact of inputs from the STWs and CSOs on water quality at the Peppenkum monitoring site. By contrast, at the Hornbach monitoring site, NH_4–N concentrations were under detection limit during low flows.

Increasing water temperature and pH move the NH_3/NH_4 equilibrium towards fish-toxic ammonia (non-ionised NH_3–N). The pH in the River Bickenalb is relatively high due to the geological conditions and therefore implicates a particularly high risk of NH_3–N forming. Especially, this applies when there is an additional pH shift due to photosynthesis. While at Hornbach monitoring site high NH_3–N concentrations are reached only temporarily, the EQS of 2 µg L^{-1} required by the German Surface Waters Ordinance (OGewV 2016) is exceeded fairly frequently and also for longer periods of time at Peppenkum. Values in excess of the EQS limit shown in Fig. 6, for example, were measured over approximately 15 h on 14 Ma y.

NH_3–N concentrations at Peppenkum exceeded the EQS limit for over 900 h (20%) with a maximum of at almost 60 µg L^{-1}within the monitoring period, at Hornbach for a total of 190 h (7%) over the shorter monitoring period there.

3.3.1. Sampling the small STWs in Germany

In 2006 to 2008, eight SWTs were built in the Saarland part of the Bickenalb catchment, mostly designed as ventilated pond or constructed wetland. To assess the influence of these STWs on water quality, an automatic sampler was installed for 1 week at each STW outlet channel and programmed to take hourly samples, which were merged to 3 mixed

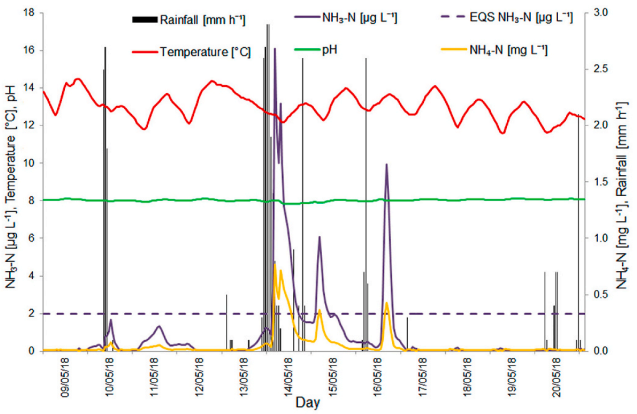

Fig. 6. NH_3–N concentrations in relation to monitored NH_4–N, water temperature and pH at Peppenkum monitoring station, and to NH_3–N EQS as stated in OGewV 2016 (9–May 20, 2018).

samples per day. Comparison of the samples showed very similar results at any time of day for all monitored STWs. It can be assumed that there are no significant negative effects on water quality from STW inputs at the monitoring sites. In this catchment it turned out to be more effective to spatially distribute these discharges because River Bickenalb and its tributaries are not abundant in water causing limitation in dilution effects.

3.4. O_2 budget

In addition to the online monitoring stations, three stand-alone onset O_2 sensors recorded water temperature and O_2 concentrations for a few months (Fig. 1: Monitoring points MP 1–3). Fig. 7 shows the O_2 curves for each monitoring point. For the comparable period, average O_2 concentrations were: 10.1 ± 0.3 mg L^{-1} at MP 1; 10.3 ± 0.9 mg L^{-1} at MP 2; 9.8 ± 1.1 mg L^{-1} at MP 3; 10.3 ± 0,8 mg L^{-1} at Hornbach monitoring station. While other authors (e.g. Wang et al., 2019) observed significant longitudinal changes in O_2 levels, in the case of the River Bickenalb only marginal differences between O_2 levels were recorded at MP 1 to 3 and Hornbach station. Monitoring at Peppenkum showed mainly similar results – from late November to early February, however, repeated periods of significantly lower O_2 levels were observed. The O_2 deficits at near-border Peppenkum station correlate with the events described above, involving inputs from surface runoff originating in the French subcatchment. Inputs of organic substances, particularly TOC and NH_4–N, lead to O_2 consumption (see e.g. Wang et al., 2019). O_2 levels recorded from 10 to December 14, 2017, for example, remained permanently below those otherwise recorded, the average concentration in this period reaching only 9.5 mg L^{-1}, in contrast to approx. 11 mg L^{-1} at all other monitoring points.

However, recorded O_2 concentrations remained below the physical saturation point at normal pressure (1013 hPa). This can be visualised by plotting high-resolution O_2 data against temperature as shown in Fig. 8a and b. O_2 concentrations were above saturation point throughout the day only occasionally during the spring weeks, when O_2 was produced from photosynthesis by algae and foliage water plants (see also Figs. S3 and S4). At Peppenkum these supersaturations occurred somewhat earlier than at Hornbach.

Similar observations were made in grab samples taken by French surveillance authorities at the Erching monitoring point during the years 2010 and 2013 to 2016.

The time of day has a significant impact on readings, especially in phases of increased photosynthetic activity, as O_2 concentrations are subject to dramatic diurnal changes. Recorded O_2 levels shown in Fig. 8a range from a supersaturation level of 125% (20 April at 15:00 h) to an undersaturation level of 64% (21 April at 6:00 h) recorded at Peppenkum. At Hornbach they range from a supersaturation level of 120% (25 March at 15:00 h) to an undersaturation level of 82% (26 March at 6:00 h) (Fig. 8b). It must be concluded that the O_2 content is inadequate, even despite the River Bickenalb's favourable morphological structure over large parts of its watercourse.

Photosynthesis also influenced pH recorded at both monitoring sites (Fig. 9) as pH too is influenced by photosynthesis, the light reaction increasing pH as a result of O_2 production.

This relationship has also been described by e.g. Moraetis et al. (2010), Halliday et al. (2015). Closer analysis of O_2 level and temperature curves shows that O_2 levels peak only slightly later than temperature. If the fluctuations in O_2 levels were influenced exclusively by physical conditions, such as e.g. temperature, the amplitudes of both parameters would have to be reciprocal.

The correlation of O_2 and temperature curves and the strong daily fluctuations in pH however suggest that O_2 concentration and pH in this period were mainly influenced by photosynthesis and indicate eutrophication. Normally, rivers' trophic status tends naturally to be higher downstream due to accumulating nutrients. In the case of the River Bickenalb, however, the observed trophic status was higher upstream (Peppenkum monitoring site) than downstream (Hornbach site), which indicates higher eutrophication status near the German-French border.

3.5. Assessment with respect to applicable EQS

As mentioned in the introductory paragraphs we aim at recording the spatial variations in subcatchments as well as the effect of diverging national approaches. For Germany, standard limit values of relevant parameters for aquatic ecosystems are set forth in the OGewV 2016. The stipulated standards are criteria for the ranking of monitored aquatic ecosystems as 'good' with respect to their ecological status and potential (see table S-4).

Peppenkum site: Over the monitoring period, NO_3–N concentrations exceeded EQS (11.3 mg L^{-1}) only in a few samples. NH_4–N concentrations exceeded EQS (0.1 mg L^{-1}) in approximately 30% of all samples. TOC concentrations exceeded EQS (7 mg L^{-1}) in approximately 8% of all

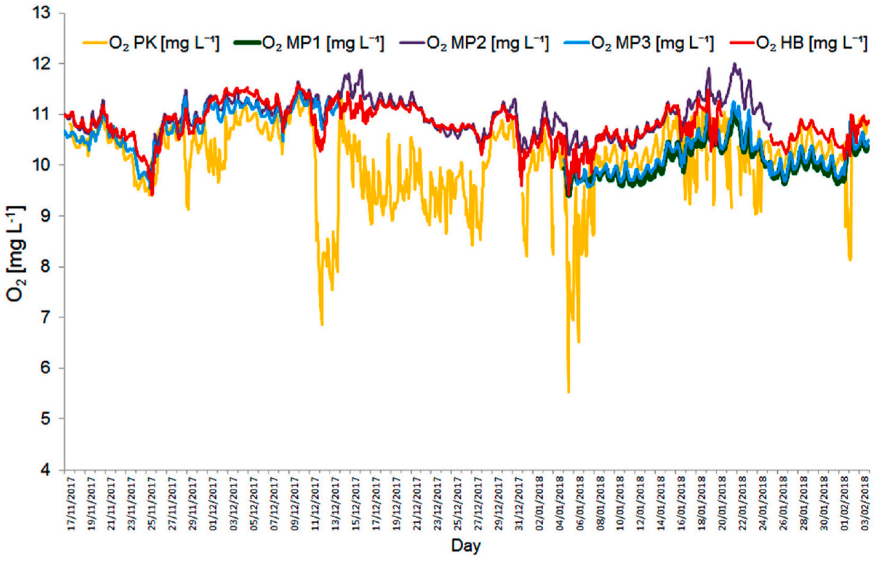

Fig. 7. O_2 levels recorded at Peppenkum (PK – yellow), MP 1 (green), MP 2 (violet), MP3 (blue) and Hornbach (HB – red) (November 17, 2017 to February 3, 2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

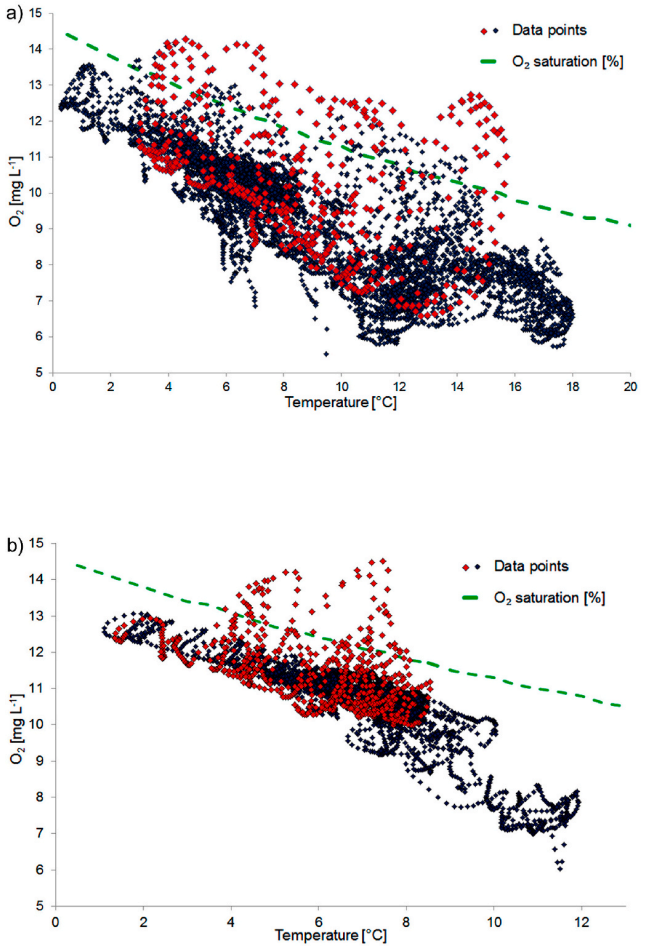

Fig. 8. Recorded O_2 concentrations in relation to temperature and physical O_2 saturation at normal pressure (1013 hPa): a) Peppenkum monitoring station; dark blue: October 4, 2017 to March 18, 2018; red: 19 March to June 27, 2018; b) Hornbach monitoring station; dark blue: October 20, 2017 to February 28, 2018; red: 1 to March 26, 2018. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

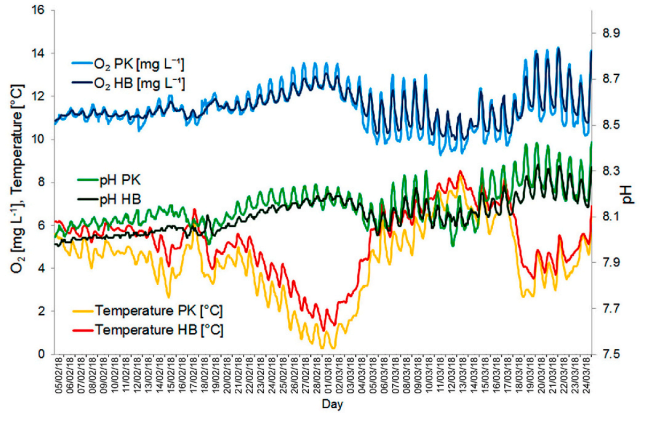

Fig. 9. Diurnal cycles for temperature (yellow), O_2 level (light blue) and pH (light green) at Peppenkum/PK, and for temperature (red), O_2 level (dark blue) and pH (dark green) at Hornbach/HB, recorded from 5 February to March 24, 2018. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

samples. Excess rates of TRP and TP are exceptional: TRP concentrations exceeded EQS in more than 70% of all samples, and TP concentrations were excessive in approximately 80% of all samples. Calculated NH_3–N levels exceeded EQS (2 μg L^{-1}) in almost 20% of all samples. Water temperatures and pH remained within approved limits. O_2 levels remained below EQS (7 mg L^{-1}) in approximately 10% of all samples.

Hornbach site: Over the monitoring period from October 20, 2017 to March 26, 2018, TP concentrations exceeded EQS in 46% of all samples, TP concentrations in 66% of all samples. NH_4–N concentrations exceeded EQS in almost 15%, TOC concentrations in 16%, and NH_3–N concentrations in 7% of all samples. NO_3–N levels remained below EQS, and pH also remained within specified limits. O_2 levels dropped below EQS in a few samples despite the monitoring in the winter half year. Moreover, recorded values do not reflect pessimal conditions for water temperatures and O_2 levels, as the monitoring was not made in summer.

Comparing the EQS excess rates compared to German standards (for O_2: deficit rates) of recorded values at Peppenkum and Hornbach within the comparable monitoring period shows that at the Peppenkum monitoring site, the EQS for NH_4–N, NH_3–N and TP are significantly more frequently exceeded, and O_2 EQS more frequently undershot than at Hornbach site, whereas TOC levels exceeded EQS more often downstream than upstream (Fig. S-5).

In contrast, the EQS required in France are not as stringent as in Germany (an overview of the relevant EQS in France and Germany is given in table S-6). This leads to some inconsistency in assessing water quality status on both sides of the border and thus also in planning of measures.

3.6. Comparison of calculated loads

High-frequency sampling also allows exact mapping of transported nutrient loads via nutrient-concentration times discharge on a detailed time-scale. Particularly in small catchments such an analysis is indispensable for an adequate determination of loads and their attribution to certain input sources (Johnes, 2007; Harmel et al., 2009; Crockford et al., 2017). For example, Ferrant et al. (2013) found that even a monitoring frequency of >3 h can produce significant errors in the analysis of NO_3–N loads. Atmospheric N and P depositions are considered to be negligible, as described e.g. by Halliday et al. (2015).

Comparison of total loads at both monitoring sites shows that nutrient pollution is already present upstream at Peppenkum, hence originating from the French subcatchment. Only in times of heavy rainfall pollutants are mobilised and transported into the river also in the Saarland subcatchment. The amount of these inputs varies in relation to intensity, duration and spatial distribution of precipitation (Fig. 10). In the time period shown, the maximum load at Peppenkum site was 47 kg h^{-1} TP and 145 kg h^{-1} NO_3–N and at Hornbach site was 77 kg h^{-1} TP and 214 kg h^{-1} NO_3–N.

For all recorded pollutants it is obvious that the major portion of loads is already present in the river when it crosses the border from France to Germany (loads recorded at Peppenkum station) (Fig. S-7); while only another third of the loads originates from the Saarland part of the catchment (difference between loads at Hornbach and Peppenkum). As most of the NH_4–N is nitrified on the transport, assessment of NH_4–N is difficult.

For the distinction of loads transported at baseflow and at storm events, the median of the flow was defined as threshold value. Consequently, storm events are defined as situations in which flow exceeds the median calculated for the entire monitoring period at the respective monitoring site (Moatar et al., 2017).

The majority of nutrient inputs occur in storm events, when flow exceeds the median. At Peppenkum, 77% of the total NH_4–N load was transported during rainfall runoff events and 84% at Hornbach; NH_4–N inputs can be attributed almost exclusively to CSOs. Only 53% of the total-TRP loads, but 71% of the TP loads were recorded during rainfall events at Peppenkum, and 70% and 88%, respectively, at Hornbach.

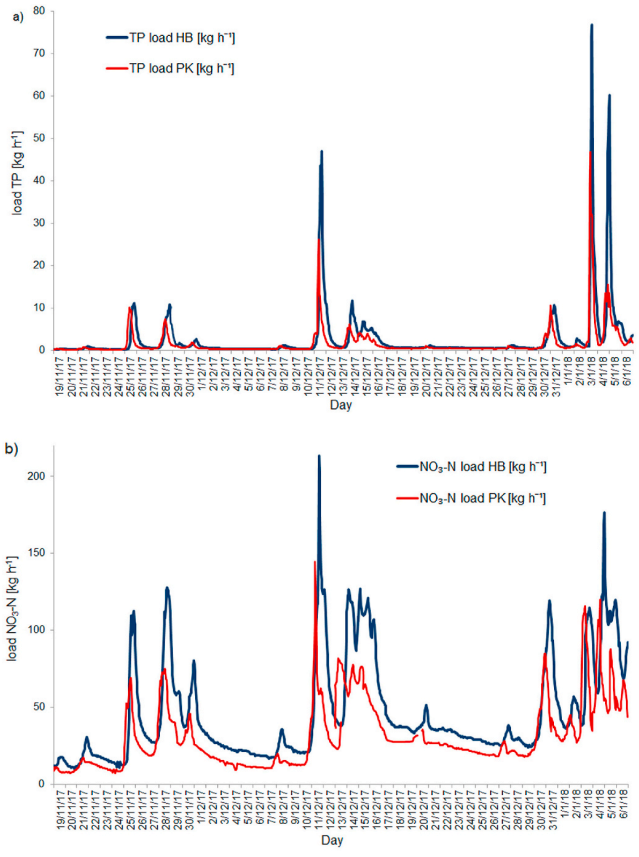

Fig. 10. Loads at Peppenkum (PK; red lines) and Hornbach (HB; blue lines) monitoring sites from November 19, 2017 to January 6, 2018: a) TP loads; b) NO_3–N loads. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

This highlights the importance of PP transportation by erosion in the whole catchment. Most of the TOC and NO_3–N loads too are transported at storm events (TOC: 85% at Peppenkum, 82% at Hornbach; NO_3–N 80% at both sites). Relocation of NO_3–N is by contrast harder to assess. In the event of interflow NO_3–N transport and the associated time lag between flow and concentration maxima, the flow median criterion does not cover the entire load curve.

The origin of P loads can also be estimated by dint of the flow median criterion. As impacts of P via interflow and groundwater as well as from industries are negligible in the catchment, nevertheless sedimentation and remobilisation processes cannot be taken into account. During baseflow and low flow periods (flow below median), the portion of P transported can be referred to the SWTs outputs. At storm events (flow above median) TRP enters the river via CSOs while PP is transported by erosion carrying P from fertilisers For the Bickenalb catchment we can assume that the biggest part of the P impacts is caused by erosion. Apart from that, in the French subcatchment one third of the P load stems from the Erching STW (Fig. 11).

However, estimating the origin of N loads is much more complex and cannot be categorised without considering e.g. STW emissions and groundwater concentrations.

4. Conclusions

This article describes how multiple stressors in a small river can be comprehensively mapped with high-frequency monitoring of electrochemical parameters and nutrient concentrations in a holistic approach. Therefore the recorded parameters were analysed in their entirety and

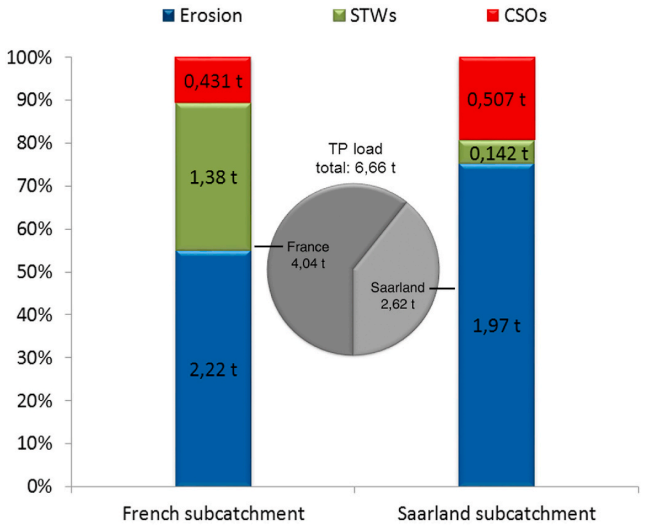

Fig. 11. Origin of the TP loads in the French and Saarland subcatchments in relation to total loads – Peppenkum and Hornbach monitoring sites from October 20, 2017 to March 26, 2018.

evaluated under various criteria, including correlations with each other and concentration-flow relationships not only for storm events but also for low flow periods. The high temporal resolution of the data also allows highly accurate calculation of loads.

The study area of the Bickenalb catchment is rural, with low population density and dominated by agriculture, and consequently suffers from pollution from multiple agricultural sources at both monitoring sites.

It could however be verified that particularly the upper reaches at the French-German border are also polluted by urban wastewater from France. To distinguish such CSO inputs from the diffuse agricultural sources at storm events, NH_4–N monitoring is indispensable. Long-term high-frequency monitoring also allows identifying interflow NO_3–N inputs from fertilisers unambiguously and in their entirety.

The comparison of loads at both monitoring sites can reliably verify that the majority of nutrient inputs originate in the French part of the Bickenalb catchment.

Sampling of STW output channels in the Saarland subcatchment revealed that total inputs from these decentralised STWs are negligible. This reflects the benefits from decentralised wastewater treatment as opposed to centralised solutions as implemented in the French part of the catchment.

However, due to the high costs incurred in operating mobile water quality monitoring stations and the considerable resources necessary for maintenance and processing, such stations can only be operated at few, carefully selected monitoring points. Operating such monitoring systems makes sense in particular at smaller rivers which usually incur a higher risk of ecological damage.

The situation described is also a striking example of the problems facing authorities in charge of transboundary river basin management. Different approaches to monitoring and assessment of water quality adopted by Member States result in differing priorities and hence differing measures implemented in cross-border catchments. Consequently, cross-border harmonisation is vital, not only as to the definition of good water quality and ecological state and potential, yet also as to monitored parameters and applicable EQS (see also Arle et al., 2016).

The findings of this study are discussed jointly by the authorities from both the Saarland and the French Grand Est region to develop measures to improve the water quality in the River Bickenalb.

CRediT author statement

Angelika M. Meyer: Writing - Original Draft, Conceptualization, Methodology, Formal analysis, Elisabeth Fuenfrocken: Data Curation, Visualization, Ralf Kautenburger: Writing - Review & Editing, Visualization, Alban Cairault: Data Curation, Horst P. Beck: Writing - Review & Editing Conceptualization Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112619.

References

Abbott, B.W., Gruau, G., Zarnetske, J.P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S., Pierson-Wickmann, A.-C., Davy, P., Pinay, G., 2017. Unexpected spatial stability of water chemistry in headwater stream networks. Ecol. Lett. 21 (2), 296–308. https://doi.org/10.1111/ele.12897.

Arle, J., Mohaupt, V., Kirst, I., 2016. Monitoring of surface waters in Germany under the water framework directive – a Review of approaches, methods and results. Water 8 (6), 217. https://doi.org/10.3390/w8060217.

Bieroza, M.Z., Heathwaite, A.L., 2015. Seasonal variation in phosphorus concentration-discharge hysteresis inferred from high-frequency in situ monitoring. J. Hydrol. 524, 333–347. https://doi.org/10.1016/j.jhydrol.2015.02.036.

Bieroza, M.Z., Heathwaite, A.L., Bechmann, M., Kyllmar, K., Jordan, P., 2018. The concentration-discharge slope as a tool for water quality management. Sci. Total Environ. 630, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256.

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Loewenthal, M., Gozzard, E., Newman, J.R., Palmer-Felgate, E.J., 2015. Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration–flow relationships. Sci. Total Environ. 511, 608–620. https://doi.org/10.1016/j.scitotenv.2014.12.086.

Campbell, J.M., Jordan, P., Arnscheidt, J., 2015. Using high-resolution phosphorus data to investigate mitigation measures in headwater river catchments. Hydrol. Earth Syst. Sci. 19, 453–464. https://doi.org/10.5194/hess-19-453-2015.

Chen, N., Wu, J., Hong, H., 2012. Effect of storm events on riverine nitrogen dynamics in a subtropical watershed, southeastern China. Sci. Total Environ. 431, 357–365. https://doi.org/10.1016/j.scitotenv.2012.05.072.

Chen, N., Wu, Y., Chen, Z., Hong, H., 2015. Phosphorus export during storm events from a human perturbed watershed, southeast China: implications for coastal ecology. Estuar. Coast Shelf Sci. 166, 178–188. https://doi.org/10.1016/j.ecss.2015.03.023.

Comber, A., Collins, A.L., Haro-Monteagudo, D., Hess, T., Zhang, Y., Smith, A., Turner, A., 2019. A generic approach for live prediction of the risk of agricultural field runoff and delivery to watercourses: linking parsimonious soil-water-connectivity models with live weather data Apis in decision tools. Front. Sustain. Food Syst. 3, 42. https://doi.org/10.3389/fsufs.2019.00042.

Crockford, L., O'Riordain, S., Taylor, D., Melland, A.R., Shortle, G., Jordan, P., 2017. The application of high temporal resolution data in river catchment modelling and management strategies. Environ. Monit. Assess. 189, 461. https://doi.org/10.1007/s10661-017-6174-1.

Daniels, M.B., Sharpley, A., Harmel, R.D., Anderson, K., 2018. The utilization of edge-of-field monitoring of agricultural runoff in addressing nonpoint source pollution. J. Soil Water Conserv. 73 (1), 1–8. https://doi.org/10.2489/jswc.73.1.1.

Drolc, A., Koncan, J.Z., Tisler, T., 2007. Evaluation of point and diffuse sources of nutrients in a river basin on base of monitoring data. Environ. Monit. Assess. 129 (1–3), 461–470. https://doi.org/10.1007/s10661-006-9376-5.

Elosegi, A., Gessner, M.O., Young, R.G., 2017. River doctors: learning from medicine to improve ecosystem management. Sci. Total Environ. 595, 294–302. https://doi.org/10.1016/j.scitotenv.2017.03.188.

European Commission, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off. J. Eur. Comm. L327, 1–22, 12.2000.

Ferrant, S., Laplanche, C., Durbe, G., Probst, A., Dugast, P., Durand, P., Sanchez-Perez, J. M., Probst, J.L., 2013. Continuous measurement of nitrate concentration in a highly event-responsive agricultural catchment in south-west of France: is the gain of information useful? Hydrol. Process. 27 (12), 1751–1763. https://doi.org/10.1002/hyp.9324.

Gao, Y., Zhu, B., Yu, G., Chen, W., He, N., Wang, T., Miao, C., 2014. Coupled effects of biogeochemical and hydrological processes on C, N, and P export during extreme rainfall events in a purple soil watershed in southwestern China. J. Hydrol. 511, 692–702. https://doi.org/10.1016/j.jhydrol.2014.02.005.

Grizzetti, B., Pistocchi, A., Liquete, C., Udias, A., Bouraoui, F., van de Bund, W., 2017. Human pressures and ecological status of European rivers. Sci. Rep. 7, 205. https://doi.org/10.1038/s41598-017-00324-3.

Halliday, S.J., Skeffington, R.A., Wade, A.J., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J., Jarvie, H.P., 2015. High-frequency water quality monitoring in an urban catchment: hydrochemical dynamics, primary production and implications for the water framework directive. Hydrol. Process. 29 (15), 3388–3407. https://doi.org/10.1002/hyp.10453.

Harmel, R.D., Smith, D.R., King, K.W., Slade, R.M., 2009. Estimating storm discharge and water quality data uncertainty: a software tool for monitoring and modeling applications. Environ. Model. Software 24 (7), 832–842. https://doi.org/10.1016/j.envsoft.2008.12.006.

Harmel, R.D., Slade, R.M., Haney, R.L., 2010. Impact of sampling techniques on measured storm water quality data for small streams. J. Environ. Qual. 39 (4), 1734–1742. https://doi.org/10.2134/jeq2009.0498.

Herndon, E.M., Dere, A.L., Sullivan, P.L., Norris, D., Reynolds, B., Brantley, S.L., 2015. Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments. Hydrol. Earth Syst. Sci. 19 (8), 3333–3347. https://doi.org/10.5194/hess-19-3333-2015.

Jarvie, H.P., Neal, C., Withers, P.J.A., 2006. Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus? Sci. Total Environ. 360 (1–3), 246–253. https://doi.org/10.1016/j.scitotenv.2005.08.038.

Johnes, P.J., 2007. Uncertainties in annual riverine phosphorus load estimation: impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. J. Hydrol. 332 (1–2), 241–258. https://doi.org/10.1016/j.jhydrol.2006.07.006.

Kralisch, S., Fink, M., Flügel, W.-A., Beckstein, C., 2003. A neural network approach for the optimisation of watershed management. Environ. Model. Software 18 (8–9), 815–823. https://doi.org/10.1016/S1364-8152(03)00081-1.

Kozak, C., Fernandes, C.V.S., Braga, S.M., do Prado, L.L., Froehner, S., Hilgert, S., 2019. Water quality dynamic during rainfall episodes: integrated approach to assess diffuse pollution using automatic sampling. Environ. Monit. Assess. 191, 402. https://doi.org/10.1007/s10661-019-7537-6.

Liu, X., Beusen, A.H.W., van Bee, L.P.H., Mogollón, J.M., Ran, X., Bouwman, A.F., 2018. Exploring spatiotemporal changes of the yangtze river (changjiang) nitrogen and phosphorus sources, retention and export to the east China sea and yellow sea. Water Res. 142, 246–255. https://doi.org/10.1016/j.watres.2018.06.006.

Lloyd, C.E.M., Freer, J.E., Johnes, P.J., Collins, A.L., 2016. Using hysteresis analysis of high-resolution water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment transfer in catchments. Sci. Total Environ. 543 (A), 388–404. https://doi.org/10.1016/j.scitotenv.2015.11.028.

Martin, G.R., Smoot, J.L., White, K.D., 1992. A comparison of surface-grab and cross-sectionally integrated streamwater-quality sampling methods. Water Environ. Res. 64 (7), 866–876.

Metadier, M., Bertrand-Krajewski, J.-L., 2012. The use of long-term on-line turbidity measurements for the calculation of urban stormwater pollutant concentrations, loads, pollutographs and intra-event fluxes. Water Res. 46 (20), 6836–6856. https://doi.org/10.1016/j.watres.2011.12.030.

Meyer, A.M., Klein, C., Fünfrocken, E., Kautenburger, R., Beck, H.P., 2018. Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers. Sci. Total Environ. 651 (2), 2323–2333. https://doi.org/10.1016/j.scitotenv.2018.10.069.

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resour. Res. 53 (2), 1270–1287. https://doi.org/10.1002/2016WR019635.

Moraetis, D., Efstathiou, D., Stamati, F., Tzoraki, O., Nikolaidis, N.P., Schnoor, J.L., Vozinakis, K., 2010. High-frequency monitoring for the identification of hydrological and bio-geochemical processes in a Mediterranean river basin. J. Hydrol. 389 (1–2), 127–136. https://doi.org/10.1016/j.jhydrol.2010.05.037.

Ockenden, M.C., Tych, W., Beven, K.J., Collins, A.L., Evans, R., Falloon, P.D., Forber, K. J., Hiscock, K.M., Hollaway, M.J., Kahana, R., Macleod, C.J.A., Villamiar, M.L., Wearing, C., Withers, P.J.A., Zhou, J.G., Benskin, C.McW.H., Burke, S., Cooper, R.J., Freer, J.E., Haygarth, P.M., 2017. Hydrol. Earth Syst. Sci. 21 (12), 6425–6444. https://doi.org/10.5194/hess-21-6425-2017.

OGewV, 2016. Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung OGewV) 20 June 2016 (BGBl. I S. 1373).

Paule-Mercado, M.C.A., Salim, I., Lee, B.-Y., Memon, S., Sajjad, R.U., Sukhbaatar, C., Lee, C.-H., 2018. Monitoring and quantification of stormwater runoff from mixed land use and land cover catchment in response to land development. Ecol. Indicat. 93, 1112–1125. https://doi.org/10.1016/j.ecolind.2018.06.006.

Ribbe, L., Delgado, P., Salgado, E., Flügel, W.A., 2008. Nitrate pollution of surface water induced by agricultural non-point pollution in the Pocochay watershed, Chile. Desalination 226 (1–3), 13–20. https://doi.org/10.1016/j.desal.2007.01.232.

Rinaldi, M., Belleti, B., Bussettini, M., Comiti, F., Golfieri, B., Lastoria, B., Marchese, E., Nardi, L., Surian, N., 2017. New tools for the hydromorphological assessment and monitoring of European streams. J. Environ. Manag. 202 (2), 363–378. https://doi.org/10.1016/j.jenvman.2016.11.036.

Rozemeijer, J.C., van der Velde, Y., van Geer, F.C., Bierkens, M.F.P., Broers, H.P., 2010. Direct measurements of the tile drain and groundwater flow route contributions to surface water contamination: from field-scale concentration patterns in groundwater to catchment-scale surface water quality. Environ. Pollut. 158 (12), 3571–3579. https://doi.org/10.1016/j.envpol.2010.08.014.

Saadat, S., Bowling, L., Frankenberger, J., Kladviko, E., 2018. Nitrate and phosphorus transport through subsurface drains under free and controlled drainage. Water Res. 142, 196–207. https://doi.org/10.1016/j.watres.2018.05.040.

Wang, J., Zhu, B., Zhang, J., Müller, C., Cai, Z., 2015. Mechanisms of soil N dynamics following long-term application of organic fertilizers to subtropical rain-fed purple soil in China. Soil Biol. Biochem. 91, 222–231. https://doi.org/10.1016/j.soilbio.2015.08.039.

Wang, J., Zhang, Z., Johnson, B., 2019. Low flows and downstream decline in phytoplankton contribute to impaired water quality in the lower Minnesota river. Water Res. 161, 262–273. https://doi.org/10.1016/j.watres.2019.05.090.

Supplementary Information

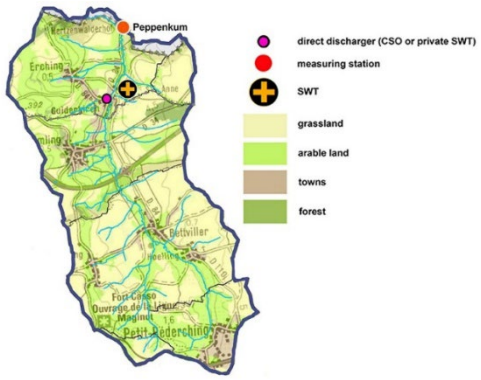

Fig. S-1a. Map of the French subcatchment showing land cover and localisation of the SWT, of the CSO and of the measuring station.

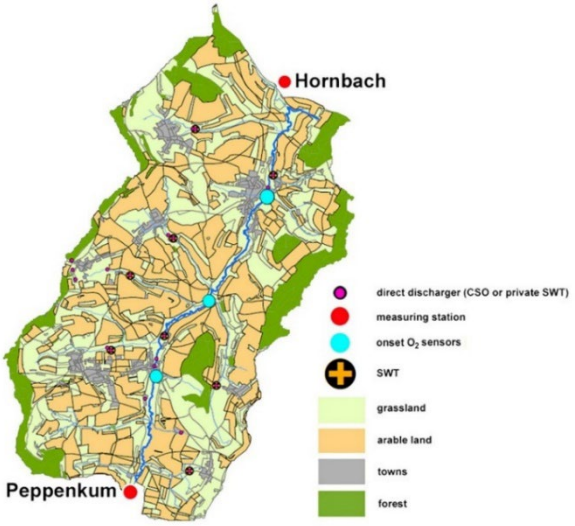

Fig. S-1b. Map of the Saarland subcatchment showing land cover and localisation of the SWTs, of the direct dischargers, of the two online measuring stations and of the three O_2 sensors.

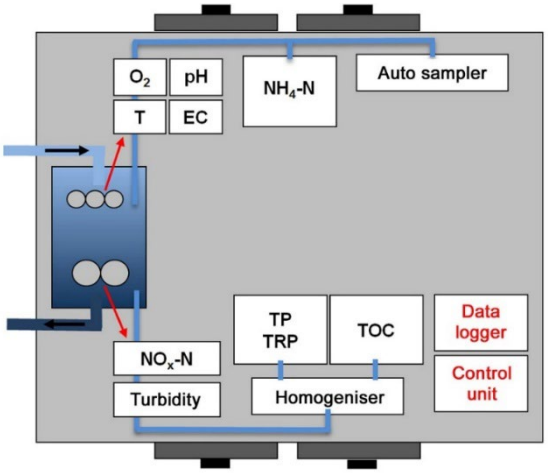

Fig. S-2. Scheme of a measuring station with sensors in the sample basin (left side) for O_2, pH, temperature and EC (above) as well as for NO_X-N and turbidity (below) and wet chemical analysers for NH_4-N (above), TOC, TRP and TP with the homogeniser (below).

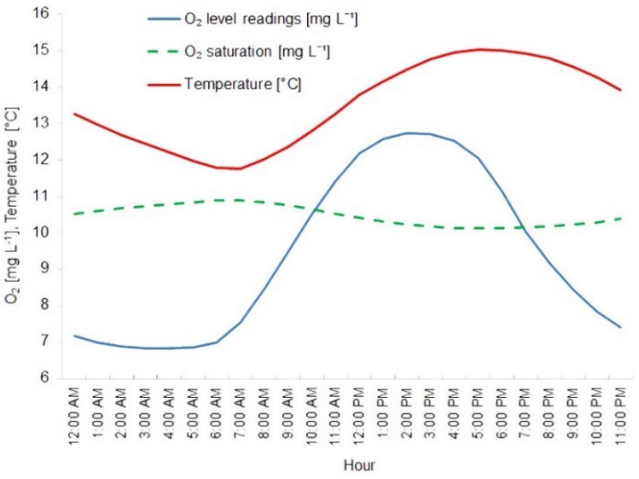

Fig. S-3. Influence of photosynthesis on O_2 concentrations: example of almost parallel daily temperature and O_2 cycles compared to the theoretical O_2 saturation at normal pressure (1013 hPa).

Table S-4.

Average, minimum and maximum hourly means by parameter as recorded at Peppenkum (4 October 2017 to 27 June 2018) and Hornbach (20 October 2017 to 26 March 2018); EQS of OGewV 2016; N = number of recorded hourly means.

Peppenkum	unit	Average	Minimum	Maximum	EQS	N
NO_3-N	[mg L^{-1}]	3.9	1.2	18.6	11.3	5771
NO_2-N	[mg L^{-1}]	0.05	0.02	0.41	0.05	34
NH_4-N	[mg L^{-1}]	0.09	BDL	>2	0.1	4994
TNb	[mg L^{-1}]	3.6	0.99	11.6	3	32
TRP	[mg L^{-1}]	0.21	0.01	1.3	0.07	5933
TP	[mg L^{-1}]	0.27	0.06	1.7	0.1	5933
TOC	[mg L^{-1}]	5.4	1.9	>25	7	5734
NH_3-N	[µg L^{-1}]	1.5	BDL	59.5	2	4926
pH		7.9	7.4	8.4	7–8.5	5875
O_2	[mg L^{-1}]	9.4	5.5	14.3	>7	5842
temperature	[°C]	9.1	0.30	18.1	<20	5867
EC	[µS cm^{-1}]	679	269	940		5933

Hornbach	unit	Average	Minimum	Maximum	EQS	N
NO3-N	[mg L^{-1}]	4.4	2.1	6.7	11.3	3676
NO2-N	[mg L^{-1}]	0.02	0.01	0.05	0.05	20
NH4-N	[mg L^{-1}]	0.06	BDL	2.0	0.1	2806
TNb	[mg L^{-1}]	3.8	1.8	6.4	3	20
TRP	[mg L^{-1}]	0.11	0.01	0.54	0.07	3393
TP	[mg L^{-1}]	0.16	0.05	2.3	0.1	3507
TOC	[mg L^{-1}]	5.4	1.5	28.2	7	3245
NH3-N	[µg L^{-1}]	0.70	0.01	22.1	2	2827
pH		7.9	7.6	8.4	7–8,5	3668
O2	[mg L^{-1}]	10.7	6.0	14.5	>7	3675
temperature	[°C]	6.9	1.1	11.9	<20	3679
EC	[µS cm^{-1}]	675	262	878		3679

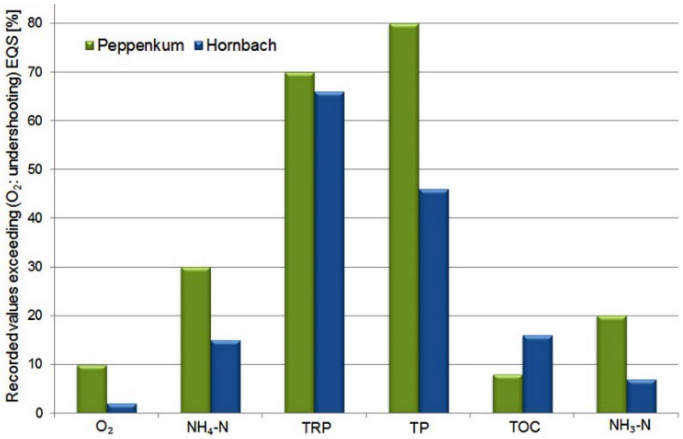

Fig. S-5. Recorded values exceeding EQS (for O2: undershooting EQS) in % of total readings for monitored parameters (hourly means) at Peppenkum and Hornbach from 20 October 2017 to 24 March 2018.

Table S-6.

Environmental quality standards in France (SEQ-Eau: Indice d'aptitude: 60*) and Germany (river type 5.1)

	unit	France	Germany
NO_3-N	[mg L^{-1}]	11.3	11.3
NO_2-N	[mg L^{-1}]	0.09	0.03
NH_4-N	[mg L^{-1}]	0.38	0.1
TRP	[mg L^{-1}]	0.17	0.07
TP	[mg L^{-1}]	0.2	0.1
TOC / DOC	[mg L^{-1}]	7	7
NH_3-N	[µg L^{-1}]	nn	2
pH		6 - 9	6.5 – 8.5
O_2	[mg L^{-1}]	6	8
temperature	[°C]	21.5	20

* Arrêté du 25 janvier 2010 relatif aux méthodes et critères d'évaluation de bon l'état écologique, de bon l'état chimique et du potentiel écologique des eaux de surface pris en application des articles R. 212-10, R. 212-11 et R. 212-18 du code de l'environnement

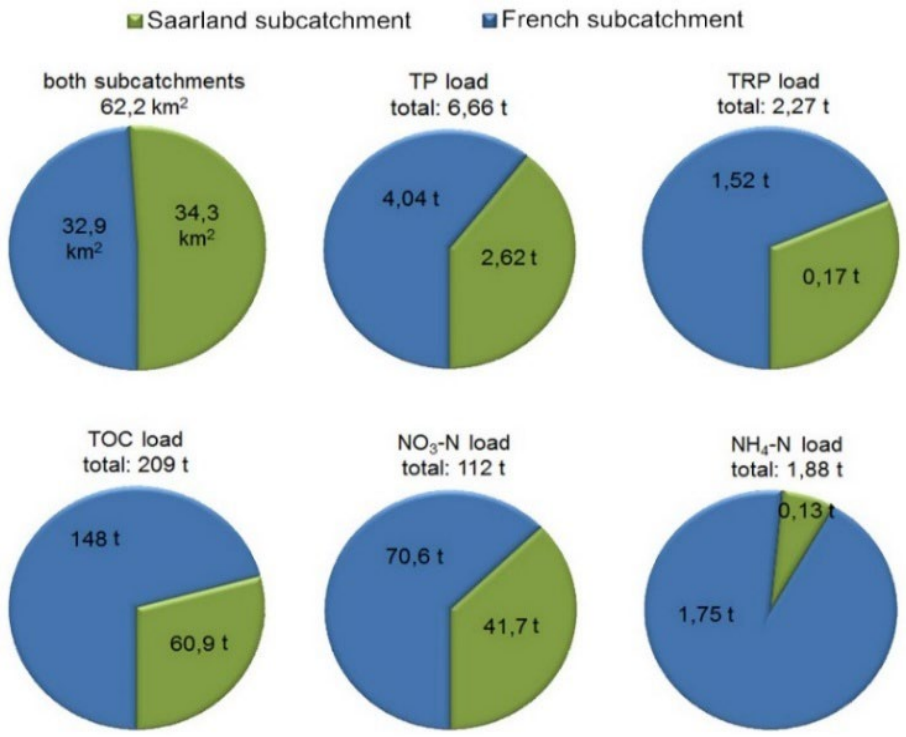

Fig. S-7. Surface portions and loads of TP, TRP, TOC, NO_3-N and NH_4-N in the French and Saarland subcatchments in relation to total loads - Peppenkum and Hornbach monitoring sites from 20 October 2017 to 26 March 2018.

2.3 In Situ Real-Time Monitoring of Ammonium, Potassium, Chloride and Nitrate in Small and Medium-Sized Rivers Using Ion-Selective-Electrodes – a Case Study of Feasibility

Extended Abstract

Small and medium-sized rivers with flashy hydrology are particularly vulnerable to anthropogenic and climatic stressors, including wastewater discharges, CSOs, agricultural runoff, road salting, and prolonged dry periods. Due to their limited dilution capacity and rapid response to external inputs, these river systems often experience abrupt and short-lived changes in water quality that are difficult to capture using conventional monitoring approaches based on manual grab sampling. High-frequency, in situ, real-time monitoring is therefore essential to identify pollution sources, understand transport pathways, and provide a sound basis for the planning of efficient and cost-effective measures to improve the chemical and ecological status of rivers.

Ion-selective electrodes (ISEs) represent a potentially attractive technology for high-frequency river monitoring. They are comparatively low in cost, compact, energy self-sufficient, and capable of measuring of multiple ions simultaneously without the need for reagents or sample pretreatment. While ISEs are well established in laboratory applications and have been successfully applied in wastewater systems and larger rivers, their long-term applicability in small and medium-sized rivers remains insufficiently explored. This is mainly due to the specific challenges posed by low analyte concentrations, strong and rapid temperature fluctuations, varying ratios of target to interfering ions, and sensor drift caused by membrane ageing and biofouling.

In this study, the suitability of ISE for in situ, real-time monitoring of ammonium, nitrate, potassium, and chloride in small rivers was systematically investigated under real field conditions. ISE systems from three different manufacturers were deployed over a five-month period (August 2022 to January 2023) at a monitoring station on the Bickenalb River (Saarland, Germany), a small rural river with a catchment area of 79 km² dominated by agricultural land use. The sensors were operated at five-minute intervals in a flow-through basin continuously supplied with untreated river water.

The ISE measurements were validated against established reference methods. Real-time ammonium data were obtained from a photometric analyser and a gas-sensitive analyser, nitrate data from an optical UV probe, and all four target ions were additionally analysed in grab samples using ion chromatography and photometric cuvette tests. The evaluation focused on key challenges relevant for small river applications: low concentration levels, temperature sensitivity, interference from non-target ions (particularly potassium interference with ammonium and chloride interference with nitrate), calibration stability, long-term drift, and sensor lifetime.

Overall, good agreement between ISE data and reference measurements was observed for nitrate and chloride across most of the monitoring period. For these ions, ISEs proved sufficiently robust for long-term deployment and reliable event detection, even under dynamic hydrological conditions. Potassium measurements were generally comparable to ion chromatography results, but several sensors showed drift after approximately five months of operation, indicating limitations in sensor lifetime in low-concentration matrices.

Ammonium measurements posed the greatest challenge. Typical background concentrations in the river were often below 0.1 mg L^{-1}, close to or below the detection limits of several ISE systems. As a result, the absolute ammonium concentrations derived from ISEs frequently deviated from those obtained by reference analysers, and some probes were unable to reliably quantify low background levels.

Nevertheless, pronounced ammonium input events, such as those associated with CSOs, were consistently detected by all ISE systems, demonstrating their suitability for qualitative event monitoring.

Temperature effects emerged as the most critical limitation for quantitative ISE application in highly dynamic small rivers. Despite built-in temperature compensation, strong diurnal and event-driven temperature fluctuations caused systematic oscillations and offsets in ISE output signals, particularly for cations at low concentrations. Interference from non-target ions was generally of secondary importance, although overcompensation for potassium interference in ammonium measurements was observed for some sensor types. In contrast, compensation for chloride interference in nitrate measurements proved to be largely adequate.

Contrary to expectations, no significant biofouling-induced drift was observed during the deployment period, likely due to regular maintenance and relatively short exposure times. However, membrane ageing and signal drift became apparent after several months, especially for ammonium and potassium sensors, limiting their effective lifetime under the given conditions.

In conclusion, ISEs show considerable potential as cost-effective tools for high-frequency river monitoring, particularly for event detection and source identification of nitrate, chloride, potassium, and ammonium. However, their current performance is insufficient for reliable quantitative assessment of low ammonium concentrations or regulatory compliance monitoring in small rivers. Further development is urgently needed, especially with regard to improved temperature compensation strategies and optimised interference correction algorithms. Advances in membrane materials and signal processing are expected to significantly enhance the robustness and accuracy of ISEs, enabling their broader application in comprehensive and economically feasible river monitoring networks.

These results have been published in Environmental Science - Advances:

Angelika M. Meyer, Elisa Oliveri, Ralf Kautenburger, Christina Hein, Guido Kickelbick, Horst P. Beck (2025)

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Table 6: Author contribution roles for the publication "In situ real-time monitoring of ammonium, potassium, chloride and nitrate in small and medium-sized rivers using ion-selective electrodes – a case study of feasibility" in form of the CRediT standard.

Contributor roles	**Author(s)**
Conceptualisation	Angelika Meyer, Elisa Oliveri, Ralf Kautenburger
Methodology	Angelika Meyer
Validation	Angelika Meyer
Formal analysis	Angelika Meyer
Investigation	Angelika Meyer, Elisa Oliveri
Writing – original draft	Angelika Meyer
Writing – review and editing	Christina Hein, Ralf Kautenburger, Guido Kickelbick, Horst P. Beck
Visualisation	Angelika Meyer
Data curation	Angelika Meyer,
Supervision	Ralf Kautenburger
Project administration	Guido Kickelbick
Resources	Guido Kickelbick
Funding acquisition	Horst P. Beck

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In situ real-time monitoring of ammonium, potassium, chloride and nitrate in small and medium-sized rivers using ion-selective-electrodes – a case study of feasibility†

Angelika M. Meyer, * Elisa Oliveri, Ralf Kautenburger, Christina Hein, Guido Kickelbick and Horst P. Beck

Real-time measurements are particularly important for monitoring especially small and medium-sized highly dynamic rivers. Their results are indispensable for planning (cost)efficient measures to improve the chemical and ecological quality of the rivers. It is therefore expedient to be able to use cost-effective, reliable equipment. In theory, ion-selective electrodes (ISEs) are excellently suited for this purpose due to their cost-effectiveness, their high spatial flexibility and their self-sufficient energy supply for the simultaneous recording of different parameters. In practice, however, malfunctions occur caused by temperature changes, interferences of non-target ions or long-term-drifts. This study investigated the applicability of ISEs for *in situ* real-time measurement of ammonium (NH_4^+), potassium (K^+), chloride (Cl^-) and nitrate (NO_3^-) in small rivers. ISEs from three different manufacturers were deployed for five months in a river monitoring station. The measured data were compared with real-time data gained from an on-line photometer, a gas-sensitive analyser and an optical UV probe as well as with grab samples analysed using ion chromatography (IC). Special attention was given to the challenges posed by low concentrations, temperature fluctuations, concentration changes of the analytes, and interfering ions, as well as to the long-term stability and the lifetime of the ISEs. For Cl^- and NO_3^- good agreements with the comparative measurements were found, and it could be shown that the ISEs are well suited for event detection of all four observed parameters. Temperature compensation is the main challenge that complicates application in highly dynamic rivers. Therefore, further optimisation is urgently needed for reliable quantitative analysis, which is part of future work.

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Environmental significance

A precise understanding of the processes taking place in water bodies is an important prerequisite for successful management measures. Since it is more feasible to implement effective measures in the upper regions of the water systems than downstream to improve chemical water quality and ecological status of the rivers, the monitoring of smaller rivers has increasingly become the focus of attention in recent years. To plan such measures, the kind and the sources of pollution and their transport pathways must be known. To this end real-time measurements in smaller rivers are indispensable. However, it is very important to have inexpensive, robust and reliable measuring devices for installation in the field. This study takes a critical look at ion-sensitive probes for *in situ* use in small and medium-size rivers. We report on advantages and drawbacks and on technical issues which may bias their performance.

1 Introduction

Rivers worldwide are exposed to manifold stressors. Inputs from wastewater treatment plants, combined sewer overflows (CSOs), road runoff and a wide variety of industrial and agricultural discharges impair water quality and endanger aquatic ecosystems. Water withdrawals and the increase of dry weather periods hinder the dilution of pollutants in water bodies. This is particularly true for small rivers (catchment area 10 to 100 km^2) and medium-sized rivers (catchment area 100 to 1000 km^2)[1] with flashy hydrology, as these respond more directly to both weather influences and human impacts than larger water bodies.

River monitoring is, at present, typically done by manual sampling.[2] This carries the risk of samples being contaminated during the sampling process itself or during transport. Critical situations, such as anthropogenic inputs, have a particularly large impact on small and medium-sized rivers and are difficult to record. Moreover, weather-related influences may lead to

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sudden and excessive changes in water temperature, oxygen budget, salt content, or other parameters. High frequency monitoring is of vital importance for capturing environmental fluctuations, as it allows the identification of pollution sources, their transport pathways and the assessment of corresponding environmental impacts. Only high frequency monitoring data provide a valid basis for planning efficient and cost-effective measures to improve the chemical and ecological status of a river.[3–6] This is true especially for land consuming measures which are usually easier to implement in smaller upstream catchments than in the downstream catchment.

For high frequency monitoring some, in particular physico-chemical, parameters such as oxygen, temperature, pH or electrical conductivity (eC) can be recorded *in situ*, at low cost and with little maintenance effort. Optical sensors also allow *in situ* real-time measurements of NO_3^-, dissolved organic matter (DOC), turbidity and chlorophyll. More complex approaches for measuring sum parameters have also been described for *in situ* application.[7,8] Other parameters relevant for source detection, such as NH_4^+ or phosphorous, are often realised by elaborated, cost-intensive measured methods, such as wet chemistry analysers.[2,9,10] This makes real-time monitoring of rivers rather complex, in particular with regard to the required infrastructure.[11,12] *In situ* ion-selective electrodes (ISEs), in contrast, offer a cost-effective, flexible alternative providing a high spatial and temporal resolution. While ISEs are widely recognised for laboratory applications in fields such as medicine, pharmacy and industry,[13–16] they have also been adapted for environmental monitoring, including handheld devices for single measurements.[17,18] Their use for online measurements in wastewater systems,[19–25] and larger rivers,[19,26] has been documented. ISEs offer distinct advantages as they can be installed *in situ*, are unaffected by turbidity and colour of the water, and, unlike analysers, do not require sample pre-treatment nor reagents. They are usually miniaturised, energy self-sufficient (powered by batteries or solar energy), and most of them even enable direct remote data transmission.[4,22,27–31]

Due to membrane ageing, reversible and irreversible biofouling the sensor accuracy is affected. Additionally, membrane bleeding in low concentration matrices influences the membrane quality. Both effects can lead to a decrease in signal stability and can cause the response time to slow down.[2,3,5,16–25,27,29,32–34]

In addition, the ISE accuracy is affected by temperature changes and interferences from other ions present in the matrix as well as from its total ion concentration (total ionic strength). These effects pose a particular challenge in small and medium-sized rivers. The concentrations in the rivers are lower than in conventional ISE applications such as wastewater systems. Abrupt changes in water temperature and concentration ratios of analytes to interfering ions are also possible, unlike in larger rivers. These increased demands on the measurement technology could be the reason why hardly any applications for intensive long-term real-time monitoring with ISEs in small rivers have been described so far.

In the present study we investigate the suitability of ISEs from three different manufacturers to monitor the concentration of NH_4^+, NO_3^-, K^+ and Cl^- in the small Bickenalb River (Saarland, Germany). The ISEs were deployed in a river monitoring station for five months (19.08.2022–03.01.2023) (Fig. S1†). The ISE data collected at a 5 minutes interval were compared with the values measured from other online measuring devices (photometric and gas-sensitive analysers for NH_4^+ and an optical UV probe for NO_3^-) and with laboratory analyses (IC and cuvette tests) of grab samples (Chapter 2.3.4).

The data measured by the ISEs for the relatively low analyte concentrations in the river were evaluated focusing on disturbances due to temperature fluctuations, dynamic concentration changes of interfering non-target ions, the calibration intervals, long-term stability, and lifetime of the ISEs.

2 Materials and methods

2.1 Working principle of ISE measurements

ISEs work on the principle of potentiometric analysis, where the measurement signal is an electrical potential (V mV^{-1}) and is converted into an ion concentration reading.

According to the Nernst eqn (1), the electrical potential E depends in a ln-linear relationship on the activity α_i of the analyte ion i in the sample solution and is calculated by:

$$E(a_i) = E^0 + \frac{RT}{zF}\ln(a_i) \quad (1)$$

where E^0 (mV) is the standard electrode potential, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), z is the ionic charge, and F is the Faraday constant (96 485C mol^{-1}).[35] The ion activity α_i is also called effective concentration. For lower ion concentrations, as they occur in small and medium-sized rivers, the ion activity can be approximated by the ion concentration in the sample solution.

As per the Nernst eqn (1), the slope of an E *vs.* $\ln(\alpha_i)$ plot is 59.2 mV per decade for monovalent cations and −59.2 mV per decade for monovalent anions at room temperature (25 °C). For divalent cations, the slope is 24.5 mV per decade and for divalent anions −24.5 mV per decade. According to literature, the slope indicating ISE sensitivity can deviate from these theoretical values due to effects within the membrane ranging between 54 and 60 mV per decade for monovalent ions such as NH_4^+, NO_3^-, K^+ and Cl^-.[14,16,17,26,29,30,36–38] The value of E^0, however, is not constant as in simple theory suggests. It depends on the type and performance of the membrane and can only be determined through calibration runs. These runs need to be repeated periodically since E^0 may furthermore change due to membrane aging during use.

Further details on the functionality of ISEs can be found in Cammann.[39] Common ISE materials and designs are presented by Bakker.[40]

2.2 Influencing parameters

2.2.1 Temperature. As can be seen from the Nernst eqn (1) the temperature has a significant influence on the measured potential, and consequently on the respective output value.[41] It is thus imperative to simultaneously record matrix temperature and adjust the measured values accordingly. To facilitate this,

most ISEs include a built-in temperature sensor that provides data values for the mathematical correction of the output data. Nevertheless, other parameters are also temperature sensitive, such as the standard electrode potential (E^0), the ion activity coefficient and the solubility of the complexes of the respective target ions.[32]

Temperature dependence of the ISEs is of particular importance for their application in small and medium-sized rivers, especially during summer, as water temperature can fluctuate by several degrees Celsius, potentially reaching an amplitude of 15 °C within just a few days.

2.2.2 Interfering ions. In addition to the temperature, non-target ions can also influence the measurement. An ISE is never completely selective for a single analyte ion. Other ions dissolved in the solution may interfere, either due to similar charge density, similar ion size or due to forming hydrate shells of similar size. The degree of interference of a non-target with the target ion can be described as cross-sensitivity. In the Nikolsky–Eisenmann eqn (2) as extension of the Nernst equation, cross-sensitivity can be described by introducing a selectivity coefficient K_{ij} for each target ion:

$$E(a_i) = E^0 + \frac{RT}{z_i F}\ln\left[a_i + \sum\left(K_{ij}\, a_j^{z_i/z_j}\right)\right] \quad (2)$$

where z_i and z_j are the ion charges and α_i and α_j the ion activities of the analyte ion i and the interfering ions j respectively.[40]

Eqn (2) describes the sum of all interfering factors affecting the measured signal. The ISE sensor's ability to distinguish the ion to be measured (target ion) from interfering (non-target) ions is described as selectivity. Since selectivity strongly depends on the structure and material of the membranes and electrodes used, selectivity coefficients specific to each ISE system must be established to define the respective ISE's ability to distinguish between target and non-target ions.[13]

A comprehensive overview of potentiometric selectivity coefficients for various ISEs is given by Umezawa *et al.*[48,49] K^+ is the predominant ion for interfering with NH_4^+ and Cl^- predominant for interfering with NO_3^-, respectively, while NH_4^+ and NO_3^- are of fundamental significance for both river monitoring and management.[19] Both K^+ and Cl^- prominently figure in freshwater ecosystems, being naturally present in all rivers in varying concentrations (natural background).[42] Typically, natural surface waters contain less than 5 mg per L K^+.[43,44] Cl^- contents in saline-free catchments range between 10 to 30 mg L^{-1} (in saline waters over 100 mg L^{-1}).[43] Human activities may result in additional K^+ and Cl^- inputs. These inputs from treated and/or untreated wastewater, fertilisers, manure (one of the main sources of K^+), road salt (one of the main sources of Cl^-), waste disposal, water softening or industrial discharges can cause abrupt rises in K^+ and Cl^- levels, decreasing with precipitations.[42,45–47] This is why it is necessary to deal with possible interferences when deploying ISEs, especially in solutions of unknown composition. Cecconi *et al.*, for example, report a cross-sensitivity of 1 : 22 for NH_4^+/K^+,[22] Winkler *et al.* a cross-sensitivity of 1 : 15 to 1 : 30 for NH_4^+/K^+ and of 1 : 300 for NO_3^-/Cl^-.[19] Papias *et al.*, on the contrary, report a cross-sensitivity of 1 : 25 for NH_4^+/K^+, while considering the cross-sensitivity for NO_3^-/Cl^- negligible.[21] Some ISE system manufacturers answer this problem by incorporating built-in measurement and compensation of the most figuring interfering non-target ion.

In case of river monitoring, the matrix to be measured contains a vast number of different substances in different concentration ranges, and thus for each target ion there may be some interfering ions. Especially in small and medium-sized rivers, the concentration ratios of many substances can change very quickly due to anthropogenic inputs or weather conditions. Other cations present in the river water such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), or anions such as sulphate (SO_4^{2-}) and carbonate (CO_3^{2-}) play a minor role as interfering ions due to their differing size or charge.

2.2.3 Drifting. Drifting can endanger the quality of the measured data, especially in long-term use. It can be caused by bleeding of the membranes due to the osmotic gradient between the internal solutions of the ISE and the ambient sample, especially during long-term measurements in low concentration matrices.[3,5,16,17,25,27,29,32–34] In the laboratory, this can be counteracted by adding a so-called (total) ion strength adjustment buffer ((T)ISAB).[22,32] However, this approach unnecessary in river monitoring, due to the naturally sufficient ion concentrations in most river waters. Additionally, drifts can occur as consequence of the incorporation of different ions into the membrane material leading to membrane ageing. Reversible und irreversible biofouling and clogging processes also influence the membrane quality and present a significant challenge, especially in *in situ* river monitoring. To counteract potential biofouling, manufacturers and/or users apply wipers, ultrasonic treatment, air flushing, or UV light to the membrane.[5,19,22]

2.2.4 Limits of detection and measuring ranges. A particular challenge considering the definition of ISEs' limits of detection (LOD) is that ISEs have a non-linear response close to the LOD. The LOD also depend on the random signal noise and the uncertainty of the instrumental parameters (*e.g.* ionophore selectivity, membrane stability and reference electrode stability) used to acquire the calibration data.[50] Therefore, all LOD estimates are subject to uncertainties. According to the IUPAC definition for ISEs, Fayose,[51] reports a LOD of 5.3×10^{-6} M (0.09 mg L^{-1}) for NH_4^+ and 3.1×10^{-6} M (0.2 mg L^{-1}) for NO_3^- as first estimates of the range within which ISEs can be meaningfully used. In literature, the LODs of NH_4^+ vary from 8×10^{-6} mol L^{-1} (0.144 mg L^{-1}),[36] *via* 10^{-5} mol L^{-1} (0.18 mg L^{-1}),[37] and 2×10^{-5} mol L^{-1} (0.36 mg L^{-1})[38] to the highest LOD of 10^{-4} mol L^{-1} (1.80 mg L^{-1}).[30] The LODs of K^+ are in a similar molar range and differ between 10^{-5} mol L^{-1} (0.39 mg L^{-1})[52] and 10^{-4} mol L^{-1} (3.9 mg L^{-1}).[30] However, all LODs found for NO_3^- are lower than the LODs for NH_4^+ and K^+. They vary between 4×10^{-6} mol L^{-1} (0.248 mg L^{-1}),[36] 10^{-5} mol L^{-1} (0.62 mg L^{-1}),[26] and 3×10^{-5} mol L^{-1} (1.86 mg L^{-1}).[14] With regard to the monitoring of NH_4^+, NO_3^-, K^+ and Cl^- in river water, the LOD may only pose a problem for NH_4^+, the other parameters generally occur in concentrations far above the LODs. Compared to other analysis techniques, ISEs provide an exceptionally wide measurement range. The measurement

range varies depending on the selected target ion as well as the electrode design and material.

ISE measuring ranges vary depending on the pH of the matrix.[6,53] However, pH limits specified by manufacturers are suitable for the typical pH range in natural rivers of pH 5 to 9.

2.2.5 Response time. Generally, ISEs have a short response time which of course makes them ideal for use in real-time monitoring. The response time also depends on the membrane material. Mettler Toledo (Columbus, US), for example, gives a response time of 3 to 5 minutes for crystalline and glass membranes, and of 5 to 8 minutes for polymer membranes. There are many different types of ISEs on the market, including for on-site use and online measurement.

2.3 Specification of the deployed ISE systems, handling and comparative measurements

2.3.1 Specifications of the deployed ISE systems. For this case study, two identic AN-ISE probes from Hach (Duesseldorf, Germany), one K16 probe from Seba (Kaufbeuren, Germany) and one AquaTROLL 600 multiparameter probe from *In Situ* (Fort Collins, USA) were used.

The Hach AN-ISE combination probe for NH_4^+ and NO_3^- was the only probe tested that features automatic and simultaneous K^+ and Cl^- compensation. All four sensors as well as the reference and the temperature sensor are combined in one cartridge to making it fully replaceable as a plug-in system. The filling solution cannot be renewed. If one sensor malfunctions, the entire cartridge must be replaced.

In addition to the AN-ISE with fixed parameter combination, the Seba K16 is a plug-in design that can accommodate up to twelve sensors. For this study, the K16 had been equipped with sensors for NH_4^+, NO_3^-, K^+, Cl^- and pH, including temperature sensor. In this system, the NO_3^- ISE is not refillable, while the NH_4^+ and the K^+ ISE can be refilled, but it is not recommended by the manufacturer.

The *In Situ* AquaTROLL 600 is a fully customisable multiparameter probe for variable sensors having been equipped with sensors for NH_4^+, Cl^- and a sensor for eC, including temperature. An add-on wiper with a wiping frequency of 5 minutes had also been attached. The AquaTROLL NH_4^+ and Cl^- sensors each have a dedicated refillable reference allowing independent measurements. The filling solution (KCl) was replaced before every calibration.

All deployed systems provide built-in temperature compensation. For further information of all ISEs tested see Table S1.†

2.3.2 ISE preparation and maintenance. Before first use, the ISEs were submerged in tap water, in conditioning solution with a specified concentration of the respective analyte, or in the matrix (as specified by manufacturer) to allow the system to swell.

During the case study, the ISEs were rinsed once a week with tap water and then carefully cleaned with a soft cloth. In addition, the membranes of the Cl^- ISEs were polished once a month according to manufacturer's instructions, since Cl^- is a solid-state electrode in contrast to the polymer membranes used for the other ions.

2.3.3 ISE calibration. Calibration was done in river water to account for matrix effects. Since the electrode response during the calibration process is temperature sensitive, calibration was carried out at the actual temperature of the river water. First, a 5-L sample of river water was filled into a bucket. If the current NH_4^+ values from the online analysers (photometric and gas-sensitive) were below 0.5 mg L^{-1}, the sample was spiked with NH_4Cl. Subsequently, photometric cuvette tests were deployed to determine the solution's exact NH_4^+, NO_3^- and Cl^- concentrations. The ISE probes were attached to a magnetic stirrer 10 512 (Fisher Bioblock Scientific, Illkirch, France) in the sample bucket to generate a flow towards the membranes. It was made sure that all sensors were always completely submerged in the solution and the membranes kept free of air bubbles. After 30 minutes for stabilisation, the first point at matrix concentration was calibrated. Then a combination standard was added to the solution (5 mg per L NH_4^+, 20 mg per L NO_3^-, 20 mg per L K^+ and 40 mg per L Cl^-), and the solution was analysed again using cuvette tests. After another 30 minutes, the second point was calibrated.

2.3.4 Comparative measuring methods and devices. The real-time, on-site ISE output data for NH_4^+ were compared with real-time data from an Amtax inter 2 photometric analyser (indophenol-blue method, measuring range 0.026–2.6 mg per L NH_4^+, Hach, Duesseldorf, Germany) and an Amtax sc gas-sensitive measurement unit (measuring range 0.026–6.4 mg per L NH_4^+, Hach, Duesseldorf, Germany) both supplied by a Hach Filtrax filtration system with ultra-filtration membranes 0.15 μm installed at the monitoring station. In contrast to the ISEs, the two Amtax systems detect both NH_4^+ and NH_3, whereby the proportion of NH_3 in river water is usually negligible. The Amtax systems measure at intervals of 10 minutes.

The ISE output data for NO_3^- were compared with real-time data from a Nitratax optical UV probe (measuring range 2–100 mg per L NO_3^-, without sample pre-treatment, Hach, Duesseldorf, Germany) measuring at 5-minutes intervals.

The ISE output data for all four ions were compared with grab samples, which were analysed in the laboratory using IC (Eco-IC Metrosep A Supp 17 and Metrosep C6, Metrohm, Herisau, Schweiz), with the following measuring ranges: NH_4^+: 0.1–10 mg L^{-1}, NO_3^-: 0.25–50 mg L^{-1}, K^+: 0.25–50 mg L^{-1} and Cl^-: 0.75–150 mg L^{-1}. Additional comparative measurements for NH_4^+, $Cl^-$and NO_3^-were made at the monitoring station using a photometric cuvette test system (LCK303, LCK304, LCK311, LCK339 tests) with a DR3900 photometer from Hach (Duesseldorf, Germany).

2.3.5 Chemicals used. All solutions required for calibration were prepared with the following salts in ultrapure water. The salts ammonium chloride (NH_4Cl), potassium nitrate (KNO_3) and potassium chloride (KCl) have a purity >99% and were supplied by Gruessing (Filsum, Germany). For the photometric analysis, the cuvette tests LCK303, LCK304, LCK311 and LCK339 from Hach (Duesseldorf, Germany) were used. For the gas-sensitive and photometric online ammonium analysis the reagent kits LCW889 and LCW802 from Hach were used for the online ammonium analysis. For the IC analysis, NH_4Cl

(Honeywell Research Chemicals, purity >98%, Morris Plaines, USA), oxalic acid dihydrate as well as sodium nitrate and potassium chloride with a purity >99%, 0.02 M dipicolinic acid, sulphuric acid (95–97%) and nitric acid (65%) (Merck, Darmstadt, Germany) were used.

2.4 Case study: Bickenalb river

The ISE systems described above were deployed in a mobile monitoring station for a period of five months from 19th August 2022 until 3rd January 2023. Due to supply bottlenecks, the device could only be used from October 24th.

With this long-term research we wanted to demonstrate the applicability of ISEs for monitoring small and medium-sized rivers under real conditions. The probes were placed into a flow-through sample basin continuously pumped with untreated river water. Further details can be found in Fig. S1† and Meyer *et al.*[11] The station was located in Altheim at river kilometre 10 (Fig. S2†), in the German–French catchment of the Bickenalb River, which covers a total area of 79 km^2. The catchment is predominantly rural with intensive agriculture on both French and German sides. Arable land covers 42%, pastures and grassland 40%, forests 14% and residential areas make up only 4% of the catchment, with a population density of less than 70 persons per km^2. Further details are described by Meyer *et al.*[12]

Although the sensors were operated in the online monitoring station, operation as well as maintenance and calibration are possible without the infrastructure of the station like current power supply.

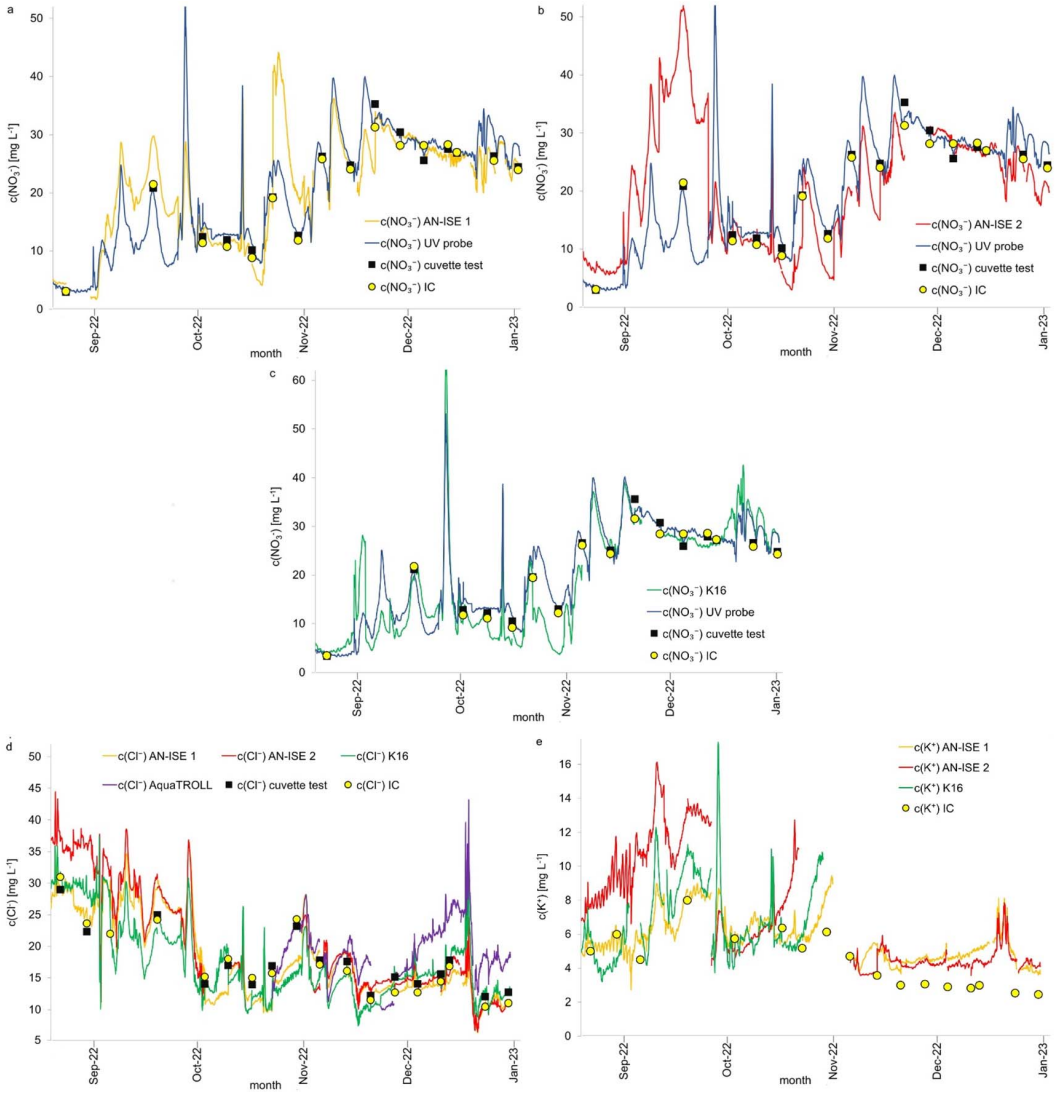

Fig. 1 Concentration data of NO_3^-, Cl^- and K^+ as given by ISEs and comparative measuring methods: comparison of NO_3^- data as given by UV probe, IC and cuvette tests with readings from (a) AN-ISE 1, (b) AN-ISE 2 and (c) K16. (d) Comparison of Cl^- data as given by IC and cuvette tests with AN-ISE 1, AN-ISE 2 and K16 readings. (e) Comparison of K^+ data as given by IC with AN-ISE 1, AN-ISE 2 and K16 readings; Bickenalb River, 19.08.2022–03.01.2023.

3 Results and discussion

3.1 Case study measuring conditions

The water temperature recorded during the case study from 19th August 2022 until 3rd January 2023 in the Bickenalb River station ranged from 1.7 to 22.5 °C, pH from 7.51 to 8.83, and eC from 180 to 907 µS cm^{-1}. NH_4^+ concentrations as measured by the gas-sensitive analyser ranged from below detection limit to 6.3 mg L^{-1}, NO_3^- (UV probe) from 2.59 to 50.9 mg L^{-1}, K^+ (IC) from 0.75 to 8.24 mg L^{-1} and Cl^- (IC) from 10.5 to 24.8 mg L^{-1}.

3.2 Validation of ISE data

All data shown are unprocessed raw data – as concentrations given by the ISEs – as it is impossible to realistically depict rapid changes in concentrations retrospectively by computer-aided data processing. In addition, the raw data can directly be compared with the data from the other measuring devices and enable to assess the suitability of the probes for a direct realistic representation of the concentrations in the river.

In order to validate recorded ISE output values, they were compared with the corresponding NO_3^- and NH_4^+ data routinely collected by the validated methods in the monitoring station. In addition, random samples were analysed for all four target ions, using cuvette tests on site and IC in the laboratory. For a more detailed description see Chapter 2.3.4.

3.2.1 NO_3^-. Plotting the ISE NO_3^- readings against the real-time data from the UV probe shows an acceptable correlation for all three probes and across most of the measurement period (Fig. 1a–c). Furthermore, grab samples were analysed for NO_3^- using IC and cuvette tests with both methods showing a good correlation with the real-time data.

3.2.2 Cl^-. The ISE Cl^- readings were validated by analysing grab samples using IC. Besides IC analysis, cuvette tests were deployed also, showing a relatively good correlation with the IC data. As evident from Fig. 1d, the ISE readings for Cl^- generally align with the values from the random samples. Larger deviations in the measured values are due to calibration problems.

3.2.3 K^+. The ISE K^+ readings were also validated through grab sampling and IC analysis. Fig. 1e shows that the background concentration values output by AN-ISE 1 and K16 are at least comparable with the IC results. However, the AN-ISE 2 showed different results initially, undergoing the same treatment and calibration as AN-ISE 1 and K16. All three ISEs developed a drift in K^+ (and also for NH_4^+) output values after 20–22 weeks of total operating time. As K16 ISEs for both K^+ and NH_4^+ could not be replaced due to supply bottlenecks, no more

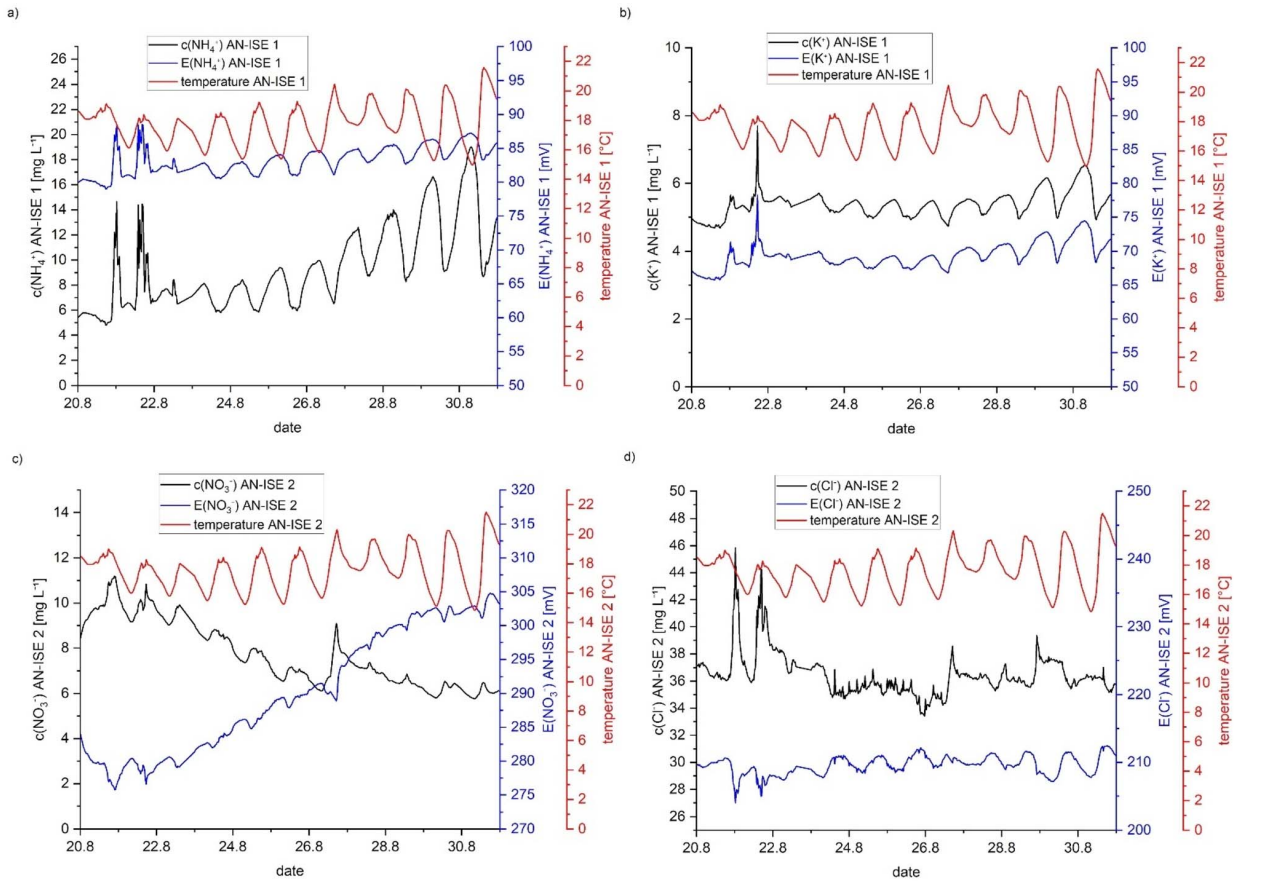

Fig. 2 Temperature dependent fluctuations in the mV signals and concentration readings of (a) NH_4^+ (AN-ISE 1), (b) K^+ (AN-ISE 1), (c) NO_3^- (AN-ISE 2), (d) Cl^- (AN-ISE 2); Bickenalb River, 20.–30.08.2022.

data could be recorded. The two AN-ISEs were upgraded with a new generation of cartridges (Chapter 3.3.4). This resulted in more reliable data.

3.2.4 NH_4^+. AN-ISE and K16 ISE readings for NH_4^+ concentrations are hard to validate, due to very low concentrations in the river water, typically below 0.1 mg L^{-1}. The AN-ISEs are unable to display or log concentration values below 0.1 mg L^{-1}, in contrast to the photometric analyser and the gas-sensitive analyser with both a detection limit as low as 0.025 mg L^{-1}. The K16 ISE was able to provide realistic data during certain periods (Fig. S3†). From the beginning of November, however, calibration was no longer possible because the lifetime of the K16 NH_4^+ electrode had expired (see K^+ data above). As the K16 ISEs for NH_4^+ and K^+ could not be replaced due to supply bottlenecks, no more data could be recorded. Only the AquaTROLL ISE, deployed from 24 October 2022, was able to measure lower concentration values. The AquaTROLL readings compare well with those from the two real-time analysers (Fig. S4†).

3.3 Common challenges of using ISE in small rivers

Apart from their practical the use of ISEs is associated with several critical challenges. The ISE method is affected by temperature changes, interferences from other ions present in the matrix, and the total ionic strength of the solution. Furthermore, ISEs tend to drift due to biofouling, membrane bleeding and aging. As these three aspects pose a major challenge, especially in small rivers, the measured values have been evaluated with regard to these aspects.

3.3.1 Calibration issues and measuring ranges. During the first two months of the present study, all sensors were two-point calibrated once a week according to the manufacturer's instructions (see Chapter 2.3.3). Sometimes, calibration led to data offsets or other incorrect measuring results. Other authors who have used ISEs in wastewater and river monitoring also report substantial calibration problems.[16,19,23,51] Therefore, the calibration intervals were extended. Additional recalibrations were performed immediately after impacts.

As expected, the measuring ranges proved sufficient, only in the case of NH_4^+ the very low basic contents of less than 0.1 mg L^{-1} could not be detected.

3.3.2 Temperature sensitivity. Due to low water levels and high air temperatures at the beginning of the field study, extensive day–night fluctuations in the water temperature were recorded. This is reflected in the mV signals from both AN-ISE probes (Fig. 2). Since the K16 gives no mV output, no data from the K16 can be shown in the figure.

This trend is evident in Fig. 2a–d: the anion concentrations (NO_3^- and Cl^-) exhibit parallel, the cation concentrations (NH_4^+ and K^+) show anti-cyclical behaviour relative to the temperature.

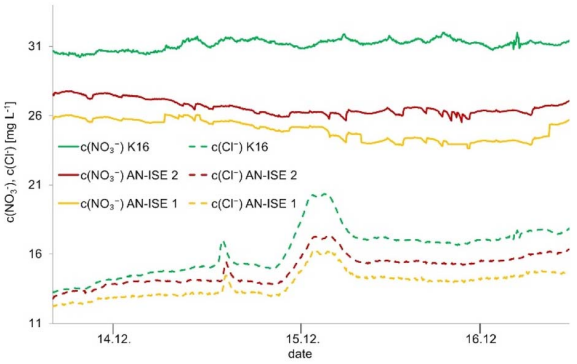

Fig. 4 Event detection: NO_3^- and Cl^- readings of AN-ISE 1, AN-ISE 2 and K16; Bickenalb River, 14.–16.12.2022.

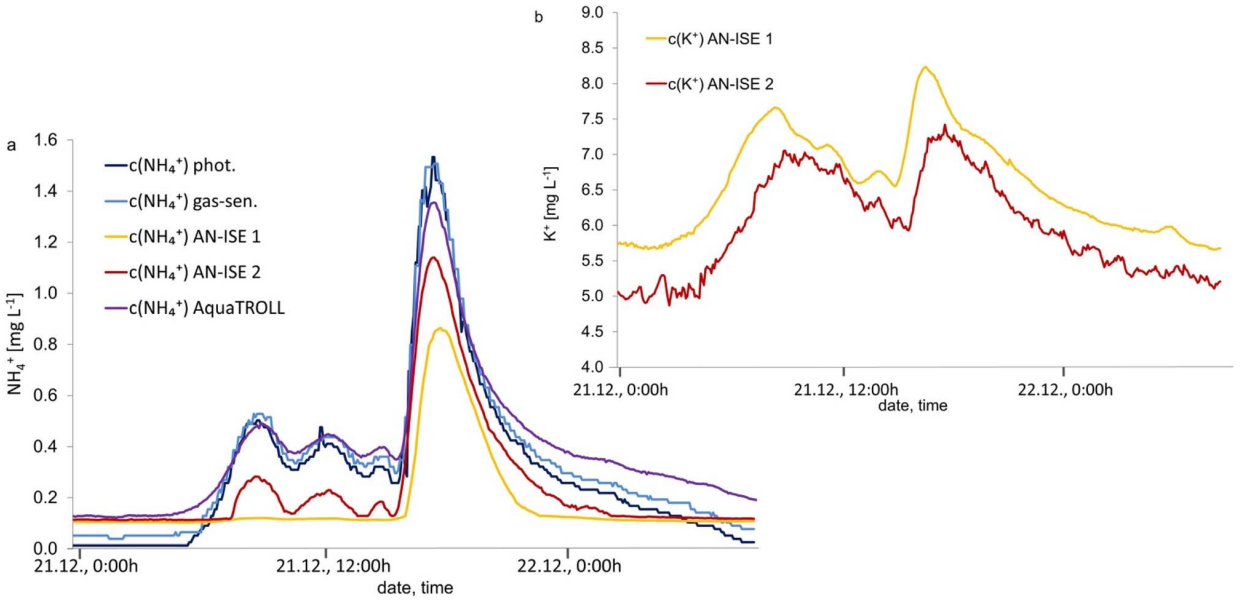

Fig. 3 (a) Event detection: NH_4^+ readings from the photometric and gas-sensitive analysers, AN-ISE 1 and AN-ISE 2 (with ion interference compensation) and AquaTROLL (without compensation), (b) K^+ readings from AN-ISE 1 and 2; Bickenalb River, 21.–22.12.2022.

Less expected, these fluctuations can also be noticed in the ISE concentration outputs, despite the presence of built-in temperature compensation. The amplitude of the cation signals is much greater, most likely due to the lower NH_4^+ and K^+ concentrations. In the case of NO_3^-, the amplitudes are less prominent, since in this period the NO_3^- concentration in the river was decreasing (Fig. 2c).

At the beginning of the measurement series (Fig. 2), two input events were recorded in close succession, with NH_4^+ and K^+, and to a lesser extent NO_3^-, being discharged into the water body. NH_4^+ concentration reached maximum values of approx. 5 mg L^{-1} (gas-sensitive analyser). This event was also recorded by the ISEs, however, there was an offset in the absolute NH_4^+ values from all three ISEs due to calibration problems. It must be pointed out that the mV signals for NH_4^+ and K^+ developed an increasing trend after this event. Due to rainfall starting at the beginning of September 2022, the water level increased while air and water temperatures decreased, with no such strong temperature fluctuations occurring in the further course of the measurement series.

As expected, temperature changes are a major problem. After having finished the field study a fit for temperature-correction of the output signals of the ISEs could empirically be determined in the laboratory. The procedure was based on an

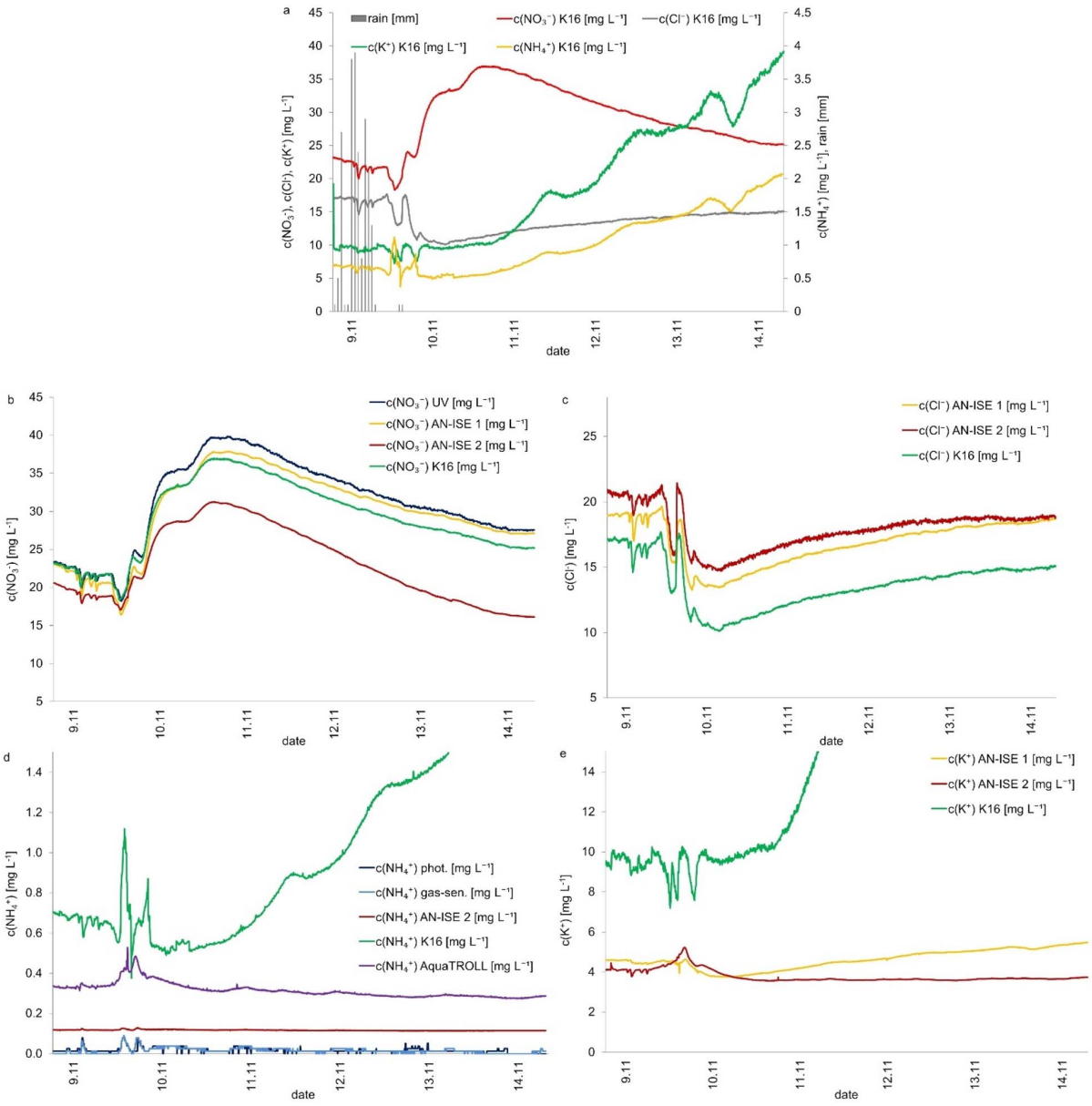

Fig. 5 Event *vs.* drift: (a) NH_4^+, NO_3^-, K^+ and Cl^- readings of K16 ISE, (b) NO_3^- readings of UV probe and AN-ISE 1, AN-ISE 2 and K16 ISEs, (c) Cl^- readings of AN-ISE 1, AN-ISE 2 and K16 ISEs, (d) NH_4^+ readings of photometric and gas-sensitive analysers and AN-ISE 2, K16 and AquaTROLL ISEs, (e) K^+ readings of AN-ISE 1, AN-ISE 2 and K16 ISEs; Bickenalb River, 09–14.11.2022.

approach of Le Goff *et al.*[32] The description of the application of this compensation to the online data is beyond the scope of this paper and will be published in a separate manuscript.

3.3.3 Influence of interfering ions. When measuring NH_4^+ and NO_3^- using ISEs, K^+ and Cl^- are the most common and relevant interfering ions. But the concentration ranges in which these interferences should become relevant vary extensively (Table S1†).

The AN-ISE probes deployed in this case study offer built-in additional sensors for the detection of the two non-target ions, which the target ion concentration output values are offset against. But this feature may also result in overcompensation and, consequently, incorrect outputs. Fig. 3 gives an example: the outputs from the AquaTROLL during an input from a CSO on 21st December accurately match the concentrations measured by both the photometer and the gas-sensitive probe, whereas the outputs from the two AN-ISEs for NH_4^+ are too low. Due to higher signal levels for K^+ and a correspondingly higher compensation in the AN-ISE 1, the resulting NH_4^+ output values are even lower than from the AN-ISE 2 (Fig. 3a and b).

It should be noted that an interference ratio of 1 : 27 is specified for the AquaTROLL, this means that 27 mg per L K^+ increases the NH_4^+ values by 1 mg L^{-1}. According to the manufactures of the AN-ISEs, 20 mg per L K^+ increase NH_4^+ values by 1.6 mg L^{-1}. Hence, the AN-ISEs are somewhat more K^+ sensitive than the AquaTROLL.

On 14th and 15th December, inputs of road salt were detected, increasing the Cl^- concentration by about 20% (Fig. 4).

However, none of the deployed sensors indicated any significant increase in NO_3^- values. The interference ratio of NO_3^- to Cl^- is typically lower than NH_4^+ to K^+, with manufacturers' specifications varying (Table S1†).

3.3.4 Drifting and lifetime. Due to their flashy hydrology, small and medium-sized rivers sensitively react to all kinds of input giving immediate leaps in the concentration of numerous substances. This makes the interpretation of online data very complex. Often, it is difficult to distinguish between real events and incorrect values, in particular with drifts involved. An example for such an event is given in Fig. 5.

After heavy rainfall on 9th November, the NO_3^- concentration increased over a longer period (Fig. 5a). This was caused by leaching and transport into the rivers *via* interflow – a phenomenon often observed in rural catchments in autumn. At the same time, Cl^- was diluted by rainfall and then slowly concentrated again. The same seemed to apply to NH_4^+ and K^+. Comparison of the K16 readings with the other ISE data and those from the UV probe and the two NH_4^+ analysers shows that the K16 data realistically represent NO_3^- and presumably also Cl^- concentrations (Fig. 5b and c). In contrast, for NH_4^+ and K^+ the K16 ISE, developed a substantial drift for both after the described event (Fig. 5d and e). The NH_4^+ readings of both K16 and AquaTROLL show an offset to the photometric and the gas-

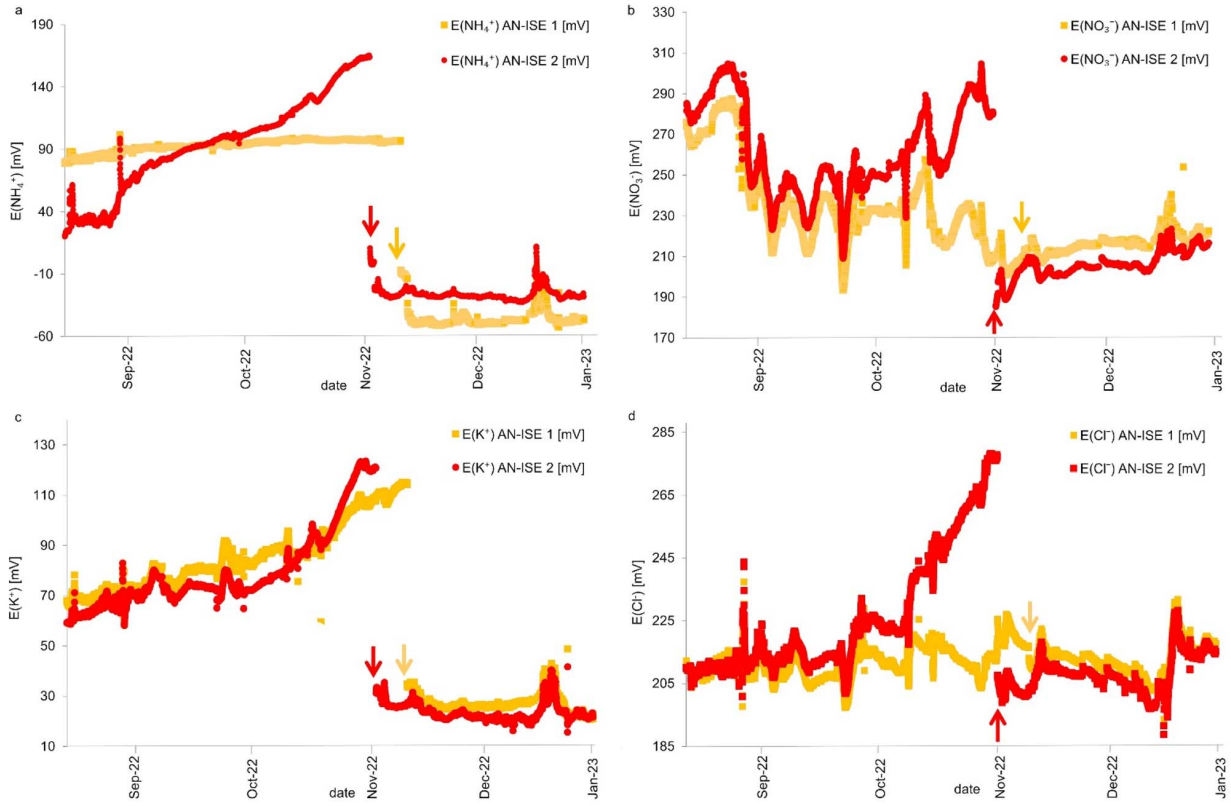

Fig. 6 Drift of mV signals: mV signals from AN-ISE 1 and 2 for (a) NH_4^+, (b) NO_3^-, (c) K^+ and (d) Cl^- over the entire measurement period (arrows: cartridge replacement).

sensitive methods due to calibration issues (Fig. 5d). The AN-ISE 2 reading is pinned to its detection limit of 0.1 mg L^{-1}.

Raw mV signals will, of course, reveal electrode drifting too, but they cannot be retrieved from every ISE system. Fig. 6 shows an example of mV signal drift: it can clearly be seen that the mV signals of the two identical AN-ISEs show a continuous drift in K^+ readings (Fig. 6c). The signals from the AN-ISE 2 show an additional drift in NH_4^+, Cl^- and NO_3^- data, despite identical treatment of both AN-ISE systems. The drift in NH_4^+ data (Fig. 6a) already occurred from the beginning of September, for Cl^- data (Fig. 6d) from mid-October, and for the NO_3^- ones (Fig. 6b) from the end of October. The reason for this could not be identified, as neither damage nor fouling could be detected. On 1st November the AN-ISE 2 cartridge was replaced, one week later the one of AN-ISE 1. According to the manufacturer, the new cartridges came with optimised NH_4^+ and K^+ sensors, which is underpinned by the larger mV range after replacing the cartridges. The new cartridge generation also helped to decrease the calibration problems with respect to NH_4^+ and K^+ readings, so that the reliability of the corresponding data improved significantly. It can be assumed that the NH_4^+ and K^+ sensors were corrupted by cation concentrations being too low, as the NH_4^+ and K^+ values from the K16 started drifting at the same time, moreover, the K16 could no longer be calibrated for NH_4^+ and K^+. Although the K16's NH_4^+ and K^+ sensors could not be replaced during the experimental timeline, the K16 continued to provide valid NO_3^- and Cl^- data. Since the K16 and the two AN-ISEs (with the first-generation cartridge) had been used in another monitoring station for two months prior to this study, it can be stated that the lifetime of the ISEs tested for NH_4^+ and K^+ in low concentration matrices is approximately 5 months and even longer for NO_3^- and Cl^-.

4 Conclusions

The present study investigates the feasibility of using commercial ISEs for real-time monitoring of NH_4^+, K^+, NO_3^- and Cl^- in small and medium-sized, highly dynamic rivers. The research was conducted over a five-month period, deploying ISEs from three different manufacturers at a water quality monitoring station at a small river. Factors such as interfering ions, temperature fluctuations, and electrode aging were investigated. During the measurement period, no drifts caused by biofouling were observed. Following the manufacturer's recommendation for weekly calibration led to unstable and incorrect results. Despite this, calibrations after significant temperature fluctuations or concentration changes showed positive effects. The device's built-in compensation for interference ion effects provided valid data for the AquaTROLL. The AN-ISE 1 and 2 overcompensated for K^+ interference in the NH_4^+ measurement, while the compensation for Cl^- in the NO_3^- measurements was acceptable across all probes. Overall, the built-in temperature compensation of all ISEs caused more problems than the interfering ions. This highlights the need for optimization with external compensatory algorithms, which are expected to be published soon. The comparison with other established online measurements showed that the absolute concentration from the ISEs can deviate considerably from the correct values. Additionally, the NH_4^+ detection limits of ISEs sensors are above river relevant concentrations. Therefore, the investigated ISEs are not reliable enough to control limit values or to serve as early warning systems, but they are suitable for event monitoring in rivers and detecting pollution sources. Ultimately, ISEs have the potential to make an important contribution to robust and comprehensive online monitoring that is also cost-effective. The development of new materials and, above all, the optimization of compensation algorithms to counteract temperature and interference would make ISEs even more suitable for river monitoring.

Data availability

All data used in this paper can be obtained from **https://www.gewaesser-monitoring.de**.

Author contributions

Angelika M. Meyer: conceptualisation, data curation, investigation, methodology, visualisation, validation, writing – original draft; Elisa Oliveri: conceptualisation, investigation; Ralf Kautenburger: conceptualisation, supervision, writing – review and editing; Christina Hein: writing – review and editing; Guido Kickelbick: project administration, resources, writing – review and editing; Horst P. Beck: funding acquisition, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 The European Parliament and The Council of the European Union, *Directive 2000/60/EC – EU Water Framework Directive*, 2000.
2 R. D. Harmel, H. E. Preisendanz, K. W. King, D. Busch, F. Birgand and D. Sahoo, A Review of Data Quality and Cost Considerations for Water Quality Monitoring at the Field Scale and in Small Watersheds, *Water*, 2023, **15**(17), 3110.
3 P. J. Blaen, K. Khamis, C. E. M. Lloyd, C. Bradley, D. Hannah and S. Krause, Real-time monitoring of nutrients and dissolved organic matter in rivers: Capturing event dynamics, technological opportunities and future

directions, *Sci. Total Environ.*, 2016, **569–570**, 647–660, DOI: 10.1016/j.scitotenv.2016.06.116.

4 G. A. Crespo, Recent Advances in Ion-selective membrane electrodes for *in situ* environmental water analysis, *Electrochim. Acta*, 2017, **245**, 1023–1034, DOI: 10.1016/j.electacta.2017.05.159.

5 J. Arndt, J. S. Kirchner, K. S. Jewell, M. P. Schluesener, A. Wick, T. A. Ternes and L. Duester, Making waves: Time for chemical surface water quality monitoring to catch up with its technical potential, *Water Res.*, 2022, **213**, 118–168, DOI: 10.1016/j.watres.2022.118168.

6 T. Forrest, T. Cherubini, S. Jeanneret, E. Zdrachek, P. Damala and E. Bakker, A submersible probe with in-line calibration and a symmetrical reference element for continuous direct nitrate concentration measurements, *Environ. Sci.: Processes Impacts*, 2023, **25**, 519–530, DOI: 10.1039/d2em00341d.

7 K. Murphy, B. Heery, T. Sullivan, D. Zhang, L. Paludetti, K. T. Lau, D. Diamond, E. Costa, N. O'Connor and F. Regan, A low-cost autonomous optical sensor for water quality monitoring, *Talanta*, 2015, **132**, 520–527, DOI: 10.1016/j.talanta.2014.09.045.

8 B. A. Pellerin, B. A. Stauffer, D. A. Young, D. J. Sullivan, S. B. Bricker, M. R. Walbridge, G. A. Clyde and D. M. Shaw, Emerging Tools for Continuous Nutrient Monitoring Networks: Sensors Advancing Science and Water Resources Protection, *J. Am. Water Resour. Assoc.*, 2016, **52**, 993–1008, DOI: 10.1111/1752-1688.12386.

9 P. Jordan and R. Cassidy, Perspectives on Water Quality Monitoring Approaches for Behavioral Change Research, *Front. Water*, 2022, **4**, 1–12.

10 A. V. Mueller and H. F. Hemond, Statistical generation of training sets for measuring NO_3(-), NH_4(+) and major ions in natural waters using an ion selective electrode array, *Environ. Sci.: Processes Impacts*, 2016, **18**, 590–599, DOI: 10.1039/c6em00043f.

11 A. M. Meyer, C. Klein, E. Funfrocken, R. Kautenburger and H. P. Beck, Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers, *Sci. Total Environ.*, 2019, **651**, 2323–2333, DOI: 10.1016/j.scitotenv.2018.10.069.

12 A. M. Meyer, E. Fuenfrocken, R. Kautenburger, A. Cairault and H. P. Beck, Detecting pollutant sources and pathways: High-frequency automated online monitoring in a small rural French/German transborder catchment, *J. Environ. Manage.*, 2021, **290**, 112619, DOI: 10.1016/j.jenvman.2021.112619.

13 G. Dimeski, T. Badrick and A. S. John, Ion Selective Electrodes (ISEs) and interferences-a review, *Clin. Chim. Acta*, 2010, **411**, 309–317, DOI: 10.1016/j.cca.2009.12.005.

14 W. Tang, J. Ping, K. Fan, Y. Wang, X. Luo, Y. Ying, J. Wu and Q. Zhou, All-solid-state nitrate-selective electrode and its application in drinking water, *Electrochim. Acta*, 2012, **81**, 186–190, DOI: 10.1016/j.electacta.2012.07.073.

15 R. V. Manurung, B. A. Prabowo, I. D. P. Hermida, D. Kurniawan, Y. Sulaeman and A. Heryana, Development ion phosphate sensor system for precision farming, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2019, **620**, DOI: 10.1088/1757-899x/620/1/012093.

16 X. Jin, A. Saha, H. Jiang, M. R. Oduncu, Q. Yang, S. Sedaghat, K. Maize, J. P. Allebach, A. Shakouri, N. Glassmaker, A. Wei, R. Rahimi and M. A. Alam, Steady-State and Transient Performance of Ion-Sensitive Electrodes Suitable for Wearable and Implantable Electro-Chemical Sensing, *IEEE Trans. Biomed. Eng.*, 2022, **69**, 96–107, DOI: 10.1109/TBME.2021.3087444.

17 R. Athavale, C. Dinkel, B. Wehrli, E. Bakker, G. A. Crespo and A. Brand, Robust Solid-Contact Ion Selective Electrodes for High-Resolution *In Situ* Measurements in Fresh Water Systems, *Environ. Sci. Technol. Lett.*, 2017, **4**, 286–291, DOI: 10.1021/acs.estlett.7b00130.

18 N. Pankratova, G. A. Crespo, M. G. Afshar, M. C. Crespi, S. Jeanneret, T. Cherubini, M. L. Tercier-Waeber, F. Pomati and E. Bakker, Potentiometric sensing array for monitoring aquatic systems, *Environ. Sci.: Processes Impacts*, 2015, **17**, 906–914, DOI: 10.1039/c5em00038f.

19 S. Winkler, L. Rieger, E. Saracevic, A. Pressl and G. Gruber, Application of ion-sensitive sensors in water quality monitoring, *Water Sci. Technol.*, 2004, **50**, 105–114.

20 M. Barjenbruch and S. Rettig, MONITOR-1: Simultaneous Monitoring of Combined Sewer Overflows and Receiving Water, *Sub-study: Test of Online Sensors for CSO and River Monitoring*, Kompetenzzentrum Wasser Berlin, 2009.

21 S. Papias, M. Masson, S. Pelletant, S. Prost-Boucle and C. Boutin, In situ continuous monitoring of nitrogen with ion-selective electrodes in a constructed wetland receiving treated wastewater: an operating protocol to obtain reliable data, *Water Sci. Technol.*, 2018, **77**, 1706–1713, DOI: 10.2166/wst.2018.052.

22 F. Cecconi, S. Reifsnyder, Y. Ito, M. Jimenez, R. Sobhani and D. Rosso, ISE-ammonium sensors in WRRFs: field assessment of their influencing factors, *Environ. Sci.: Water Res. Technol.*, 2019, **5**, 737–746, DOI: 10.1039/c8ew00763b.

23 J. W. Pedersen, L. H. Larsen, C. Thirsing and L. Vezzaro, Reconstruction of corrupted datasets from ammonium-ISE sensors at WRRFs through merging with daily composite samples, *Water Res.*, 2020, **185**, 116227, DOI: 10.1016/j.watres.2020.116227.

24 F. Cecconi and D. Rosso, Soft Sensing for On-Line Fault Detection of Ammonium Sensors in Water Resource Recovery Facilities, *Environ. Sci. Technol.*, 2021, **55**, 10067–10076, DOI: 10.1021/acs.est.0c06111.

25 W. Boenne, N. Desmet, S. Van Looy and P. Seuntjens, Use of online water quality monitoring for assessing the effects of WWTP overflows in rivers, *Environ. Sci.: Processes Impacts*, 2014, **16**, 1510–1518, DOI: 10.1039/c3em00449j.

26 T. Le Goff, J. Braven, L. Ebdon and D. Scholefield, Automatic continuous river monitoring of nitrate using a novel ion-selective electrode, *J. Environ. Monit.*, 2003, **5**, 353–358, DOI: 10.1039/b211140n.

27 R. De Marco, G. Clarke and B. Pejcic, Ion-Selective Electrode Potentiometry in Environmental Analysis, *Electroanalysis*, 2007, **19**, 1987–2001, DOI: 10.1002/elan.200703916.

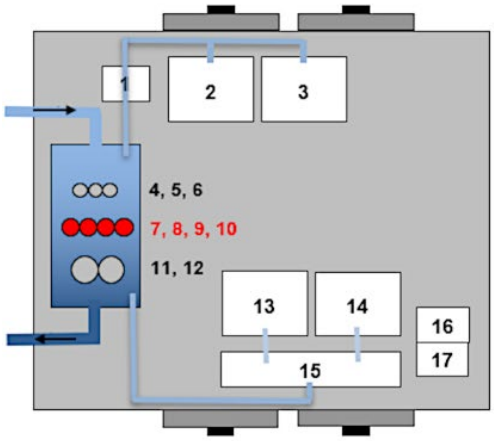
28 M. Cuartero and E. Bakker, Environmental water analysis with membrane electrodes, *Curr. Opin. Electrochem.*, 2017, **3**, 97–105, DOI: **10.1016/j.coelec.2017.06.010**.
29 M. Cuartero, N. Colozza, B. M. Fernandez-Perez and G. A. Crespo, Why ammonium detection is particularly challenging but insightful with ionophore-based potentiometric sensors - an overview of the progress in the last 20 years, *Analyst*, 2020, **145**, 3188–3210, DOI: **10.1039/d0an00327a**.
30 C. Feller and U. Partsch, Ceramic multilayer technology as a platform for miniaturized sensor arrays for water analysis, *J. Sens. Sens. Syst.*, 2021, **10**, 83–91, DOI: **10.5194/jsss-10-83-2021**.
31 A. Radu, T. Radu, C. McGraw, P. Dillingham, S. Anastasva-Ivanova and D. Diamond, Ion selective electrodes in environmental analysis, *J. Serb. Chem. Soc.*, 2013, **78**, 1729–1761, DOI: **10.2298/Jsc130829098r**.
32 T. Le Goff, J. Braven, L. Ebdon, N. P. Chilcottt, D. Scholefield and J. W. Wood, An accurate and stable nitrate-selective electrode for the *in situ* determination of nitrate in agricultural drainage waters, *Analyst*, 2002, **127**, 507–511, DOI: **10.1039/b201899n**.
33 F. Cecconi, S. Reifsnyder, R. Sobhani, A. Cisquella-Serra, M. Madou and D. Rosso, Functional behaviour and microscopic analysis of ammonium sensors subject to fouling in activated sludge processes, *Environ. Sci.: Water Res. Technol.*, 2020, **6**, 2723–2733, DOI: **10.1039/d0ew00359j**.
34 G. Weber, U. Honecker and J. Kubiniok, Nitrate dynamics in springs and headwater streams with agricultural catchments in southwestern Germany, *Sci. Total Environ.*, 2020, **722**, 137858, DOI: **10.1016/j.scitotenv.2020.137858**.
35 W. Nernst, Die elektromotorische Wirksamkeit der Jonen, *Z. Phys. Chem.*, 1889, **4U**, 129–181, DOI: **10.1515/zpch-1889-0412**.
36 J. Schwarz, H. Kaden and G. Pausch, Development of miniaturized potentiometric nitrate- and ammonium selective electrodes for applications in water monitoring, *Fresenius. J. Anal. Chem.*, 2000, **367**, 396–398, DOI: **10.1007/s002160000367**.
37 D. P. Quan, C. X. Quang, L. T. Duan and P. H. Viet, A conductive polypyrrole based ammonium ion selective electrode, *Environ. Monit. Assess.*, 2001, **70**, 153–165, DOI: **10.1023/a:1010622422561**.
38 Y. Kan, C. Han, Y. Ye, X. Zhang, Y. Huang, L. Xing, Y. Zhou and H. Qin, An All-Solid-State Ammonium Ion-Selective Electrode Based on Polyaniline as Transducer and Poly (o-phenylenediamine) as Sensitive Membrane, *Int. J. Electrochem. Sci.*, 2016, **11**, 9928–9940, DOI: **10.20964/2016.12.03**.
39 K. Cammann, *Working with Ion-Selective Electrodes*, 1979, DOI: **10.1007/978-3-642-67276-7**.
40 E. Bakker, Electroanalysis with Membrane Electrodes and Liquid-Liquid Interfaces, *Anal. Chem.*, 2016, **88**, 395–413, DOI: **10.1021/acs.analchem.5b04034**.
41 B. P. Nikolsky, M. M. Shultz, A. A. Belyustin and A. A. Lev, *Recent developments in the ion-exchange theory of the glass electrode and its application in the chemistry of glass*, 1967.
42 A. Hamid, S. U. Bhat and A. Jehangir, Local determinants influencing stream water quality, *Appl. Water Sci.*, 2019, **10**, 41, DOI: **10.1007/s13201-019-1043-4**.
43 P. Skowron, M. Skowrońska, U. Bronowicka-Mielniczuk, T. Filipek, J. Igras, A. Kowalczyk-Juśko and A. Krzepiłko, Anthropogenic sources of potassium in surface water: The case study of the Bystrzyca river catchment, *Agric., Ecosyst. Environ.*, 2018, **265**, 454–460, DOI: **10.1016/j.agee.2018.07.006**.
44 P. Schneider, P. Neitzel, M. Schaffrath and H. Schlumrecht, *Leitbildorientierte physikalisch-chemische Gewässerbewertung – Referenzbedingungen und Qualitätsziele*, 2003.
45 N. Khatri and S. Tyagi, Influences of natural and anthropogenic factors on surface and groundwater quality in rural and urban areas, *Front. Life Sci.*, 2014, **8**, 23–39, DOI: **10.1080/21553769.2014.933716**.
46 V. Nava, M. Patelli, T. Bonomi, G. A. Stefania, C. Zanotti, L. Fumagalli, V. Soler, M. Rotiroti and B. Leoni, Chloride Balance in Freshwater System of a Highly Anthropized Subalpine Area: Load and Source Quantification Through a Watershed Approach, *Water Resour. Res.*, 2020, **56**(1), 2019WR026024.
47 Z. Yang, Z. Liang, L. Gao, R. Li, Z. Wang, A. Zhu, S. Li, Z. Xie, J. Chen and Z. Wang, Quantifying the impacts of anthropogenic activity on chemical weathering based on source identification of hydrochemistry: the Liuxi river basin, southern China, *Environ. Sci.: Processes Impacts*, 2020, **22**, 2406–2417, DOI: **10.1039/d0em00332h**.
48 Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda and S. Amemiya, Potentiometric Selectivity Coefficients of Ion-Selective Electrodes. Part I. Inorganic Cations (Technical Report), *Pure Appl. Chem.*, 2000, **72**, 1851–2082, DOI: **10.1351/pac200072101851**.
49 Y. Umezawa, K. Umezawa, P. Bühlmann, N. Hamada, H. Aoki, J. Nakanishi, M. Sato, K. P. Xiao and Y. Nishimura, Potentiometric selectivity coefficients of ion-selective electrodes. Part II. Inorganic anions (IUPAC Technical Report), *Pure Appl. Chem.*, 2002, **74**, 923–994, DOI: **10.1351/pac200274060923**.
50 P. W. Dillingham, B. S. O. Alsaedi, S. Granados-Focil, A. Radu and C. M. McGraw, Establishing Meaningful Limits of Detection for Ion-Selective Electrodes and Other Nonlinear Sensors, *ACS Sens.*, 2020, **5**, 250–257, DOI: **10.1021/acssensors.9b02133**.
51 T. Fayose, E. Thomas, T. Radu, P. Dillingham, S. Ullah and A. Radu, Concurrent measurement of nitrate and ammonium in water and soil samples using ion-selective electrodes: Tackling sensitivity and precision issues, *Anal. Sci. Adv.*, 2021, **2**, 279–288, DOI: **10.1002/ansa.202000124**.
52 Y. Chen, *Potassium Ion Measurement with Flexible Printed Ion-Sensitive Electrode and ISFET Sensors*, McGill University Libraries, 2021.
53 G. de Vera, M. A. Climent, C. Antón, A. Hidalgo and C. Andrade, Determination of the selectivity coefficient of a chloride ion selective electrode in alkaline media simulating the cement paste pore solution, *J. Electroanal. Chem.*, 2010, **639**, 43–49, DOI: **10.1016/j.jelechem.2009.11.010**.

Supplementary Information

Table S1 Technical specifications of the ISEs used according to the manufacturer's information

	ISE	Potential dissipation	Membrane	Measuring range [mg L^{-1}]	Accuracy	Resolution	Operat. pH range	Response time	Interferences (factor 1 : ...)	Temp. compensation via
ANI-SE 1 and 2 (Hach)	NH_4^+	Ag/AgCl	PVC-	0 – 780	±5% or +0.2 mg L^{-1}	±5% or +0.2 mg L^{-1}	5 – 9	< 3 min (5 – 50 mg L^{-1})	K^+: 12 – 17	integrated temp. sensor
	NO_3^-	Ag/AgCl	PVC-	0 – 225	±5% or +0.2 mg L^{-1}	±5% or +0.2 mg L^{-1}	5 – 9	< 3 min (5 – 50 mg L^{-1})	Cl^-: 250 NO_2^-: 5	
	K^+	Ag/AgCl	PVC-	0 – 1000	±5% or +0.2 mg L^{-1}	±5% or +0.2 mg L^{-1}	5 – 9	< 3 min (5 – 50 mg L^{-1})		
	Cl^-	Ag/AgCl	AgCl/Ag_2S pellet	0 – 1000	±5% or +0.2 mg L^{-1}	±5% or +0.2 mg L^{-1}	5 – 9	< 3 min (5 – 50 mg L^{-1})		
K16 (Seba)	NH_4^+	electrolyte	PVC with org. ion exchanger	0.2 – 18000	±5%	0.01 mg L^{-1}	3 – 8		K^+: 22 Na^+: 10^3 Mg^{2+}: 10^4 Ca^{2+}: 10^4 Cl^-: 57 NO_2: 7.4	pH sensor
	NO_3^-	solid	PVC with org. ion exchanger	0.4 – 60000	±5%	0.01 mg L^{-1}	3 – 10			
	K^+	electrolyte	PVC with org. ion exchanger	0.4 – 39000	±5%	0.01 mg L^{-1}	3 – 8		NH_4^+: 5 Na^+: 6 x 10^2 Mg^{2+}: 10^4 Ca^{2+}: 10^4 H^+: 10^1	
	Cl^-	solid	AgCl/Ag_2S pellet	1 – 35000	±5%	0.01 mg L^{-1}	3 – 10		OH^-: 40 Cu^{2+} 27	
AquaTROLL 600 (in-Situ)	NH_4^+	electrolyte	PVC	0.14 – 14000	±10%	0.01 mg L^{-1}		T95 < 30 s	K^+: 27 Na^+: 10^5	eC sensor
	NO_3^-	electrolyte	PVC	0.14 – 14000	±10%	0.01 mg L^{-1}		T95 < 30 s	Cl^-: 7.6 x 10^3 NO_2^-: 230	
	Cl^-	electrolyte	AgCl/Ag_2S pellet	0.35 – 35500	±15%	0.01 mg L^{-1}		T95 < 30 s	NH_3: 6	

All the information taken from the manufacture's manuals and brochures at www.hach.com, www.seba-hydrometrie.com and www.in-situ.com in July 2024.



1: Filtrax (filtration system, Hach)
2: Amtax inter 2 (photometer for NH_4^+, Hach)
3: Amtax sc (gas-sensitive analyser for NH_4^+, Hach)
4-6: SC1000 (multiparameter controller with display module) with probes for oxygen, pH, eC (each with integrated temperature measurement, Hach)
7-10: ISEs tested: An-ISE 1 and 2 (for NH_4^+, NO_3^-, K^+, Cl^- and temperature, Hach), K16 (for NH_4^+, NO_3^-, K^+, Cl^-, pH and temperature, Seba), AquaTROLL (for NH_4^+, NO_3^-, Cl^-, eC and temperature, In-Situ)
11: Nitratax (optical sensor for NO_3^-, Hach)
12: Solitax (optical sensor for turbidity, Hach)
13: Phosphax sigma (photometer for PO_4-P and total Phosphorus, Hach)
14: Bioctector (photometer for TOC and TIC, Hach)
15: Sigmatax (sampling and homogenisation system, Hach)
16,17: Control unit and data logger (Ott Hydrometry, Germany)

Fig. S1 Design and equipment of a mobile measuring station.

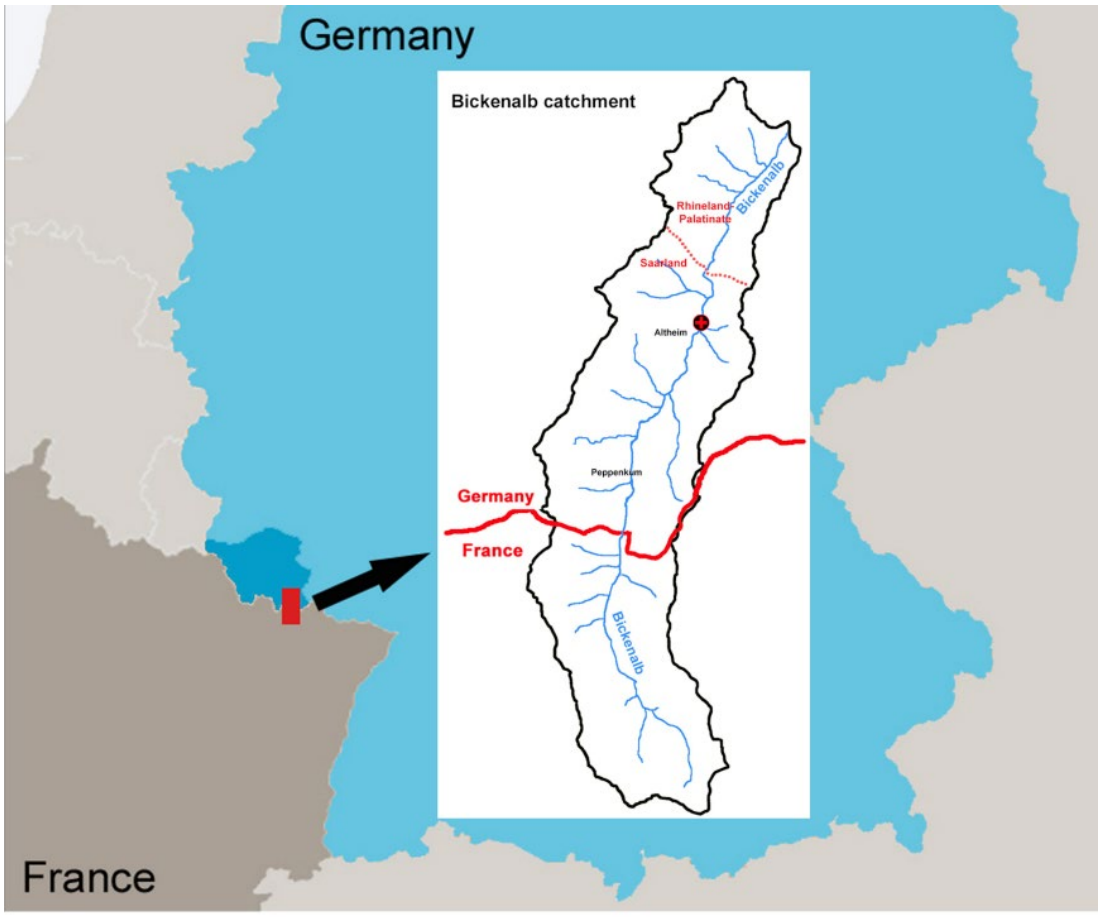


Fig. S2 Schematic illustration of the German-French catchment of the Bickenalb River and location of the measuring station (red dot).

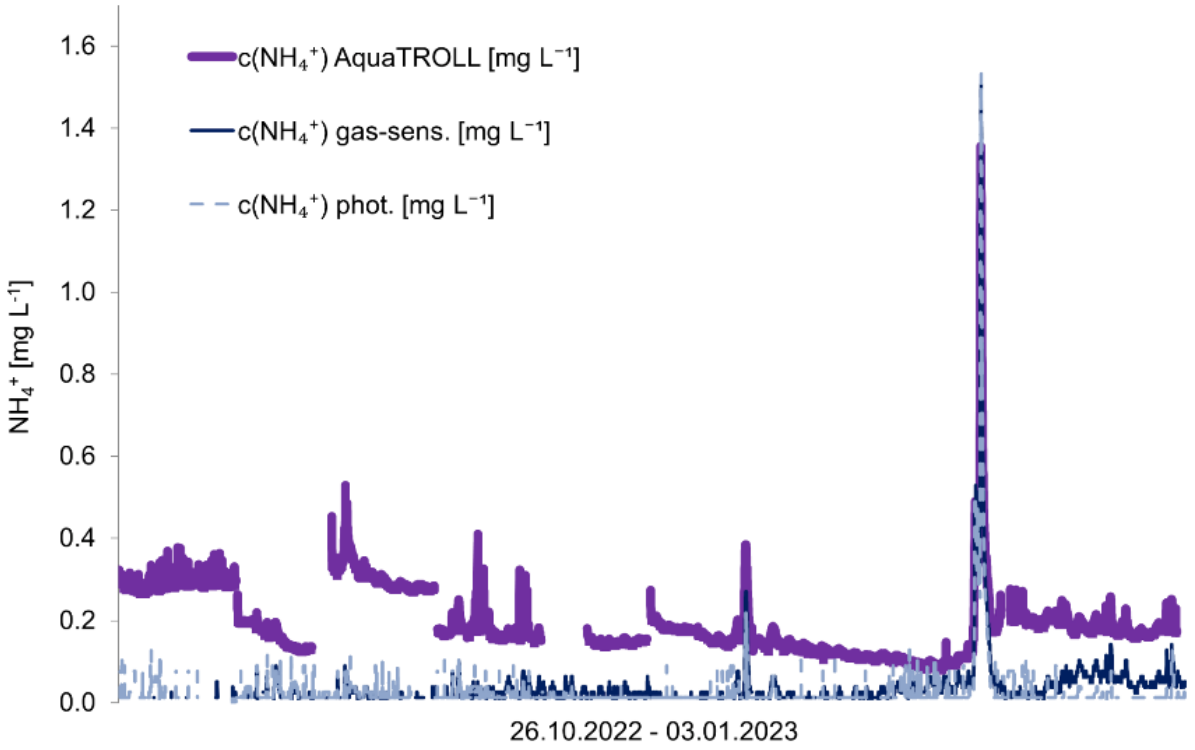


Fig. S4 Comparison of NH_4^+ concentrations as given by the photometric and the gas-sensitive analyser with AquaTROLL ISE readings; Bickenalb River, 26.10.2022 – 03.01.2023

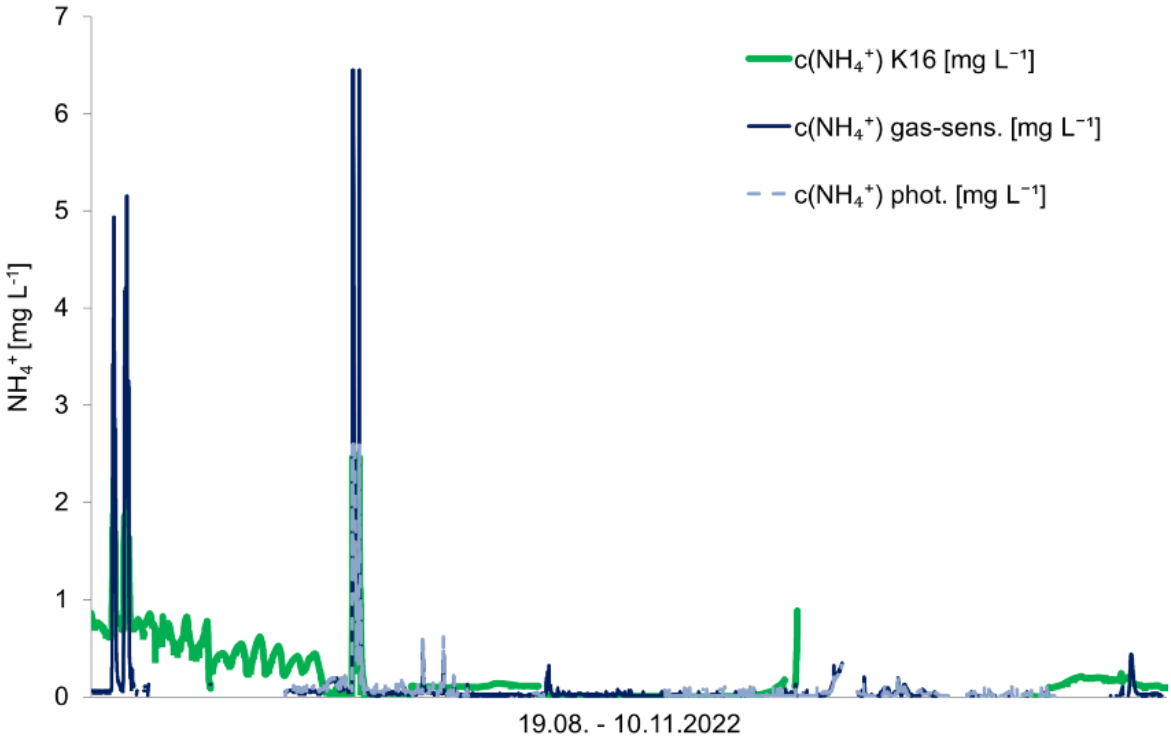


Fig. S3 Comparison of NH_4^+ concentrations as given by the photometric and the gas-sensitive analyser with K16 ISE readings; Bickenalb River, 19.08. – 10.11.2022.

3. Conclusions and Outlook

The dynamics and vulnerability of small and medium-sized rivers require a paradigm shift from traditional, infrequent monitoring strategies to sophisticated, high-resolution real-time monitoring.

Small and medium-sized rivers, which make up the majority of European waterways, are not simply smaller versions of larger rivers, but have unique hydrological and chemical characteristics. Due to their flashy hydrology and low dilution capacity, they are extremely sensitive to a variety of pressures, including seasonal fluctuations, diurnal cycles and event-related pollution such as CSOs, agricultural runoff and effluent from STPs. The traditional sampling method required for monitoring and operational control under the WFD is fundamentally unsuitable for detecting the rapid and significant changes in concentration that are characteristic of these systems. These diagnostic shortcomings inevitably lead to erroneous assessments and thus misguided management decisions or incorrect action planning.

In this work, arguments for real-time monitoring are therefore presented not as a luxury, but as a necessity for accurate water quality assessment and effective integrated water resource management.

This work presents different strategies and technologies for real-time monitoring that have been in use over many years at numerous different rivers for longer time periods. Thereby, very different measuring devices were used: complex on-site analysers (e.g. for ammonium via photometry), installed in mobile measuring stations, as well as in situ sensors (e.g. for temperature, dissolved oxygen, turbidity, nitrate via UV absorption), some of which are used directly in the water, while others are used in stations. Each approach has its advantages and disadvantages: in situ sensors offer high temporal resolution and lower operating costs but are limited to a narrower range of parameters. In contrast, at-site analysers offer greater analytical flexibility and sensitivity for a broader spectrum of pollutants, but this comes with higher costs and maintenance requirements and requires a certain infrastructure (pump with supply line, power supply, sample preparation if necessary).

However, to ensure optimal spatial and temporal monitoring, cost-effective and low-maintenance technologies are required. In this context, ISEs represent a promising approach and were therefore examined in particular detail in this work. The advantages of ISEs, including a large measuring range, fast response times and relatively low costs, face certain challenges, especially in small and medium-sized rivers. It is therefore necessary to assess whether ISEs are also suitable in practice for prolonged use under the dynamic and rapidly changing conditions of small rivers. To this end, different ISE systems were integrated into one of the mobile measuring stations and the real-time data obtained was compared with that from the other measuring systems (wet chemical analysers for ammonium, optical probe for nitrate). For chloride and potassium, which are not measured in real-time at the stations, weekly samples were taken and analysed in the laboratory using ion chromatography. The sub-study showed that, in contrast to initial assumptions, no interference from other ions was observed for any of the ISE systems. Rather, the two biggest problems were temperature effects and the limited lifetime of the ISEs. Despite integrated temperature compensation, diurnal temperature fluctuations, which are particularly pronounced in small watercourses in summer, led to significant cyclical disturbances in the concentration output. On the other hand, the limited lifetime of all ISE systems led to signal drift, which resulted in unreliable data after only about five months and was particularly pronounced for the ammonium and potassium sensors. This is probably due to the fact that these two ions were present in very low concentrations in the sample water to be measured. Since the ISEs were placed in the sample pot inside the measuring station rather than directly in the water, and were also cleaned regularly, gross contamination and increased biofouling of the membranes, commonly observed during in situ use of ISEs, can be ruled out.

Despite these challenges, the conclusion is not that ISEs are unsuitable for small and medium-sized river monitoring, but that their use requires careful consideration, regular and careful calibration, and an awareness of their limitations. When used properly, they can provide valuable, continuous data for nitrate and chloride and, under certain conditions, also for ammonium. This sub-study emphasises that ISE data must be validated using reference methods (e.g. photometry, ion chromatography) and interpreted by trained personnel who can distinguish real trends from instrumental deviations.

Overall, this paper demonstrates how extremely efficient and profitable real-time monitoring is, especially for small and medium-sized rivers. All of the technologies used have proven to be reliable and robust over the years when maintained and calibrated appropriately (weekly). By combining sensors and wet chemical analysers, a wide range of different parameters can be reliably recorded. Although all the rivers investigated over the years differ greatly in terms of catchment conditions and anthropogenic pressure, real-time monitoring has always been able to provide fundamental insights and an understanding of the key processes that influence the chemical status and ecological situation in each river. The gathered data enable the differentiation of various sources of pollution, as well as a clear determination of the duration of pollution events and an assessment of their impact on the chemical status and the aquatic ecosystem, for both storm events and low water periods. Furthermore, it has been shown that accurate calculation of substance loads, which is crucial for the management of the entire catchment area and the evaluation of the effectiveness of measures, can only be carried out reliably with continuous concentration and discharge data.

It is also made clear that, for an effective interpretation of real-time data, not only different parameters must be compared with each other, but they must also be correlated with supplementary data streams such as discharge and weather data, and they must be linked to further information from the catchment area such as geogenic background, land use, dischargers, etc. It could be demonstrated that real-time monitoring is not only indispensable for pure control of limit values, but also for planning measures and monitoring their success, and for identifying long-term trends. The latter is also of particular importance in view of the effects of climate change on these very vulnerable water bodies and all their ecosystem functions.

Furthermore, it has been shown that complex measuring stations can only be operated at a few carefully selected measuring points due to the high acquisition and operating costs. Therefore, future research focus must be on developing inexpensive but reliable, robust and durable technologies that are suitable for in situ use in flowing waters turbulent systems and on low-cost nanotechnology sensors to realise closing the current spatio-temporal data gaps. Improvements in energy generation through solar and water-powered energy systems will also have a positive impact on the autonomous, long-term operation of real-time monitoring systems. Extensive standardisation of data transmission and data formats would also be desirable in order to ensure interoperability between systems from different providers, thereby facilitating the combination of different measurement systems.

The findings can be used

- to improve the chemical status assessment in environmental legislation by further developing the legal assessment framework
- to develop new strategies and technologies for targeted measures and to derive further recommendations for action to reduce pollutant inputs
- to achieve a sound calibration of water chemistry in computer-aided models and enable realistic modelling of scenarios, e.g. through changes due to climate change or changes in discharges into or withdrawals from water bodies (Piniewski et al., 2019).

The protection and renaturation of small and medium-sized rivers, which provide important ecosystem services (e.g. protection of biodiversity, flood protection, recreation), depends on the ability to understand these complex and sensitive systems. The work presented here shows that this understanding cannot be achieved through sporadic snapshot monitoring. The future of river monitoring lies in the strategic implementation of real-time technologies with high spatial and temporal resolution to ensure the unique identification of pollution sources and transport pathways, the accurate assessment of chemical and ecological status, and the effective targeting of remediation measures for preserving and/or restoring these important water bodies and to preserve and restore their immensely important ecosystem functions.

With regard to the WFD, it can be said that it is regarded as one of the most successful pieces of EU legislation in terms of environmental policy issues and has become a global model for the implementation of water protection (Brack et al., 2017; Carvalho et al., 2019).

As Carvalho et al. (2019) stated, various aspects have emerged that influence the implementation of the WFD since its introduction:

- "Increased recognition of the importance of specific pressures, including climate change and associated flood and drought risks, invasive species and a wide range of emerging pollutants.
- New perspectives on environmental management have been developed, including ecosystem services, nature-based solutions and adaptive and resilience-based approaches.
- The UN Sustainable Development Goals have been set, in which many targets are related to water, or affect waters in positive and negative ways.
- Other EU policies on biodiversity, renewable energy and flood management have been developed, influencing how we manage aquatic systems".

However, the WFD has been implemented in the EU Member States with very different strategies and ambitions, and progress in management measures and improving ecological quality has been much slower than originally anticipated.

A revision or even redesign of the WFD from 2027 onwards therefore offers an opportunity to build on the sound conceptual foundations in terms of monitoring, priority setting, assessment and management (Carvalho et al., 2019).

A key approach here is to promote safer and more cost-effective monitoring, supported by the integration of passive sampling, screening of non-target chemicals and impact-oriented analysis, among other things (Brack et al., 2017). The inclusion of real-time data in the assessments pursuant to Annex V and the financing of dense monitoring networks are just as crucial steps as the establishment of comparable measurement techniques and data protocols. This is important not only for describing current conditions, but also for maintaining good status and addressing emerging pressures. This, in turn, requires a long-term perspective that certainly extends well beyond 2027.

In addition, the regulatory shortcomings of the WFD with regard to the management of transboundary waters must be remedied. An essential part of this is the harmonisation of EU-wide limit values and assessment keys.

All these developments provide the scientific and practical basis that will enable the important objectives of the WFD to be finally achieved across the EU.

4. References

Ao, X., Grimmond, C.S.B., Ward, H.C., Gabey, A.M., Tan, J., Yang, X.-Q., Liu, D., Zhi, X., Liu, H., Zhang, N., 2018. Evaluation of the Surface Urban Energy and Water Balance Scheme (SUEWS) at a Dense Urban Site in Shanghai: Sensitivity to Anthropogenic Heat and Irrigation. J. Hydrometeorol. 19, 1983–2005. https://doi.org/10.1175/JHM-D-18-0057.1

Arle, J., Mohaupt, V., Kirst, I., 2016. Monitoring of Surface Waters in Germany under the Water Framework Directive—A Review of Approaches, Methods and Results. Water 8, 217. https://doi.org/10.3390/w8060217

Arndt, J., Gerloff, A.-L., Zavarsky, A., Schlüsener, M.P., Wick, A., Duester, L., 2026. Online high-resolution real-time monitoring techniques for anions in river water. Environ. Monit. Assess. 198, 121. https://doi.org/10.1007/s10661-025-14954-y

Babitsch, D., Sundermann, A., 2020. Chemical surveillance in freshwaters: small sample sizes underestimate true pollutant loads and fail to detect environmental quality standard exceedances. Environ. Sci. Eur. 32, 3. https://doi.org/10.1186/s12302-019-0285-y

Bakker, E., Bühlmann, P., Pretsch, E., 1997. Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics. Chem. Rev. 97, 3083–3132. https://doi.org/10.1021/cr940394a

Bakker, E., Pretsch, E., 2007. Modern Potentiometry. Angew. Chem. Int. Ed. 46, 5660–5668. https://doi.org/10.1002/anie.200605068

Barjenbruch, M., Rettig, S., 2009. Test und Bewertung von moderner Online-Sensorik zum Kanalnetz- und Gewässermonitoring (Techreport No. RN181). Technische Universität Berlin, Berlin.

Benisch, J., Helm, B., Chang, X., Krebs, P., 2024. Can Short-Term Online-Monitoring Improve the Current WFD Water Quality Assessment Regime? Systematic Resampling of High-Resolution Data from Four Saxon Catchments. Water 16, 889. https://doi.org/10.3390/w16060889

Biggs, J., Nicolet, P., Mlinaric, M., Lalanne, T., 2014. Report of the workshop on the protection and management of Small Water Bodies, Brussels, 14th November 2013. The European Environmental Bureau (EEB) and the Freshwater Habitats Trust.

BMU, 2013. Wasserwirtschaft in Deutschland Teil 2 -Gewässergüte. Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, Bonn.

Boahen, E., Owusu, L., Adjei-Anim, S.O., 2025. A comprehensive review of emerging environmental contaminants of global concern. Discov. Environ. 3, 144. https://doi.org/10.1007/s44274-025-00259-x

Bold, L., 2025. Zielgerichtetes Monitoring zur repräsentativen Beurteilung und Analyse des Cadmiumeintrages im Kondeler Bach (Bachelorarbeit). Universität des Saarlandes.

Brack, W., Aissa, S.A., Backhaus, T., Dulio, V., Escher, B.I., Faust, M., Hilscherova, K., Hollender, J., Hollert, H., Müller, C., Munthe, J., Posthuma, L., Seiler, T.-B., Slobodnik, J., Teodorovic, I., Tindall, A.J., De Aragão Umbuzeiro, G., Zhang, X., Altenburger, R., 2019. Effect-based methods are key. The European Collaborative Project SOLUTIONS recommends integrating effect-based methods for diagnosis and monitoring of water quality. Environ. Sci. Eur. 31, 10. https://doi.org/10.1186/s12302-019-0192-2

Brack, W., Dulio, V., Ågerstrand, M., Allan, I., Altenburger, R., Brinkmann, M., Bunke, D., Burgess, R.M., Cousins, I., Escher, B.I., Hernández, F.J., Hewitt, L.M., Hilscherová, K., Hollender, J., Hollert, H., Kase, R., Klauer, B., Lindim, C., Herráez, D.L., Miège, C., Munthe, J., O'Toole, S.,

Posthuma, L., Rüdel, H., Schäfer, R.B., Sengl, M., Smedes, F., Van De Meent, D., Van Den Brink, P.J., Van Gils, J., Van Wezel, A.P., Vethaak, A.D., Vermeirssen, E., Von Der Ohe, P.C., Vrana, B., 2017. Towards the review of the European Union Water Framework Directive: Recommendations for more efficient assessment and management of chemical contamination in European surface water resources. Sci. Total Environ. 576, 720–737. https://doi.org/10.1016/j.scitotenv.2016.10.104

Briem, E., 2003. Gewässerlandschaften der Bundesrepublik Deutschland: morphologische Merkmale der Fließgewässer und ihrer Auen, ATV-DVWK-Arbeitsbericht. ATV-DVWK Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V, Hennef.

Bui, L.T., Tran, D.L.T.H., Nguyen, D.P., 2024. Role of self-cleaning factors in river water environmental capacity assessment: A case of Sai Gon basin, Vietnam. Case Stud. Chem. Environ. Eng. 9, 100689. https://doi.org/10.1016/j.cscee.2024.100689

Bumberger, J., Abbrent, M., Brinckmann, N., Hemmen, J., Kunkel, R., Lorenz, C., Lünenschloss, P., Palm, B., Schnicke, T., Schulz, C., Van Der Schaaf, H., Schäfer, D., 2025. Digital ecosystem for FAIR time series data management in environmental system science. SoftwareX 29, 102038. https://doi.org/10.1016/j.softx.2025.102038

Burkert, 2025. Type MS09 - Nitrate sensor [WWW Document]. URL https://www.burkert.com/en/type/MS09 (accessed 03.11.2025).

Carvalho, L., Mackay, E.B., Cardoso, A.C., Baattrup-Pedersen, A., Birk, S., Blackstock, K.L., Borics, G., Borja, A., Feld, C.K., Ferreira, M.T., Globevnik, L., Grizzetti, B., Hendry, S., Hering, D., Kelly, M., Langaas, S., Meissner, K., Panagopoulos, Y., Penning, E., Rouillard, J., Sabater, S., Schmedtje, U., Spears, B.M., Venohr, M., Van De Bund, W., Solheim, A.L., 2019. Protecting and restoring Europe's waters: An analysis of the future development needs of the Water Framework Directive. Sci. Total Environ. 658, 1228–1238. https://doi.org/10.1016/j.scitotenv.2018.12.255

Cassidy, R., Jordan, P., 2011. Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. J. Hydrol. 405, 182–193. https://doi.org/10.1016/j.jhydrol.2011.05.020

CCME, 2015. Guidanc Manual for Optimizing Water Quality Monitoring Program Design. Canadian Council of Ministers of the Environment.

Corday, J., 2024. Restoring western headwater streams with low-tech process-based methods: a review of the science and case study results, challenges, and opportunities (No. Version 2.0). American Rivers.

Curtis, J.A., Burns, E.R., Sando, R., 2020. Regional patterns in hydrologic response, a new three-component metric for hydrograph analysis and implications for ecohydrology, Northwest Volcanic Aquifer Study Area, USA. J. Hydrol. Reg. Stud. 30, 100698. https://doi.org/10.1016/j.ejrh.2020.100698

Datry, T., Boulton, A.J., Bonada, N., Fritz, K., Leigh, C., Sauquet, E., Tockner, K., Hugueny, B., Dahm, C.N., 2018. Flow intermittence and ecosystem services in rivers of the Anthropocene. J. Appl. Ecol. 55, 353–364. https://doi.org/10.1111/1365-2664.12941

Dong, J., Tang, J., Wu, G., Xin, Y., Li, R., Li, Y., 2024. Effective correction of dissolved organic carbon interference in nitrate detection using ultraviolet spectroscopy combined with the equivalent concentration offset method. RSC Adv. 14, 5370–5379. https://doi.org/10.1039/D3RA08000E

DWA (Ed.), 2017. Gewässermonitoring - Strategien und Methoden zur Erfassung der physikalisch-chemischen Beschaffenheit von Fließgewässern, DWA-Regelwerk. Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V, Hennef.

EC, 2024. Directive 2024/3019 of the European Parliament and of the Council of 27 November 2024 concerning urban wastewater treatment.

EC, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. Waterframework Directive (WFD).

ECRR, 2025. What is (ecological) river restoration? [WWW Document]. Eur. Cent. RIver Restor. URL https://www.ecrr.org/River-Restoration/What-is-river-restoration (accessed 02.12.2025).

EEA, 2025. Data Dictionary - Vocabulary [WWW Document]. Eur. Environ. Agency. URL https://dd.eionet.europa.eu/vocabularyconcept/gemet2/concept/2882/view (accessed 17.11.2025).

EEA, 2024. Europe's state of water 2024: the need for improved water resilience [WWW Document]. Eur. Environ. Agency. URL https://www.eea.europa.eu/en/analysis/publications/europes-state-of-water-2024.

EPA, 2026. 5.6 Phosphorus | Monitoring & Assessment [WWW Document]. Unites States Environ. Prot. Agency. URL https://archive.epa.gov/water/archive/web/html/vms56.html?utm_source=chatgpt.com (accessed 07.01.2026).

EPA, 2013. Aquatic Life Ambient Water Quality Criteria For Ammonia – Freshwater 2013 (No. EPA-822-R-13-001). United States Environmental Protection Agency.

EPA, 2004. Impacts and Control of CSOs and SSOs (Report to Congress No. EPA 833-R-04-001). United States Environmental Protection Agency.

EPA 180.1-1, 1993. Determination of Turbidity by Nephelometry.

EVS, 2025. Die Kläranlagenstandorte des EVS [WWW Document]. Entsorgungsverband Saar. URL https://www.evs.de/abwasser/klaeranlagen/klaeranlagenstandorte (accessed 31.10.2025).

Fan, J., Yang, J., Cheng, F., Zhang, S., 2023. The Source, Distribution, and Environmental Effects of Suspended Particulate Matter in the Yangtze River System. Water 15, 3429. https://doi.org/10.3390/w15193429

Fauth, H., 1985. Geochemischer Atlas Bundesrepublik Deutschland: Verteilung von Schwermetallen in Wässern und Bachsedimenten.

Feio, M.J., Hughes, R.M., Callisto, M., Nichols, S.J., Odume, O.N., Quintella, B.R., Kuemmerlen, M., Aguiar, F.C., Almeida, S.F.P., Alonso-EguíaLis, P., Arimoro, F.O., Dyer, F.J., Harding, J.S., Jang, S., Kaufmann, P.R., Lee, S., Li, J., Macedo, D.R., Mendes, A., Mercado-Silva, N., Monk, W., Nakamura, K., Ndiritu, G.G., Ogden, R., Peat, M., Reynoldson, T.B., Rios-Touma, B., Segurado, P., Yates, A.G., 2021. The Biological Assessment and Rehabilitation of the World's Rivers: An Overview. Water 13, 371. https://doi.org/10.3390/w13030371

Gu, W.-Z., Liu, J.-F., Lin, H., Lin, J., Liu, H.-W., Liao, A.-M., Wang, N., Wang, W.-Z., Ma, T., Yang, N., Li, X.-G., Zhuo, P., Cai, Z., 2018. Why Hydrological Maze: The Hydropedological Trigger? Review of Experiments at Chuzhou Hydrology Laboratory. Vadose Zone J. 17, 1–27. https://doi.org/10.2136/vzj2017.09.0174

Hach, 2026a. Nitratax sc Nitrat-Sonden | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/nitrat-sonden/nitratax-sc-nitrat-sonden/family?productCategoryId=23358150297 (accessed 01.02.2026).

Hach, 2026b. Optical oxygen measurement in power plants l Hach [WWW Document]. URL https://mena.hach.com/power-dissolved-oxygen (accessed 01.02.2026).

Hach, 2026c. AN-ISE SC Sensoren | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/ammonium-sonden/an-ise-sc-sensoren/family?productCategoryId=23357946664 (accessed 01.02.2026).

Hach, 2026d. Phosphax sigma Prozess-Photometer für Gesamt-Phosphor und Ortho-Phosphat, 0,01-5 mg/L PO_4-P, Profibus DP | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/phosphax-sigma-prozess-photometer-fur-gesamt-phosphor-und-ortho-phosphat-0-01-5-mg-l-po-p-profibus-dp/product?id=26370469076&callback=qs (accessed 01.02.2026).

Hach, 2026e. Sigmatax 2 Steuereinheit Probennahme und Ultraschall-Homogenisierung | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/sigmatax-2-steuereinheit-probennahme-und-ultraschall-homogenisierung/product?id=26370809331&callback=qs (accessed 01.02.2026).

Hach, 2026f. Amtax inter2 Ammonium-Analysator | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/ammonium-analysatoren/amtax-inter2-ammonium-analysator/family?productCategoryId=23955609936 (accessed 01.02.2026).

Hach, 2026g. Amtax sc Ammonium analyser, outdoor, 0.05 - 20 mg/L NH_4-N, 1-channel [WWW Document]. URL https://uk.hach.com/p-amtax-sc-ammonium-analyser/LXV421.99.13001 (accessed 01.02.2026).

Hach, 2026h. Sulfat-Analysatoren der EZ-Serie | Hach Deutschland – Übersicht | Hach [WWW Document]. URL https://de.hach.com/analysatoren-der-ez-serie/sulfat-analysatoren-der-ez-serie/family?productCategoryId=55073004817 (accessed 01.02.2026).

Harris, D.C., 2014. Lehrbuch der Quantitativen Analyse. Springer Berlin Heidelberg, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-37788-4

Harvey, D., 2013. Schematic Diagram of a Membrane Electrode. URL https://asdlib.org/imageandvideoexchangeforum/schematic-diagram-of-a-membrane-electrode/ (accessed 02.02.2026).

Hoffmann, D., 2021. Experten warnen: Gefahr von Hochwasser und Überflutung steigt – wie wir uns davor schützen können [WWW Document]. Saarbr. Ztg. URL https://www.saarbruecker-zeitung.de/saarland/saarbruecken/problem-flaechenversiegelung-umwelt-experten-fordern-massnahmen_aid-63401713 (accessed 18.10.2025).

ISO 5667-3:2018, 2018. Water quality - Sampling.

ISO 5814-2012, 2012. Water quality — Determination of dissolved oxygen — Electrochemical probe method.

ISO 5815-1:2020-11, 2020. Bestimmung des biochemischen Sauerstoffbedarfs nach n Tagen (BSB_n) - Teil 1: Verdünnungs- und Impfverfahren mit Zugabe von Allylthioharnstoff.

ISO 7027-1:2016, 2016. Water quality - Determination of turbidity. Part 1: Quantitative methods.

ISO 7888:1985, 1985. Water quality - Determination of electrical conductivity.

ISO 10523:2008, 2008. Water quality — Determination of pH.

ISO 11905-1:1997, 1997. Water quality - Determination of nitrogen -Part 1: Method using oxidative digestion with peroxodisulfate.

IUPAC, 2026. Beer–Lambert law (B00626) [WWW Document]. Int. Union Pure Appl. Chem. https://doi.org/10.1351/goldbook.B00626 (accessed 01.02.2026)

IUPAC, 2025. pH (P04524) [WWW Document]. Int. Union Pure Appl. Chem. https://doi.org/10.1351/goldbook.P04524 (accessed 11.11.2025)

Khosrovyan, A., 2024. Biodiversity and Ecosystem Services in Rivers. Water 16, 2091. https://doi.org/10.3390/w16152091

Kirchner, J.W., Feng, X., Neal, C., Robson, A.J., 2004. The fine structure of water-quality dynamics: the (high-frequency) wave of the future. Hydrol. Process. 18, 1353–1359. https://doi.org/10.1002/hyp.5537

Kumar, R., Qureshi, M., Vishwakarma, D.K., Al-Ansari, N., Kuriqi, A., Elbeltagi, A., Saraswat, A., 2022. A review on emerging water contaminants and the application of sustainable removal technologies. Case Stud. Chem. Environ. Eng. 6, 100219. https://doi.org/10.1016/j.cscee.2022.100219

Lassaletta, L., García-Gómez, H., Gimeno, B.S., Rovira, J.V., 2010. Headwater streams: neglected ecosystems in the EU Water Framework Directive. Implications for nitrogen pollution control. Environ. Sci. Policy 13, 423–433. https://doi.org/10.1016/j.envsci.2010.04.005

LAWA, 2021. Teil B Bewertungsgrundlagen und Methodenbeschreibungen, Rahmenkonzeption Monitoring. Länderarbeitsgemeinschaft Wasser.

LAWA, 2015. Arbeitspapier 1: Berücksichtigung von natürlichen Hintergrundkonzentrationen bei der Beurteilung von Überschreitungen der Umweltqualitätsnormen nichtsynthetischer Schadstoff, Technische Anleitung zur Oberflächengewässerverordnung,. Länderarbeitsgemeinschaft Wasser.

LAWA, 2003. Ermittlung von Stoff-Frachten in Fließgewässern, Probenahmestrategien und Berechnungsverfahren. Länderarbeitsgemeinschaft Wasser.

Lepore, M., Delfino, I., 2022. Optical Sensors Technology and Applications. Sensors 22, 7905. https://doi.org/10.3390/s22207905

Li, X., Shen, X., Jiang, W., Xi, Y., Li, S., 2024. Comprehensive review of emerging contaminants: Detection technologies, environmental impact, and management strategies. Ecotoxicol. Environ. Saf. 278, 116420. https://doi.org/10.1016/j.ecoenv.2024.116420

Libelium, 2025. Libelium Smart Water Sensor Platform Adds Ion Monitoring. Libelium. URL https://www.libelium.com/libeliumworld/smart-water-ions-sensors-calcium-fluoride-chloride-nitrate-iodide-lead-bromide-cupric-silver/ (accessed 12.10.2025).

LUBW, 2015. Fischsterben in der Jagst - Vorläufige Abschätzung der ökologischen Auswirkungen des Großbrandes in der Lobenhausener Mühle. Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Karlsruhe.

Marshak, S., 2022. Essentials of geology, Seventh edition. ed. W.W. Norton & Company, New York, NY London.

Meybeck, M., 2003. Global Occurrence of Major Elements in Rivers, in: Treatise on Geochemistry. Elsevier, pp. 207–223. https://doi.org/10.1016/B0-08-043751-6/05164-1

Meyer, A.M., Fuenfrocken, E., Kautenburger, R., Cairault, A., Beck, H.P., 2021a. Detecting pollutant sources and pathways: High-frequency automated online monitoring in a small rural French/German transborder catchment. J. Environ. Manage. 290, 112619. https://doi.org/10.1016/j.jenvman.2021.112619

Meyer, A.M., Fünfrocken, E., Beck, H.P., Hegetschweiler, K., 2019a. Überwachung von Fließgewässern im Saarland - Abschlussbericht Theel - Ill - Alsbach (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Fünfrocken, E., Beck, H.P., Hegetschweiler, K., 2014. Überwachung von Fließgewässern im Saarland - Fischbach (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Fünfrocken, E., Beck, H.P., Hegetschweiler, K., 2013a. Überwachung von „at risk"-Gewässern im Saarland in einem online-Monitoring Programm - Bist (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Fünfrocken, E., Beck, H.P., Kickelbick, G., Kautenburger, R., 2021b. Überwachung von Fließgewässern im Saarland - Erbach (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Fünfrocken, E., Beck, H.P., Kickelbick, G., Kautenburger, R., 2020. Überwachung von Fließgewässern im Saarland - Blies in Neunkirchen und Bierbach (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Fünfrocken, E., Kickelbick, G., Kautenburger, R., Beck, H.P., 2023. Überwachung von Fließgewässern im Saarland - Oster in Wiebelskirchen (Im Auftrag des Ministeriums für Umwelt, Klima, Mobilität, Agrar und Verbraucherschutz). Universität des Saarlandes.

Meyer, A.M., Klein, C., Fünfrocken, E., Kautenburger, R., Beck, H.P., 2019b. Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers. Sci. Total Environ. 651, 2323–2333. https://doi.org/10.1016/j.scitotenv.2018.10.069

Meyer, A.M., Megel, N., Hein, C., Fünfrocken, E., Oberhausen, B., Kickelbick, G., Kautenburger, R., 2024. Überwachung von Fließgewässern im Saarland - Mandelbach (Im Auftrag des Ministeriums für Umwelt, Klima, Mobilität, Agrar und Verbraucherschutz). Universität des Saarlandes.

Meyer, A.M., Neurohr, S., Fünfrocken, E., Beck, H.P., Hegetschweiler, K., 2013b. Überwachung von "at-risk"-Gewässern im Saarland - Einzugsgebiet Losheimer Bach (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

Meyer, A.M., Oliveri, E., Kautenburger, R., Hein, C., Kickelbick, G., Beck, H.P., 2025. *In situ* real-time monitoring of ammonium, potassium, chloride and nitrate in small and medium-sized rivers using ion-selective-electrodes – a case study of feasibility. Environ. Sci. Adv. 4, 1238–1249. https://doi.org/10.1039/D5VA00021A

Meyer, J.L., Strayer, D.L., Wallace, J.B., Eggert, S.L., Helfman, G.S., Leonard, N.E., 2007. The Contribution of Headwater Streams to Biodiversity in River Networks[1]. JAWRA J. Am. Water Resour. Assoc. 43, 86–103. https://doi.org/10.1111/j.1752-1688.2007.00008.x

Mishra, R.K., Mentha, S.S., Misra, Y., Dwivedi, N., 2023. Emerging pollutants of severe environmental concern in water and wastewater: A comprehensive review on current developments and future research. Water-Energy Nexus 6, 74–95. https://doi.org/10.1016/j.wen.2023.08.002

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. Water Resour. Res. 53, 1270–1287. https://doi.org/10.1002/2016WR019635

MUKMAV, 2021. Anhang VI - Methodenhandbuch für das Saarland, 3. Bewirtschaftungsplan Nach § 83 Wasserhaushaltsgesetz Für Das Saarland. Ministerium Für Umwelt- Und Verbraucherschutz in Zusammenarbeit Mit Dem Landesamt Für Umwelt- Und Arbeitsschutz.

Nernst, W., 1889. Die elektromotorische Wirksamkeit der Jonen. Z. Für Phys. Chem. 4U, 129–181. https://doi.org/10.1515/zpch-1889-0412

Nikolsky, B.P., Shultz, M.M.-, Belyustin, A.A., Lev, A.A., 1967. Recent developments in the ion-exchange theory of the glass electrode and its application in the chemistry of glass 174–222.

NORMAN, 2025. Emerging substances [WWW Document]. Netw. Ref. Lab. Res. Cent. Relat. Organ. Monit. Emerg. Environ. Subst. URL https://www.norman-network.net/?q=node/19 (accessed 12.12.2025).

Oberhausen, B., Meyer, A.M., Fünfrocken, E., Kickelbick, G., Kautenburger, R., Beck, H.P., 2023. Einfluss von Haldenwässern auf kleine Fließgewässer am Beispiel des Trenkelbachs und des Lochwiesbachs (Im Auftrag des Ministeriums für Umwelt und Verbraucherschutz des Saarlandes). Universität des Saarlandes.

OGewV, 2016. Verordnung Zum Schutz Der Oberflächengewässer (German Surface Water Ordiance) - Oberflächengewässerverordnung.

Patella, B., Parisi, A., Moukri, N., Gitto, F., Busacca, A., Aiello, G., Russo, M., O'Riordan, A., Inguanta, R., 2023. Phosphate ions detection by using an electrochemical sensor based on laser-scribed graphene oxide on paper. Electrochimica Acta 461, 142600. https://doi.org/10.1016/j.electacta.2023.142600

Piniewski, M., Marcinkowski, P., Koskiaho, J., Tattari, S., 2019. The effect of sampling frequency and strategy on water quality modelling driven by high-frequency monitoring data in a boreal catchment. J. Hydrol. 579, 124186. https://doi.org/10.1016/j.jhydrol.2019.124186

RAG, 2014. Konzept zur langfristigen Optimierung der Grubenwasserhaltung der RAG Aktiengesellschaft für das Saarland. Ruhrkohle AG, Herne.

Rodríguez, J.P., Beard, Jr., T.D., Bennett, E.M., Cumming, G.S., Cork, S.J., Agard, J., Dobson, A.P., Peterson, G.D., 2006. Trade-offs across Space, Time, and Ecosystem Services. Ecol. Soc. 11, art28. https://doi.org/10.5751/ES-01667-110128

Romanowski, J., 2015. Probenehmer für Wasser, Abwasser und Flüssigkeiten von WaterSam [WWW Document]. WaterSam. URL https://www.watersam.com/ (accessed 08.02.2026).

Rozemeijer, J., Jordan, P., Hooijboer, A., Kronvang, B., Glendell, M., Hensley, R., Rinke, K., Stutter, M., Bieroza, M., Turner, R., Mellander, P.E., Thorburn, P., Cassidy, R., Appels, J., Ouwerkerk, K., Rode, M., 2025. Best practice in high-frequency water quality monitoring for improved management and assessment; a novel decision workflow. Environ. Monit. Assess. 197, 353. https://doi.org/10.1007/s10661-025-13795-z

Schönenberger, M., 2024. Suitability Verification and Method Optimisation of Ion-Selective Electrodes (ISE) for the Online Measurement of Nitrate, Chloride, Ammonium, and Potassium in Small and Middle Scale Rivers (Masterarbeit). Universität Trier.

Shaad, K., Souter, N.J., Vollmer, D., Regan, H.M., Bezerra, M.O., 2022. Integrating Ecosystem Services Into Water Resource Management: An Indicator-Based Approach. Environ. Manage. 69, 752–767. https://doi.org/10.1007/s00267-021-01559-7

Shawul, A.A., Chakma, S., Melesse, A.M., 2019. The response of water balance components to land cover change based on hydrologic modeling and partial least squares regression (PLSR) analysis in the Upper Awash Basin. J. Hydrol. Reg. Stud. 26, 100640. https://doi.org/10.1016/j.ejrh.2019.100640

Shumilova, O., Tockner, K., Gurnell, A.M., Langhans, S.D., Righetti, M., Lucía, A., Zarfl, C., 2019. Floating matter: a neglected component of the ecological integrity of rivers. Aquat. Sci. 81, 25. https://doi.org/10.1007/s00027-019-0619-2

Silva-Júnior, R.O.D., Souza-Filho, P.W.M.E., Salomão, G.N., Tavares, A.L., Santos, J.F.D., Santos, D.C., Dias, L.C., Silva, M.S.D., Melo, A.M.Q.D., Costa, C.E.A.D.S., Rocha, E.J.P.D., 2021. Response of Water Balance Components to Changes in Soil Use and Vegetation Cover Over Three Decades in the Eastern Amazon. Front. Water 3, 749507. https://doi.org/10.3389/frwa.2021.749507

Sousa, M.C., Martins, R., Simões, N.E., Feio, M.J., 2025. Ecosystem services of urban rivers: a systematic review. Aquat. Sci. 87, 10. https://doi.org/10.1007/s00027-024-01138-y

Su, G., Logez, M., Xu, J., Tao, S., Villéger, S., Brosse, S., 2021. Human impacts on global freshwater fish biodiversity. Science 371, 835–838. https://doi.org/10.1126/science.abd3369

Tomei, A., Fornasaro, S., Arrighi, S., Ghezzi, L., Cogorno, M., Petrini, R., Petrov, M., Shukurov, N., Giannarelli, S., 2026. Legacy, Distribution and Risk Assessment of Persistent Organic Pollutants in River Sediments in a Mixed Sources Area. Water. Air. Soil Pollut. 237, 133. https://doi.org/10.1007/s11270-025-08737-x

UBA, 2025. Stabilizing our Landscape Water Balance [WWW Document]. Umweltbundesamt. URL https://www.umweltbundesamt.de/en/topics/water/extreme-events-climate-change/stabilizing-our-landscape-water-balance (accessed 15.10.2025).

UBA, 2024. Nasse Deposition saurer und säurebildender Regeninhaltsstoffe [WWW Document]. Umweltbundesamt. URL https://www.umweltbundesamt.de/daten/luft/nasse-deposition-saurer-saeurebildender (accessed 11.12.2025).

UBA, 2022. Water Framework Directive The Status of German Waters 2021 Progress and Challenges. Umweltbundesamt.

UBA, 2021. PMT and vPvM substances under REACH [WWW Document]. Umweltbundesamt. URL https://www.umweltbundesamt.de/en/PMT-substances (accessed 02.02.2026).

UN, 2025. Goal 6: Clean water and sanitation. Glob. Goals. URL https://globalgoals.org/goals/6-clean-water-and-sanitation/ (accessed 19.11.2025).

UN/ECE, 2003. Environmental monitoring and reporting: Eastern Europe, the Caucasus and Central Asia. United Nations, New York.

Vidmar, J., Zuliani, T., Novak, P., Drinčić, A., Ščančar, J., Milačič, R., 2017. Elements in water, suspended particulate matter and sediments of the Sava River. J. Soils Sediments 17, 1917–1927. https://doi.org/10.1007/s11368-016-1512-4

Walker, P.J., 2003. WATER SUPPLIES | Chemical Analysis, in: Caballero, B. (Ed.), Encyclopedia of Food Sciences and Nutrition (Second Edition). Academic Press, Oxford, pp. 6111–6117. https://doi.org/10.1016/B0-12-227055-X/01278-5

Wilcock, P., Pitlick, J., Cui, Y., 2009. Sediment transport primer: estimating bed-material transport in gravel-bed rivers (No. RMRS-GTR-226). U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, Ft. Collins, CO. https://doi.org/10.2737/RMRS-GTR-226

WISE, 2024. Water Framework Directive [WWW Document]. URL https://water.europa.eu/freshwater/freshwater/europe-freshwater/water-framework-directive (accessed 10.12.2024).

Zak, D., Hupfer, M., Cabezas, A., Jurasinski, G., Audet, J., Kleeberg, A., McInnes, R., Kristiansen, S.M., Petersen, R.J., Liu, H., Goldhammer, T., 2021. Sulphate in freshwater ecosystems: A review of sources, biogeochemical cycles, ecotoxicological effects and bioremediation. Earth-Sci. Rev. 212, 103446. https://doi.org/10.1016/j.earscirev.2020.103446

Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., Yao, X., 2020. Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. Glob. Ecol. Conserv. 22, e00925. https://doi.org/10.1016/j.gecco.2020.e00925