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Making waves: Time for chemical surface water quality monitoring to catch up with its technical potential

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ABSTRACT

A comprehensive real-time evaluation of the chemical status of surface water bodies is still utopian, but in our opinion, it is time to use the momentum delivered by recent advanced technical, infrastructural, and societal developments to get significantly closer. Procedures like inline and online analysis (*in situ* or in a bypass) with close to real-time analysis and data provision are already available in several industrial sectors. In contrast, atline and offline analysis involving manual sampling and time-decoupled analysis in the laboratory is still common practice in aqueous environmental monitoring. Automated tools for data analysis, verification, and evaluation are changing significantly, becoming more powerful with increasing degrees of automation and the introduction of self-learning systems. In addition, the amount of available data will most likely in near future be increased by societal awareness for water quality and by citizen science. In this analysis, we highlight the significant potential of surface water monitoring techniques, showcase “lighthouse” projects from different sectors, and pin-point gaps we must overcome to strike a path to the future of chemical monitoring of inland surface waters.

1. Current status vs. potential applications

Regulatory and scientific chemical monitoring serves societal and ecological needs, focusing on surface water bodies and dissolved chemical species in industrialized and populated areas. A highly visible challenge is the protection of drinking water resources and the avoidance of adverse ecological effects in the context of global climate change and the associated changing water distribution. Erfurt et al. (2019) describe the impact of drought events from 1800-2018 on southwestern Germany and emphasize: “Droughts […] cause impacts on ecology, economy, health, governance, and social behavior.” Consequently, while recognizing increasingly competing interests for water use and re-use (e.g., temperature (Zavarsky and Duester 2020)) and raising societal awareness for global water distribution, chemical water monitoring (regulatory and scientific) is increasingly important in transnational decision-making processes. Strategies on how to monitor the almost unmanageable multitude of anthropogenic chemical species from different sources are available. Usually, at different levels of complexity, they aim to provide robust data of the current chemical water quality status in order to (i) deliver long-term data on trends, (ii) detect patterns of chemical substances, (iii) detect potential threats to humans, biota, and ecosystem health, (iv) evaluate the current risk potential for the water bodies, (v) deliver inputs for prediction tools, and (vi) support decision-making on the political, environmental, and economic level.

In past monitoring activities, the decoupling of sampling, analysis, and data provision was self-evident and a consequence of the clear separation between the *in situ* (sampling) and *ex situ* (laboratory) workload. Prominent examples of drawbacks caused by this practice are, discontinuous monitoring schemes with grab samples and large time intervals, or the failing to address discontinuously released chemical species (e.g., pesticides). Moreover, the delayed availability of data, impedes authorities and downstream waterworks to immediately respond to spill events. Additionally, current chemical routine monitoring often provides only a small glimpse of the chemical burden in surface waters. So far, it focuses on regulated substances and as a direct consequence, it usually misses the multitude of emerging contaminants such as precursor species, by-products of industrial processes or the various transformation products. Taking this into account, it is time to look ahead at potential solutions, from technical innovations to verified monitoring approaches. Nowadays, time gaps between sampling, sample preparation, analysis, quality management, data-processing, and

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-provisioning are decreasing through significant technical improvements. These key technologies for improvements are also crucial for development towards the fourth industrial revolution (e.g., digitalization, big data and artificial intelligence analytics, from offline to inline and atline analyses, Internet of Things). Routine surface water monitoring already includes continuous real-time inline (*in situ*) and online (in a bypass, e.g., a monitoring station) measurements as well as automated data processing of basic physicochemical water quality parameters such as temperature, pH, conductivity, dissolved oxygen (DO), and turbidity. In some river basins, like at the river Rhine, international alert and warning plans are in place based on flow time models fed by chemical analyses at seven international stations along the river (https://www.iksr.org/en/topics/pollution/international-warning-and-alarm-plan), including close to real-time, on- and atline analysis (definitions in Fig. 1). Following this example, within the last decades each year between 16 and 61 alerts were triggered. These alerts included events from shipping, industries, agriculture, others, and unknown sources. However, as explained later this only includes visible (e.g., oil films) or target pollutants and systematic non-target approaches are urgently needed to complete the picture.

This article raises awareness for the high innovation potential visible in the chemical surface water quality monitoring, provided by the fourth industrial revolution. The most significant bottlenecks are addressed to deliver a basis for further discussion between different interest groups (e.g., science, administration, industry, politics). The aim is to create a common ground for future activities both in regulative and scientific surface water quality monitoring. We share the vision, within a timeframe of ten to twenty years, the chemical surface water quality monitoring can catch up with its technical potential, if we set the right course today.

2. Current routine? Today's sensor-based monitoring

To address the classical physicochemical parameters, well-established sensor designs are often preferred when large maintenance intervals are needed, e.g., in areas with limited infrastructure. These sensors form the basis of almost every chemical surface water monitoring network, and the technical development has a significant overlap with the wastewater treatment market segment. In the last decades, the set of sensors was extended by ion selective electrodes (ISEs) and optical detection methods (UV-VIS, IR, fluorescence) for detection of specific chemical species or sum parameters (Finch et al. 1998, Jannasch et al. 1994, Langmuir and Jacobson 1970). However, sensitivity, selectivity, interferences, and fouling effects may significantly limit their application (DeMarco et al. 2007, Pellerin et al. 2013). An example for interferences limiting ISEs is an over-estimation of the analyte's concentration due to ionic interferences (Pellerin et al. 2013), e.g., by K^+ while monitoring NH_4^+ (Wang et al. 2020). Optical sensors for nitrite own often detection limits in the mg L^{-1} range, which is rarely reached in European natural waters and can be impacted by fouling effects on the optical measurement windows. However, anti-fouling techniques are already in practice or included in prototypes. They make use of fouling resistant materials, UV light from LEDs, or turbulences from air flushing (Meyer 2003). In summary, certain parameters are still difficult to be analyzed with sensors, but several recent technical approaches improve the measurements. Reagent-free or colorimetric optical sensors provide data for nutrients and optically visible substances (e.g., Boënne et al. (2014), Rieger et al. (2008)). Giving higher precision compared to ISEs (Pellerin et al. 2016), they are, sensitive to turbidity and colored water, i.e., high concentrations of suspended matter or humic substances dominant in wetlands or during floods, e.g., Blaen et al. (2016). Sensors based on fluorescence spectroscopy are employed to quantify aromatic organic compounds, chlorophyll α (Blaen et al. 2016), and algae

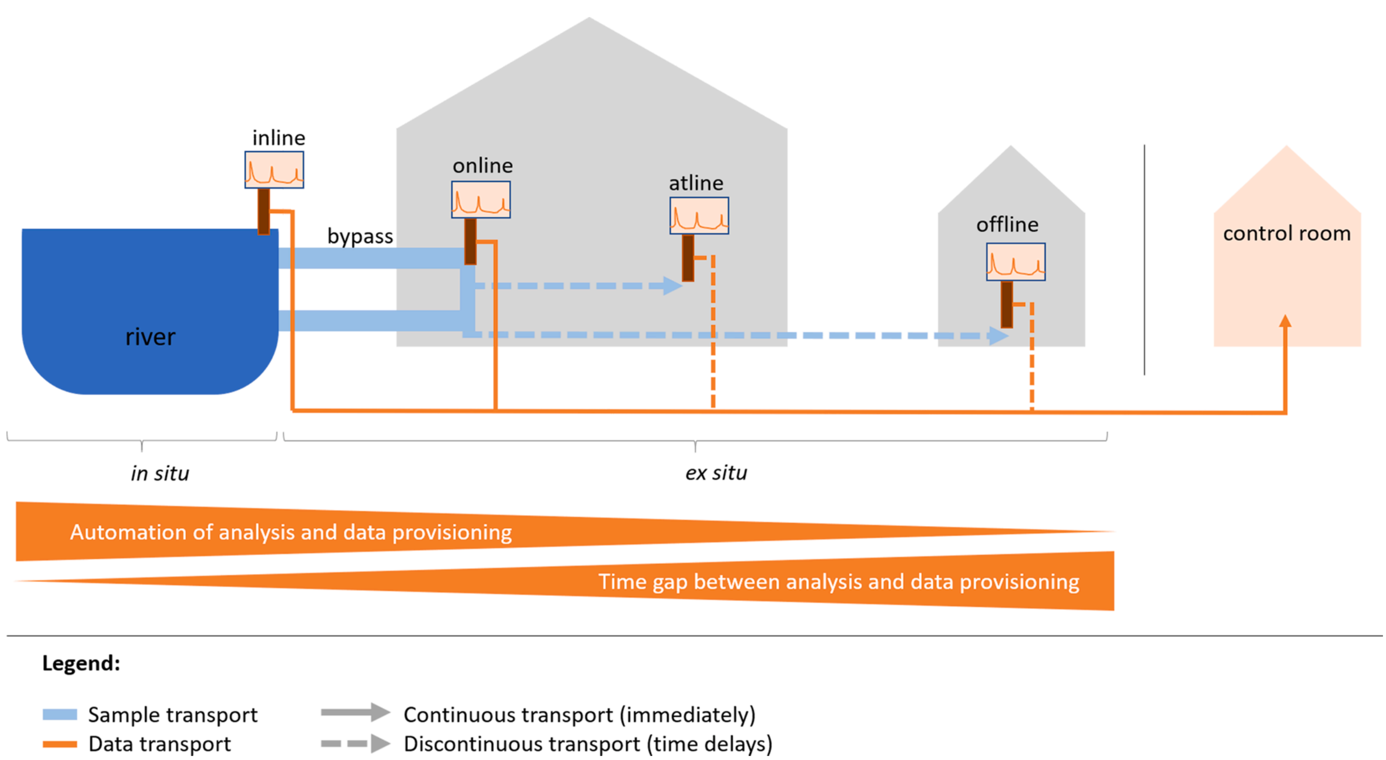

Fig. 1. Categories in surface water monitoring analogous to process technologies. An *in situ* technique is inline (automated continuous analysis directly in the river, e.g., by sensors, and automated data provisioning), *ex situ* methods are online (continuous automated sample supply and analysis in a bypass with automated data provisioning, e.g., colorimetric methods with chemical addition), atline (more complex discontinuous analysis with either automated or manual sample preparation and supply and often discontinuous data provisioning), or offline (sample transport is mostly done manually to a different building or laboratory for analysis, resulting in time delays in data provisioning).

(Besmer et al. 2014, Ye et al. 2014). A validation of the sensor-based online techniques in direct comparison to the respective offline methods must therefore always be undertaken within the respective catchment area. As an example, for optical dissolved organic carbon (DOC) sensors the sum parameter is calibrated in the laboratory with a single substance. In contrast, in every surface water this sum parameter consists of several substances varying in composition and therefore results may differ significantly. This also applies to turbidity, which is also a sum parameter. In addition, cross-comparison to remote sensing activities are needed to be able to monitor also inaccessible surface waters (e.g., due to topography; Gholizadeh et al. (2016)). Sensors are comparably easy to use, usually cheaper than the alternatives, run continuously (Blaen et al. 2016), and can be applied *in situ*, online in monitoring stations, or mobile on trailers/ships or autonomous vehicles (e.g., Meyer et al. (2019), Petersen (2014)). Even if sensor-based measurements still sometimes lack precision, they already are used to trigger event-based sampling during extreme events, spills, droughts, or algae blooms (e.g., by water level sensors; Gunold et al. (2019)). As an example, they own a significant potential to enhance the precision of river basin balances. Taking it together, to improve "routine" monitoring, better knowledge of the limits of accuracy for the sensors (interfering factors and common practice to correct data, e.g., Shaughnessy et al. (2019)) and improved solutions to suppress fouling must be available.

3. From offline to online

Usually, the most analytically accurate methods (providing often also the lowest limits of detection (LODs)) are laboratory offline techniques. If feasible, these techniques can be transferred to automated online monitoring techniques and adapted to tolerate extended maintenance intervals. Basically, injection systems are modified, software is adapted for 24/7 runtimes, process and quality control (QC) as well as the data processing and evaluation need to be automated. In contrast to many fourth industrial revolution trends, e.g., in the semiconductor industry (Wiederin and Otaki 2017), surface water is biologically active, delivering its own challenges, for which filtration or disinfection (e.g., with UV light) may improve the analytical stability.

To transfer laboratory methods to online monitoring methods, a higher degree of freedom than in conventional method development is needed. This can be supported, e.g., by 3D-printing of low-cost autosamplers run by open-source software (Carvalho and Murray 2018), designing self-cleaning autosamplers with integrated sample filtering controlled by RaspberryPi (Stadler et al. 2017), or using cost-effective pipetting robots (Steffens et al. 2017). To foster these processes, more scientists and institutions must support open-source software development and open-access technology sharing trends, beyond the information usually delivered in publications.

3.1. Inorganic substances

Using common analysis techniques, robust *in situ* lab-on-a-chip devices have recently been 3D-printed for the detection of Pb, Cd, Zn, Cu, Hg (Katseli et al. 2020, Lee et al. 2017), NH_4^+ (Fornells et al. 2020), and algae (Schaap et al. 2012). Automated online IC has recently been developed for anion and cation monitoring in rivers (Floury et al. 2017, Murray et al. 2020). As an example for single element analyses, total Hg has been analyzed online by cold vapor atomic absorption spectrometry (CV-AAS) for 5 days at the river Elbe, Germany (Elsholz et al. 2000). For less polluted water bodies, enrichment or the more sensitive atomic fluorescence spectrometry detector (AFS) are suitable online alternatives. The most commonly used instrument in single-run, multi-element analysis of trace elements is inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS has been applied online for trace elements in environmental aerosols (Mishra et al. 2018) and is already automated in the semiconductor industry atline for vapors and liquids (Wiederin and Otaki 2017). Single run multi-element analysis with 20-70 analytes by ICP-MS (Belkouteb et al. in prep., Fabricius et al. 2020) and online preconcentration solutions (Wuttig et al. 2019) are first steps towards real multi-element online analysis of the almost complete surface water element balance. For automated online voltammetric determination of trace elements, commercial techniques exist for about 20 elements down to ppt concentrations (e.g., Metrohm Process Analytics, 2016). For some elements, speciation (i.e., oxidation state) is possible (e.g., As, Sb, Fe, Cr, Mo, Se) and also *in situ* sensors exist (Illuminati et al. 2019, Tercier--Waeber et al. 2021). In addition to total element concentration analysis, isotopic analysis can provide evidence for the origin of the water and impacts from different tributaries. The first online injection techniques for stable water isotopes without isotopic fractionation have already been evaluated 9 years ago for potential field application (Herbstritt et al. 2012, Koehler and Wassenaar 2011), while online application was first performed in 2017 (von Freyberg et al. 2017). A similar setup was used for the analysis of $\delta^{13}C$ in dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC, Hartland et al. (2012)) and therefore also has the potential to be run online. Total radioactivity of water currently is surveilled continuously by the widely used scintillation analysis with probes in real-time within networks across large areas (e.g., Doll et al. (2013), Wedekind et al. (1999)). Most important aspects to be improved in the next 10 to 15 years are: reduce the price and raise the robustness as well as further promote online preconcentration and matrix removal methods.

3.2. Organic substances

Organic micropollutants in water are usually analyzed by gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS). The automation of sample preparation by online solid-phase-extraction–LC-MS for the analysis of a variety of pesticides, pharmaceuticals, biocides, and industrial chemicals in surface water bodies has recently made enormous progress (as reviewed by Elpa et al. (2020)). While the technical equipment for such setups is commercially available, the automation of the entire workflow, including sampling but especially data processing and evaluation, is more challenging and requires custom-built solutions (see Section 3.3). Nonetheless, almost entirely automated laboratories are operating on a continuous basis, in one example for the monitoring of specific organic compounds in industrial production water (Wortberg and Kurz 2019).

In contrast to *target* analysis, which is restricted to a limited selection of known analytes, *non-target-screening* (NTS), based on the detection by high-resolution mass spectrometry (HRMS), enables the analysis of all compounds amenable to the chosen chromatographic method and detected by the MS applied. Thus, the data can be screened post-analysis for any known or suspected contaminant, a process which can be automated by employing a substance library (Jewell et al. 2019). In addition, NTS enables the detection of unknown contaminants by searching the data for characteristic emission patterns or unexpected changes and then identifying these unknowns with the help of the acquired mass spectra (Ruppe et al. 2018, Schlüsener et al. 2015). NTS is thereby both a powerful tool for (in a sense) digitally storing samples for post-analysis screening (Hollender et al. 2017) and also to increase the breadth of chemical monitoring. Only recently, Stravs et al. (2021) developed a trailer-based automated sampling and HRMS measurement system for surface water, e.g., for the deployment in remote locations. To make use of the full potential of NTS, we must address the following challenges: Especially for automated online monitoring, optimized and robust algorithms for automated processing and evaluation of NTS data are essential (see Section 3.3). There is a need to increase the comparability of NTS data by strategies for quality assurance such as the application of (automated) quality control charts (e.g., for mass deviation and resolution, absolute and relative intensities) as well as the evaluation of false positives and false negatives, i.e. erroneous detections or non-detections due to errors in the data evaluation algorithms. Moreover, freely available mass-spectral libraries tailored to surface water monitoring must be continuously extended and be easily accessible to overcome the bottleneck of compound identification. Finally, databases for storing quality-assured NTS data combined with powerful and easy-to-use online dashboards for user-specific data evaluation and prioritization would foster the inter-regional and retrospective evaluation of both known and unknown organic water contaminants.

3.3. Automation of data processing and evaluation

Next to instrumental automation, online routines in quality assurance and quality control (QA/QC), process control, and data processing must be adapted. Regarding the high throughput of samples, automated data processing, data QA/QC, its evaluation, and close to real-time availability are becoming more common (Fleischer and Thurow 2018). Sometimes, commercial solutions are applied (Ehmann et al. 2006), but usually at the moment at least parts of the setups must be adopted or developed from scratch (Wortberg and Kurz 2019). Fortunately, the lack of commercial software applications is filled by several open-source automation solutions for both instrument control and data evaluation (Rijkenberg (2016), e.g., ms-utils.org, https://bio.tools, ms-utils.org, 2022, Ison et al. (2016)). Open-access journals and exchange platforms may help to accelerate knowledge sharing and thereby foster automation of data processing and evaluation techniques which is urgently required for real-time data provisioning. QA/QC can involve regularly analyzed standards, redundant systems, or statistical data (history) evaluation like classification of river water composition based on principal component analysis and linear discriminant analysis, e.g., Filella et al. (2014). Automated data evaluation may end up in, e.g., pure warning systems by comparing with threshold values (Wortberg and Kurz 2019) or forecasting and early warning systems based on artificial neural network or inferential modeling in addition to threshold values (Recknagel et al. 2017, Xia et al. 2015, Zhu et al. 2010). To be able to use automated data evaluation systems on all monitored parameters, significantly more time and money must be invested into transdisciplinary collaboration between, e.g., data- and environmental scientists. Here, large societal expectations lead in some cases to financial backing in areas like adaptive decision support systems, bayesian network modeling, machine-, deep-, or self-learning (incl. artificial neural network as reviewed in Ighalo et al. (2020)), often misleadingly summarized as “artificial intelligence” (Adeyemi et al. 2017, Kim and Lee 2018, Marcot and Penman 2019, Quinn and Hanna 2003, Yekeen and Balogun 2020). Next to transdisciplinary collaboration, transboundary collaboration must be intensified to successfully apply these emerging techniques for the benefit of our rivers and surface waters.

4. Non-stationary monitoring

Usually, stationary platforms are employed for surface water monitoring and sampling. Besides these, mobile infrastructures (e.g., trailer-based *ex situ* or autonomous *in situ*) equipped with GPS trackers, self-sustaining energy supply and data transmission via satellite or cellular network, depending on how remote the location is (Nam et al. 2005), are employed. Non-stationary examples from marine monitoring include buoys, autonomous gliders, and sailing boats or ferries. The latter provide more infrastructure and the water utilized for engine cooling or daily needs can be sampled and analyzed without changing processes on the ships (Petersen 2014, Steffen 2018). Buoys are also employed in rivers (Apel et al. 2012) while autonomous gliders, e.g., for microplastic screening with near-IR-light sensors and optional sampling (Edson and Patterson 2015), are difficult to realize for waterways where the challenges are less of technical nature, but more about legal challenges due to increased traffic densities compared to oceans. Remote-controlled boats already monitor small rivers/lakes for topography, hydrometry, and routinely for water quality (Degel and Hofmann 2017, Kutschera et al. 2017, Wiek et al. 2019). This on-site *in situ* monitoring is complemented by remote sensing towards spatially comprehensive monitoring with optically active parameters like chlorophyll, turbidity or drought monitoring (reviewed in Gholizadeh et al. (2016), Wieland and Martinis (2020)). To develop and optimize more robust non-stationary deployable techniques, again transdisciplinary research efforts as well as a close collaboration between science and industry is needed, while legal restrictions for autonomous vessels in inland waters must be overcome. In addition, it is for foreseeable that satellite-based monitoring merged with ground-based monitoring will play a more significant role in the future.

5. Citizen science

There are already examples of successful citizen science projects to monitor river water levels using modern smartphone capabilities (Etter et al. 2020, Strobl et al. 2019), routine water quality parameters by employing test kits (EarthEchoInternational, 2014), or biological parameters such as bacterial DNA or blooms of cyanobacteria (http://www.my-osd.org; https://cyanos.org/) are addressed. Several challenges and restrictions are still visible (i) only easy-to-determine parameters are addressed, (ii) a carefully designed, well-explained experimental setup to avoid temporal and spatial data biases is needed, (iii) data/ sample transmission must be easy to use, (iv) a complex data evaluation including provisions for potential sampling differences is usually involved and (v) discussions about integrity of research and intellectual properties need to be overcome (Guerrini et al. 2018). Even though the quality of citizen-based data is an ongoing point of discussion (Kosmala et al. 2016, Quinlivan et al. 2020, Thornhill et al. 2018), it is self-evident the overall data quality will increase once a higher degree of automatization and of “plug and play” solutions are implemented. Initiatives like “MyH2O“, are already beyond science by bridging the gap between data collection and provisioning, delivering more security for the local population (https://www.unenvironment.org/youngchampions/news/story/turning-data-drinking-water-china). Undoubtedly, fostered by commonly used high-tech devices, by higher robustness and lower prices of analytical devices and by big data mining, data created by non-scientists shows the greatest and so far, mostly unexploited, potential for our future environmental monitoring.

6. Can we draw the full picture?

Progress has been made and is still ongoing in the development, improvement, and evaluation of monitoring techniques. Diverse lighthouse projects already prove that automated online water monitoring is possible. However, adaption to routine online monitoring is often missing. Now is the right time to take the available techniques as a basis and add, step-by-step, innovative approaches from different sources (Fig. 2). This includes monitoring from different (autonomous) platforms (especially in remote areas), citizen science projects, utilizing existing infrastructures (like freighters), or creating new structures (like trailers). Inclusion of remote sensing techniques complement already *in situ* data, especially for areas with no possibility for area-wide *in situ* monitoring.

Demands in chemical water monitoring depend on hydrological conditions, the degree and kind of contamination expected, the monitoring aim, and last but not least the political will and financial means. Employed monitoring techniques and selection of monitoring parameters must vary significantly depending on the system monitored, e.g., major rivers need many parameters with lower time resolution, while at small rivers fewer parameters with a high time resolution are needed. In the current, far too long-lasting situation, countries downstream suffer from upstream chemical discharge. Therefore, especially at borders, networks of automated close-to-real-time monitoring stations will improve trust-based relations between countries. These joint projects are always also peace projects, especially in times of global change.

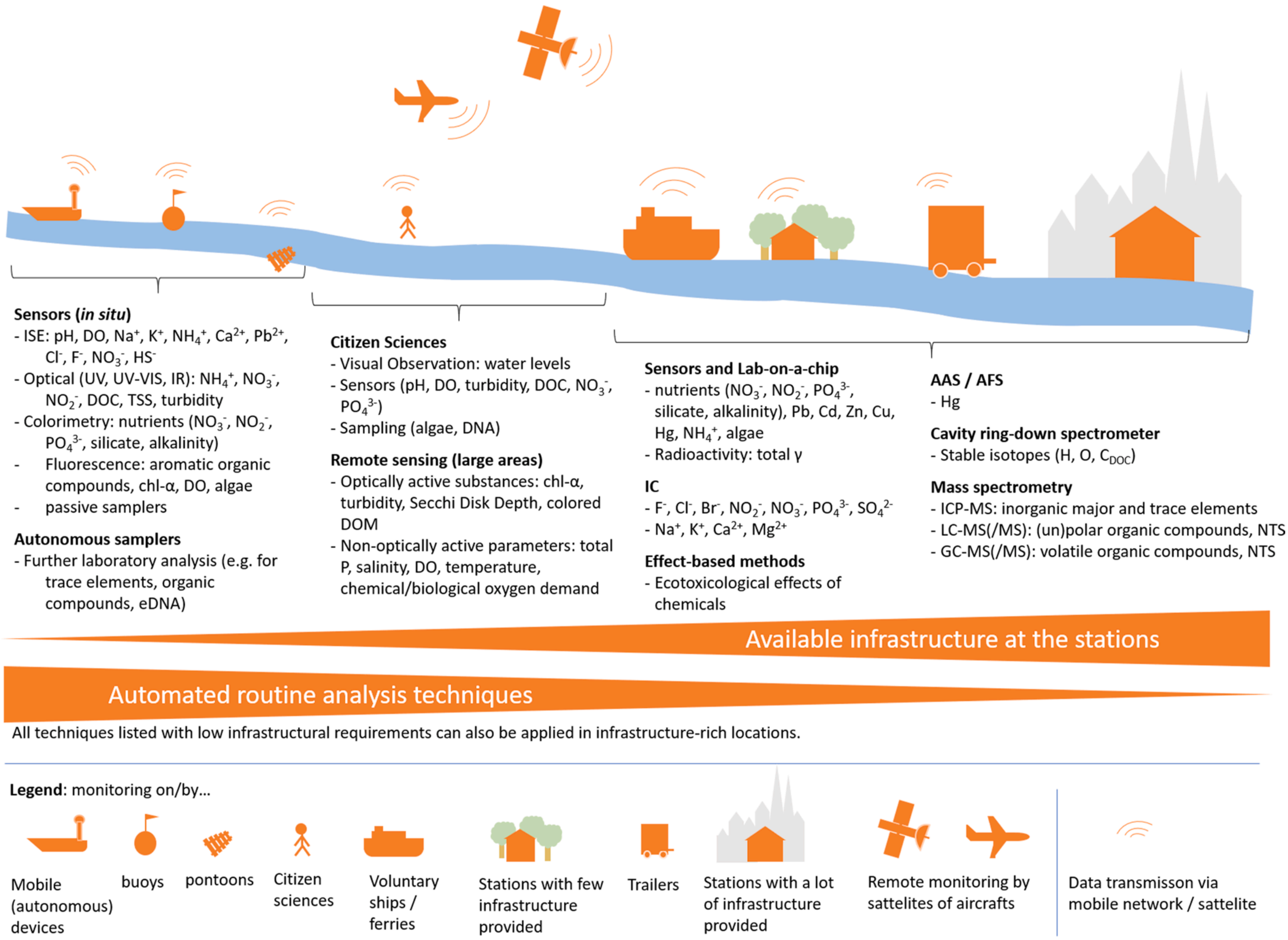

Fig. 2. Summary of techniques and parameters available for chemical real-time surface water monitoring. These are *in situ* techniques with monitoring from boats, buoys and pontoons, data collection through citizen science and remote sensing, as well as techniques currently known from laboratories requiring more infrastructure which is provided in ships, trailers and monitoring stations.

Regulative monitoring (based on the verification of compliance with limit values) can profit from scientific monitoring (based on a scientific question, usually not directly connected to regulation) to describe the current water status in much more detail. By using robust online techniques, threats towards goods worth of protection can be minimized and decision-making processes are improved. On the other hand, scientific monitoring can profit from regulative monitoring by its long-term data to, e.g., calibrate models and prediction tools. Cooperation and scientific exchange between different interest groups such as authorities, researchers, and industry will not only foster the innovation processes, but will also create a branched monitoring network where every single branch, and also in the end the environment, profit.

Future monitoring should focus on close to real-time (online) data provisioning with (if needed) high time-resolution and low LOQs. Following the utopia of data transport instead of sample transport, in long-term perspective, this will save energy, time and money. The data created will enable a more comprehensive communication of evaluations and prognosis to stakeholders and the public. Currently, in several industrialized countries, trace-level concentrations and the detection of so-far unknown substances are often of highest concern. Once implemented, automated monitoring may quickly pay back their substantial initial costs, as in industrialized countries personnel expenses are high and can be significantly reduced by automation. For countries with less infrastructure and significantly different, often well-known pollution patterns, a reduction of costs of the available techniques will presumably enable improvement in surface water monitoring. Here, after price reductions, communities supported by citizen science tools are more often likely to take matters into their own hands.

7. Conclusions

To exploit the whole range of the potentials given by the so-called fourth industrial revolution for chemical surface water quality monitoring, we must improve the following aspects within this decade:

- Improve the technical equipment:
- lower costs, raise robustness, and save resources via miniaturization,
- enable automated online analysis of previously offline techniques,
- automate matrix removal and analyte enrichment.
- Exploit additional information from the complementary online monitoring by including not only chemical but also hydrological, (micro)biological, ecotoxicological, and sedimentological parameters.
- Provide automated data processing and on-the-fly evaluation concepts like self-/ deep-/ machine-learning. Make these openly available to increase the impact.
- Create networks across all borders (countries and stakeholders) and address whole catchment areas to increase the efficiency of warning and forecasting approaches.

- Most of all, time and money must be spent on an intensified knowledge exchange between different scientific fields and interest groups.

CRediT authorship contribution statement

Julia Arndt: Investigation, Writing – original draft, Validation, Project administration. **Julia S. Kirchner:** Investigation, Writing – original draft, Validation. **Kevin S. Jewell:** Writing – original draft. **Michael P. Schluesener:** Writing – original draft. **Arne Wick:** Conceptualization, Writing – review & editing, Funding acquisition. **Thomas A. Ternes:** Conceptualization, Writing – review & editing, Funding acquisition. **Lars Duester:** Conceptualization, Investigation, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

None.

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