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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†

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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.

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:

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

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:

$$E(a_{\mathrm{i}}) = E^0 + \frac{RT}{z_{\mathrm{i}}F}\ln\left[a_{\mathrm{i}} + \sum\left(K_{\mathrm{ij}}\, a_{\mathrm{j}}^{z_{\mathrm{i}}/z_{\mathrm{j}}}\right)\right] \tag{2}$$

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.

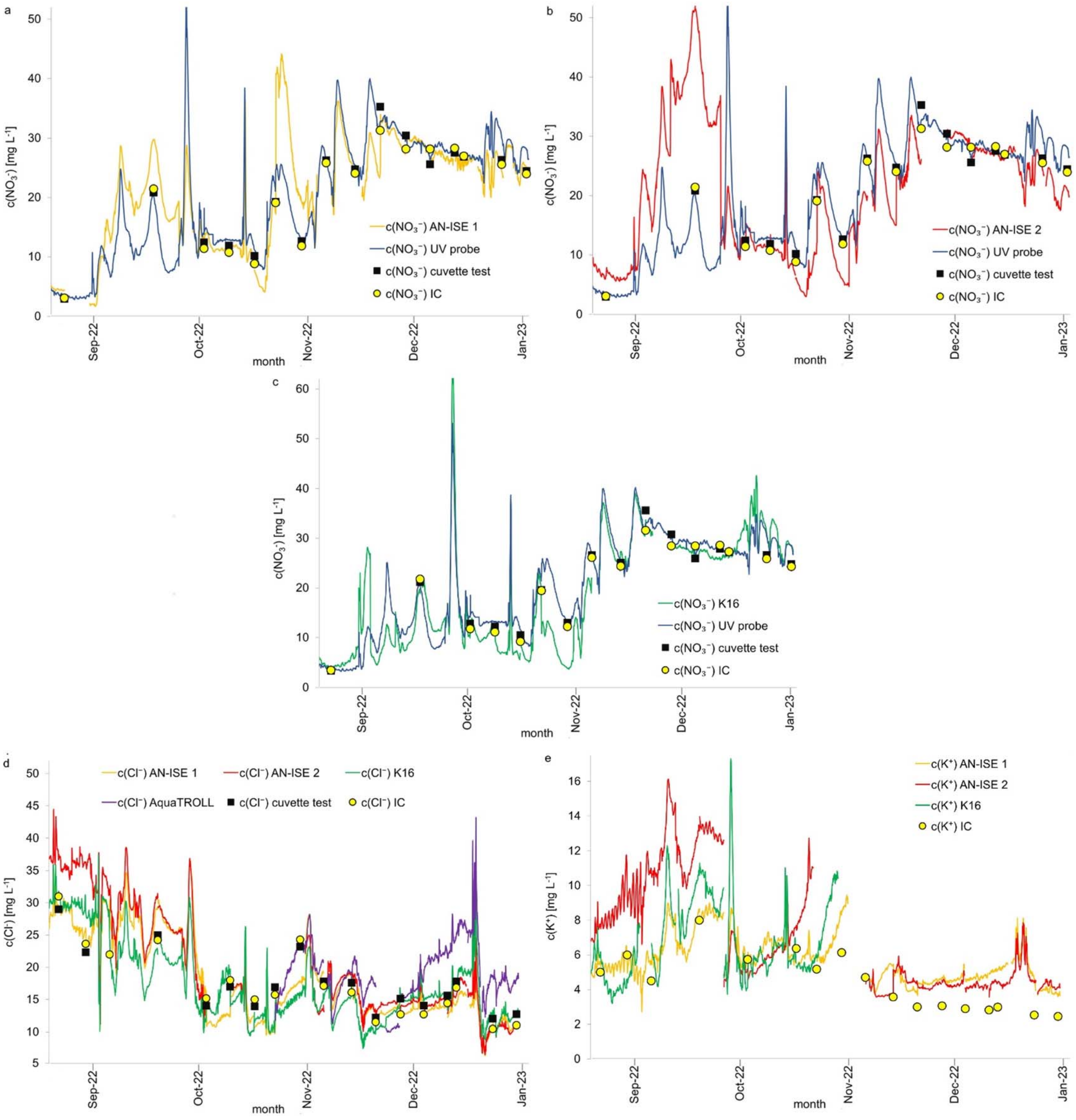

Fig. 1 Concentration data of NO_3^-, Cl^- and K^+ as given by ISEs and comparative measuring methods: comparison of NO_3^- data as given by UV probe, IC and cuvette tests with readings from (a) AN-ISE 1, (b) AN-ISE 2 and (c) K16. (d) Comparison of Cl^- data as given by IC and cuvette tests with AN-ISE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

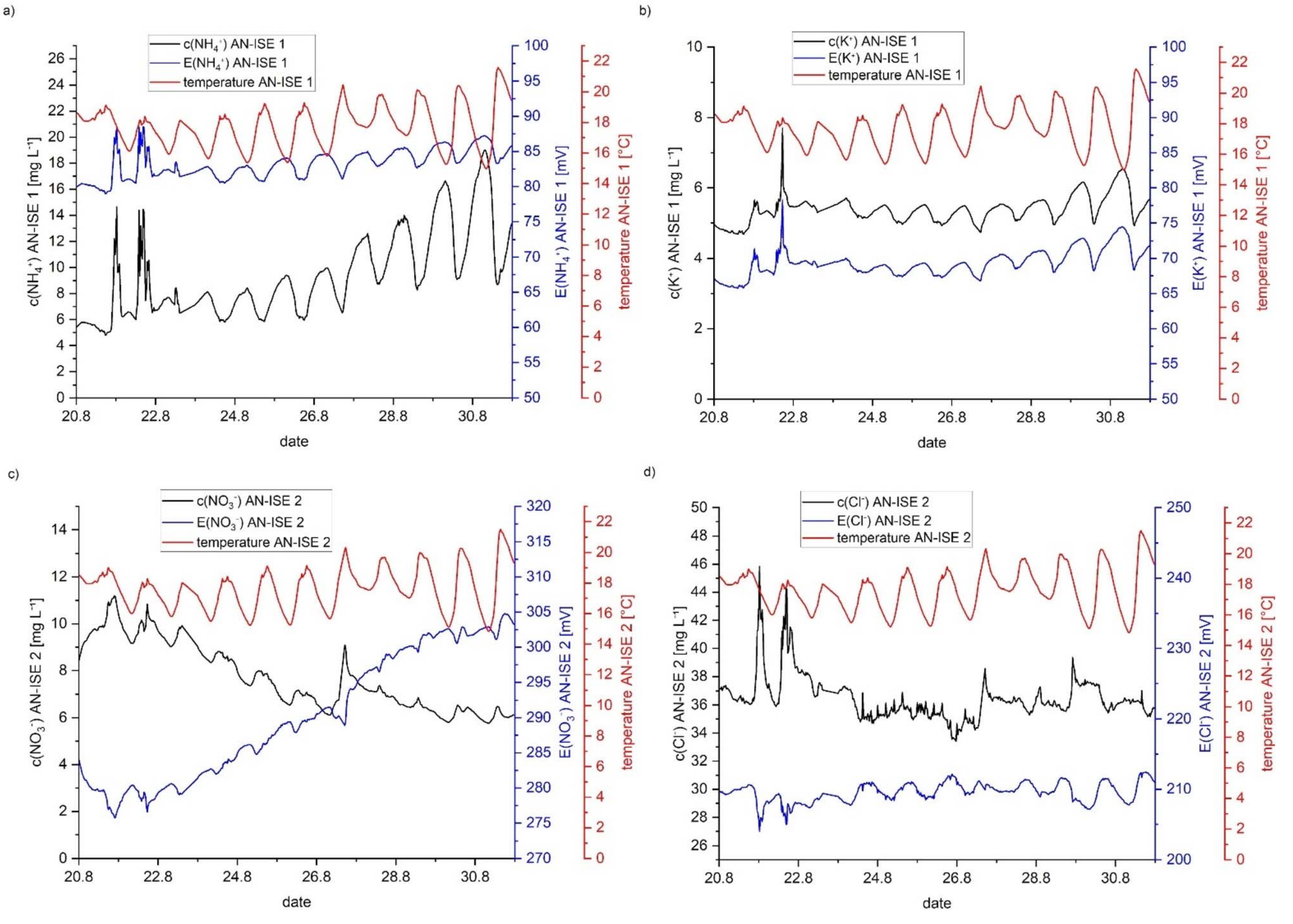

Fig. 2 Temperature dependent fluctuations in the mV signals and concentration readings of (a) NH_4^+ (AN-ISE 1), (b) K^+ (AN-ISE 1), (c) NO_3^- (AN-ISE 2), (d) Cl^- (AN-ISE 2); Bickenalb River, 20.–30.08.2022.

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.

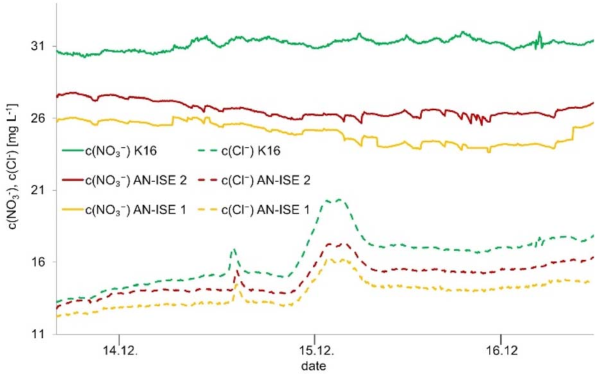

Fig. 4 Event detection: NO_3^- and Cl^- readings of AN-ISE 1, AN-ISE 2 and K16; Bickenalb River, 14.–16.12.2022.

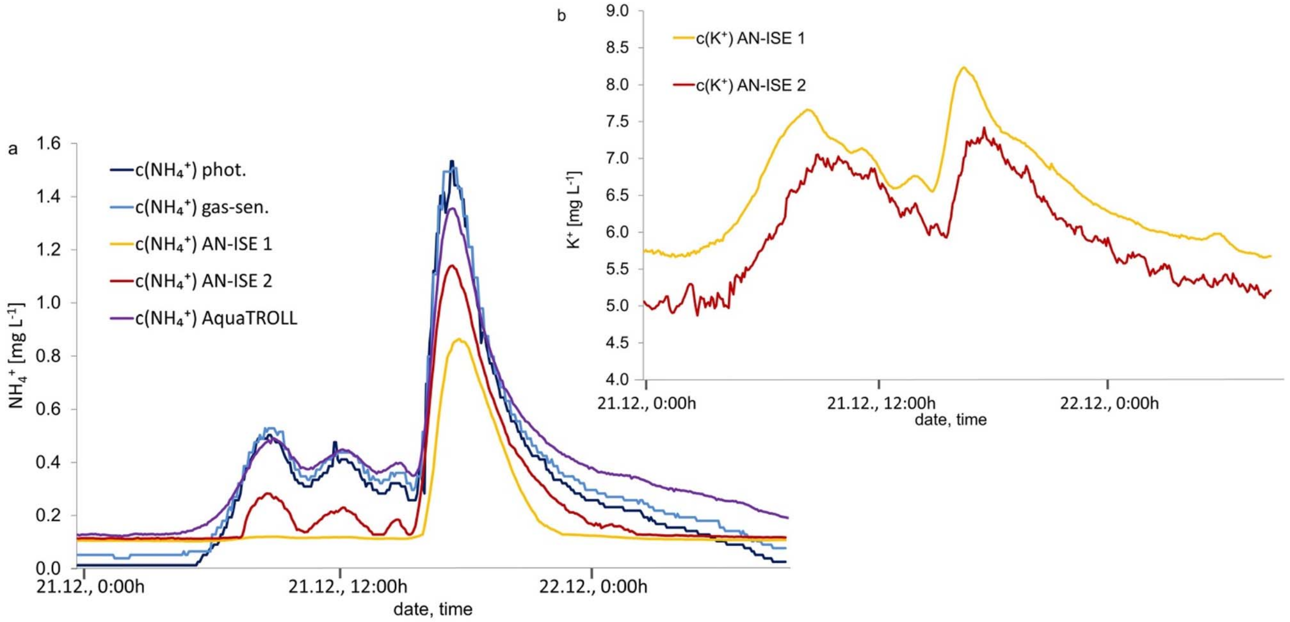

Fig. 3 (a) Event detection: NH_4^+ readings from the photometric and gas-sensitive analysers, AN-ISE 1 and AN-ISE 2 (with ion interference compensation) and AquaTROLL (without compensation), (b) K^+ readings from AN-ISE 1 and 2; Bickenalb River, 21.–22.12.2022.

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

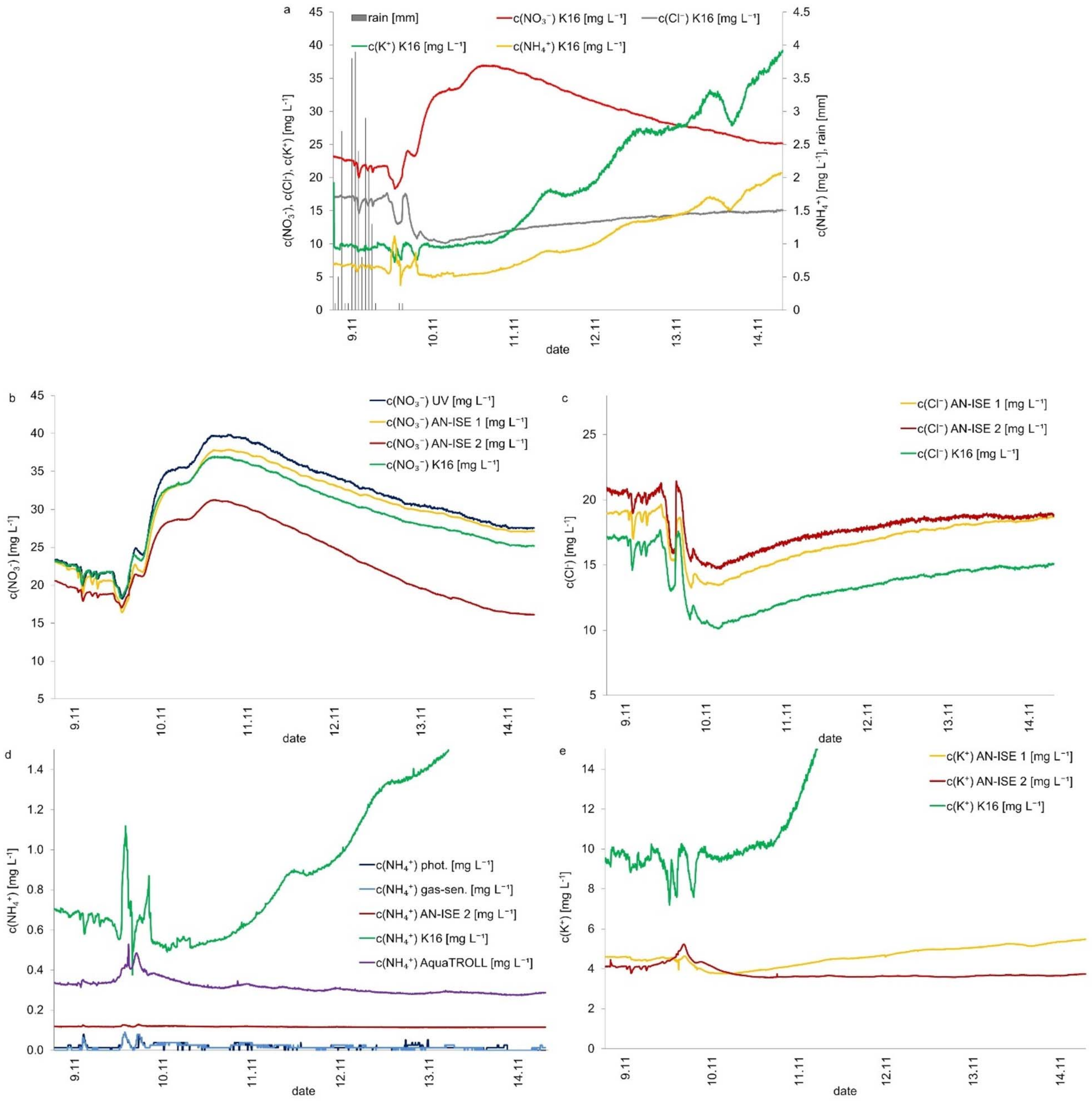

Fig. 5 Event *vs.* drift: (a) NH_4^+, NO_3^-, K^+ and Cl^- readings of K16 ISE, (b) NO_3^- readings of UV probe and AN-ISE 1, AN-ISE 2 and K16 ISEs, (c) Cl^- readings of AN-ISE 1, AN-ISE 2 and K16 ISEs, (d) NH_4^+ readings of photometric and gas-sensitive analysers and AN-ISE 2, K16 and AquaTROLL ISEs,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

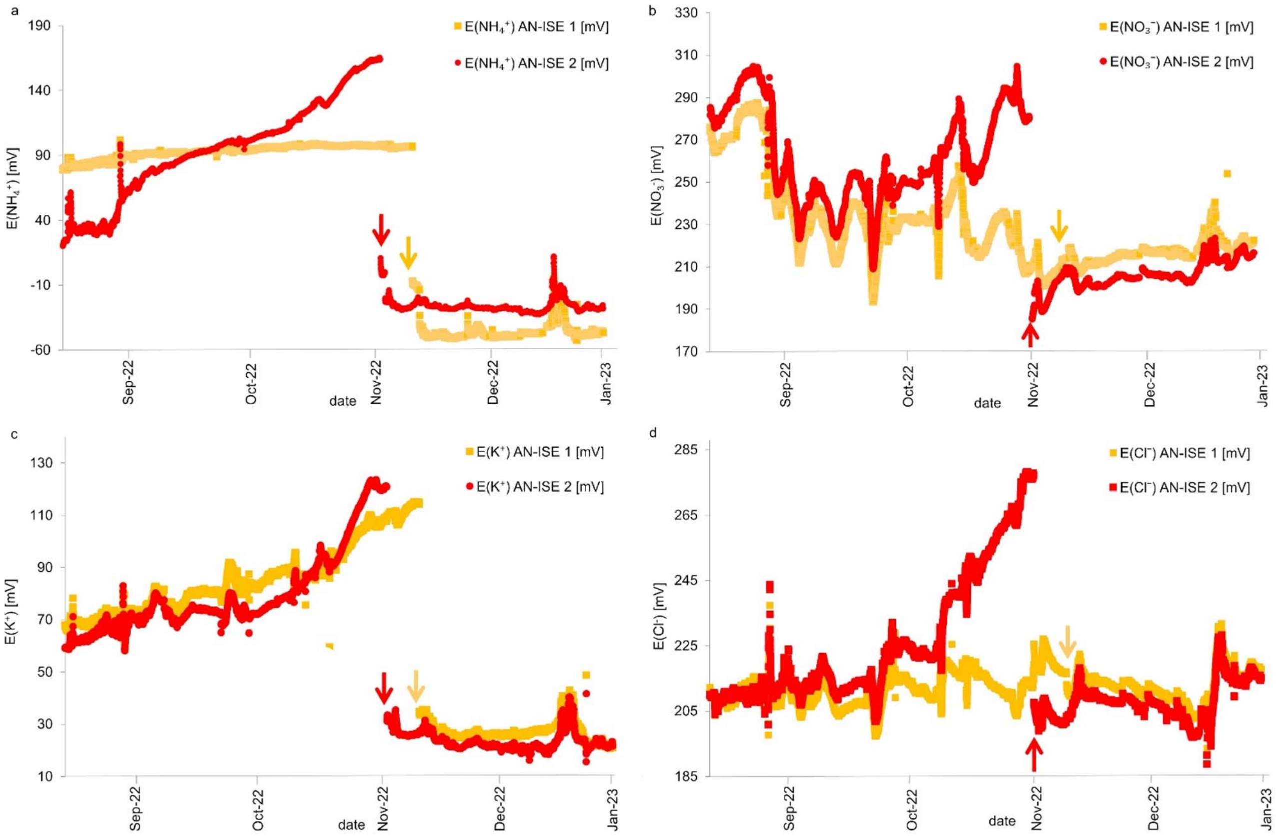

Fig. 6 Drift of mV signals: mV signals from AN-ISE 1 and 2 for (a) NH_4^+, (b) NO_3^-, (c) K^+ and (d) Cl^- over the entire measurement period (arrows: cartridge replacement).

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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