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Advances in Water Quality Monitoring of Inorganics: Current Trends

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ABSTRACT

New methods of analysis for water quality monitoring to detect inorganic substances are required to meet the demands of determining concentration, particularly at low detection limits, analysing speciation and even identifying the pollution source. Such information is essential to inform public health decisions and to comply with more stringent legislation. This paper concentrates on two case studies, reviewing the development in monitoring methods, and predicting future trends. Arsenic and nitrates detection was selected as these pollutants are particularly problematic from a human health perspective. Additionally, the challenges faced in developing monitoring methods for these chemicals are relevant to a wide range of other inorganics. The current state of the art in detection approaches for these chemicals are discussed along with recommendations for future research to further improve the methods.

Keywords: Water Quality; Monitoring; Detection Methods; Arsenic; Nitrates; Speciation; Source Tracking

1. Introduction

In water quality monitoring simply determining the presence of pollutants is often insufficient. Accurate determination of concentrations, speciation or sources can all be critical information to determine, for example, drinking water safety or identify the origin of pollution. Pollutants include pathogens, organics and inorganics.

Pathogen monitoring has been a recent subject of focus with a large EU grant recently awarded to develop new microbial methods of detection. This has been driven by the onset of molecular methods and the growing realisation that faecal indicator monitoring is insufficiently well-correlated with the presence of certain pathogens [1]. At the same time concern regarding emerging pollutants, many of which are trace level organics have been mounting worldwide [2,3]. These chemicals are extremely challenging to detect at environmentally relevant ng/L, and extraction and concentration methods are a key part of addressing this problem.

However, inorganics are another major class of waterborne pollutants, many of which have long-term chronic impacts upon human health [4]. The aim of this paper is to review the challenges facing monitoring for inorganic compounds in water by focusing on two key case studies. Arsenic has been selected due to the widespread nature, and huge scale, of the issue. This example describes the challenges of meeting low detection limits, especially for field instruments, and the issues relating to speciation. This is a common problem for the detection, and analysis, of inorganic waterborne contaminants. Speciation can impact upon the fate and transport of an inorganic in the environment as well as be a key determinant in the health risk. Nitrates have been selected as this chemical represents one the few short-term acute exposure risks. This example also highlights the challenges of environment forensics in identifying the source of pollution to meet ever-increasing legislation.

2. The Problems of Arsenic Concentration and Speciation Detection

Arsenic contamination of drinking water, which leads to chronic poisoning, affects more than 140 million people across 70 countries in all six continents and is considered as the most challenging water pollutant on a global scale [5]. Arsenic in groundwater is a widespread contaminant in South East Asia affecting the quality of drinking water in Bangladesh, India [6] and Cambodia [7] and is also present to a lesser degree in the USA [8] and in parts of

the UK. In Bangladesh, where the contamination is most acute, tube-wells were dug to access shallow aquifers with the aim of providing a microbial-free source of drinking water. However, the groundwater has high levels of arsenic; over 45% of these wells exceed the World Health Organisation (WHO) recommendation of 10 μg/l and 27% exceed the 50 μg/l limit set by the Bangladeshi authorities [5]. The high concentrations of arsenic in the main drinking water source for over 50 million people in Bangladesh has been referred to as the largest manmade environmental disaster in the world and "the largest mass poisoning of a population in history" [5]. Recent studies have estimated that arsenic groundwater contamination in Bangladesh causes 1 in 5 deaths in the country and a Lancet study by Argos *et al.* showed that those in the top quartile of exposure suffered a 70 percent higher mortality rate than would be expected in the population as a whole [9]. Furthermore, it has been estimated that morbidity from polluted water consumption reduces the labour supply by 8% [10].

Detrimental effects arising from chronic exposure to low doses of arsenic have been demonstrated in epidemiological studies, and include an array of health problems such as skin lesions, skin, bladder, kidney and lung cancer, neurological disorders and cardiovascular disease [5]. Furthermore, such health problems generate many issues both at an individual level (e.g. social stigma, loss of income, lowered educational attendance) and at a national level (e.g. reduced labour supply, decreased productivity, rising healthcare costs) [10,11]. Thus, provision of potable water is an essential component of poverty alleviation and sustainable growth.

The release of arsenic into the environment is controlled by both natural and anthropogenic processes. Arsenic is commonly found as part of sulphur or organic compounds in nature and can be unleashed in a number of ways, the mechanisms of which can be contentious. The most commonly espoused mechanism in Bangladesh is that of geogenic reduction of deep aquifer rocks, which releases the arsenic into the groundwater [12]. Arsenic compounds can be mobilised by a variety of processes including mining runoff [13], weathering interactions, biological activity, geochemical reactions, volcanic emissions and anthropogenic processes [1], with erosion and leaching being the largest contributing processes at 612×10^8 and 2380×10^8 g/year respectively [14]. Arsenic is most commonly found in the +3 and +5 oxidation states while −3 and 0 contribute a smaller amount of the naturally occurring species [14]. Adsorption onto metal oxides is the most common arsenic remediation technology as it is both cheap and effective. For a full review of the performance of adsorbent materials see Mohan and Pittman [12].

Arsenic is sensitive to mobilisation across the pH range of groundwater (pH 6.5 to 8.5) [14] and under both oxidising and reducing conditions. The speciation of arsenic in natural waters is controlled by redox potential and pH, as seen in **Figure 1**, with As (III) being the dominant species in reducing conditions, such as groundwater, and As (V) more prevalent in oxidising conditions such as surface water. Trivalent arsenic is typically found as $As(OH)_3$, $As(OH)_4^-$, AsO_2OH^{2-} and AsO_3^{3-}, while pentavalent arsenic typically forms AsO_4^{3-}, $HAsO_4^{2-}$ and $H_2AsO_4^-$ [1] as described in **Figure 1**.

The dominance of the uncharged As(III) species H_3AsO_3 across pH 0 to ~pH 9 compared to the dominance of the charged As(V) species $H_2AsO_4^-$ and $HAsO_4^{2-}$ provides a significant problem for the removal of toxic arsenic species from drinking water through adsorption. Negatively charged As(V) has a preferred affiliation for positively charged iron oxide, a common adsorbent material, compared to the uncharged H_3AsO_3 As(III) molecule. As(III) is the dominant oxidation state in relatively reducing groundwater, is known to be 60 times more toxic than As(V) as well as more mobile [15]. Arsenic is therefore of significant concern for countries which obtain the majority of their drinking water at depth through tube wells that sample groundwater [16].

A large part of the arsenic problem is characterised by the presence of both As(III) and As(V) at concentrations exceeding the national and WHO threshold limits. The two species behave very differently, in terms of adsorption behaviour which is the dominant removal technology whilst As(III) is very difficult to remove through adsorption but also difficult to detect. Discrete measurement of As(III) and As(V) is not facile. Standard arsenic analysis techniques such as atomic absorption spectro-

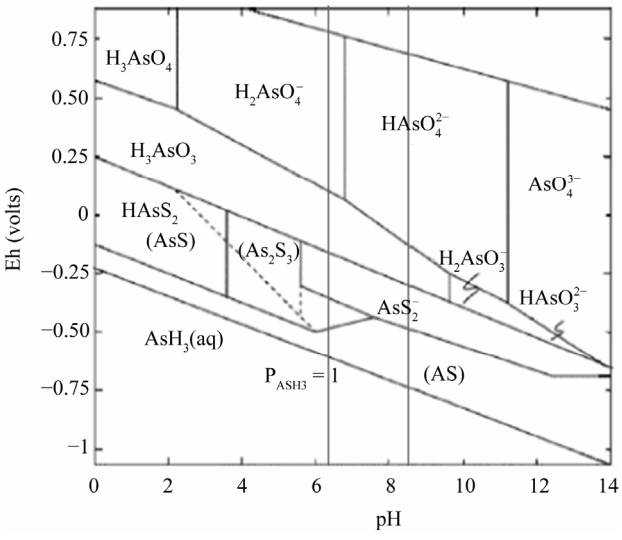

Figure 1. The redox potential-pH plot for Arsenic at 25˚ and 101.3 Pa [14]. Red lines delineate the typical pH of groundwater.

metry (AAS); atomic fluorescence spectrometry (AFS); atomic emission spectrometry (AES); differential pulse polarography (DPP); electrothermal atomic absorption spectrometry (ETAAS) and mass spectrometry (ICP-MS) [17] do not measure individual species and much be used with front-end separation techniques, such as high pressure liquid chromatography (HPLC), to separate the As(III) and As(V) oxidation states.

Following the recent reduction in threshold limit from 50 μg/L to 10 μg/L, the need for cheap and accurate species determination of arsenic has become intensified. The presence of As(III) at toxic levels in parts of Bangladesh [18] has created a greater need for discrete analysis as opposed to total arsenic. Many of the existing technologies, including Gutzeit method and the aforementioned method are either unable to provide this distinction or complex and expensive. Due to the nature of much of arsenic contamination being in areas of the world with poor infrastructure and funds for remediation technology, arsenic analysis techniques need to be cheap, reliable, portable as much as possible and with a very low detection limit, below 10 μg/L.

One method that has been proposed to deliver field-tests of the bioavailable arsenic is that of genetically modified whole-cell biosensors [19,20]. In this approach bacteria are engineered such that a reporter gene, which generates a signal, is paired with a contaminant sensing component. In the presence of arsenic, the biosensors emit a signal, which could be emission of visible light or a pH change of the water sample. pH changes can also be easily visualised using an indicator dye [21]. Modified cells can be grown and then freeze dried to facilitate transportation. Reconstitution in the field, followed by over-night incubation (at ambient temperature), revives the cells and activates the biosensor. Such sensors are cheap and easy to use; however, there are challenges in achieving low detection limits as well as the issue of permissions for field use of genetically modified organisms.

Alternatively, low detection limits can be achieved by the voltammetric analytical technique which has been found to accurately detect As(III) and As(V) discretely at sub 10 μg/L concentrations [22].

Voltammetry, as a form of elemental analysis, has been known to chemists for over 50 years [16]. It has received more attention in recent years, particularly in the analysis of arsenic, due to its sensitivity, low cost, reliability, relatively short analysis time [17] and its unique sensitivity for As(III) [16]. It has become particularly useful in the area of water contamination and remediation because of its portability, which allows sample analysis to take place at, or close to the sampling point [16]. This avoids the issue of sample preservation between sample taking and measurement in a laboratory. In addition to its selectivity for arsenic oxidation states, the development of voltammetry for stand-alone field use is of particular interest for the detection of arsenic in groundwater [16]. This is highly significant for measuring samples in situ without issues of preservation or alteration of the arsenic in the sample vessel.

Stripping Voltammetry exploits the electrochemically active nature of certain metal species to determine concentrations. It involves the electrochemical deposition, on application of a current, through reduction of the element of interest on an electrode, for a given deposition time. The element is then oxidised back into the solution by a reverse potential scan [16]. During the deposition time the arsenic is pre-concentrated at the electrode which accounts for the sensitivity of the method [23]. The oxidation current which causes the stripping of the arsenic from the electrode back into solution is recorded and plotted against scan potential [16] to give an analytical signal.

The analysis of As(III) and As(V) is controlled through the potential at which the solution is held prior to stripping, where the potential is low enough to reduce the analyte and deposit it at the electrode [16]. In our system the As(III) determination is held at a potential −0.2 V and total arsenic (As(III) + As(V)) determination is held at −1.2 V. In both cases the arsenic is reduced to As(0) when it is deposited at the electrode at ~−0.1 V. The differential pulse anodic stripping voltammetric system (DPASV), used in the work by Alves *et al.* and also Saluan *et al.* [24] uses a three electrode system, a working electrode, on to which the element of interest is deposited, a reference electrode and an auxiliary electrode all of which vary depending on the type of determination being carried out [16]. The system is calibrated through standard addition [18] whereby once the sample has been analysed, an aliquot of a known stock solution of known concentration is added to the voltammetric cell: the resultant concentration is measured twice and then the process is repeated again. The benefit of the standard addition calibration is that each sample is calibrated individually at the time of analysis as opposed to a calibration line which can incur more drift. This means that some of the differences in relative conditioning of the electrode should be removed through the standard addition method.

Electrode conditioning is a potential issue with the reproducibility of voltammetric determinations. When not being used, the reproducibility of data using solid electrodes can be impeded due to the formation of a surface oxide on the electrode surface, which limits sensitivity [25]. This can cause sensitivity issues both within runs and over the long term [16]. Electrodes are conditioned by either immersing the electrode in an appropriate acid or base over a period of time or electrochemically by

running voltammetric cycles in a pre-determined solution. No standard electrode pre-treatment has been established with many researcher using acids or bases with variations in the strength of the conditioning solution [16]. All voltammetric techniques require efficient mass transfer of ions in the cell so that the working electrode can effectively pre-concentrate the analyte of interest. This is primarily achieved by a magnetic stirrer or a rotating electrode. This local motion enhances metal deposition [25] and can also minimise the H_2 bubble formation at the working electrode, resulting in reduced noise and increased signal [26].

Much research has gone into optimising many parts of the process including the material the electrode is made from. Most commonly an Au electrode is used due to its stability and sensitivity. In recent publications, particularly from Salaun *et al.* they have tested an alternative Au microwire electrode. These studies found that As(III) could be determined in freshwaters and seawaters at any pH, thus excluding the addition of corrosive acids as electrolytes [27]. Optimum conditions included a deposition potential of −1.0 kv for As(III) and As(V) and 30 s deposition time. They reported the use of 0.01 M HCl as an electrolyte with limits of detection of 14.98 ng·L^{-1} for As(III) and 22.47 ng/L for As(V) [27]. Later work developed the use of cathodic stripping voltammetry (CSV) at a vibrating gold microwire electrode, where arsenite determination was possible with no pre-treatment of the sample at its original pH and open to ambient air [22]. This means that this method is suitable for on-site analysis. Total arsenic is then determined through the addition of acid to pH 1. The data compared well (within 10%) with the ASV method. To highlight the issue of sample preservation, a study in West Bengal waters showed that if analysed immediately then As(III) was the dominant species, however, upon storage there was significant oxidation to As(V) and adsorption on particulate matter in the solution [22]. Immediate analysis of the arsenic samples without the need for pre-treatment or expensive lab techniques for countries such as Bangladesh would be an important contribution to the ongoing effort to provide safe drinking water.

3. The Challenge of Nitrate Source Determination

Nitrate (NO_3^-) occurs naturally within the environment. However, concern regarding its ever-increasing entry into the natural environment as a result of various anthropogenic sources, such as inorganic fertilisers and effluents from wastewater treatment plants, have led to it being considered a contaminant of concern. This is largely as it has been linked to various environmental and health concerns. High nitrate concentrations within water bodies have been linked to such occurrences as eutrophication [28,29]. High nitrate concentrations within drinking water have also been linked to methemoglobinemia in children (blue-baby disease) [30] and cancer [31] amongst other diseases. However, the presence of a direct link is still a factor for debate [32]. These factors have led to increasing interest in the development of environmental forensics techniques for nitrate source determination, largely in relation to legislative requirements related to the Water Framework (2000/60/EC) and Nitrates Directives (91/676/EEC).

To date, various approaches have been adopted in an effort to distinguish between different sources of nitrate. The use of nitrate stable isotope compositions has been one of the most successful in this regard [33]. The dual isotope approach is the most successful approach for identifying the various sources of nitrate contamination, where isotopic fractionation for both the nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) atoms within the nitrate ion is considered (**Figure 2**) e.g. [33-37].

In particular, the dual isotope approach has been useful for the identification of hydrologic pathways [38-41]. The isotopic composition of a particular water body does not only reflect the composition of the original source or of mixed sources having different compositions but can also be influenced by isotopic fractionation during the transport and chemical transformation of the compounds [42,43]. Therefore, it allows for the source of contamination and the pathways undertaken to be identified. However, this method is not suitable for differentiating closely related sources of contamination, such as sewage and manure [44]. This is because both sewage and manure undergo similar isotopic fractionation processes leading to overlapping isotopic compositions (as seen in **Figure 2** where these elements cannot be distinguished) [44].

A range of approaches has been utilised for specifically achieving faecal source tracking. The use of faecal indicator bacteria (FIB) represents the most commonly

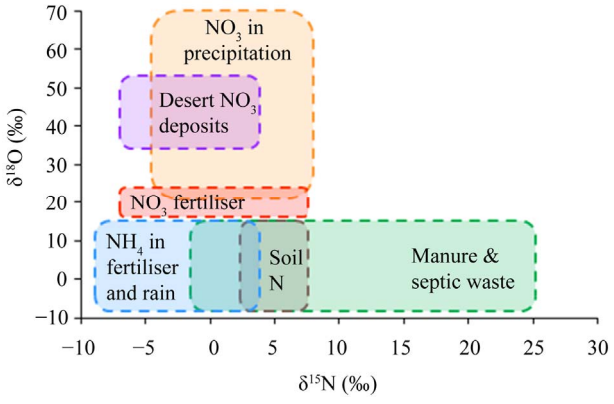

Figure 2. A general depiction of the normal range of $\delta^{18}O$ and $\delta^{15}N$ values for the dominant sources of nitrate [45].

adopted faecal contamination markers of water bodies. However, whilst it is useful for the detection of faecal contamination, it is currently not possible to distinguish between microbial pathogens arising from human (sewage) or animal (manure) sources on this basis. This is because FIB such as *Escherichia coli* and enterococci, which represent the commonly used FIB, do not discriminate between human and animal faecal matter sources [46]. The ratio of faecal coliforms (FC) to faecal streptococci (FS) was also proposed as a way to differentiate sewage and manure [47]. However, as a result of variable survival rates of the bacterial species and the differences in FC-FS ratios within different animals, the use of these ratios is no longer considered to be suitable [46]. For this reason, other tracers must be used to achieve this differentiation.

The use of molecular techniques for Microbial Source Tracking (MST) through a variety of library dependent and library independent methods has also been investigated [48]. These include antibiotic resistance, biochemical fingerprinting, DNA fingerprinting, bacteriophage occurrence and the use of genetic markers. However, the application of MST for achieving faecal source tracking has met a number of challenges. Host specificity is one of the major challenges in the development of MST techniques. This is because, whilst it is commonly the case that differential distribution of the particular source identifier is present within the various sources, such that it is found at a higher frequency or density within certain hosts [49], it is known that a significant level of cosmopolitan strains (strain sharing) is present, such that incorrect source attribution might result [50, 51].

Furthermore, particular molecular source identifiers often also vary on temporal and spatial scales. Differences in dietary regimes are amongst the major contributors to this variability. This is because different dietary regimes would include the presence and levels of bacterial groups within the intestinal tract [49]. Hence, source identifiers that would be relevant within a specific temporal period and geographical area might not be relevant in a different scenario [49,50]. The environmental persistence of the various source identifiers selected is another consideration. This is because the clonal composition of the species commonly differs between the environmental samples and the host populations [49,52]. Lastly, practical considerations, in particular related to the method's transferability and applications must be taken into account. These include factors such as the technique's availability and complexity, the cost of analysis and the level of expertise required for successful data interpretation [46].

Therefore, whilst the use of molecular techniques for MST allows for highly specific information on the presence of faecal indicators, a number of challenges have been identified. In fact, although multiple LDMs and LIMs are currently available, many have not yet been fully tested and validated to the stage of application in field studies [48,49] and no specific method has been shown to be superior enough to be adopted as a standard [46]. In fact, a number of studies carried out by the US Geological Survey project to assess available techniques concluded that none of the methods investigated were ready for field application [51,53]. An additional consideration of using molecular techniques, is that they can only function in the identification of the host from which the source of nitrate (or faecal) contamination is initiated. Therefore, using such techniques it would not be possible to differentiate between raw and treated sources of contamination.

A review of recent literature has identified the use of a suite of chemical markers, namely pharmaceuticals and related compounds such as caffeine, as providing the greatest potential in this regards [45]. The use of pharmaceuticals and related compounds, such as food additives, as chemical markers of co-occurring discriminators of sewage and manure is believed to provide the greatest potential in this regards. They are ideal for such an application as they are generally relatively water soluble and non-volatile, and their natural background levels are low. The adoption of such an approach also renders increased temporal and spatial stability of the source identifiers, as opposed to the use of molecular markers, since consumption of pharmaceuticals and related compounds such as food additives is largely stable, at least within the developed world.

Furthermore, due to the wide variety of such compounds available, through an understanding of the chemical marker's environmental persistence, biodegradation and environmental fate, it would be possible to select the most appropriate suite of chemical markers for achieving identification of the required input. To date, most such environmental forensics studies have focussed on a single tracer approach. Caffeine has been one of the most studied chemical tracers of sewage to date [54,55]. However, it is only through the use of a suite of chemical markers, that it would be possible to achieve further characterisation of the sewage or manure input. For example, indicating the effectivity and the level of treatment being undergone within the DWWTS.

The use of immunoassays for chemical marker detection is an emerging technique for this purpose. Immunoassays have been widely applied in other areas of science, in particular clinical analyses [56]. However, despite the first studies on using immunoassays to detect pharmaceutical in surface waters showing up around 10 years ago [57] for the detection on Diclofenac, they have received limited further attention [58-60]. This may be due

to the limited availability of antibodies showing reactivity to e.g. pharmaceuticals, as well as the skills set of environmental scientists.

However, the use of immunoassays renders a number of advantages. Since the antibody-antigen complexes form through relatively weak interactions, which function over short distances, a close antibody-antigen fit is required for complex formation [61]. This confers a high degree of specificity to antibody-antigen binding. Therefore, they have the capability of measuring antigens within complex matrices, with limited or no pre-treatment, extraction, purification or concentration, due to the potential for low detection limits being achieved [56]. Furthermore, they have the potential for high-throughput analysis [56]. This is particularly related to the use of 96 (and less commonly 384) well-plates for analysis and multi-channel pipettes, which greatly facilitate reagent and sample handling [62]. Combined with this are multichannel-spectrophotometers, which allow for the complete sample plates to be read within a few seconds [62].

As with all analytical techniques, the use of immunoassay techniques has a number of limitations, which need to be considered. One of the main limitations is the potential for cross-reactivity or interference within immunoassay analyses. Therefore, factors such as the uniqueness of the epitope used are critical, as they determine antibody-antigen selectivity. Furthermore, the level of confirmatory detail on the presence of a particular analyte within a sample is reduced as compared to that obtained through mass spectrometric analyses. This is especially true when considering the potential variability in surface water matrices. However, the use of immunoassays has wide potential as a fast-screening method for sample analysis, allowing for samples requiring chromatographic analysis to be decreased. This is particularly true, with the advent of multiplex screening which is a recent development and the potential for incorporation in lab-on-a-chip systems [63] augurs for high potential for such screening techniques.

4. Conclusions and Future Outlook

As our two case studies illustrate, new methods of analysis for inorganics in water samples are required. While existing techniques can successfully detect the presence of compounds, new approaches are needed to meet the demands of determining concentration, particularly at low detection limits, analysing speciation and even identifying the pollution source. This information is essential to inform public health decisions and to comply with more stringent legislation. Our first case study, arsenic detection, illustrated the first two challenges of low detection limit analysis in addition to the need to obtain species information. Our second case study, nitrate source determination, discussed how chemical markers can be applied to identify the origin of pollution. In addition to these factors, new detection approaches also have to be cheap, reliable and ideally portable. Portability enables detection in the field negating the challenges of sample processing and transportation.

This paper concentrated on two case studies and reviewed the challenges as well as the existing state-of-the-art in detection technologies. For arsenic we have seen that detection at low concentration along with speciation were key challenges, essential to appropriate risk assessments and public health interventions. From a review of the literature we found that voltammetry is one of the most promising potential solutions to this challenge as it offers many advantages including sensitivity, ability to speciate, low-cost and short analysis times. Whole-cell biosensors are also interesting from the perspective of field testing instrument.

This paper summarised many of the recent developments to optimise the voltammetric detection approach for arsenic. The current state of this technology still requires significant research and testing to move towards analysis with less pre-treatment of samples so as to improve detection in real sea-water and terrestrial water samples. In order to deliver field-ready instrumentation, the stability of the samples and equipment in field scenarios needs to be tested as well as the reproducibility of concentrations in complex real water samples.

For nitrate, we have seen that new environmental forensics methods are required to meet recent legislation and enable tracing of sources of pollution. Our literature review revealed that various methods are available including isotope approaches, molecular methods and detection of a range of chemical markers. Overall, it is expected that no single method would allow for complete source characterisation. The most appropriate approach largely depends upon the specific scenario and the context of the study. The use of chemical markers is a relatively recent development. Its use for such studies is particularly promising as it allows for the entry pathway to be identified, such as the differentiation of raw and treated sewage inputs. At present this approach has been applied to a number of small scale studies and would benefit from further research into field testing and validation of alternative analytical techniques, such as immunoassay analyses, to replace costly and time-intensive chromatographic and mass spectrometric analysis, which would facilitate catchment scale studies.

In conclusion, it is clear from this review of waterborne inorganics detection that current approaches are moving towards more detailed analysis and this demand for improved information raises significant challenges for detection technologies. However, for all the case studies discussed here, progress is being made towards this goal. Further research developing, characterising and

validating such new techniques, for these case studies as well as other inorganic substances, should be a priority.

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