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The Present and Potential Future of Aqueous Mercury Preservation: A Review

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Abstract

Mercury is considered to be one of the most toxic elements to human health. Due to pollution from industry and artisanal gold mining, mercury species are present globally in waters used for agriculture, aquaculture, and as drinking water. This review summarises methods reported for preserving mercury species in water samples and highlights the associated hazards and issues with each. This includes the handling of acids in an uncontrolled environment, breakage of sample containers, and the collection and transport of sample volumes in excess of 1 L, all of which pose difficulties to both *in-situ* collection and transportation. Literature related to aqueous mercury preservation from 2000 – 2021 was reviewed, as well as any commonly cited and relevant references. Amongst others, solid-phase extraction techniques were explored for preservation and preconcentration of total and speciated mercury in water samples. Additionally, the potential as a safe, *in-situ* preservation and storage method for mercury species was summarised.

The review highlighted that the stability of mercury is increased when adsorbed on a solid-phase and therefore the metal and its species can be preserved without the need for hazardous reagents or materials in the field. The mercury species can then be eluted upon return to a laboratory, where sensitive analytical detection and speciation methods can be better applied. Developments in solid phase extraction as a preservation method for unstable metals such as mercury will improve the quality of representative environmental data, and further improve toxicology and environmental monitoring studies.

1. Introduction

1.1. Background (Mercury in the environment)

Mercury (Hg) is ubiquitous in the environment and is one of the most toxic elements to human health, being described as one of the 13 priority hazardous substances under the Water Framework Directive. Concentrations in drinking water are restricted to just 2 µg L^{-1} total Hg for acute poisoning[1] and a tolerable intake set at 2 µg total Hg kg^{-1} body weight per day[2]. Both acute and long-term exposure to the metal can result in severe, irreversible neurological and developmental complications, commonly referred to as Minamata disease. It is therefore one of the most widely studied and monitored environmental pollutants. There are three main species of Hg found in natural waters: inorganic mercury (Hg^{2+}), elemental mercury (Hg^0), and organic species such as methylmercury ($MeHg^+$) and dimethylmercury (Me_2Hg). These species are often highly mobile[3] and their most significant environmental interactions are shown in Figure 1. Making up 1-40 % of the total Hg fraction, $MeHg^+$ is considered the most toxic Hg species. Organic Hg species are highly bioaccessible and prone to bioaccumulation. For example, predatory fish can have up to 10^6 times higher concentrations of total Hg than the surrounding waters, with 95 % of this being methylmercury[4]. Total aqueous Hg concentrations are usually less than 10 ng L^{-1} Hg in uncontaminated natural freshwaters, with polluted waters generally being defined as higher than 100 ng L^{-1} and even being reported at over 50 µg L^{-1} Hg[1, 5-7]. Monitoring total Hg and speciation data is vital to prevent human and environmental exposure to harmful concentrations of the metal. Due to the naturally low concentrations of total and speciated Hg, sample pre-treatment and preparation are vital to ensure accurate and precise measurement with appropriate detection limits. Many preservation and preparation techniques for Hg recommend filtration of the water sample. Dissolved Hg concentrations may adsorb to particulate matter over time, altering the measurable dissolved concentration and posing different analytical challenges[8-10]. The potential for toxicity of particulate-bound Hg is not well researched[11, 12], with toxicity studies focusing on dissolved species concentrations. For speciation analysis, sample pre-treatment methods should generally avoid inter-species conversion, to provide representative species data of the sample.

1.2. Preservation and storage: importance and challenges

Preventing losses of Hg from water samples has been an ongoing problem for many years[13-15]. Safely preserving and storing Hg concentrations in water samples is particularly difficult. Many species are unstable in water, with total Hg (Hg_T) concentrations can show losses of >70 % within 1 week[13, 15]. Elemental Hg^0 is volatile in solution and so readily escapes from uncapped samples or into any container headspace[13, 16]. Inorganic Hg^{2+} is the most stable species in solution but is still prone to losses through sorption to the container walls or reduction to the less stable species Hg^0 [13, 17, 18]. Methylmercury and other organomercurials can undergo photolytic reduction to Hg^0 and can adsorb to container walls, as well as minor losses occurring from coagulation with humic acids[13, 18, 19]. Any loss of Hg from the sample or contamination of the sample will produce erroneous results and limit the usefulness of the data, especially for samples used in environmental monitoring and human health studies.

Wall-sorption of Hg has been extensively studied in the past[10, 13, 15, 17, 20-22] and the choice of sample container material has been noted as a major factor in mitigating this. Glass and PTFE containers are preferred for sampling Hg in waters, as wall sorption is greatly reduced in these materials[8]. However, PTFE is relatively expensive when compared to other materials such as polyethylene, as demonstrated in **Error! Reference source not found.**. Glass containers are heavier and will become hazardous should breakage occur. Polyethylene (PE) and polypropylene (PP) are relatively more affordable alternatives than PTFE or glass, are often used in water sampling[9] and are more robust than glass containers, but can pose a significant risk of Hg loss if the sample is untreated[15, 22].

Table 1 Approximate price comparison of container materials from online suppliers (sourced from FischerScientific on 4th March 2022)

Container material	Approximate price per 100 mL sample bottle*
High density polyethylene (HDPE)	$1.50
Polypropylene (PP)	$2
Borosilicate glass	$1
Polytetrafluoroethylene (PTFE)	$40

* Prices are obtained from online vendors (SigmaAldrich, FischerScientific) and converted from GBP (£) to USD ($) (4th March 2022)

1.3. Scope of the Review and Methodology

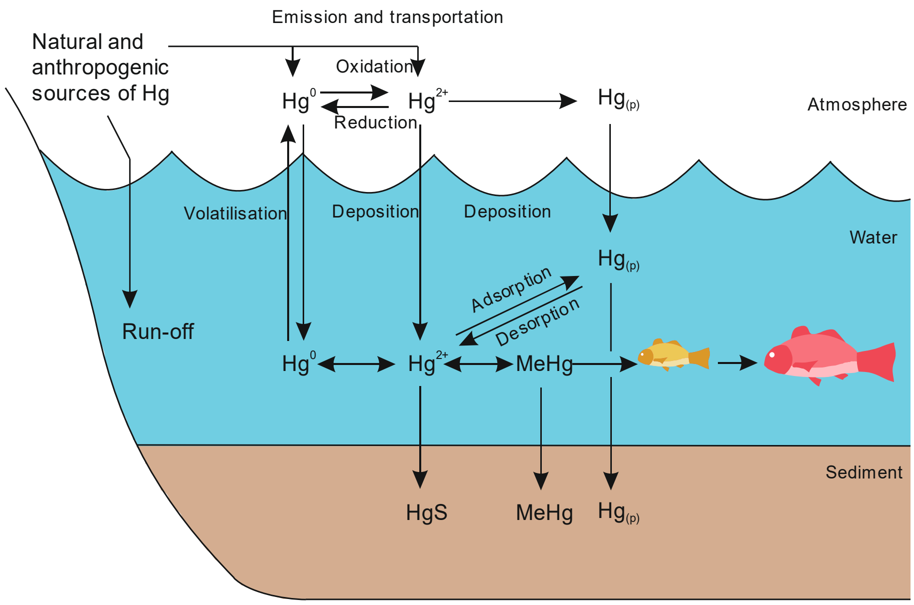

Figure 1 Biogeochemical cycle of mercury in the environment. Species descripted: Elemental mercury, Hg0; inorganic mercury, Hg2+; methylmercury, MeHg; particulate bound mercury, Hg(p); mercury sulfide, HgS (Adapted from Kim and Zoh (2012)[3])

The aim of this review was to critically assess the current literature related to the sampling, preservation and storage of Hg samples during transport from field to laboratory, to improve the likelihood of obtaining representative concentration and speciation data.

For the current preservation and pre-treatment methods, key benefits were highlighted and limitations associated with the different methods were considered. Using ScienceDirect literature database, Scopus, the WorldCat Library database and NERC library services, peer-reviewed, published literature from 2000 to 2021 was reviewed using the search terms "mercury", "water" or "aquatic", and "preservation", "storage" or "speciation". Literature that involved the preservation and storage of aqueous Hg was reviewed. Any papers that were frequently cited throughout the reviewed literature were also assessed and included if relevant. The benefits of the preservation methods were explored, and any hazards associated with *in-situ* use and transportation were highlighted. The current applications of solid-phase extraction (SPE) in Hg analysis were examined and the potential benefits of the sorbents for sampling and preservation were explored. For solid-phase methods, the search terms "mercury", "preconcentration" or "speciation" or "removal" or "recovery", "water" or "aquatic" were used, and similarly any common and relevant references were assessed and included. Some key considerations of the reviewed SPE methods were: the retention of the target analyte, the recovery of the analyte upon desorption, and the compatibility of the desorption method with analysis techniques.

A summary of literature on the preservation of Hg and its species by addition of a reagent is given in **Error! Reference source not found.** and a summary of literature on the solid-phase extraction of Hg and its species is given in **Error! Reference source not found.**2.

2. Current trends for field measurement, sampling and preservation

2.1. Field measurements

Analysis of analytes and their species *in-situ* eliminates the need for preservation and reduces the risk of inter-species conversion and loss of analyte over time, providing a more accurate representation of real-world chemistry. However, there is a greater risk of sample contamination and a greater difficulty maintaining appropriate analytical conditions, due to a lower control over the environment when compared to a laboratory.

Commercially available field probes have been developed for *in-situ* Hg^{2+} stripping voltammetry analysis. These are reported to measure Hg^{2+} in the field with detection limits of 5 µg L^{-1}, as well as other trace and transition metals. For pristine waters, these probes will likely struggle to produce an accurate quantitative result as mercury concentrations can be as low as 1 ng L^{-1} Hg^{2+}. Rocha et al. (2019) reported detection limits of 5 µg L^{-1} Hg^{2+} in river water using a portable analyser[23], unsuitable for the WHO guideline value[1] of 2 µg L^{-1} Hg but may be useful for indicating severe Hg pollution. A similar detection limit was reported by Bhardwaj et al. (2020) in pond and drain water[24]. Gold nanoparticle electrodes have been developed by Hwang et al. (2021) for Hg^{2+} determination, achieving detection limits of 1.7 µg L^{-1} Hg^{2+} with a linear response between 10-100 µg L^{-1} in landfill leachates[25]. This highlights the ability for these technologies to be used in difficult matrices, however detection limits are currently unsuitable for speciation analysis or for Hg concentrations found in most natural waters.

Other methods of Hg field analysis use headspace Hg vapor analysers, relying on the evolution of elemental Hg vapour from water samples[26]. These probes have been reported to achieve detection limits of approximately 0.09 µg L^{-1} Hg^0, but are designed specifically for Hg concentration in air; preparative chemicals are required for other matrices to evolve Hg vapour and the data must be converted to other units for comparison to other analysis methods and water studies[1, 5-7].

2.2. Acidification

As field measurement of Hg in natural waters is not currently possible, preservation of the dissolved metal is vital for Hg analysis. Recommended methods for preservation of Hg in natural water samples generally follow the guidance of other trace metals, namely acidifying water samples with nitric (HNO_3), hydrochloric (HCl), or sulphuric acid (H_2SO_4)[8-10]. The choice of acid is important for Hg stability; the use of HNO_3 has been found to still be susceptible to large losses of Hg from water samples through both volatilisation and sorption to container walls[13, 15, 17, 27].

Hydrochloric acid is recommended as a suitable preservation method for dissolved Hg species in freshwater samples[20]. Inorganic Hg^{2+} can complex with chloride ions to form the stable $HgCl_2$ complex, and tri- or tetra-chloromercury complexes if the chloride concentration is further increased[21, 28]. These are more stable in solution than other species and are not co-precipitated by metal oxides and hydroxides[29-31]. A 1 % (v/v) HCl solution was reported to prevent loss of Hg^{2+} over 55 days in 500 mL HDPE containers[28]. The lower pH and the presence of chloride ions increases the stability of Hg^{2+}, as demonstrated by the preservative abilities of HNO_3 (6% v/v HNO_3) for Hg in seawater reported by Gardner and Gunn (1997)[32] and 20 mg L^{-1} NaCl + 0.15% (v/v) HNO_3 for Hg in deionised water reported by Louie et al. (2012)[28].

These conditions also increase the stability of MeHg in water samples. In a 0.5% (v/v) HCl solution stored in Teflon containers at 1-4 °C in the dark, MeHg is reported to be stable for up to 250 days in both freshwater and seawater[10]. Sulphuric acid has also been recommended for the preservation of aqueous MeHg in saline media, as hydrochloric acid (>0.4% v/v) may result in the artificial formation of monomethyl mercury during the distillation and ethylation process typically used for MeHg speciation[10].

When considering speciation, Bloom et al.[5] reported that acidification may alter labile Hg(II) resulting in desorption from particulates in unfiltered samples, oxidation of Hg^0 or coagulation of dissolved organic carbon and humic acids which can precipitate Hg from solution.

3. Solid-phase extraction

Solid-phase extraction offers the potential for reagent-free field sampling of Hg from water samples. Sorbents and solid-phase methods are frequently used in the analysis of dissolved Hg for sample preparation and pre-treatment, such as preconcentration[33-39], speciation[34, 36, 37, 40-43] and removal of Hg[37, 44-49]. Solid-phase extraction was previously studied for retention and stabilisation of heavy metals for analysis at a later date[33, 50]. Adsorption of Hg to a solid-phase mitigates the risk of loss from wall sorption; there is less chance of contact between an analyte bound to a solid-phase and the container walls when compared to an analyte in an aqueous-phase. This approach has been investigated in the past[14, 33, 51], but is not in widespread use.

3.1. Thiol- functionalised resins

A common approach to Hg-selectivity in sorbents is to exploit the affinity for Hg of thiol-containing compounds; diphenylthiocarbazone (dithizone)[42, 52, 53], 2-mercaptoethanol[54], diethyldithiocarbamate[33], and other compounds have been used to either functionalise resins or for complexation with aqueous Hg. These reagents provided recoveries of inorganic, methyl-, ethyl- and phenyl- species of Hg of over 70 %, with preconcentration factors suitable for aqueous Hg concentrations of between 0.1 – 50 µg L^{-1} [33, 42, 54, 55]. While most work focuses on a deionised water matrix, Margetínová et al. (2008)[54] successfully extracted Hg from natural freshwaters, by complexing Hg with 2-mercaptophenol before passing samples through C18 columns. The use of 2-mercaptophenol as a complexing agent comes with separate risks as the reagent is volatile, has a strong odour, and the concentrated solution is highly toxic, so was reportedly diluted to a 5 mM 2-mercaptophenol solution before use. The high organic concentration of the methanol eluent solution limits the analytical techniques available to this method, relying on HPLC/CV-AAS for speciation analysis.

Blanco et al. (2000)[33] achieved a similar extraction by immobilising diethyldithiocarbamate onto homemade C18 microcolumns. The C18 immobilised diethyldithiocarbamate column used a 50 mL sample volume to achieve recoveries of >70 % for Hg^{2+} and >65 % for $MeHg^{+}$ from freshwater river samples, with detection limits of 0.2 µg L^{-1}. The diethyldithiocarbamate modified C18 columns showed potential as an in-field preservation method, as samples could be readily passed through the microcolumns in the field and inorganic Hg^{2+} is stablised for approximately 2 weeks. The detection limits are unsuitable for typical concentrations in many unpolluted natural water samples, primarily being suitable for areas of moderate to high Hg pollution. There was a substantial decline in recovery of MeHg after 2 weeks of storage, even when held at 4°C in the dark[33]. Over 85 % of the spiked MeHg could be recovered within 7 days of extraction to the cartridge, declining to <50 % by 14 days. This trend was also seen with Hg^{2+}, albeit much less significant with a recovery of 80 % Hg^{2+} after 30 days storage. This method was applied to LC-ICP-MS, allowing for a fraction of the sample volume required from the technique reported by Margetínová et al. (2008)[54]. In addition, the eluent composition (0.5% v/v HCl + 5% w/v sodium thiosulphate) is compatible with a wide variety of analytical techniques, so is suitable for a broader scope of laboratories.

Dithizone functionalised C18 columns were developed by Yin et al. (2010) to effectively recovery Hg species from tap water samples (Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$)[42]. The method used just 3 mL 100 mmol L^{-1} sodium thiosulphate solution to elute the retained species, from sample volumes of 100 mL. This eluent choice allows a wide variety of analytical techniques to be applied but may show limitations where acidification or oxidation of the sample is required, due to the formation of solid sulphur which may decrease Hg concentrations by formation of solid Hg_2S. Using HPLC-ICP-MS analysis, detection limits of 3 ng L^{-1} Hg were reported from sample injection volumes of just 20 µL. This work supported by Wang et al. (2022), using a 1% (v/v) 2-mercaptoethanol eluent for elution of Hg species[53]. This eluent is still compatible with a wide range of analytical techniques with some careful adjustments, such as use of organic introduction systems for ICP-MS analysis for routine use.

3.2. Commercially available chelating resins

Commercially available ion exchange resins have been developed for the removal of Hg from industrial wastewaters; Duolite GT-73™ and AmberSep GT-74™ are examples of these. The recovery and preconcentration of Hg in solution using these resins has been explored as diffusive gradient thin-film cartridges[35, 45, 56]. Pelcová et al.[56] reported that both Duolite GT-73™ and AmberSep GT-74™ can remove inorganic, methyl-, ethyl-, and phenylmercury from both tap and river waters with limits of detection between 30 – 50 ng L^{-1} Hg concentrations. The loading capacities for Hg are often high, >70 mg Hg g^{-1} resin[57], as these resins were designed for the treatment of wastewaters with high Hg concentrations, often greater than 500 µg L^{-1}. These efficiently and selectively extract Hg^{2+} from a variety of water matrices but some studies reported difficulty in recovery from the resins by elution[35, 56], instead resorting to either digestion of the resin prior to analysis or direct absorption spectrometry measurement of the resin. From solutions containing up to 100 µg L^{-1} Hg^{2+}, over 92 % of the total Hg concentration could be readily recovered by digestion of the Duolite GT-73 resin™, with negligible losses in the digestion step[35]. Duolite GT-73™ is now out of production, but AmberSep GT-74™ and other variations of this resin are still available[56, 58].

3.3. Cationic exchange resins

As Hg species are predominantly cationic in the aquatic environment, cation exchange resins offer a method to remove these from solution. These resins are effective at removing cationic Hg species such as $Hg(OH)_2^{2+}$ complexes, but there may be issue with the sorption of uncharged complexes and species, such as $HgCl_2$ or MeHgCl. The conditioned resins are often washed with deionised water prior to extraction, as this decreases the likelihood of forming uncharged or negatively charged Hg complexes in the resin which impede sorption[21, 28].

A commercially available resin, Dowex 50W X4™, was found to remove inorganic Hg and some organic Hg species from a variety of natural water matrices whilst allowing for elution using 0.1 % thiourea and 8 % hydrochloric acid[59]. Gomez et al.[60] used the commercially available Dowex Marathon™ cation exchange resin as comparison to activated carbon and treated and non-treated coals. They reported the cationic exchange resin had the best sorption capacity, 98 µg Hg g^{-1} resin, and recoveries, >95 % Hg^{2+}, of the studied sorbents. These experiments used 50 mL sample volume but used a high Hg concentration, between 0.1 – 998.4 mg L^{-1}.

Cationic exchange columns have been used for online preconcentration of Hg species in sea waters, achieving detection limits of 42 pg L^{-1} when using HPLC-ICP-MS analysis[61]. This indicates suitability for the analysis of low Hg concentrations in waters. Ion exchange sorbents, columns and cartridges are commercially available and often relatively inexpensive. Some technical knowledge and training are required for field use, but use of hazardous materials is limited in field applications. Other cations present may compete for the active sites of the resin, but high loading capacities would overcome this. Issues may also arise in samples with high chloride concentrations due to the formation of uncharged complexes that would not be retained by the sorbent and pass through to the effluent[21]. Metals are eluted from these columns using strong acids, such as hydrochloric acid. While this is compatible with many analysis techniques, the concentrations of acid may require a dilution and thus reduce the overall sensitivity of the method.

3.4. Polyaniline

Polyaniline is a readily available polymeric sorbent that can be used for removal of metals from aqueous solutions and preconcentration of trace metals. Studies have primarily examined inorganic Hg species by addition of a bulk resin to a water sample, but separation of methylmercury is also possible[36, 41]. Mercury analyses using polyaniline for preconcentration have achieved 2-3 ng L^{-1} Hg limits of detection using CV-AAS and FAAS, suitable for uncontaminated natural water and drinking water; these matrices usually show Hg concentrations below 10 ng L^{-1} [62]. Mercury has been successfully preconcentrated with polyaniline from a variety of matrices including bottled water, lake and groundwaters, seawater, and even fish tissue using 100 mL sample and 10 mL 0.3 % HCl + 0.5 % thiourea eluent[36, 41]. The eluent is suitable for a wide range of analytical detection methods, due to the relatively low organic compound concentration and acid concentration.

Some polyaniline composites have also been examined for Hg removal, to improve resin stability, Hg selectivity and efficiency of sorption. Polyvinyl alcohol[63], humic acid[15], polystyrene[64], and other reagents have been used to create polyaniline composites, usually with an optimal pH range of 4-7. The predominant Hg species at this pH range is $Hg(OH)_2$ species, which will form Hg-N bonds with the polyaniline units and other bonds such as Hg-S with the composite molecules. At pH <4 the polyaniline nitrogen may be protonated, reducing the number of possible Hg-N bonds that can be formed.

3.5. Magnetic SPE

In the past decade, developments for solid-phase extraction technologies have incorporated the use of magnetic particles. By functionalising magnetic particles, the sorbent can be added to a sample to sorb Hg and then be readily removed by applying a magnetic field. The selectivity and efficiency of the sorbent is dictated by the functionalisation; some previously used compounds include 1,2-ethanedithiol[65], 3-mercaptopropyltrimethoxysilane[43], 1,5-diphenylcarbazide[66], and other task-specific monoliths[67]. These have achieved 0.1-100 ng L^{-1} Hg^{2+} detection limits of inorganic Hg in real-world aquatic matrices such as lake, river water and for spiked tap water. The 1,2-ethanedithiol functionalised particle also adsorbed cadmium (Cd) and lead (Pb) ions from solution with 0.82 ng L^{-1} Cd and Pb limits of detection[65], making the method more desirable commercially and for heavy metal pollution studies. Song, et al.[68] synthesised a task specific monolith with vinylboronic anhydride pyridine complex for functionalising the magnetic particles. This was synthesised for magnetic solid-phase extraction microextraction of inorganic Hg^{2+}, methyl-, ethyl- and phenyl- Hg. Using the chelating sorbent, recoveries of up to 94 % and detection limits of 20-160 ng L^{-1} could be achieved.

Magnetic solid-phase particles can be readily removed from solution with a magnetic field and can be used to achieve detection limits of <100 ng L^{-1} Hg. Speciation of Hg^{2+} and MeHg can be achieved and changing functional groups on the sorbent can allow for multi-elemental extraction. The sorbent can be applied to a water sample collected in a container, allowed to sit in the sample for an appropriate length of time, and then the enriched sorbent can be removed using a magnet. Elution from magnetic sorbents is generally achieved using HCl or HNO_3 and thiourea in relatively low concentrations. Analysis is typically conducted using ICP-MS techniques, however the composition of eluent and the preconcentration of the metal make the methods compatible with less sophisticated techniques such as AAS. The main limitation for magnetic SPE is the multi-step synthesis required to produce the sorbent, as the methods used often produce approximately 1 g of sorbent and scaling-up the synthesis has not yet been explored[65]. The product must also be characterised before use to ensure a homogenous and effective sorbent.

3.6. Gold-based SPE

Many metals form amalgams with Hg and this property is frequently exploited for solid-phase extraction of Hg vapour. Cold vapour (CV) methods use gold to amalgamate reduced Hg vapour, trapping the analyte in place and allowing release of the preconcentrated Hg by thermal desorption. As the amalgam is formed on the solid particles, problems arising from interferents are often negligible and so can be readily applied to environmental matrices. This has been examined and exploited in the form of gold nanoparticle columns[38, 69, 70], greatly increasing the surface area when compared to a bulk solid. Similarly, columns made using gold nanosheets offer a relatively simple method of extracting and preconcentrating aqueous Hg with very good sensitivity, as low as 80 pg L^{-1} Hg^{2+} [71]. Schlathauer et al.[51] developed a dipstick of immobilised gold nanoparticles, allowing for a simple field-sampling method that can achieve levels of sensitivity suitable for pristine waters and sea waters. As a simple dipstick, this method is easily conducted in the field without the need for extensive training or technical competency, as well as posing little hazard to the operator or during transport. While technically capable, the cost and complexity of manufacturing the dipstick alongside the need for annealing at 600 °C before each measurement currently prevents this from being easily reproduced. Additionally, gold-based SPE typically uses thermal desorption to liberate Hg from the solid-phase. While this effectively eliminates potential interferences, the detection method becomes limited to those suited for gases and vapors, such as CV-AAS.

3.7. Critical review of sample preservation and solid-phase extraction

While acidification of water samples for Hg analysis is commonly recommended, the handling and transportation of acids is becoming increasingly more regulated, particularly where controls over health and safety are more difficult, i.e. handling concentrated acids outside of a laboratory setting, and where limitations are imposed for international transportation of acids (**Error! Reference source not found.**). Any handling of acids comes with inherent hazards and risks due to their corrosive nature. This makes preservation methods that require concentrated acids particularly difficult to conduct in the field, as well as for transportation of acids and acidified samples particularly transport by air where regulations are becoming stricter[72]. Historically, oxidising agents were also recommended for Hg preservation[73] by oxidising the Hg species to the stable Hg^{2+}, however this destroys speciation data and so has fallen out of favour. Other reagent-based methods for preservation show potential, but have not been fully explored[13]. For example, increasing the ionic strength of solution by addition of ionic salts, i.e. NaCl, allows for a less hazardous method to preserve Hg[15], but literature primarily focuses on Hg^{2+} in spiked and synthetic matrices with little assessment of un-spiked water environmental samples. In addition, elevated chloride concentrations can co-precipitate in MeHg distillation and ethylation procedures[10], making the procedure unsuitable for traditional speciation analysis.

Due to the importance of Hg speciation analysis for toxicity studies, there is a concern for interspecies conversion and loss of sample integrity during preparation and storage of water samples[74-77]. Individual samples are often taken for each desired species and preserved using different methods[78]. This approach allows the operator to collect speciation data for Hg, but vastly increases same volumes required and limits the environments in which Hg studies can be conducted. For example, studies in developing countries and remote area must ship samples internationally for analysis[79, 80]. If samples are shipped unpreserved, then speciation data may not be considered as representative of the sampled environment.

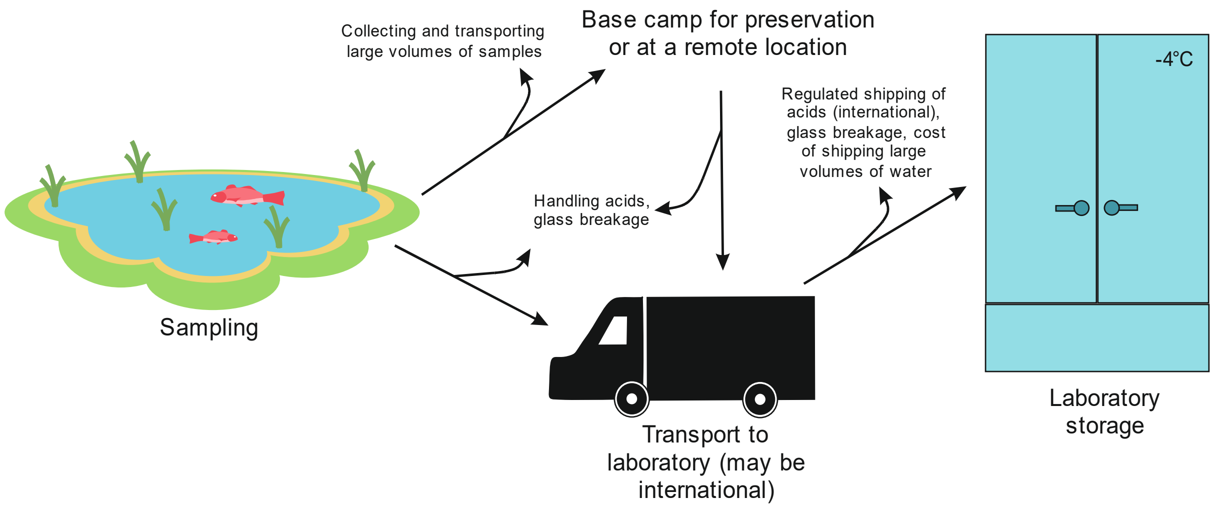

Figure 2 The sampling and preservation process, with key challenges highlighted

Recent developments in SPE for Hg analysis have focused on preparative methods such as online-speciation and -preconcentration; hyphenating a chromatographic separation to the detection method to enrich the analyte, improving detection limits and analytical sensitivity. The SPE preparation methods often operate in a broad pH range, usually optimal at pH 4-7 so suitable for many natural waters. These methods are often developed for mass spectrometry techniques[33, 65, 68] and atomic absorption and fluorescence techniques[33, 39, 52, 54, 81, 82] , due to their comparatively high sensitivity for environmental metal analysis.

Ion exchange resins sorbents and columns are commercially available and have been shown to sorb both inorganic and organic Hg species from aquatic media. Chelating resins are the more prominent choice for Hg sorption in the literature, as the affinity for sulphur allows for selective extraction of Hg[33, 42, 53, 54]. Some chelating resins, however, require synthesis or processing to create columns and cartridges for field use[33, 42]. Commercially available resins are available but have shown difficulty in eluting retained Hg species, requiring digestion processes to liberate the adsorbed Hg[56, 58] which may affect speciation data through oxidation of the retained species. Cation exchange resins only require an acid, HCl in this case, and thiourea to efficiently elute Hg[59], but these may be more susceptible to competition with other cations in the sample. Typically, ion exchange resins use dilute acids and weak organic concentrations to elute immobilised Hg species. The eluent composition allows for analysis using a wide range of instruments and can therefore be applied in most laboratories.

Functionalised magnetic sorbents can be added to a collected water sample and then readily removed by application of a magnetic field, either an electro-magnet or a strong, permanent magnet[43, 65-67]. These sorbents are relatively simple to use in the field, with minimal training requirements and a high Hg extraction efficiency. The eluent can typically be used with a wide variety of analysis techniques, although some developed sorbents require methanol[67] which will limit the compatibility of the methods. The synthesis of these sorbents is often more complicated than other sorbent materials, and may require work to scale-up synthesis to be viable as a widespread sampling procedure.

Gold-based sorbents are some of the most selective and efficient sorbents available for Hg extraction and preservation, but come with a considerable cost due to the raw materials price[38, 51, 71]. Therefore, a high reusability is necessary to offset the cost. Desorption of the retained Hg is conducted via thermal desorption, which limits the compatible analysis techniques to those which can measure Hg vapour, such as AAS.

Another technology, diffusive gradient thin-film (DGT), was investigated for the sorption and storage of Hg in the field[56, 83], with analysis after transport to the laboratory. These are usually deployed into a water source, for example a river or waste treatment water tank, for 4 – 24 hours, where the Hg species become bound to the resin[58, 84]. For some DGT resins, Hg is irreversibly bound and so must be digested before analysis or alternative analysis methods must be used[56, 58]. For other resins, Hg species are elutable with either thiourea or HCl the latter being preferable for many analysis techniques and when ethylation of the Hg species is required for MeHg quantification[84].

A current deficiency in literature is the exploration of adequate storage capacities and times for SPE methods (Supplementary Table 2). When investigating sorption of Hg species, there is a tendency to focus on trace metal concentrations, such as <0.1 µg L^{-1} Hg^{2+} [43, 51, 69, 71]. While this is adequate for unpolluted waters, the usefulness of the developed methods for contaminated water samples is in question. Resins developed for Hg removal show comparatively higher storage capacities, often over 10 mg Hg g^{-1} resin[36, 48, 63-66], and storage capacities of functionalised columns are dependent on the amount of functionalising agent immobilised on the solid phase[33, 42, 53]. Storage times are also under-represented in literature, often only being investigated for around 1-week of storage[33, 42, 51, 53]. Filling this gap in knowledge will provide necessary information for applying SPE as an offline field sampling and preservation method.

4. Future perspectives of field analysis and preservation

4.1. The future of Hg field analysis

Emerging technologies use nanoparticles and colorimetric methods to determine Hg^{2+} in natural waters. Fluorescence probes have been developed for Hg^{2+} determination, for example Kaewnok et al.[85] developed a [5]helicene-based probe highly selective for Hg^{2+} which can be used as a test-strip with a detection limit of 6.5 µg L^{-1} Hg^{2+}. This work requires development for the in-field screening of Hg^{2+} in environmental samples. Rhodamine nanoparticles have been developed for smartphone-based colorimetric analysis, as a method to detect Hg^{2+} in pristine water matrices[86, 87]. These nanoparticles are highly selective for Hg^{2+}, showing little interference with other metals. Recoveries of over 95 % were reported for both drinking water and dam water with a limit of detection of 1.3 µg L^{-1} Hg^{2+} [87], and 0.1 µg L^{-1} Hg^{2+} in spiked deionised water with recoveries >80 % Hg^{2+} in river and lake water[86]. Lopreside et al. reported colorimetric smartphone detection of Hg^{2+} using an orthogonal paper biosensor[88]. Using three different biotic "reagents", Hg^{2+} concentrations and toxicity can be evaluated simultaneously. The sensors each determine Hg over different periods of time, between 17 – 60 minutes, and with varying limits of detection, 0.58 – 17 µg L^{-1} Hg^{2+}. This allows for either quantitative or semi-quantitative analysis, if required. The use of multiple sensors reduces the chance of interference by other compounds and elements in the matrix, however silver and cadmium reportedly inhibit the activity of the sensors.

With the prevalence of smartphones and simplicity of use, colorimetric methods are likely to become a mainstay in field analysis methods for trace metals in the future. The biggest challenges to analysis in the field are the limit of detection in relevant matrices, determination of different Hg species and contamination of the sample. While good practice can overcome sample contamination issues, the sensitivity of portable instruments is currently not suitable for mercury concentrations less than the WHO guideline limit of 2 µg L^{-1} total Hg, or for speciation analysis. Current field analyses of Hg species are unable to achieve appropriate sensitivity, as Hg species are often found in concentrations <10 ng L^{-1} particularly in unpolluted sites. The portable instruments tend to favour analysis of Hg^{2+}, neglecting the determination of MeHg and other relevant species. This limits their usefulness for toxicological and monitoring studies, as organic Hg species data is vital for assessing the health impact of Hg concentrations in waters. With these current restraints, analysts must weigh up improved analysis and sensitivity in laboratory measurements versus representative but less accurate data measured in the field.

4.2. Solid-phase extraction as a sampling and preservation method

Solid-phase extraction shows potential as future reagent-free sampling methods for Hg in natural water samples, as columns and microcolumns[33, 38, 42, 54, 59, 71], as DGT cartridges[56, 58], particles added directly to samples[43], or as a dipstick[51]. The ability to extract Hg from solution and retain the metal on a solid bed reduces the likelihood of Hg loss over time; volatilisation is reduced due to strong interactions with the stationary phase and wall sorption is reduced as the analyte is immobilised on a solid phase with little interaction with the container walls. By immobilising the analyte to a solid phase, the likelihood of chemical changes is reduced, and speciation data can be preserved[33, 43, 53]. Most column-based SPE methods are relatively simple to conduct and, once prepared, can be used in the field to extract dissolved Hg without the need for additional reagents. The use of columns and cartridges also eliminate the need for glass containers, reducing hazards from breakages.

One promising SPE methods for Hg preservation, gold-nanoparticle dipsticks, are effective at removing Hg from natural water samples[51]. The dipsticks can be simply dipped into a water sample, with little knowledge required for field-use, few possible interferents and is a relatively quick method at only 10 – 20 minutes per sample. The dipstick must be annealed at 600 °C to ensure gold nanoparticle formation and the synthesis was reported to require a system for depositing a gold vapour to a defined area on the stick. This limits the ability to scale-up production of the dipstick for routine use, however the article reported excellent reusability at 145 cycles of sampling and annealing without performance loss. While offering superb extraction and recovery, the gold-based sorbents are limited to techniques for analysing Hg vapours, such as AAS, due to the requirement for thermal desorption. This may limit the overall usefulness of the technique, as other analysis methods cannot be used as readily.

Other sorbents, such as thiol-functionalised sorbents or funtionalised magnetic solid-phases, are typically compatible with a wider variety of analytical techniques due to eluent composition. Often, the eluents used are a dilute acid[33, 36, 43, 59, 63, 65] or a low organic compound concentration[33, 36, 42, 43, 59, 65], so are not as restricted as thermal desorption. In addition, inorganic and methyl- Hg species were retained and stored on diethyldithiocarbamate immobilized C18 microcolumns for up to 2-weeks and 1 week respectively before elution[33], highlighting the potential for reagent-free field sampling while preserving speciation. These columns, microcolumns, and cartridges are simple to use in the field, with minimal training requirements and little-to-no risk to the operator. With high recoveries and readily incorporating preconcentration of Hg species, SPE methods offer the ability to collect and preserve representative Hg concentration and speciation data, while being suitable to many analysis techniques and laboratory settings.

The cost of the SPE methods is often higher than that of sample acidification but the reduction in storage space and sample volume, as well as reduced risk to the operator and simpler field-application, offset the cost (Table 2). Preconcentration, usually via SPE, may be required for samples only treated by acidification, so sorbents may already be required. A currently unexplored risk of columns and cartridges is the accumulation of Hg from ambient storage conditions; this is likely mitigated by choice of casing material and appropriate storage, but further work on this is needed. However, avoiding storage in areas of with Hg vapour contamination may make this concern negligible.

Another important, yet unresolved issue is the lack of validated *in-situ* analytical techniques that can accurately measure Hg species concentrations. Without the determination of species concentration at the point of collection, interspecies conversion during storage and transportation cannot be fully validated for environmental samples and so speciation data determined in the laboratory may not be representative of the real-world concentrations.

Table 2 Approximate cost-per-sample of some suggested Hg preservation and solid-phase extraction methods

Preservation/ preparation method	Relevant species	Main costs	Approximate reagent cost per sample*	Sample holding time	Application in the field	Cost-benefit
Acidification (HCl and HNO_3)	Total Hg, Hg^{2+}, MeHg	HCl and HNO_3 divided by samples at 1 %	$2.50 per 500 mL sample	6-12 months	Addition of 1% (v/v) acid to a collected water sample, either at a base-camp or in a laboratory after shipping	+ Relatively cheap per sample + Recommended – Separate samples are usually required for speciation techniques (i.e. distillation for MeHg) – Needs to be added to samples when at a base-camp or laboratory, to ensure safety measures – Potential difficulties and regulations in transportation of samples
Thiol-functionalised ion exchange cartridges	Hg^{2+}, MeHg	Price of cartridges and approximate price of functionalising reagents	$5 per sample	Not investigated beyond 2 weeks	Water samples are passed through homemade microcolumns or cartridges in the field, transported to a laboratory for elution	+ Highly selective for Hg and can be filled with water prior to sampling, reducing the amount of hazardous waste in-field. + Can be re-used and regenerated several times, improving cost-effectiveness – Preservation and storage of Hg species has not been fully explored – A time-cost must be considered for preparation of SPE-phases, albeit relatively labour unintensive
Commercially available resins	Total Hg, Hg^{2+}	Initial price of resin	$10 per sample	Not investigated	Water samples passed through preprepared DGT cartridges, or applied as a batch sorbent	+ Selective for Hg in water samples, usually applied for Hg removal in waste-water + High analyte capacity relative to other resins and sorbents – Resins are often expensive (~$500 for 250g resin) – For a column/cartridge, column loading and preparation time must be considered

Gold sorbents	Total Hg, Hg^{2+}	Price of gold metal for synthesising sorbent	\$5 for sample	Not investigated	A dipstick, which can be dipped into a water sample, or passing water through preprepared microcolumns or cartridges	+ These offer high levels of reusability (>145 cycles), and Hg desorption can be conducted thermally + Minimal interference/competition for the sorbent, due to selective amalgamation – Synthesis requires controlled sputtering and vapour deposition technologies, which may not be readily available – Gold is an expensive reagent, not readily available in most laboratories for preparation of the columns/dipsticks, therefore has a high initial cost

*Prices are obtained from online vendors (sigmaaldrich.com, fishersci.co.uk, accessed 21 August 2022) converted from GDP (£) to USD ($)

5. Conclusion

While the mechanisms for dissolved Hg loss have become more well defined over the years, safe methods for preservation, storage and transportation of samples to the laboratory for measurement of both total Hg and individual Hg species still remains a challenge. Different species require separate preservation methods, hazardous or expensive materials, and large sample volumes to improve detection limits for trace and ultra-trace Hg analysis and speciation analysis. This makes routine Hg studies and monitoring impractical in challenging environments such as remote locations or lower- and middle-income countries. Current literature on preserving Hg species in water samples has shown minimal developments on limiting the use of hazardous materials, instead highlighting the need for rapid transportation to a laboratory for preservation. In remote areas and uncontrolled environments, the use of concentrated acids can pose a significant risk to the operator and increase the challenges of transporting samples to laboratories in a timely manner.

Solid-phases methods and sorbents are already used in Hg analysis for preconcentration, removal, and speciation of Hg, immobilising the chemical species without altering the chemical forms. Mercury-specific functionalized sorbents, in particular functionalisation with diethyldithiocarbamate or diphenylthiocarbazone, have shown effective extraction of Hg^{2+} and some organic Hg species from natural water samples and suitable recovery after 1 week of storage. There is a lack of literature on the concentrations of adsorbed Hg species after 1-week of storage, therefore research into the long-term storage of Hg-species, particularly MeHg, is necessary for the development of SPE as a preservation method. However, SPE is a relatively inexpensive and safe method for *in-situ* sampling and preserving Hg species from natural water samples for transport from field-to-laboratory and obtaining representative dissolved Hg data.

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References

1. WHO, *Mercury in Drinking-water*, WHO, 2005.
2. J. F. Risher, *Elemental mercury and inorganic mercury compounds: human health aspects*, WHO, 2003.
3. M. K. Kim and K. D. Zoh, Fate and transport of mercury in environmental media and human exposure, *J Prev Med Public Health*, 2012, **45**, 335-343.
4. USEPA, *Mercury update: impact on fish advisories [Fact sheet]*, USEPA, 1999.
5. N. Bloom, in *Mercury pollution integration and synthesis*, ed. J. W. H. C. J. Watras, Lewis Publishers, Boca Raton, 1994, pp. 541-552.
6. C. T. Driscoll, Y. Han, C. Y. Chen, D. C. Evers, K. Fallon Lambert, T. M. Holsen, N. C. Kamman, R. K. Munson, Mercury contamination in remote forest and aquatic ecosystems in the northeastern US: sources, transformations and management options, *Bioscience*, 2007, **57**, 17-28.
7. V. Ngure, T. Davies, G. Kinuthia, N. Sitati, S. Shisia, E. Oyoo-Okoth, Concentration levels of potentially harmful elements from gold mining in Lake Victoria Region, Kenya: Environmental and health implications, *J. Geochem.*, 2014, **144**, 511-516.
8. USEPA, *Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapour atomc fluorescence spectrometry*, USEPA, 2002.
9. USEPA, *Method 1669 Sampling ambient water for trace metals at EPA water quality criteria levels*, USEPA, 1996.
10. J. L. Parker and N. S. Bloom, Preservation and storage techniques for low-level aqueous mercury speciation, *Sci Total Environ*, 2005, **337**, 253-263.
11. C. Bosch, A. Olivares, M. Faria, J. M. Navas, I. del Olmo, J. O. Grimalt, B. Pina and C. Barata, Identification of water soluble and particle bound compounds causing sublethal toxic effects. A field study on sediments affected by a chlor-alkali industry, *Aquat Toxicol*, 2009, **94**, 16-27.
12. B. Gworek, O. Bemowska-Kalabun, M. Kijenska and J. Wrzosek-Jakubowska, Mercury in marine and oceanic waters—a review, *Water Air Soil Pollut*, 2016, **227**, 371.
13. L. Yu and X. Yan, Factors affecting the stability of inorganic and methylmercury during sample storage, *TrAC*, 2003, **22**, 245-253.
14. K. Leopold, M. Foulkes and P. Worsfold, Methods for the determination and speciation of mercury in natural waters—a review, *Anal Chim Acta*, 2010, **663**, 127-138.
15. J. Zhang, J. Chao, Y. Tang, P. Wan, X. J. Yang, C. Wong, M. Bruce and Q. Hu, Quantification of Trace Mercury in Water: Solving the Problem of Adsorption, Sample Preservation, and Cross-Contamination, *Glob Chall*, 2020, **4**, 1900061.
16. F. Beckers and J. Rinklebe, Cycling of mercury in the environment: Sources, fate, and human health implications: A review, *Crit. Rev. Environ.*, 2017, **47**, 693-794.
17. J. M. Lo and C. M. Wai, Mercury loss from water during storage. Mechanisms and prevention, *Anal. Chem.*, 1975, **47**(11), 1869-1870.
18. M. Leermakers, P. Lansens and W. Baeyens, Storage and stability of inorganic and methylmercury solutions, *Fresnius J. Anal. Chem.*, 1994, **336**, 655-662.
19. A. Riscassi, C. L. Miller and S. C. Brooks, Impact of collection container material and holding times on sample integrity for mercury and methylmercury in water, *Limnol.*, 2014, **12**, 407-420.
20. R. A. Carr and P. E. Wilkniss, Mercury. Short-term storage of natural waters, *Environ. Sci. Technol.*, 1973, **7**, 62-63.

21. M. H. Bothner and D. E. Robertson, Mercury contamination of sea water samples stored in polyethylene containers, *Anal. Chem.*, 1975, **47**, 592-595.
22. C. R. Hammerschmidt, K. L. Bowman, M. D. Tabatchnick and C. H. Lamborg, Storage bottle material and cleaning for determination of total mercury in seawater, *Limnol.*, 2011, **9**, 426-431.
23. C. H. B. Rocha, H. F. Costa and L. P. Azevedo, Heavy metals in the São Mateus Stream Basin, Peixe River Basin, Paraiba do Sul River Basin, Brazil, *Rev. Ambiente Água*, 2019, **14**(3).
24. S. Bhardwaj, R. Soni, S. K. Gupta and D. P. Shukla, Mercury, arsenic, lead and cadmium in waters of the Singrauli coal mining and power plants industrial zone, Central East India, *Environ Monit Assess*, 2020, **192**, 251.
25. J. H. Hwang, D. Fox, J. Stanberry, V. Anagnostopoulos, L. Zhai and W. H. Lee, Direct Mercury Detection in Landfill Leachate Using a Novel AuNP-Biopolymer Carbon Screen-Printed Electrode Sensor, *Micromachines (Basel)*, 2021, **12**, 649.
26. A. A. Kriger and R. R. Turner, Field analysis of mercury in water, sediment and soil using static headspace analysis, *Water Air Soil Pollut.*, 1995, **80**, 1295-1304.
27. V. Krivan and H. F. Haas, Prevention of loss of mercury(II) during storage of dilute solutions in various containers, *Fresnius J. Anal. Chem.*, 1988, **332**, 1-6.
28. H. Louie, C. Wong, Y. J. Huang and S. Fredrickson, A study of techniques for the preservation of mercury and other trace elements in water for analysis by inductively coupled plasma mass spectrometry (ICP-MS), *Anal. Methods*, 2012, **4**, 522-529.
29. R. Addis Lockwood and K. Y. Chen, Adsorption of Hg (II) by hydrous manganese oxides, *Environ. Sci. Technol.*, 1973, **7**, 1028-1034.
30. Y. Inoue and M. Munemori, Coprecipitation of mercury (II) with iron (III) hydroxide, *Environ. Sci. Technol.*, 1979, **13**, 443-445.
31. L. D. Hylander, M. Meili, L. J. Oliveira, E. de Castro e Silva, J. R. D. Guimaraes, D. M. Araujo, R. P. Neves, R. Stachiw, A. J. P. Barros and G. D. Silva, Relationship of mercury with aluminum, iron and manganese oxy-hydroxides in sediments from the Alto Pantanal, Brazil, *Science of the Total Environment*, 2000, **260**, 97-107.
32. M. Gardner and A. Gunn, Stability of mercury in seawater samples, *Analytical Communications*, 1997, **34**, 245-246.
33. R. M. Blanco, M. T. Villanueva, J. E. Sánchez Urıa and A. Sanz-Medel, Field sampling, preconcentration and determination of mercury species in river waters, *Anal. Chim. Acta*, 2000, **419**, 137-144.
34. D. M. Sánchez, R. Martín, R. Morante, J. Marín and M. L. Munuera, Preconcentration speciation method for mercury compounds in water samples using solid phase extraction followed by reversed phase high performance liquid chromatography, *Talanta*, 2000, **52**, 617-679.
35. P. Pohl and B. Pruisisz, reconcentration of Mercury Using Duolite GT-73 in the Analysis of Water Samples by Inductively Coupled Plasma Atomic Emission Spectrometry., *Anal. Sci.*, 2004, **20**, 1367-1370.
36. M. V. Balarama Krishna, D. Karunasagar, S. V. Rao and J. Arunachalam, Preconcentration and speciation of inorganic and methyl mercury in waters using polyaniline and gold trap-CVAAS, *Talanta*, 2005, **68**, 329-335.
37. B. R. Vermillion and R. J. Hudson, Thiourea catalysis of MeHg ligand exchange between natural dissolved organic matter and a thiol-functionalized resin: a novel method of matrix removal and MeHg preconcentration for ultratrace Hg speciation analysis in freshwaters, *Anal. Bioanal. Chem.*, 2007, **388**, 341-352.

38. K. Leopold, M. Foulkes and P. Worsfold, Gold-Coated Silica as a Preconcentration Phase for the Determination of Total Dissolved Mercury in Natural Waters Using Atomic Fluorescence Spectrometry, *Anal. Chem.*, 2009, **81**, 3421-3428.
39. N. Basadi, K. Ghanemi and Y. Nikpour, l-Cystine-functionalized graphene oxide nanosheets for effective extraction and preconcentration of mercury ions from environmental waters, *Chem. Zvesti.*, 2020, **75**, 1083-1093.
40. W. R. Cairns, M. Ranaldo, R. Hennebelle, C. Turetta, G. Capodaglio, C. F. Ferrari, A. Dommergue, P. Cescon and C. Barbante, Speciation analysis of mercury in seawater from the lagoon of Venice by on-line pre-concentration HPLC-ICP-MS, *Anal. Chim. Acta*, 2008, **622**, 62-69.
41. M. V. Balarama Krishna, K. Chandrasekaran and D. Karunasagar, On-line speciation of inorganic and methyl mercury in waters and fish tissues using polyaniline micro-column and flow injection-chemical vapour generation-inductively coupled plasma mass spectrometry (FI-CVG-ICPMS), *Talanta*, 2010, **81**, 462-472.
42. Y. Yin, M. Chen, J. Peng, J. Liu and G. Jiang, Dithizone-functionalized solid phase extraction-displacement elution-high performance liquid chromatography-inductively coupled plasma mass spectrometry for mercury speciation in water samples, *Talanta*, 2010, **81**, 1788-1792.
43. S. Zhang, H. Luo, Y. Zhang, X. Li, J. Liu, Q. Xu and Z. Wang, In situ rapid magnetic solid-phase extraction coupled with HPLC-ICP-MS for mercury speciation in environmental water, *Microchemical Journal*, 2016, **126**, 25-31.
44. J. A. Ritter and J. P. Bibler, Removal of mercury from wastewater: large-scale performance of an ion exchange process, *Water Sci. Technol.*, 1992, **25**, 165-172.
45. S. Chiarle, M. Ratto and M. Rovatti, Mercury removal from water by ion exchange resins adsorption, *Water Res.*, 2000, **43**, 2971-2978.
46. J. M. Monteagudo and M. J. Ortiz, Removal of inorganic mercury from mine waste water by ion exchange, J. *Chem. Technol. Biotechnol.*, 2000, **75**, 767-772.
47. J. Wang, B. Deng, H. Chen, X. Wang and Z. Jianzhong, Removal of aqueous Hg (II) by polyaniline: sorption characteristics and mechanisms, *Environ. Sci. and Technol.*, 2009, **43**, 5223-5228.
48. Y. Zhang, Q. Li, L. Sun, R. Tang and J. Zhai, High efficient removal of mercury from aqueous solution by polyaniline/humic acid nanocomposite, *J. Hazard Mater.*, 2010, **175**, 404-409.
49. M. Rajasimman, N. Rajamohan, Parametric, equilibrium and kinetic studies on the removal of mercury using ion exchange resin, *Water Pract.*, 2017, **12**, 305-313.
50. E. Hanhauser, M. S. Bono, Jr., C. Vaishnav, A. J. Hart and R. Karnik, Solid-phase extraction, preservation, storage, transport, and analysis of trace contaminants for water quality monitoring of heavy metals, *Environ Sci Technol*, 2020, **54**, 2646-2657.
51. M. Schlathauer, J. Friedland, M. Lindén and K. Leopold, Sustainable and reagent-free mercury trace determination in natural waters using nanogold dipsticks, *Microchem. J.*, 2019, **147**, 253-262.
52. M. E. Mahmoud, M. M. Osman and M. E. Amer, Selective pre-concentration and solid phase extraction of mercury (II) from natural water by silica gel-loaded dithizone phases, *Anal. Chim. Acta*, 2000, **415**, 33-40.
53. Y. Wang, A. Zhu, Y. Fang, C. Fan, Y. Guo, Z. Tan, Y. Yin, Y. Cai and G. Jiang, Dithizone-functionalized C18 online solid-phase extraction-HPLC-ICP-MS for speciation of ultra-trace organic and inorganic mercury in cereals and environmental samples, *J. Environ. Sci. (China)*, 2022, **115**, 403-410.
54. J. Margetínová, P. Houserová-Pelcová and V. Kubáň, Speciation analysis of mercury in sediments, zoobenthos and river water samples by high-performance liquid chromatography

hyphenated to atomic fluorescence spectrometry following preconcentration by solid phase extraction, *Anal. Chim. Acta*, 2008, **615**, 115-123.

55. M. E. Mahmoud, Selective solid phase extraction of mercury (II) by silica gel-immobilized-dithiocarbamate derivatives, *Anal. Chim. Acta*, 1999, **398**, 297-304.
56. P. Pelcova, H. Docekalova and A. Kleckerova, Development of the diffusive gradient in thin films technique for the measurement of labile mercury species in waters, *Anal. Chim. Acta*, 2014, **819**, 42.
57. F. Fondeur, W. Van Pelt and S. Fink, *Mercury Removal Performance of Amberlite™ GT-73A, Purolite™ S-920, Ionac™ SR-4 and SIR-200™ Resins*, Westinghouse Savannah Rover Company, 2002.
58. P. Pelcova, H. Docekalova and A. Kleckerova, Determination of mercury species by the diffusive gradient in thin film technique and liquid chromatography – atomic fluorescence spectrometry after microwave extraction, *Anal. Chim. Acta*, 2015, **866**, 21-26.
59. A. Krata, K. Pyrzynska and E. Bulska, Use of solid-phase extraction to eliminate interferences in the determination of mercury by flow-injection CV AAS, *Anal. Bioanal. Chem*, 2003, **377**, 735-739.
60. L. M. Gomez, F. Colpas-Castillo and R. Fernandez-Maestre, Cation exchange for mercury and cadmium of xanthated, sulfonated, activated and non-treated subbituminous coal, commercial activated carbon and commercial synthetic resin: effect of pre-oxidation on xanthation of subbituminous coal, *Int. J. Coal. Sci. Technol.* 2014, **1**, 235-240.
61. X. Y. Jia, D. R. Gong, Y. Han, C. Wei, T. C. Duan and H. T. Chen, Fast speciation of mercury in seawater by short-column high-performance liquid chromatography hyphenated to inductively coupled plasma spectrometry after on-line cation exchange column preconcentration, *Talanta*, 2012, **88**, 724-729.
62. K. Leopold, M. Foulkes and P. J. Worsfold, Preconcentration techniques for the determination of mercury species in natural waters, *TrAC*, 2009, **28**, 426-435.
63. H. Vafaei Molamahmood, T. Ebadi and R. Eskandari, Adsorption of mercury by polyaniline/polyvinyl alcohol in an aqueous environment, *Water Air Soil Pollut.*, 2018, **229**, 106.
64. R. Gupta, R. Singh and S. Dubey, Removal of mercury ions from aqueous solutions by composite of polyaniline with polystyrene, *Sep. Purif.*, 2004, **38**, 225-232.
65. Y. Chen, M. He, B. Chen and B. Hu, Thiol-grafted magnetic polymer for preconcentration of Cd, Hg, Pb from environmental water followed by inductively coupled plasma mass spectrometry detection, *Spectrochim.*, 2021, **177**, 10671.
66. Y. Zhai, S. e. Duan, Q. He and X. Yang, Solid phase extraction and preconcentration of trace mercury (II) from aqueous solution using magnetic nanoparticles doped with 1, 5-diphenylcarbazide, *Mikrochim. Acta*, 2010, **169**, 353-360.
67. X. Song, J. Wu, J. Pang, Y. Wu and X. Huang, Task specific monolith for magnetic field-reinforced in-tube solid phase microextraction of mercury species in waters prior to online HPLC quantification, *Journal of Hazard. Mater.*, 2021, **411**, 125141.
68. Y. Song, Q. Ma, H. Cheng, J. Liu and Y. Wang, Simultaneous enrichment of inorganic and organic species of lead and mercury in pg L−1 levels by solid phase extraction online combined with high performance liquid chromatography and inductively coupled plasma mass spectrometry, *Anal. Chim. Acta*, 2021, **1157**, 338388.
69. N. Panichev, M. M. Kalumba and K. L. Mandiwana, Solid phase extraction of trace amount of mercury from natural waters on silver and gold nanoparticles, *Anal. Chim. Acta*, 2014, **813**, 56-62.

70. V. Stock, A. Mutschler, M. Lindén and K. Leopold, Photoactive Titanium Dioxide Films with Embedded Gold Nanoparticles for Quantitative Determination of Mercury Traces in Humic Matter-Containing Freshwaters, *Nanomaterials*, 2021, **11**, 512.
71. A. Zierhut, K. Leopold, L. Harwardt and M. Schuster, Analysis of total dissolved mercury in waters after on-line preconcentration on an active gold column, *Talanta*, 2010, **81**, 1529-1535.
72. IATA, *Dangerous Goods Handling*, 2022.
73. C. Feldman, Preservation of dilute mercury solutions, *Anal. Chem.*, 1974, **46**, 99-102.
74. J. A. Colman, L. Barber and N. S. Bloom, Artifact formation of methyl mercury during aqueous distillation and alternative techniques for the extraction of methyl mercury from environmental samples, *Fresnius J. Anal. Chem.*, 1997, **358**, 371-377.
75. H. Hintelmann, Comparison of different extraction techniques used for methylmercury analysis with respect to accidental formation of methylmercury during sample preparation, *Chemosphere*, 1999, **39**, 1093-1105.
76. J. P. Snell, E. Björn and W. Frech, Investigation of errors introduced by the species distribution of mercury in organic solutions on total mercury determination by electrothermal vaporisation– inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.*, 2000, **15**, 397-402.
77. C. R. Hammerschmidt and W. F. Fitzgerald, Formation of artifact methylmercury during extraction from a sediment reference material, *Anal. Chem.*, 2001, **73**, 5930-5936.
78. E. Mladenova, I. Dakova, D. Tsalev and I. Karadjova, Mercury determination and speciation analysis in surface waters, *Open Chem.*, 2012, **10**, 1175-1182.
79. J. C. Bonzongo, B. S. Ojiambo, W. B. Lyons, S. Wilder and K. Welch, Mercury concentrations in waters of Lake Naivasha watershed, Kenya, *Geophys.*, 1996, **23**, 1581-1584.
80. J. Kotnik, M. Horvat, E. Tessier, N. Ogrinc, M. Monperrus, D. Amouroux, V. Fajon, D. Gibičar, S. Žižek, F. Sprovieri and N. Pirrone, Mercury speciation in surface and deep waters of the Mediterranean Sea, *Mar. Chem.*, 2007, **107**, 13-30.
81. F. J. Black, K. W. Bruland and A. R. Flegal, Competing ligand exchange-solid phase extraction method for the determination of the complexation of dissolved inorganic mercury (II) in natural waters, *Anal. Chim. Acta*, 2007, **598**, 318-333.
82. B. Duval, A. Gredilla, S. Fdez-Ortiz de Vallejuelo, E. Tessier, D. Amouroux and A. de Diego, A simple determination of trace mercury concentrations in natural waters using dispersive Micro-Solid phase extraction preconcentration based on functionalized graphene nanosheets, *Microchem. J.*, 2020, **154**, 104549.
83. Y. Gao, E. De Canck, M. Leermakers, W. Baeyens and P. Van Der Voort, Synthesized mercaptopropyl nanoporous resins in DGT probes for determining dissolved mercury concentrations, *Talanta*, 2011, **87**, 262-267.
84. Y. Gao, S. De Craemer and W. Baeyens, A novel method for the determination of dissolved methylmercury concentrations using diffusive gradients in thin films technique, *Talanta*, 2014, **120**, 470-474.
85. N. Kaewnok, J. Sirirak, S. Jungsuttiwong, Y. Wongnongwa, A. Kamkaew, A. Petdum, W. Panchan, S. Sahasithiwat, T. Sooksimuang, A. Charoenpanich and N. Wanichacheva, Detection of hazardous mercury ion using [5] helicene-based fluorescence probe with "TurnON" sensing response for practical applications, *J. Hazard. Mater.*, 2021, **418**, 126242.
86. X. Zhao, Y. Liu, B. Shu, Z. Guo, C. Song, X. Huang and Z. Jiao, Portable smartphone-based device for on-site detection of Hg2+ in water samples, *Int. J. Environ. Anal. Chem.*, 2020, **102**(11), 1-10.

87. D. Aydin, I. Yilmaz, Simple synthesis and sensing applications of a new and low cost fluorescent chemosensor for selective recognition and facile removal of Hg2+, *J. Photochem.*, 2021, **414**, 113280.
A. Lopreside, L. Montali, B. Wang, A. Tassoni, M. Ferri, M. M. Calabretta and E. Michelini, Orthogonal paper biosensor for mercury (II) combining bioluminescence and colorimetric smartphone detection, *Biosens. Bioelectron.*, 2021, **194**, 113569.

Supplementary information

Supplementary Table 1 Reagent-based preservation methods for Hg, reported storage times, analytical merit and challenges

Reagent	Mercury species	Storage time	Sample volume reported	Analytical merit and challenges	References
Acidification				• Recommended for many metals and trace elements • In an uncontrolled environment, there is a risk of acid burns and skin irritation from spills • A pH <4 promotes stable chloro-mercury complexes in the presence of chloride ions	
Hydrochloric acid (0.4-1 %)	Hg^{2+} in freshwater	6-12 months (>90 % recovery)	0.5-1 L in polytetrafluoroethylene (PTFE) or glass containers	• >90 % recovery over long term storage (12 months) • Recommended container materials are either hazardous (glass, risk of cuts from breakage) or expensive (PTFE, £15-30 per bottle)	8-10,28
Nitric (1 %) and hydrochloric acid (0.005 %)	Hg^{2+} in deionised water	53 days (>90 % recovery)	500 mL in high-density polyethylene (HDPE) containers	• Recoveries of >90 % Hg^{2+} can be obtained with small quantities of acid • A nitric and hydrochloric acid mixture is a common matrix for ICP-MS analysis, which is sensitive enough for Hg analysis	8,9,28
Sulphuric acid (0.2 %)	MeHg in seawater	6 months	Not specified as a series of different experiments – PE container material	• Mitigates formation of artificial MeHg during speciation by distillation and ethylation • This speciation method is less prevalent nowadays, due to the development of HPLC speciation	10
Oxidising agent				• Oxidises species to inorganic Hg^{2+} (comparatively more stable than Hg^0) • Risk of oxidising atmospheric Hg^0 and artificially increasing Hg concentration (particularly for trace Hg concentrations of relatively high atmospheric Hg^0 concentrations) • Oxidising chemicals are often harmful, risk of spillage and harm to the operator	
Potassium permanganate-persulphate digestive solution	Hg^{2+} in deionised water	560 days (negligible losses)	50 mL in polypropylene (PP) containers	• Negligible losses by adsorption for 0.2 – 1 µg L^{-1} Hg^{2+} • Improves cost-effectiveness by allowing use of polypropylene containers • Increased risk of spills and harm to the operator in an uncontrolled environment	15

Potassium dichromate solution (0.05 % w.v, acidified)	Hg^{2+} in deionised water	21 days (>95 % recovery)	100 mL in borosilicate glass and PE containers	• Effectively preserves Hg for up to 21 days, further investigation has not been conducted • As a strong oxidising agent, there is a risk to the operator, especially in an uncontrolled environment	17,73
Increased ionic strength				• Mitigates wall sorption by reducing the number of active sites in container walls • Formation of $Hg(OH)_x^{2-x}$ can be limited with the introduction of different complexing agents	
Sodium nitrate (3 %)	Hg^{2+} in deionised water	90 days (95 % recovery in PP, >95 % recovery in glass)	50 mL in PP or glass containers	• An initial loss of 5 % Hg is seen over 7 days (likely stabilisation and losses to with container walls) • Below 3 % sodium nitrate, the recovery of Hg drops to <90 % in PP containers	15
Sodium chloride (1-3 g L^{-1})	Hg^{2+} in deionised water	180 days (>95 % recovery)	50 mL in PP containers	• Chloro-mercury complexes are promoted, improving stability of the metal • The initial loss of Hg is decreased to <2 % over 7 days	15,28
Sodium chloride (20 mg L^{-1}, acidified)	Hg^{2+} in deionised water	35 days (>98 % recovery)	500 mL in PP containers	• Low pH and increased chloride concentrations further promotes chloro-mercury complexes • Stability was only recorded up to 35 days, but further preservation is likely possible	28

Supplementary Table 2 Solid-phase extraction sorbents for Hg, reported recoveries, detection limts, analyical merits and difficulties

Sorbent/Solid-phase functionalization	Hg species	Matrix	Eluent/digestion	Detection limit	Recovery	Mesh/pore/particle size	Analytical merits and difficulties	References
Thiol functionalised resins								

Dithizone functionalised silica (for preconcentration)	Hg^{2+}, MeHg, EtHg	DI water, tap water (**filtered** waters)	100 mmol L^{-1} sodium thiosulphate or 1% 2-mercaptoethanol	3 ng L^{-1} by HPLC-ICP-MS	83.4 % Hg^{2+} 93.7 % MeHg 71.7 % EtHg	Storage capacity: not investigated, dependent on load of functional reagent, 20 µg L^{-1} Hg tested with a 12.5 µg dithizone load Pore size: 60 Å Particle size: 45 µm	+ Selective for Hg and its species + Extraction efficiency and elution were not affected after 7 days storage at 4 °C – Must be functionalised before use, so time between functionalisation and sampling needs to be accounted for – Optimised for pH 4 samples, higher and lower pH values may affect performance – High chloride concentration lowers Hg adsorption	42,53
2-mercaptophenol-Hg complex on C18 microcolumn (for preconcentration)	Hg^{2+}, MeHg, EtHg, PhHg	Sediments, zoobenthos, river water (**filtered** and acidified to pH3 with HCl)	Solid samples were microwave digested with HCl (3 mol L^{-1}), citric acid (0.2 mol L^{-1}), methanol (50%) (10 mL). Elution with methanol	Hg^{2+}=0.9 µg L^{-1}, MeHg=4.3 µg L^{-1}, EtHg=1.4 µg L^{-1}, PhHg=0.8 µg L^{-1} by AMA mercury analyser and HPLC/CV-AFS	>90 %	Storage capacity: up to 155 µg Hg (500 mL sample) with 20 mL 14 mmol L^{-1} complexing agent Pore size: 80 Å Particle size: 5 µm	+ No functionalisation of resin is required, instead a complexing agent (2-mercaptophenol) is added to the sample + ~95 % extraction efficiency was reported with preconcentration factors of up to 1000 using 500 mL sample – 2-mercaptoethanol has a strong, unpleasant odour and is harmful in high concentrations and must be diluted before use – Any iron may compete with Hg for complexation with the 2-mercaptoethanol and interfere with extraction	54
Diethyldithiocarbamate functionalised C18 microcolumn (for preservation and storage)	Hg^{2+}, MeHg	River water (**filtered** waters)	5% (v/v) thiosulphate + 0.5% (v/v) HCl	Hg^{2+}=5.2 ng L^{-1}, MeHg=5.6 ng L^{-1} by LC-ICP-MS	97 %	Storage capacity not investigated, but 30 ng Hg successfully recovered Unspecified pore and particle sizes.	+ The sorbent operates under a wide range of pH values, so suitable for a variety of matrices + Spiked river waters showed >80 % Hg^{2+} recovery reported for up to 30 days storage at 4°C in the dark (80 % MeHg recovery up to 7 days storage) – Must be functionalised before use, so time between functionalisation and sampling must be accounted for – MeHg recovery significantly decreases after 7 days to 50 % recovery at 14 days	33
Commercially available resins								
Duolite GT-73™ as a diffusive gradient thin film (for preconcentration and removal)	Hg^{2+}	DI water, tap water, river water (**filtered** in the DGT apparatus)	Thermal decomposition (total Hg)	0.05 µg L^{-1} by LC-AFS	95 %	Storage capacity: 2.4 mg per DGT disk Particle size: sieved to <150 µm	+ The resin has a high sorption capacity and is selective for Hg + Can be synthesised as a diffusive thin film, so can be immersed directly into the water source – The resin is no longer commercially available, but alternatives are available – Desorption of Hg is difficult, so the resin must be digested using a nitric and hydrochloric acid mixture, eliminating the possibility of re-use	56

AmberSep GT-74™ as a diffusive gradient thin film (for preconcentration and removal)	Hg^{2+}, MeHg EtHg PhHg	DI water, tap water, river water (**filtered** in the DGT apparatus)	Thermal decomposition (total Hg), microwave extraction with 6 mol L^{-1} HCl	Hg^{2+}=13 ng L^{-1}, MeHg=38 ng L^{-1}, EtHg=34 ng L^{-1}, PhHg=30 ng L^{-1} by Advanced Mercury Analyser (AMA245) for absorption spectroscopy	>95 %	Storage capacity: 3.8 mg per DGT disk Particle size: sieved to <150 µm	+ The resin has a high sorption capacity and is selective for Hg + Can be synthesised as a diffusive thin film, so can be immersed directly into the water source – The resin is no longer commercially available, but alternatives are available – The resin is reluctant to release Hg, so other analysis methods are required such as thermal desorption and atomic absorption	56, 58
Cationic exchange resins								
Dowex 50W X4™ as a microcolumn (for preconcentration and removal)	Hg^{2+}	Mineral, spring and tap-water	0.1% thiourea + 8% HCl	27 ng L^{-1} by CV-AAS	>79 %	Storage capacity: Not investigated, but 860 µg Hg was totally adsorbed by 0.5 g sorbent Particle size: 150-300 µm	+ Recoveries of >79 % were reported for natural water samples spiked to 10 µg L^{-1} Hg^{2+} + As a non-specific sorbent, multi-elemental analysis is possible – Copper and iron significantly decrease the recovery of Hg by direct determination and selenium (IV) cause signal suppression in CV-AAS analysis – A sequential elution is required to remove interfering ions	59
Polyaniline								
Polyaniline (PANi) as a microcolumn (for preconcentration and removal)	Hg^{2+}, MeHg	Lake water, groundwater, seawater, fish tissue	0.3% HCl (for MeHg) and 0.3% HCl + 0.02% thiourea (for Hg^{2+})	0.05 ng L^{-1} by CV-AAS	>96 %	Storage capacity: 100 mg Hg^{2+} g^{-1} resin, 2.5 mg MeHg g^{-1} resin Particle size: 100-150 µm	+ The resin has a high sorption capacity (100 mg g^{-1} Hg^{2+} and 2.5 mg g^{-1} MeHg) + A 100 mL sample can be used to achieve preconcentration factors of 120 for Hg^{2+} and 60 for MeHg from lake water, ground water and seawater – Lower pH values (<2) significantly affect the Hg removal ratio to <20 %, higher pH values (>6) also decrease the Hg removal ratio (<80 %) – A pH of 4-5 is preferred to ensure nitrogen atoms are not fully protonated and can bind to Hg from solution – The sorbent must be synthesised and homogenised before use	36

Polyaniline-polyvinyl alcohol (PANi-PVA) as batch sorbent applied to solution (for removal)	Hg^{2+}	DI water	0.1 mol L^{-1} HNO_3	FAAS. No detection limit was reported	90 % Hg removal after 30 mins contact time	Storage capacity: 7.5 mg Hg g^{-1} resin No specification for particle or pore size	+ The sorbent has a high sorption capacity (>90 % removal from a 35 mg L^{-1} Hg^{2+} solution at pH 6) + Desorption of Hg was reported with 0.1 M HNO_3, although this required 90 minutes to achieve 90 % recovery – Chloride at 30 mmol L^{-1} significantly decreases adsorption of Hg to <15 %, likely due to chloro-mercury complexation – The sorbent must be synthesised and homogenised before use	63
Polyaniline-humic acid (PANi-HA) as batch sorbent applied to solution (for removal)	Hg^{2+}	DI water	No desorption investigated	AFS of supernatant. No detection limit was reported	95 %	Storage capacity: 671 mg Hg g^{-1} resin Particle size: 50-60 nm	+ The addition of humic acid widens the operable pH range to between 4 – 7, with Hg removal at >90 %. + The additional humic acid stabilises PANi by mitigating aggregation of the sorbent + The sorption capacity is high (671 mg g^{-1} Hg^{2+}) and most other ions in samples do not significantly affect Hg removal – Chloride concentrations of 50 mg L^{-1} significantly decrease removal of Hg from samples to <20 % – Desorption from the composite has not been explored, nor stability of retained Hg species over time – Humic acid is a broad term to define many naturally occurring organic molecules, so extraction efficiency may vary between batches of synthesised sorbent	48
Polyaniline-polystyrene (PANi-PE) as batch sorbent applied to solution (for removal)	Hg^{2+}	DI water	DI water, no desorption noted	β-activity by an end window Geiger-Müller counter. No detection limit was reported	67 %	Storage capacity: 0.15 mg Hg g^{-1} resin No particle size specified	+ The stability of the sorbent is improved, as polyethylene prevents aggregation of PANi + The composite was reported to adsorb 79 % Hg from a 10 ng L^{-1} Hg^{2+} solution – Mercury is not readily desorbed from the composite. 47 % was desorbed with 0.1 M HNO_3 after 30 minutes – Interfering ions and characteristics have not been explored	64

Magnetic SPE

1,2-ethanedithiol as batch sorbent applied to solution (for preconcentration)	Hg^{2+}	DI water, lake water (**filtered** waters)	0.1 mol L^{-1} HNO_3 + 2% (m/v) thiourea	0.82 ng L^{-1} by ICP-MS	>90 %	Storage capacity: 254 mg Hg g^{-1} resin Particle size: 400 nm	+ >95 % adsorption of Hg over pH 2 – 8 and >95 % recover using a 4 % thiourea, 0.5 M HNO_3 eluent solution + Common cations and anions do not significantly impact the adsorption or recovery of Hg at 5000 mg L^{-1} Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, Na^+, NO_3^+, 10 mg L^{-1} Al^{3+}, Zn^{2+}, $Fe^{2+ \text{ or } 3+}$, and 1 mg L^{-1} Cu^{2+} + The sorbent has a high sorption capacity (254 mg g^{-1} Hg) and can extract lead and cadmium, so is potentially suitable for multi-elemental analysis + Recoveries of >93 % were reported for river water and lake waters spiked with 50 – 1000 ng L^{-1} Hg^{2+} – The multi-step synthesis has a yield of <50 % and may not be readily scaled up – The stability of the sorbent and of Hg retained on the sorbent has not been investigated – Speciation analysis has not been investigated for this sorbent, so the usefulness for toxicity studies and monitoring is not fully defined	65
3-mercaptopropyl-trimethoxysilane as batch sorbent applied to solution (for removal)	Hg^{2+}, MeHg	DI water, lake water, tap water, sea water (**unfiltered** waters)	0.5 mol L^{-1} HCl + 1% thiourea	0.1, 0.3 ng L^{-1} by HPLC-ICP-MS	>90 %	Storage capacity: Not investigated, focused on trace Hg (10 ng L^{-1} Hg, 500 mL sample) No particle size specified	+ A >90 % recovery of Hg^{2+} and MeHg using 500 mL of a 20 ng L^{-1} Hg spiked tap, sea and lake waters + The sorbent can be freely added to the sample and removed with a magnet after 10 minutes stabilisation time + The sorbent can be reused up to 5 times without significant degradation of performance – The sorbent requires a multi-step synthesis and characterisation, which may not be readily scaled up – Common ions and interferences were not investigated	43

1,5-diphenylcarbazide as batch sorbent applied to solution (for preconcentration)	Hg^{2+}	DI water, river water, tap water, (oxidised with H_2O_2, acidified to pH1 with HCl, **filtered**) vegetation (microwave digested with HNO3)	Regeneration with 0.5 mol L^{-1} HNO_3 (No elution assessed)	0.16 µg L^{-1} by CV-AAS	>95 %	Storage capacity: 44 mg Hg g^{-1} resin Particle size: 60-80 nm	+ Common ions in water (Ca^{2+}, Mg^{2+}, Cl^-) have no significant effect on Hg adsorption up to 4 mg L^{-1} interferent + Other metals (Cu^{2+}, Zn^{2+}, Cd^{2+}) have no significant effect on Hg adsorption up to 50 µg L^{-1} interferent + The sorbent can be reused up to 8 times without noticeable degradation in performance + The sorbent is stable up to 6 months – The sorbent is sensitive to pH, with adsorption of Hg decreasing from 95 % at pH >6 to <40 % at pH <5 (active sites become protonated at lower pH values) – Speciation and MeHg sorption were not investigated	66
Task-specific monolith with vinylboronic anhydride pyridine complex as a microcolumn (for preconcentration)	Hg^{2+}, MeHg, EtHg, PhHg	DI water, seawater, river water, lake water (**filtered** and acidified to pH4 with HCl)	Methanol	102, 22, 28, 162 ng L^{-1} by HPLC-diode array detector	>80 %	Storage capacity: Not investigated, 100 ng Hg per prepared column fully sorbed Pore size: 230 nm	+ >94 % of Hg^{2+}, MeHg, ethylmercury and phenylmercury can be recovered under optimised conditions + Recovery of Hg from river, sea, lake and tap water is >80 % Hg – A complexing agent is required to promote Hg extraction, which may be a source of contamination and is not readily useable in an uncontrolled environment – A pH of 4 is necessary, as lower pH values promote H^+-complexing agent formation and higher pH values may hydrolyse Hg species	67
Gold-based SPE								
Gold nanoparticles as a microcolumn (AuNP) (for preconcentration)	Total Hg	DI water, river water (**filtered** and acidified with 0.5% v/v HCl)	Thermal desorption	180 pg L^{-1} by AFS	>90 %	Storage capacity: Not investigated, 0.007 ng Hg fully recovered from 1 g sorbent Particle size: 100-350 µm Pore size: 60 Å	+ Highly selective for Hg due to Au-Hg amalgamation + A >99 % Hg recovery can be achieved from river waters + No additional reagents are required for extraction of Hg + Extracted Hg is stable for at least 2 days with no significant losses + Speciation analysis is possible, as Hg^{2+} thermally desorbs at approximately 550 °C and MeHg thermally desorbs at approximately 20 °C (columns should be stored at 4 °C in the dark to mitigate loss of MeHg) + The column can be reused 180 times without loss of precision or sensitivity – Synthesis of column should be done in Hg vapour-free conditions and reagents require purging before use	38

Gold nano-sheets as a column (for preconcentration)	Hg^{2+}, MeHg	DI water, seawater, river water, lake water (**filtered** and acidified with 0.5% v/v HCl)	Thermal desorption	0.08 ng L^{-1} by AFS	>96 %	Storage capacity: Not investigated, work focused on trace Hg, 0.002 ng Hg adsorbed per column "Mesh size": 1024 meshes cm−2	+ + – –	The columns are highly selective for Hg with a high tolerance for interfering matrix components >95 % recovery Hg can be achieved from river, sea and lake waters at trace concentrations (0-3 ng L^{-1} Hg^{2+}) The columns were developed for online preconcentration, so may not be suitable for offline extraction and storage Reusability of the column was not fully explored	71
Immobilised gold nanoparticle dipstick (for preservation and storage)	Total Hg	DI water, river water, seawater (**unfiltered** water, acidified with 0.5% v/v HCl)	Thermal desorption	0.06 ng L^{-1} by AFS	>94 %	Storage capacity: Not investigated, work focused on trace Hg, 0.0015 ng Hg per dipstick Particle size: 38 nm (14 µg Au cm^{-2})	+ + + + – –	The dipstick is highly selective for Hg with little interferences Hg is thermally desorbed form the stick, so limits the opportunity for contamination Low variation was reported between individually prepared dipsticks The dipsticks can be reused 145 times without significant degradation to Hg recovery Specialised sputtering technology is required to synthesise the dipsticks, so synthesis may not be readily scaled up The dipsticks must be annealed at 600 °C before each use, which may be challenging in the field and so must be stored in Hg-free conditions during transport to and from the field	51