

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				<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> >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	<ul style="list-style-type: none"> Recoveries of >90 % Hg²⁺ 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	<ul style="list-style-type: none"> 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				<ul style="list-style-type: none"> Oxidises species to inorganic Hg²⁺ (comparatively more stable than Hg⁰) Risk of oxidising atmospheric Hg⁰ and artificially increasing Hg concentration (particularly for trace Hg concentrations of relatively high atmospheric Hg⁰ 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	<ul style="list-style-type: none"> Negligible losses by adsorption for 0.2 – 1 µg L⁻¹ Hg²⁺ 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) Increased ionic strength	Hg ²⁺ in deionised water	21 days (>95 % recovery)	100 mL in borosilicate glass and PE containers	<ul style="list-style-type: none"> 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 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 	17,73
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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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 limits, analytical 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	<ul style="list-style-type: none"> + + – – – 	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	<ul style="list-style-type: none"> + + – – 	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.	<ul style="list-style-type: none"> + + – – 	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	<ul style="list-style-type: none"> + + – – 	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	<ul style="list-style-type: none"> + + – – 	<p>The resin has a high sorption capacity and is selective for Hg</p> <p>Can be synthesised as a diffusive thin film, so can be immersed directly into the water source</p> <p>The resin is no longer commercially available, but alternatives are available</p> <p>The resin is reluctant to release Hg, so other analysis methods are required such as thermal desorption and atomic absorption</p>	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	<ul style="list-style-type: none"> + + – – 	<p>Recoveries of >79 % were reported for natural water samples spiked to 10 µg L⁻¹ Hg²⁺</p> <p>As a non-specific sorbent, multi-elemental analysis is possible</p> <p>Copper and iron significantly decrease the recovery of Hg by direct determination and selenium (IV) cause signal suppression in CV-AAS analysis</p> <p>A sequential elution is required to remove interfering ions</p>	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	<ul style="list-style-type: none"> + + – – – 	<p>The resin has a high sorption capacity (100 mg g⁻¹ Hg²⁺ and 2.5 mg g⁻¹ MeHg)</p> <p>A 100 mL sample can be used to achieve preconcentration factors of 120 for Hg²⁺ and 60 for MeHg from lake water, ground water and seawater</p> <p>Lower pH values (<2) significantly affect the Hg removal ratio to <20 %, higher pH values (>6) also decrease the Hg removal ratio (<80 %)</p> <p>A pH of 4-5 is preferred to ensure nitrogen atoms are not fully protonated and can bind to Hg from solution</p> <p>The sorbent must be synthesised and homogenised before use</p>	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	<ul style="list-style-type: none"> + + – – 	<p>The sorbent has a high sorption capacity (>90 % removal from a 35 mg L⁻¹ Hg²⁺ solution at pH 6)</p> <p>Desorption of Hg was reported with 0.1 M HNO₃, although this required 90 minutes to achieve 90 % recovery</p> <p>Chloride at 30 mmol L⁻¹ significantly decreases adsorption of Hg to <15 %, likely due to chloro-mercury complexation</p> <p>The sorbent must be synthesised and homogenised before use</p>	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	<ul style="list-style-type: none"> + + + – – – 	<p>The addition of humic acid widens the operable pH range to between 4 – 7, with Hg removal at >90 %.</p> <p>The additional humic acid stabilises PANi by mitigating aggregation of the sorbent</p> <p>The sorption capacity is high (671 mg g⁻¹ Hg²⁺) and most other ions in samples do not significantly affect Hg removal</p> <p>Chloride concentrations of 50 mg L⁻¹ significantly decrease removal of Hg from samples to <20 %</p> <p>Desorption from the composite has not been explored, nor stability of retained Hg species over time</p> <p>Humic acid is a broad term to define many naturally occurring organic molecules, so extraction efficiency may vary between batches of synthesised sorbent</p>	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	<ul style="list-style-type: none"> + + – – 	<p>The stability of the sorbent is improved, as polyethylene prevents aggregation of PANi</p> <p>The composite was reported to adsorb 79 % Hg from a 10 ng L⁻¹ Hg²⁺ solution</p> <p>Mercury is not readily desorbed from the composite. 47 % was desorbed with 0.1 M HNO₃ after 30 minutes</p> <p>Interfering ions and characteristics have not been explored</p>	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	<ul style="list-style-type: none"> + >95 % adsorption of Hg over pH 2 – 8 and >95 % recover using a 4 % thiourea, 0.5 M HNO₃ eluent solution + Common cations and anions do not significantly impact the adsorption or recovery of Hg at 5000 mg L⁻¹ Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, Na⁺, NO₃⁻, 10 mg L⁻¹ Al³⁺, Zn²⁺, Fe^{2+ or 3+}, and 1 mg L⁻¹ Cu²⁺ + 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 Hg²⁺ – 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	<ul style="list-style-type: none"> + A >90 % recovery of Hg²⁺ 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 ₂ O ₂ , acidified to pH1 with HCl, filtered) vegetation (microwave digested with HNO ₃)	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	<ul style="list-style-type: none"> + + + + – – 	<p>Common ions in water (Ca²⁺, Mg²⁺, Cl⁻) have no significant effect on Hg adsorption up to 4 mg L⁻¹ interferent</p> <p>Other metals (Cu²⁺, Zn²⁺, Cd²⁺) have no significant effect on Hg adsorption up to 50 µg L⁻¹ interferent</p> <p>The sorbent can be reused up to 8 times without noticeable degradation in performance</p> <p>The sorbent is stable up to 6 months</p> <p>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)</p> <p>Speciation and MeHg sorption were not investigated</p>	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	<ul style="list-style-type: none"> + + – – 	<p>>94 % of Hg²⁺, MeHg, ethylmercury and phenylmercury can be recovered under optimised conditions</p> <p>Recovery of Hg from river, sea, lake and tap water is >80 % Hg</p> <p>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</p> <p>A pH of 4 is necessary, as lower pH values promote H⁺-complexing agent formation and higher pH values may hydrolyse Hg species</p>	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	<ul style="list-style-type: none"> + + + + + – 	<p>Highly selective for Hg due to Au-Hg amalgamation</p> <p>A >99 % Hg recovery can be achieved from river waters</p> <p>No additional reagents are required for extraction of Hg</p> <p>Extracted Hg is stable for at least 2 days with no significant losses</p> <p>Speciation analysis is possible, as Hg²⁺ 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)</p> <p>The column can be reused 180 times without loss of precision or sensitivity</p> <p>Synthesis of column should be done in Hg vapour-free conditions and reagents require purging before use</p>	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 from 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