Determination of Mercury in Selected Polluted Sediments using HPLC-ICP-MS in Westbank Area, Western Cape, South Africa

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ABSTRACT

High selectivity, excellent linearity and reproducibility were achieved using HPLC-ICP-MS method for mercury in sediments. The HPLC-ICP-MS method reported previously for mercury in biota analysis was adapted in terms of operational consumables and optimized for the efficient mercury determination in riverbed sediments; a first for South Africa. Results obtained for real environmental samples, were verified by Direct Mercury Analysis (DMA) by an accredited laboratory. The determination of inorganic and organic mercury compounds in sediments was based on the complexation of mercury compounds with cysteine. The separation was achieved on a reversed-phase C₁₈ column (15 cm × 4.6 mm id) using aqueous 0.1 % w/v L-cysteine·HCl + 0.1 % w/v L-cysteine mobile phase at a flow rate of 0.8 mL min⁻¹ at ambient temperature. The method was found to be suitable for the routine analysis of Hg compounds in sediments as well as aqueous media and was developed to determine the influence of humic substances on the bioavailability of mercury species. The results were comparable and consistent with those determined with a Direct Mercury Analyzer. The detection limit for methylmercury, ethylmercury and inorganic mercury were lower than 10 ng L⁻¹ and recoveries for spiked samples was >90 %. The accuracy of the method was assessed by the analysis of certified reference material (European Reference Material ERMCC580 and Tort-2) and found to be in good agreement. Mercury concentration was determined in sediments collected from the Eerste Kuils River, Westbank area, Kuilsriver, Western Cape, South Africa. Mercury concentration was determined to vary from 2–14 ng g⁻¹ (w.wt).

KEYWORDS

Speciation, validation, complexation, bioavailability.

1. Introduction

Anthropogenic sources as well as natural contributions (e.g. volcanic activity and evaporation from the oceans) have increased Hg levels in the environment. Mercury (Hg) is widely used as a catalyst in the manufacture of sodium hydroxide, gold mining, manufacture of batteries and thermometers, as fungicides, herbicides and disinfectants.¹ As a highly toxic metal, it is considered to be a global pollutant^{2,3}. South Africa is the world's sixth largest producer of coal;^{3,4,5,6} coal provides about 75 % of the country's primary energy needs and over 90 % of its electricity is coal-driven.^{3,7} Almost all the Hg present in the coal, >90 %⁸ is vaporized and released in the form of elemental Hg. The largest emissions of Hg in South Africa are from coal-fired power plants, with an estimated contribution of 78 %.⁶ Anthropogenic Hg emissions are likely to increase as human dependency or demand for energy increases. Masekoameng *et al.*⁶ studied the trends in the anthropogenic mercury emission for South Africa and showed a general increase in emissions with a contribution of up to 2 % of total global emissions. There are not many reported studies⁹ about the Hg emissions from natural sources although they could be an important contribution to total Hg emission.⁶ Health impacts of potentially harmful elements, stemming from sulphide mineralization, mining or ore processing and mine waste disposal are generally not well documented.⁹ Disposal of mine waste in tailing dams could be a large risk to the adjacent environment due to the potential of

migration of these toxic, heavy metals to the surrounding area. Inadequate management of these tailing dams has led to serious environmental problems.¹⁰ It is important to understand the environmental impact of heavy metals entering the surrounding area from these tailing dams.^{11,12} In South Africa and neighboring countries there is an increase in illegal small-scale mining of disused gold mines.¹³ These mining operations use entirely Hg extraction methods for gold recovery. In the population at three sites along the South Africa coast Channa *et al.*¹³ determined Hg levels of 1.15 µg L⁻¹ and 1.67 µg L⁻¹ in maternal and cord blood, respectively. Other possible sources of Hg emissions include products of the incineration and treatment of waste at a municipal waste site and medical waste incinerators. Kuhn¹⁴ found excessive levels of Hg in some of the residents of an area in Cape Town (South Africa) living in close proximity to a waste disposal site, an industrial site that housed a brick factory that burned fossil fuels, and to an oil reclamation plant (potentially resulting in airborne Hg)¹⁵ (Dalvie and Ehrlich¹⁵). Dalvie and Ehrlich¹⁵ found that the urinary Hg levels of residents in the exposure area however were not a major health factor as the levels determined were below levels associated with adverse health effects.

Mercury deposits mainly in sediments, where it finally ends up in aquatic systems.^{16,17} Sediments are capable of immobilizing toxic metals but this does not guarantee that the metals are safely removed from aquatic systems. Metals can be reintroduced into the aquatic systems if the solubility, mobility and bioavailability

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increase due to different environmental factors such as pH, salt concentration, the presence of complexing agents, and changes in redox potential or chemical form.¹⁸ Sediments can be a long-term source of Hg to surface waters.¹⁹ Walters *et al.*²⁰ mapped the spatial patterns of Hg distribution and bioaccumulation in water resources in the 19 designated Water Management Areas (WMAs) across South Africa. Higher Hg concentration where reported in areas closer to coal-fired power stations and gold mining.^{3,5,20–22}

A metal's mobility, accumulation, bioavailability and toxicity depend on the chemical form of the metal.^{1,23,24} Mercury occurs in three chemical forms, metallic or elemental mercury (Hg^0), inorganic mercury (Hg^{2+}), and methylated forms that include the organic forms of Hg such as, methylmercury (MeHg), ethylmercury (EtHg) and dimethylmercury (DMHg).^{25–26} The organic forms are more toxic than their inorganic counterparts, and have been shown to affect the central nervous system of humans.²⁵ Mercury speciation studies are therefore essential to monitor the levels of these species in water, soil and biota to determine the toxic effect of Hg on the environment. Monitoring of the distribution of metals, including Hg species, is important in order to control pollution from industrial processes.

There are a number of very efficient analytical techniques capable of determining Hg levels in different matrices. The United States Environmental Protection Agency (USEPA) has published methods for measuring low levels of Hg and MeHg in water and biota, using gas chromatography (GC) and cold-vapour atomic fluorescence spectrophotometry (CVAFS) (USEPA Method 1631 and 1630, 1999). The best established and most widely used method for mercury speciation analysis is gas chromatography with an electron capture detector in methods modified from the Westö procedure. The disadvantage is that it is time-consuming, uses hazardous organic solvents and it requires volatile, thermally stable derivatives.^{27,28} Another disadvantage is that the detector is not selective for Hg but responds to any compounds containing halogens. By using this method, time-consuming clean-up procedures are used to eliminate interferences.^{29,30}

New methods are constantly being developed and HPLC is one that can rapidly and efficiently separate a variety of compounds. A disadvantage of the HPLC-method is that it lacks sufficient concentration detection sensitivity. Several detectors have been developed that can substantially lower the sensitivity of this analytical technique, including inductively coupled plasma (ICP), inductively coupled plasma mass spectrometry (ICP-MS), and electrochemical detection. These methods have shown high selectivity, excellent linearity and reproducibility in analysis for MeHg and other forms of Hg.³¹ A disadvantage of using ICP as a detector for HPLC is that the mobile phase should be carefully chosen as solvents such as methanol and acetonitrile are not compatible with the argon plasma.² Mobile phases which contain high concentrations of salts and buffers can clog the cones of the nebulizer which can produce changes in sensitivity.³²

The popular analytical method for the determination of total mercury used to be by gold trap amalgamation followed by cold-vapour atomic absorption or cold-vapour atomic fluorescence spectroscopy.^{33–35} Time-consuming digestion of the sample however is required. The use of the direct mercury analyzer (DMA) is becoming very popular for total mercury analysis.³ It is the standard method employed by the CSIR (Council for Scientific and Industrial Research; Natural Resources and the Environment) for total mercury analysis. No pre-treatment of the sample is required and it is suitable for solid and liquid samples. Because

no digestion of the sample is needed there is no need for corrosive chemicals and the production of hazardous waste is thus minimized. The method also has a very good detection limit.¹

Here we present for the first time a simplified method for the analysis of MeHg, EtHg and Hg^{2+} in environmental samples by HPLC-ICP-MS. The method describe here has been adapted in terms of solvents used for extraction, efficiency of extraction as well as simplification of sample handling. A lower injection volume and lower flow rate gave excellent separation within 12 min. An Agilent 7900 ICP-MS system used in the analysis is fitted with standard nickel cones, glass concentration nebulizer with a generator collision/reaction cell, a 4th generator, octopole reaction system which provides optimized operating conditions for helium (He) collision mark. It uses an advanced collision/reaction technology to ensure accurate results with minimal polyatomic interferences derived from the sample matrix. Here we report on the improved sensitivity (<5 %) achieved as a result of method modification.

2. Sampling Site

Sediments samples were collected using standard CSIR protocols,⁵ up to a depth of 12 cm. Sediment samples were transferred to acid cleaned sample jars, stored frozen in plastic bags until digestion and analysis. The sampling site was at the Eerste Kuils River, Westbank area, Kuilsriver, Western Cape, South Africa (Fig. 1). The Eerste River rises on Dwarsberg 60 km east of Cape Town at the head of Jonkershoek Nature Reserve. The Eerste River is a short river; with a length of 40 km. The major tributary, the Kuils River, is approximately 30 km long to its point of flowing together with the Eerste River. The Eerste River site (33°05'S, 18°46'E) is approximately 36 km southeast of Cape Town.

3. Experimental

3.1. Reagents

The CuSO_4 , HNO_3 (65 %), CH_2Cl_2 , cysteine and cystein-HCl were reagent grade purity and purchased from Merck. Stock solutions of MeHg, EtHg and Hg^{2+} were prepared from the respective chloride salts obtained from Aldrich-Sigma at a concentration of 1.0 g L^{-1} each. A stock solution of Hg^{2+} was prepared by dissolving its chloride salt in 0.1 % HCl. Stock solutions of MeHg, EtHg and PhHg were prepared by dissolving the respective salts in HPLC grade methanol and diluting with ultrapure water purified by a Milli-Q (Millipore) system. All stock solutions were stored in a refrigerator. The standard solutions were prepared daily by appropriate dilutions with purified water.

3.2. Sample Preparation and HPLC-ICP-MS Analysis

A 0.5–1.5 g sediment sample was weighed into a 50 mL polypropylene centrifuge tube to which 2 mL of CuSO_4 (1M), 10 mL of HNO_3 (3M) and 10 mL of CH_2Cl_2 was added. The centrifuge tube was tightly capped and vigorously shaken for 30 min on a Gerhardt mechanical shaker. The mixture was then centrifuged at 3000 rpm for 30 min. About 5 mL of the CH_2Cl_2 was pipetted into 40 mL of deionized water. The water/ CH_2Cl_2 mixture was heated in a waterbath (Memmert WNB 7-45, Germany) at 45 ° for solvent evaporation until no visible layer of CH_2Cl_2 solvent was left. The temperature of the water bath was increased to 75 °C, the sample purged with N_2 to remove the solvent residue, and the sample was diluted to 40 mL with deionized water before analysis. These samples were used for analysis by HPLC-ICP-MS. Analysis was performed on an Agilent 1100 series. Separation was achieved by using a Synergi Hydro-RP C₁₈, $150 \times 4.6 \text{ mm i.d.}$ column.

Figure 1 Map of the sampling area, Eerste Kuil River, in the Western Cape, South Africa (map supplied by CSIR databases, at a fixed fee).

The chromatographic operating conditions used for the determination are listed in Tables 1 & 2. The mobile phase used was prepared in the same way as a method described by Hight and Cheng²⁸. The mobile phase was prepared by volume and consisted of aqueous 0.1 % w/v L-cysteine-HCl + 0.1 % w/v L-cysteine. The mobile phase was filtered through a 0.45 μm Millipore membrane and sonicated before use. To obtain reproducible results the mobile phase and the standards were prepared daily.

3.3. Direct Mercury Analyzer

The sediment samples were analyzed for total mercury concentration with a direct mercury analyzer. The DMA uses a dual cell atomic absorption spectrometer to determine elemental Hg and absorption was measured at a wavelength of 253.65 nm. A 0.2–0.5 g sediment sample was placed into quartz boats, the sample was weighed, dried for a set period and then thermally decomposed. This process heated the sample to release the mercury and the vapours were carried by an oxygen flow to an amalgamator for selective trapping of mercury on a gold trap. After a short heating period, the mercury released was measured by atomic absorption.^{1,3} Triplicates were run on all of the samples, and standards reference material was run between every eight samples.

4. Results and Discussion

4.1. Chromatograms of a Mixed Standard and a Sediment Sample obtained by HPLC-ICP-MS

The retention time of MeHg, EtHg and inorganic Hg was verified by single standard analysis. A cocktail standard was prepared by mixing MeHg, EtHg and inorganic Hg. A 20 μL of the prepared standard was injected and analyzed. The peaks of the mixed standards were well resolved and the different mercury species all elute within 10 min (Fig 2). In all the sediment standards analyzed only inorganic Hg (Fig 3) was detected in the sediment samples.

4.2. Linearity and Detection Limits

Calibration curves for each mercury species were constructed. The calibration graphs containing the information for the determination of the mercury species is illustrated in Figs. 4–6. The optimum conditions for separation as mentioned in Tables 1 & 2 were used to obtain the required data.

Chromatographic separation of the three compounds was achieved within 12 min at ambient temperature. Retention times were 2.5 min, 4.5 min and 10.8 min for Hg^{2+} , MeHg and EtHg, respectively. Linear regression data for Hg^{2+} , MeHg and EtHg are presented in Table 3. A calibration curve for each of the four

Figure 2 Chromatogram of a 10 ppm standard solution of MeHg, EtHg and Hg^{2+} determined with HPLC-ICP-MS and using best conditions established (Tables 1 & 2).

Figure 3 Chromatogram of a sediment sample obtained from the Westbank area determined with HPLC-ICP-MS and using best conditions established (Tables 1 & 2).

mercury species were obtained from three standards and were found to be linear over the concentration range $0.5\text{--}20\ \mu\text{g L}^{-1}$. The correlation coefficient was higher than 0.99 for the three compounds.

The analytical protocols produced calibration data which leads to the statistic results as presented in Tables 1 & 2. All statistical data were reported at 95 % confidence level. The detection limit defined as the calculated amount of the analyte which corresponds to a signal equal to three times the standard deviation of six representative blank samples³³ is listed in Tables 3 & 4 and was found to be $2\ \text{ng L}^{-1}$ or less for all the species. The limit of detection (LOD) and limit of quantification (LOQ) values were determined using a signal-to-noise ratio of 3 and 10, respectively.

4.3. Sediment Analysis, Recovery Efficiency and Accuracy Studies

The sediment was spiked with known quantities of the mercury species in order to determine the recovery efficiency. All analysis was done in duplicate and injected into the HPLC in triplicate. Total mercury determination was done in triplicate in the DMA. The analyte recovery rate from the spiked samples was 97.54 %. For all the samples only Hg^{2+} could be detected.

Reported values are for the mean, $n = 3$. Results for the percentage recovery was within 80–100 % (Tables 5 & 6), and the percentage difference of the analysis results between the two

Table 1 The operating ICP-MS conditions for the determination of Hg compounds.

RF power (W)	1550
Argon plasma gas flow rate/ min^{-1}	151
Argon auxiliary gas flow/ min^{-1}	0.91
Argon nebulizer flow rate/ min^{-1}	1.171
Sampling depth/mm	8
Solution uptake – tuning (peristaltic pump)/ mL min^{-1}	0.4
Solution uptake – analysis (HPLC pump)/ mL min^{-1}	1.0
Solution drain – analysis/ mL min^{-1}	>1.0
Spray chamber temperature/K	275.15
Mass-to-charge ratio/ m/z	199; 200; 202
Chromatographic integration time/s point ⁻¹	1.55

Table 2 The optimum operating HPLC chromatographic conditions for the determination of Hg compounds.

Column	Phenomenex Synergi Hydro-RP C_{18} , $150 \times 4.6\ \text{mm}$, $4\ \mu\text{m}$
Column temperature	Ambient temperature
Injection volume / μl	20
Flow rate/ mL min^{-1}	0.8
Pump mode	Isocratic
Mobile phase	0.1 % w/v L-cysteine·HCl + 0.1 % w/v L-cysteine
Run time/min	12

methods were within 10 % difference. The confidence interval levels calculated and reported for the DMA results falls within the mean for the HPLC-ICP-MS method which implies that the two methods are statistically comparable (Table 7). The analysis of the reference sample by DMA shows a similar low value of recovery to the HPLC analysis (Tables 5 & 6). The low recovery for the HPLC method of the reference sample could be due to the high concentration of Hg^{2+} in the reference sample and under recovery due to extraction.

5. Conclusion

The sediment samples were provided by the CSIR, Natural Resources and the Environment, CSIR, Stellenbosch, South Africa. The sampling sites (at Eerste Kuil River, Westbank area, Kuilsriver, Western Cape, South Africa) are close to a landfill site, which may explain the relatively high levels of mercury obtained. The method was developed for the determination of MeHg, EtHg and Hg^{2+} in soil samples. The method was validated for accuracy by analyzing reference material and spiked samples. The mobile phase used in the method used no hazardous organic materials and the extraction method was relatively quick and easy to use.

Although the method is able to determine both the organic as well as the inorganic form of mercury, none of the organic forms were found in the samples. It could be that the method was not sensitive enough to detect any organic forms present. The concentration of the Hg^{2+} found in the soil samples show a steady increase in concentration levels at lower depth (Figs. 7–9).

Table 3 From the calibration curves, the following analytical parameters were obtained. Linear regression data of MeHg, EtHg and Hg^{2+} .

Compound	Range/ $\mu\text{g L}^{-1}$	Linear regression equation	Correlation coefficient/ r	LOD/ ng L^{-1}	LOQ/ ng L^{-1}	Sensitivity/ ng L^{-1}
MeHg	0.5–20	$8.116x + 59.35$	0.9992	0.02	0.20	0.022
EtHg	0.5–20	$5.205x + 56.05$	0.9997	0.01	0.10	0.083
Hg^{2+}	0.5–20	$5.738x + 67.50$	0.9996	0.02	0.20	0.120

Figure 4 Calibration curve of Hg^{2+} standards determined with HPLC-ICP-MS under operating conditions as reported in Tables 1 & 2. Results are the mean of three determinations and insert shows the linear range from 0.5–20 μL (error bars represent standard error, $n = 3$).

Figure 5 Calibration curve of MeHg determined with HPLC-ICP-MS obtained with operating conditions as reported in Tables 1 & 2. Results are the mean of three determinations and insert shows the linear range from 0.5–20 μL (error bars represent standard error, $n = 3$).

Figure 6 Calibration curve of EtHg standards determined with HPLC-ICP-MS determined with operating conditions as reported in Tables 1 & 2. Results are the mean of three determinations and insert shows the linear range from 0.5–10 μL (error bars represent standard error, $n = 3$).

Figure 7 Variation in vertical mercury concentration distribution vs. sediments core depth at sampling site EKA, Kuils River system (error bars represent standard error, $n = 3$).

Figure 8 Variation in vertical mercury concentration distribution vs. sediments core depth at sampling site EK 2, Kuils River system (error bars represent standard error, $n = 3$).

Figure 9 Variation in vertical mercury concentration distribution *vs.* sediments core depth at sampling site EKC, Kuils River system (error bars represent standard error, $n = 3$).

Table 4 From the calibration curves, the following statistical results were obtained. Relative standard deviation values of MeHg, EtHg and Hg^{2+} .

	Relative standard deviation/% Concentration/ $2 \mu\text{g L}^{-1}$	Relative standard deviation/% Concentration/ $4 \mu\text{g L}^{-1}$
MeHg	3.01	4.12
EtHg	4.15	5.02
Hg^{2+}	1.25	2.52

At a depth of 8 cm a slight decrease in concentration occurred at all sites except for EKC. Highest concentrations were found at levels 10–12 cm. The dispersion of Hg as a function of depth as presented in Fig. 10 at the four sites showed no distinguishable

trend, due to the limited sample set. Selected sediment samples provided by the CSIR, revealed an increasing trend in Hg concentration within the first 12 cm depth in riverbed samples. The samples provided by the CSIR were not specifically sampled for this work, but was in fact drawn from a wider sample base which formed part of a separate independent CSIR investigation.^{5,20} The samples provided were from four separate locations and taken at 2 cm intervals up to a depth of 12 cm, providing us with a sample set of 17 samples which were deemed sufficient to prove the application of the method. Surprisingly an increasing trend in Hg concentration was observed even in this limited depth dispersion. This trend is supported by previous studies^{3,38} which shows an increase in Hg concentration up to a depth of 0–15 cm and then a decrease at lower depth. Each sample was analyzed three times with a RSD < 5 % indicating the suitability of the method for riverbed samples.

Soil samples were spiked with both MeHg and Hg^{2+} . Spike recoveries of the soil samples were 98 %. The recovery rate increased with less of the reference material used for extraction and on using microwave extraction. On a separate analysis using microwave digestion and the same operating conditions the recovery was determined to be 99 %. The method was developed for the determination of Hg^{2+} , MeHg and EtHg in sediments. The extraction process was reasonably quick and easy. The method worked well for the precision of analysis as well as the accuracy determined by spiking the samples. Although the method of analysis provides for the determination of Hg^{2+} , MeHg and EtHg only the inorganic form of mercury was detected in the soil samples. Total mercury was determined by DMA. The values obtained are in good agreement with those obtained with the DMA.

Figure 10 Variation in the distribution of mercury concentration *vs.* sediments core depth in sampling sites, EKA, EKB, EKC and EK, at Kuils River system.

Table 5 Certified reference sample (European Reference Material ERM-CC580) for Hg^{2+} and MeHg analyzed in triplicates with HPLC-ICP-MS.

	Recovery value of Hg^{2+}	Recovery value for MeHg
European Reference Material ERM-CC580	69.8 % $\pm$ 15.2 (mass 0.1007 g)	89.3 % $\pm$ 0.0281 (mass 1.0003 g)
Certified value in ERM-CC580	132 $\text{mg kg}^{-1} \pm 3 \text{ mg kg}^{-1}$	0.0755 $\text{mg kg}^{-1} \pm 0.0037 \text{ mg kg}^{-1}$

Table 6 Certified reference sample (European Reference Material ERM-CC580) and Tort 2 for Hg^{2+} analyzed in triplicates with DMA.

European Reference Material ERM-CC580		Tort-2	
Recovery Hg^{2+}	77.5 % $\pm$ 12.8	Recovery Hg^{2+}	98.1 % $\pm$ 21.1
Certified value in ERM-CC580	132 $\text{mg kg}^{-1} \pm 3 \text{ mg kg}^{-1}$	Certified value in Tort-2	270.00 $\text{ng g}^{-1} \pm 60.00$

Table 7 Sediment concentration of Hg²⁺ in Westbank area, Kuilsriver, Western Cape, South Africa determined by HPLC-ICP-MS and verified by analysis on DMA. Results are for duplicates and the mean of three determinations.

Location	HPLC-ICP-MS Conc./ng g ⁻¹ (w.wt)	DMA Conc./ng g ⁻¹ (w.wt)	% Difference between methods methods
EKA 0–2 cm	7.280 ± 0.250	7.481 ± 1.752	2.76
EKA 2–4 cm	3.055 ± 0.022	3.352 ± 1.764	5.65
EKA 4–6 cm	5.641 ± 1.021	5.979 ± 0.622	1.71
EKA 6–8 cm	4.644 ± 1.015	4.725 ± 0.617	3.88
EKA 8–10 cm	14.112 ± 0.025	14.167 ± 0.406	8.90
EKB 0–2 cm	3.251 ± 1.520	3.602 ± 0.434	9.74
EKB 4–6 cm	5.181 ± 1.250	5.235 ± 1.703	1.03
EKB 6–8 cm	2.824 ± 1.250	3.069 ± 1.830	7.98
EKB 8–10 cm	n/a	n/a	
EKC 0–2 cm	7.344 ± 1.520	7.351 ± 1.055	0.10
EKC 4–6 cm	6.080 ± 1.051	6.130 ± 1.459	0.82
EKC 6–8 cm	9.003 ± 0.037	9.034 ± 0.888	0.34
EKC 8–10 cm	n/a	n/a	
EK 2 0–2 cm	3.260 ± 0.015	3.342 ± 0.330	–2.52
EK 2 2–4 cm	2.081 ± 0.172	2.074 ± 0.290	0.34
EK 2 6–8 cm	4.522 ± 0.021	4.410 ± 0.240	2.48
EK 2 8–10 cm	7.472 ± 0.032	7.354 ± 0.210	1.59

Reported values are for the mean ± S.D. of three determinations.

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