This version is available at https://strathprints.strath.ac.uk/63530/

OPTIMISATION AND APPLICATION OF A LOW COST, COLORIMETRIC SCREENING METHOD FOR MERCURY IN MARINE SEDIMENT

CAVOURA, Olga[a,c], DAVIDSON, Christine M.[b], KATSIRIS, Nicholas[a], KEENAN, Helen E.[c]

[a]*Department of Sanitary Engineering and Environmental Health, National School of Public Health, Athens, Greece*
[b]*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK*
[c]*Department of Civil and Environmental Engineering University of Strathclyde, Glasgow, UK*

*corresponding author email: okavoura@esdy.edu.gr

Keywords

mercury; screening; colorimetric; marine; sediment; Elefsina

Abstract

A rapid, inexpensive, colorimetric screening method for mercury (Hg) has been optimised to provide a semi-quantitative measurement of Hg concentration in marine sediment within the range 0.038 to 1.5 mg kg^{-1} encompassing the interim sediment quality guideline (ISQG) value of 0.13 mg kg^{-1} (CCME 1999) and the probable effects level (PEL) of 0.7 mg kg^{-1} for Hg in marine sediment (CCME 1999). Neither salinity (up to 41 practical salinity units (psu)) nor sediment organic matter (OM) content (up to 10%) affected the performance of the method. Accurate results were obtained for spike recovery experiments and analysis of certified reference material (CRM) BCR 580 Estuarine Sediment. The method was applied to sediment samples from Elefsina Bay, Greece. Screening results indicated Hg contamination in the bay, with concentrations exceeding the PEL value. Findings were confirmed by quantitative analysis of the samples by cold vapour atomic absorption spectrometry (CV-AAS), where results in the range 1.4–2.96 mg kg^{-1} were determined.

Introduction

Sediment is the main environmental sink for Hg, containing an estimated >90% of the total Hg in the environment (Faust and Osman 1981). Aquatic organisms can be exposed to Hg through direct contact with sediment and Hg species can be biomagnified through the marine food chain, resulting in high levels in higher trophic level organisms. The main source of human exposure to Hg is through the consumption of contaminated fish, where regular consumption could exceed acceptable levels of intake currently set at 0.1 µg kg body weight^{-1} day^{-1} (EPA 2001). Assessment of sediment Hg levels is therefore necessary in order to determine potential for exposure of aquatic organisms, and ultimately human exposure to this potentially toxic element. Rapid, inexpensive screening is necessary to allow such assessments to be made in areas where resources are limited but the risk of exposure through the consumption of contaminated fish can be high (WHO 2013).

Over the last decade there has been much interest in developing portable sensors for rapid identification of Hg. These sensors work by registering an output such as light emission (Huange et al. 2016; Singh *et al*. 2014), or electrochemical response (Duarte et al. 2015; Zhou et al. 2013), or are based on colorimetry (Choi et al. 2014; Duan and Zhan 2015; Yallouz et al. 2008). The challenging step in the use of such sensors is application to 'real' samples. In the environment, their use is primarily limited to aqueous media (Bazzicalupi et al. 2013; Choi et al. 2014; Deng et al. 2013; Ding et al., 2016; Huber and Leopold 2016; Sedghi et al. 2017). Even then, in complex aqueous matrices such as groundwater and marine waters, difficulties are encountered: colorimetric sensors containing functionalized metal nanoparticles for example can become unstable when dissolved solids content is high (Duan and Zhan 2015) whilst filtration and dilution of samples is often necessary prior to analysis when using chemoluminescent sensors (Li et al. 2016; Huang et al. 2016; Jayabel et al. 2015). The analysis of solid samples adds extra difficulty, since an additional step is necessary to release Hg species for determination. To screen marine sediment for Hg, a method must incorporate both an initial digestion step, and a subsequent analysis step that is unaffected by the salt content of the marine environment and the chemicals used for sample digestion.

A Hg screening method that has been applied to freshwater sediment is the colorimetric paper-based sensor using copper(I)iodide (Yallouz et al. 2008). The reaction involved, which is specific for Hg (Gettler and Kaye 1950), produces cuprous mercury iodide, $Cu_2[HgI_4]$, a Hg complex with a characteristic orange colour. Not only can Hg be identified, but also, since the intensity of the colour produced on reaction with

74 copper(I)iodide is proportional to the Hg concentration, by comparing the colour obtained

75 from a sample with colours obtained using standards of known concentration, a semi-

76 quantitative determination of Hg content can be made, expressed as a concentration

77 range. The method requires only basic laboratory glassware and a power supply and is

78 therefore low cost and easy to implement. Its suitability has been demonstrated for the

79 screening of fish (Yallouz et al. 2000; Ferreira et al. 2017), gold mining residues and

80 fluvial sediments (Yallouz et al. 2008; Ferreira et al. 2017).

81 The aims of the current study were to more fully characterize the cuprous iodide

82 based colorimetric Hg screening method, to assess its applicability to marine sediment,

83 and to implement the method for screening of Hg levels in marine sediment from Elefsina

84 Bay, Greece.

85

86 **Materials and methods**

87

88 General procedures

89

90 Chemicals were of analytical grade or higher purity. Glassware was soaked in 10% (v/v)

91 HNO_3 (> 65%, for trace analysis, Sigma-Aldrich Company Ltd. Dorset, UK) overnight and

92 rinsed with deionised (DI) water before use. Glass containers were used for storing Hg

93 samples, standard solutions and reagents. A 10 mg L^{-1} Hg stock solution in 10% (v/v)

94 HNO_3 was prepared from a 1000 mg L^{-1} commercial Hg standard solution ($Hg(NO_3)_2$,

95 Certipur, Merck, Leicester, UK). Reagent-matched standard solutions with Hg

96 concentration < 10 mg L^{-1} were prepared daily by apporpriate dilution of the stock

97 solution in DI water.

98

99 Screening procedure

100

101 The apparatus (Fig. 1), reagents and procedures used for the screening method were

102 based on the method described by Yallouz *et al.* (2008). Briefly, 10 g test portions of

103 solid samples were weighed accurately into a conical flask, fitted with a water-filled cold

104 finger, and digested in 25 mL a*qua regia* at 80 ^{o}C for 30 min. using a water bath. After

105 cooling to room temperature, 50 mL DI water was added and Hg^{II} species were reduced

106 to Hg^0 with 5 mL $SnCl_2$ (50% w/v in HCl) without filtration of the digest. By using an

107 aquarium pump and aeration duct to bubble air through the sample, Hg^0 was transferred

108 *via* a condenser to a preconditioned detecting paper coated with copper(I)iodide and held

109 in a specially constructed holder (Cetem, Centro de Tecnologia Mineral, Brazil), where

110 $Cu_2[HgI_4]$ was formed on reaction with the coating.

111

112

113

114
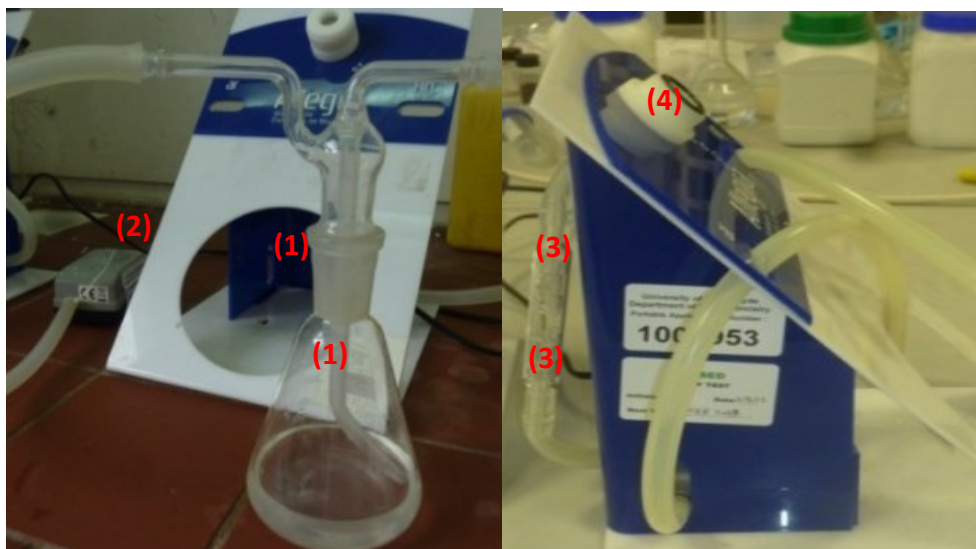
116 **Fig. 1** Apparatus for Hg reduction and determination as described by Yallouz et al. (2008). An
117 aeration duct is positioned inside the conical flask (1). One arm of the duct is connected through
118 tubing to an aquarium pump (2) and the other arm is connected to the condenser (3), which is
119 attached to the detecting paper holder (4)

120

121 Since the intensity of the colour was proportional to the amount of Hg in the sample, a
122 semi-quantitative determination of Hg concentration was obtained by comparison of the
123 colour intensity produced from Hg in standard solutions, analyzed in the same manner
124 (but omitting the digestion step) (Fig. 2). Sample Hg concentrations were reported as a
125 range corresponding to the lower and higher standard solution concentrations producing
126 less and more intense colors respectively than the sample. For example, if the color
127 intensity obtained from sample analysis lay 'in between' the intensities of colors obtained
128 for two standard Hg concentrations of 10 and 30 µg L^{-1} respectively, a semi-quantitative
129 sample concentration of 10–30 µg L^{-1} was reported.

130

131

Fig. 2 Increasing colour intensity of Hg complex formed on copper(I)iodide-coated detecting papers following analysis of standards with increasing Hg concentration (from left to right: blank, 15, 35, and 55 µg L^{-1})

Method characterization

Flow rate and repeatability

The effect of aeration pump flow rate on the reproducibility of the colour obtained from reaction of Hg^0 vapor with the detecting papers was tested using two, fixed-flow rate aquarium pumps: an Elite Pro that operated at a flow rate of 2.5 L min^{-1} (provided with the detecting papers and holder by Cetem, Centro de Tecnologia Mineral, Brazil) and an AquaAir Mini (Interpet, Surrey, UK) that operated at a flow rate of 1 L min^{-1}. Three replicate analyses of a 40 µg L^{-1} Hg standard were performed using each pump and flow rate.

Method range and concentration discrimination

The range of the method was assessed using standard solutions (75 mL) containing from 5 to 300 µg L^{-1} of Hg. For a 10 g sediment sample this corresponds to a sediment Hg concentration range of 0.038 to 2.25 mg kg^{-1}. This range covers background (unpolluted) mercury sediment concentrations, considered to be 0.01–0.2 mg kg^{-1} (Boszke et al. 2003), samples with Hg content around the ISQG value of 0.13 mg kg^{-1} and contaminated sediment samples with Hg content above the PEL of 0.7 mg kg^{-1} (CCME 1999). Colour discrimination was tested by analyzing standard solutions differing in concentration by various amounts e.g. 10 µg L^{-1}, 20 µg L^{-1}, 50 µg L^{-1}, within the above range.

Effect of sediment organic matter content

Sediment OM contributes significantly to adsorption of Hg (Skyllberg et al. 2006), hence can alter the efficiency of Hg extraction from sediment samples, leading to incorrect results being obtained. To investigate whether this affected the screening method, results for the determination of Hg in synthetic sediment containing no OM (sand pit sand, B&Q, Glasgow, UK) and in synthetic sediment containing 10% OM (75% sand + 10% silt + 5% clay + 10% humus) were compared. This selection covered typical sediment OM content. Duplicate 10 g test portions of each synthetic sediment were spiked with 3 µg Hg by

5

169 addition of 300 µL of the 10 mg L^{-1} Hg stock solution (to give a resultant Hg concentration

170 of 0.3 mg kg^{-1}) then mixed well, covered and left overnight before digestion and analysis.

171 Synthetic sediment and sand blanks (without addition of Hg) were also analysed.

172

173

174

175 Applicability of method to the marine environment

176

177 *Effect of salinity and seawater on method performance*

178

179 The effect of increasing salinity on the screening method was first tested by using

180 potassium chloride (KCl, GPR, BDH Laboratory Supplies, Poole, UK) to prepare a series

181 of Hg standard solutions (40 µg L^{-1}) with increasing salinities from 0.01 to 41 psu (the

182 latter representing the salinity of seawater). The salinity was determined based on an *in*

183 *situ* electrical conductivity measurement at 20 °C and P = 10 kPa, and converted to

184 salinity using Flinders conductivity converter (http://www.es.flinders.edu.au).

185   Performance was also compared for analysis of series of DI and sea water

186 standard solutions. Seawater obtained from the intertidal zone at Loutsa, Greece

187 (37.969° N, 24.008 ° E) and DI water were spiked with appropriate volumes of 10 mg L^{-1}

188 Hg stock solution to produce pairs of test solutions with Hg concentrations in the range

189 5–200 µg L^{-1}. The colours obtained for pairs of the same concentration were compared to

190 assess potential interferences from sea water.

191

192 Method performance for marine sediment

193

194 Method efficiency in marine sediment was tested by both spike recovery experiments

195 and analysis of a CRM. The sediment was obtained from the intertidal zone at

196 Lochgilphead, UK (56.02° N, 5.44° W), air dried, and passed through a 2 mm mesh

197 stainless steel sieve before use. Portions (10 g) were spiked with 1.5 and 6 µg Hg (by

198 addition of 150 or 600 µL of the 10 mg L^{-1} Hg stock solution), mixed thoroughly, covered

199 and left overnight, before being digested and screened for Hg. Blank sediment was also

200 analyzed. The CRM was BCR 580 Estuarine Sediment (Institute for Reference Materials

201 and Measurements, Geel, Belgium) containing 132 ± 3 mg kg^{-1} Hg. Smaller test portions

202 (approximately 0.02 and 0.04 g) of the CRM were analysed because of its high Hg

203 content.

204

205 Application

Study site

Sediment was taken from the Elefsina Bay (also known as the Gulf of Elefsina), 20 km west of Athens, Greece. With the island of Salamina to the south, the bay is sheltered and water mixing is poor. Two na_____ Gulf (Fig. 3).

Fig. 3 Elefsina Bay, Greece, showing sampling locations

The bay has a surface area of 67 km^2, a maximum depth of 33 m and receives effluent from some of the largest industrial plants in Greece, such as shipyards, oil refineries, paper and cement industries and metal extraction facilities. The main municipal effluent from Athens, which until 1995 was without treatment, is also discharged into the bay. In 2005, the bay was recognised as an area of major environmental concern (EEA 2005).

Sampling

Nearshore locations were selected along the bay in the vicinity of specific industries and sample coordinates recorded (Garwin eTrex 10 GPS unit). Specifically, locations A1 and A11 were in the vicinity of ship yards; A2 and A4 were in the area of oil refineries; A8 was

7

near a ship disassembly unit; and A5 was the location receiving the outfall from the Agios Georgios stream that contains effluent from many industries. Samples were taken at approximately 500–1000 m from the shore from a naval motor launch using a grab sampler and placed in glass wide mouth bottles for transport to the laboratory.

Sediment preparation

Sediment samples were dried in a natural convection drying oven (Binder E28, VWR International GmbH) at 30 °C and sieved (2 mm mesh, stainless steel) before storage in glass bottles. Each dried, sieved sample was coned and quartered to obtain a representative test portion for analysis.

Quantitative determinations

To assess the performance of the screening test, quantitative determination of total Hg concentration was performed using CV-AAS (PE 2006). Briefly, after microwave assisted digestion of 0.5 g test portions with 10 mL HNO_3 (175 °C, 20 min) (Berghoff Speedwave MWS-2 microwave system), 10 mL DI water was added to each digest, following which digests were filtered and diluted to a final volume of 50 mL with further DI water. Analysis was performed following reduction with 3% $NaBH_4$ using a MHS-10 Hg/Hydride system (Perkin Elmer, Massachusetts, USA) operated in cold vapour mode. Moisture content was determined on dried, sieved test portions (BS 2000) and OM content was estimated by loss on ignition (Schumacher 2002).

Results and discussion

Method characterization

Flow rate and repeatability

Results obtained for triplicate analysis of the 40 µg L^{-1} standard solution using a flow rate of 2.5 L min^{-1} proved unsatisfactory. Colour development was uneven and there was no distinct edge to the coloured complex formed (Fig. 4, paper 1). Delivering the Hg^0 vapor to the detecting paper more slowly (1 L min^{-1}) yielded reproducible results, a generally uniform response across the sensitive area of the detecting paper, and a spot with distinct edges (Fig. 4, papers 2, 3, 4). The lower flow rate was therefore selected for future use.
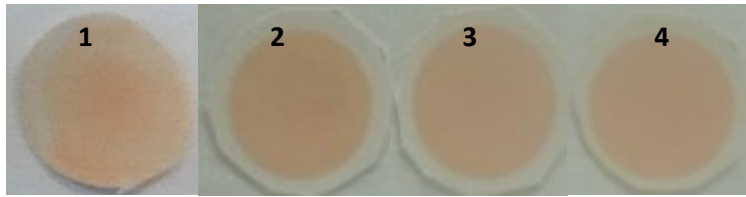
Fig. 4 Response obtained for analysis of a 40 µg L^{-1} standard solution using the Elite Pro pump at a flow rate of 2.5 L min^{-1} (paper 1) and the AquaAir Mini pump at a flow rate of 1 L min^{-1} (papers 2, 3, 4)

Method range and concentration discrimination

Concentrations of 5 µg L^{-1} Hg were distinguishable from the blank, making this the lower limit of screening in solution (equivalent to a limit of detection around 0.04 mg kg^{-1} for analysis of a 10 g sediment sample). A difference in colour intensity visible to the eye could be seen between standards differing in Hg concentration by 20 µg L^{-1}, up to a Hg concentration of 150 µg L^{-1} (Fig. 5, top row). Above a Hg concentration of 150 µg L^{-1} colour differences became harder to discern. There was no obvious increase in colour intensity between 200 and 300 µg L^{-1}, indicating that 200 µg L^{-1} (which is equivalent to 1.5 mg kg^{-1} for analysis of a 10 g sediment sample) was the effective upper limit of sensitivity for the sensor.

Effect of sediment organic matter content

After spiking 10 g test portions of synthetic sediment without OM, and 10 g test portions of synthetic sediment containing 10% OM, with 3 µg Hg, the screening method was applied both to the sediment samples and to standards containing 1.1, 2.6 and 4.1 µg. The colours intensities obtained for the samples were indicative of a Hg content in the range 2.6–4.1 µg per sample, which corresponds well to the 3 µg added. At least for the specific samples and contact time studied, the presence of up to 10% OM did not appear to affect the method performance. No Hg was detected in either the reagent blank or the unspiked synthetic samples.

Applicability of screening method to the marine environment

*Effect of salinity and seawater on method performance*

298   A series of 40 µg L^{-1} Hg standard solutions was prepared with differing salinities; 0.01,

299   10, 21, 30, 33 and 41 psu. Regardless of the salinity, all standards produced the same

300   colour intensity on screening indicating that salinity does not affect intensity.

301   Two series of standard solutions with Hg concentrations ranging from 5 to 200 µg

302   L^{-1} were prepared, one series in DI water and the other in seawater. Similar intensities

303   were obtained for standard solutions of the same concentration, regardless of the matrix

304   (DI water or seawater) (Fig. 5) indicating that the seawater matrix did not interfere with

305   the screening method.

306

| µg L^{-1} | blank | 5 | 10 | 30 | 50 | 70 | 90 | 110 | 130 | 150 | 200 |
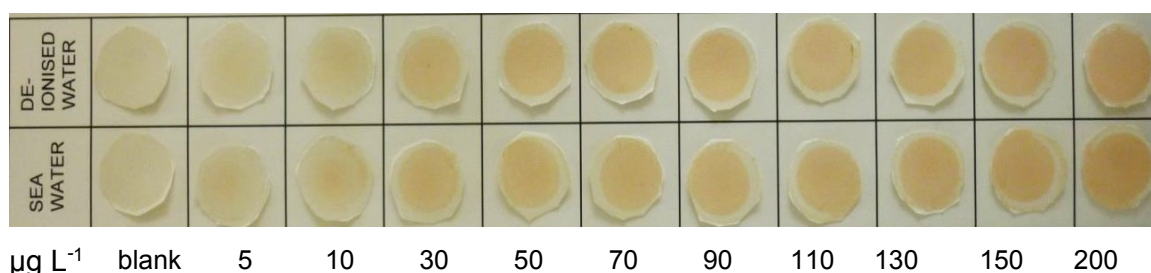
308 **Fig. 5** Increase in colour intensity obtained from screening standard solutions containing 5, 10, 30,

309 50, 70, 90, 110, 130, 150 and 200 µg L^{-1} of Hg prepared in deionised water and seawater

310

311 Method performance for marine sediment

312

313   Marine sediment (10 g portions) was spiked with 1.5 µg and 6 µg Hg. The colour

314   intensities produced on screening were compared to intensities obtained for standard

315   solutions containing 0.75, 3.75 and 7.5 µg Hg. The samples spiked with 1.5 µg Hg gave

316   colour intensities indicative of a Hg content in the range 0.75–3.75 µg, and samples

317   spiked with 6 µg Hg gave colour intensities indicative of a Hg content in the range 3.75–

318   7.5 µg, corresponding to the amount of Hg added.

319   Portions of CRM BCR 580 Estuarine Sediment containing 2.81 and 5.48 µg Hg

320   were screened and the colours obtained compared to intensities obtained for standard

321   solutions containing 1.1, 2.6 and 4.1 µg Hg. The samples containing 2.81 µg Hg gave

322   colour intensities indicative of a Hg content in the range 2.6–4.1 µg, and the samples

323   containing 5.48 µg Hg gave colour intensities indicative of a Hg content > 4.1 µg Hg,

324   corresponding to the expected range (Table 1). The procedure was therefore considered

325   suitable to screen sediment samples from Elefsina Bay.

326

327 **Table 1** Screening results for Hg in marine sediment spiked with 1.5 µg and 6 µg Hg and for

328 certified reference material (CRM) BCR 580 containing 132 ± 3 mg kg^{-1} Hg

Spiked sediment weight	Hg added (µg)	Hg found (µg)[a]

10 g (replicate 1)	0	< LOD
10 g (replicate 2)	0	< LOD
10 g (replicate 1)	1.5	0.75–3.75
10 g (replicate 2)	1.5	0.75–3.75
10 g (replicate 1)	6	3.75–7.50
10 g (replicate 2)	6	3.75–7.50
CRM weight (g)	Hg content (µg)	Hg found (µg)[b]
0.0210	2.81	2.6–4.1
0.0412	5.48	> 4.1

[a] Sediment results compared to those for standard solutions containing 0.75, 3.75 and 7.5 µg Hg
[b] CRM results compared to those for standard solutions containing 1.1, 2.6 and 4.1 µg Hg

Application

Screening of sediment samples from Elefsina Bay identified Hg contamination at all locations. Initial screening was performed using 10 g test portions, as in method development, and comparison made with the colour obtained from standard solutions (75 mL) containing up to 70 µg L^{-1} of Hg (equivalent to a maximum sediment Hg concentration of 0.5 mg kg^{-1}). Since sediment concentrations appeared to be either very close to or above this value, screening was repeated using 1 g sediment samples and standard solutions (75 mL) of Hg concentration 10, 50 and 100 µg L^{-1} (equivalent to sediment concentrations of 0.75, 3.75 and 7.5 mg kg^{-1} Hg). Results for locations A2 and A5 gave Hg concentrations in the range 0.75–3.75 mg kg^{-1}, while sediments from A1, A4, A8 and A11 had Hg concentrations between 0.38 mg kg^{-1} (the procedural LOD for analysis of a 1 g samples) and 0.75 mg kg^{-1} (the response for the lowest concentration standard solution) (Table 2).

Table 2 Screening results for Hg content, Hg concentration as determined by cold vapour atomic spectrometry (CV-AAS) and sediment organic matter (OM) content in samples from Elefsina Bay

Locations (E to W) and potential pollution source in brackets	Coordinates (lat., long.)	Screening result (mg kg^{-1}) (1 g sample)	Total Hg by CV-AAS[a] (mg kg^{-1})	OM (%)
A1 (shipyard)	38.010° N, 23.590° E	0.38–0.75	1.93 (1.77, 2.08)	8.36 (8.06, 8.66)
A2 (oil refinery)	38.020° N, 23.595° E	0.75–3.75	1.88 (1.73, 2.03)	8.96 (7.51, 10.4)
A5 (Agios Georgios stream)	38.030° N, 23.590° E	0.75–3.75	2.96 (2.19, 3.73)	7.23 (6.76, 7.71)
A8 (dissassembly unit)	38.038° N, 23.554° E	0.38–0.75	1.40 (1.15, 1.66)	8.09 (7.36, 8.87)
A4 (oil refinery)	38.038° N, 23.507° E	0.38–0.75	1.50 (1.38, 1.61)	11.8 (11.0, 12.6)
A11 (shipyard)	38.029° N, 23.495° E	0.38–0.75	2.86 (2.20, 3.51)	9.08 (8.07, 10.1)

[a]CV-AAS and OM results given as mean of two values (individual results shown in brackets)

Mercury concentrations determined by CV-AAS ranged from 1.40 to 2.96 mg kg^{-1}, with highest concentrations found in locations A5 (outfall of Agios Georgios stream) and A11

(shipyard). High Hg concentration at position A5 is probably a result of effluent discharge from industries known to release Hg such as cement manufacture and metal extraction while the use of phenylmercury acetate as an anitfouling agent in ship paints, which was common until the 1990s, may explain the higher results at locations A11. Although there was variation between results for duplicate analyses, the concentration of Hg in all samples exceeded not only the ISQG value of 0.13 mg kg^{-1}, but also the PEL of 0.7 mg kg^{-1} for Hg in marine sediment (CCME 1999), the latter being the concentration above which adverse effects are frequently observed in aquatic organisms. The OM content of the samples ranged from 7.23 to 11.8%, with highest OM content at position A4. The proximity of this location to an oil refinery could explain the higher OM observed in this area.

Screening and quantitative Hg determination gave consistent results for samples A2 and A5. Although screening identified the presence of Hg for samples A1, A4, A8 and A11, the screening results were lower than the results obtained from quantification (Table 2). Lower results are not thought to be a consequence of OM content, since samples for which screening gave a result in the correct range did not differ markedly in OM content from those for which screening gave a lower assessment. A possible explanation for the lower screening results is that the digestion procedure used in the screening method was less vigorous: while digestion in the screening method was performed at a relatively low temperature of 80 ℃ (using *aqua regia*), for quantitative determination microwave digestion was carried out at 175 ℃ (using concentrated HNO$_3$). Harsh digestion conditions are necessary if the determination of all forms of Hg, including less mobile forms, such as HgS, is desired. However, insoluble, stable forms of Hg are less likely to be released under environmental conditions and are not available for biomethylation. Milder extraction conditions, such as those used in the screening method, are more representative of environmental mobility and give a clearer indication of potential for exposure.

Conclusions

A colorimetric screening method for semi-quantitative determination of Hg in the marine sediment was found to have a sensitivity range from 0.038 to 1.5 mg kg^{-1}. Method performance was unaffected by salinity up to 41 psu, the presence of a seawater matrix and sediment OM content up to 10%. Results in the expected ranges were obtained when the method was applied to spiked (uncontaminated) marine sediment samples, and CRM BCR 580 Estuarine Sediment. Results obtained for screening of sediments from the Elefsina Bay, Greece, sometimes underestimated the true Hg content as determined

390 by CV-AAS, probably due to milder digestion conditions used. However Hg

391 contamination potentially exceeding the PEL level of 0.7 mg kg^{-1} (CCME 1999) was

392 identified at all locations sampled and the determination of Hg concentration using milder

393 digestion conditions is more indicative of environmentally mobility Hg concentrations and

394 potential for exposure. Quantitative analysis confirmed sediment Hg concentrations in

395 Elefsina Bay ranged from 1.4 to 3.0 mg kg^{-1}. Further work will explore the use of battery-

396 powered aerating pumps and portable sample digestion/extraction apparatus with the

397 goal of developing a methodology that can be fully implemented in the field to allow initial

398 identification of contaminated marine sediment that can then be taken to a laboratory for

399 quantitative analysis where necessary.

400

401

409

410

411 **References**

412 Bazzicalupi, C., Caltagirone, C., Cao, Z. F., Chen, Q. B., Di Natale, C., Garau, A., Lippolis, V.,
413 Lvova, L., Liu, H. L., Lundstrom, I., Mostallino, M. C., Nieddu, M., Paolesse, R., Prodi, L., Sgarzi,
414 M. and Zaccheroni, N. (2013). Multimodal Use of New Coumarin-Based Fluorescent
415 Chemosensors: Towards Highly Selective Optical Sensors for Hg2+ Probing, *Chemistry -a*
416 *European Journal*, 19, 14639–14653.

417

418 Boszke, L., Kowalski, A., Glosinska, G., Szarek, R. and Siepak, J. (2003). Environmental factors
419 affecting speciation of mercury in the bottom sediment; an overview, *Polish Journal of*
420 *Environmental Studie*s, 12, 5–13.

421

422 BS (2000). British Standards ISO 12880:2000: Characterisation of sludges – Determination of dry
423 residue and water content. British Standards Institution, London.

424

425 CCME (1999). Canadian sediment quality guidelines for protection of aquatic life, Mercury.
426 Available at http://ceqg-rcqe.ccme.ca/download/en/241. Accessed June 2016.

427

428 Choi, Y. W., You, G. R., Lee, M. M., Kim, J., Jung, K. D. and Kim, C. (2014). Highly selective
429 recognition of mercury ions through the "naked-eye", *Inorganic Chemistry Communications*, 46,
430 43–46.

431

432 Deng, L., Ouyang, X. Y., Jin, J. Y., Ma, C., Jiang, Y., Zheng, J., Li, J. S., Li, Y. H., Tan, W. H. and
433 Yang, R. H. (2013). Exploiting the Higher Specificity of Silver Amalgamation: Selective Detection
434 of Mercury(II) by Forming Ag/Hg Amalgam, *Analytical Chemistry*, 85, 8594–8600.

435

Ding, Y., Wang, S., Li, J. and Chen, L. (2016). Nanomaterial-based optical sensors for mercury ions, *TrAC Trends in Analytical Chemistry*, 82, 2016, 175–190.

Duan, J. and Zhan, J. (2015). Recent developments on nanomaterials-based optical sensors for Hg2+ detection, *Sci China Mater*, 58, 223–240.

Duarte, K., Justino, C. I. L., Freitas, A. C., Gomes, A. M. P., Duarte, A. C. and Rocha-Santos, T.A.P. (2015). Disposable sensors for environmental monitoring of lead, cadmium and mercury, *TrAC Trends in Analytical Chemistry*, 64, 183–190.

EEA (2005). UNEP/MAP, Priority issues in the Mediterranean environment, Report no. 5/2005, Office for the Official Publications of the European Communities, Luxembourg.

EPA (2001), methylmercury, Oral RfD assessment, Integrated Risk Information System. Available from http://www.epa.gov/iris/subst/0073.htm.

Faust, S. D. and Osman, M. A. (1981). Mercury, arsenic, lead, cadmium, selenium, and chromium in aquatic environments in King, J. K., Kostka, J. E., Frischer, M. E. and Saunders, F. M. (2000). Sulfate-reducing bacteria methylate mercury at variable rates in pure culture and in marine sediments, *Applied and Environmental Microbiology*, 66, 2430-2437.

Ferreira, C. M. A., Egler S. G., Yallouz, A. V., Ignácio, A. R. A. (2017). Semiquantitative determination of total mercury in *Pygocentrus nattereri* Kner, 1858 and sediment at the plateau of Upper Paraguai River, Brazil, *Chemosphere*, 174, 604-612.

Gettler, A. O. and Kaye, S. (1950). A simple and rapid analytical method for Hg, Bi, Sb, and As in biologic materials, *Journal of Laboratory and Clinical Medicine*, 35, 146–151.

Huange, Y. Q., Yin, J. C., Wang, Y. S., Xiao, X. L., Zhou, B., Xue, J. H., Tang, X., Wang, X. F., Zhu, Y. F. and Chen, S. H. (2016). Streptavidin and gold nanoparticles-based dual signal amplification for sensitive magnetoelastic sensing of mercury using a specific aptamer probe, *Sensors and Actuators B: Chemical*, 235, 507–514.

Huber, J. and Leopold, K. (2016). Nanomaterial-based strategies for enhanced mercury trace analysis in environmental and drinking waters, *TrAC Trends in Analytical Chemistry*, 80, 280–292.

Jayabal, S., Pandikumar, A., Lim, H. N., Ramaraj R., Sund, T. and Huang, N. M. (2015). A gold nanorod-based localized surface plasmon resonance platform for the detection of environmentally toxic metal ions, *Analyst*, 140, 2540–2555.

Li, Q., Wang, J., He, Y. (2016). Selective chemiluminescent sensor for detection of mercury(II) ions using non-aggregated luminol-capped gold nanoparticles, *Sensors and Actuators B: Chemical*, 231, 64–69.

PE (2006). AAnalyst 200 User's Guide, PerkinElmer, Inc., 710 Bridgeport Avenue, Connecticut, USA. Available from http://www.che.ntu.edu.tw/ntuche/equip_booking/files/AAnalyst%20200%20.pdf

Schumacher, B. (2002). Methods for the determination of total organic carbon (TOC) in soil and sediment, US EPA, 2002, Ecological risk assessment support centre, Office of Research and Development, US EPA.

Sedghi, R., Kazemi, S and Heidari, B. (2017). Novel selective and sensitive dual colorimetric sensor for mercury and lead ions derived from dithizone-polymeric nanocomposite hybrid, *Sensors and Actuators B: Chemical*, 245, 860–867.

Singh, V., Srivastava, P., PrakashVerma, S., Misra, A., Das, P. and Singh, N. (2014). A new fluorescent pyrene-pyridine dithiocarbamate probe: A chemodosimeter to detect Hg2+ in pure aqueous medium and in live cells, *Journal of Luminescence*, 154, 502–510.

495
496 Skyllberg, U., Bloom, P. R., Qian, J., Lin, C. M. and Bleam, W. F. (2006). Complexation of
497 mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur
498 groups, *Environmental Science & Technology*, 40, 4174–4180.
499
500 WHO (2013). Mercury Exposure and Health Impacts among Individuals in the Artisanal and
501 Small-Scale Gold Mining (ASGM) Community, World Health Organization, Public Health and
502 Environment, 20 Avenue Appia, 1211 Geneva 27, Switzerland. Available at
503 http://www.who.int/ipcs/assessment/public_health/mercury_asgm.pdf. Accessed June 2014.
504
505 Yallouz, A. V., Cesar, R. G. and Egler, S. G. (2008). Potential application of a semiquantitative
506 method for mercury determination in soils, sediments and gold mining residues, *Environmental
507 Pollution*, 151, 429–433.
508
509 Yallouz, A. V., de Campos, R. C. and Paciornik, S. (2000). A low-cost non instrumental method for
510 semiquantitative determination of mercury in fish, *Fresenius Journal of Analytical Chemistry*, 366,
511 461–465.
512
513 Zhou, N., Chen, H., Li, J. H. and Chen, L. X. (2013). Highly sensitive and selective voltammetric
514 detection of mercury(II) using an ITO electrode modified with 5-methyl-2-thiouracil, graphene
515 oxide and gold nanoparticles, *Microchimica Acta*, 180, 493–499.