

# ASSESSING MERCURY MOBILITY IN SEDIMENT OF THE UNION CANAL, SCOTLAND, UK BY SEQUENTIAL EXTRACTION AND THERMAL DESORPTION

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## Abstract

The mobility of mercury (Hg) was assessed in sediment from the Union Canal, Scotland, UK. Samples collected from the vicinity of a former munitions factory that manufactured mercury fulminate detonators were subjected to sequential extraction followed by cold vapor atomic absorption spectrometry (CVAAS) and direct analysis using thermal desorption (TD). The sequential extraction indicated that >75% of mercury (up to 429 mg kg<sup>-1</sup>) was in mobile forms, with <12% semi-mobile and <23% non-mobile species. In the TD method, >67% of the total Hg content was desorbed in the temperature range 100–250 °C consistent with species weakly attached to the mineral matrix (tentatively identified as an iron (oxy)hydroxide-associated species). This predominance of mobile mercury species may arise from a lack of association between Hg and either organic matter or sulfur in the sediments. Further investigation of Hg mobilization, transport and assimilation/biomagnification is required both to determine whether there is a need for remediation of the sediment and to improve understanding of the biogeochemical cycling of Hg in shallow, oxic, freshwater systems.

## 1. Introduction

Mercury (Hg) is a potentially toxic element distributed throughout the environment in different chemical species, where species refers to the 'specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure' (IUPAC, 1997). With characteristics including global transfer and neurotoxicity, Hg is ranked third on the priority list of substances that pose a potential threat to human health (ASTDR 2013). The methylated form is especially of concern because it can be bioaccumulated and biomagnified up the food chain, ultimately resulting in the main source of human population Hg exposure through the consumption of contaminated fish.

Between 90 and 95% of the total Hg in the environment is associated with sediment (Faust and Osman 1981) where interactions are governed almost exclusively by affinity for reduced sulfur (S) ligands (Dyrssen and Wedborg 1991). In sediment, HgS, an insoluble sulfide with very limited mobility is commonly encountered. Reduced S ligands in organic matter (OM) also contribute significantly to strong sediment adsorption of Hg (Ravichandran, M. 2004). After saturation of the reduced S ligands, O and N ligand associations are formed between Hg and OM (Skylberg *et al.* 2006). In heavily polluted areas, weaker Hg adsorption to the inorganic matrix may occur if binding sites on OM become saturated (Hissier and Probst 2006).

Mobility, or ease of extractability, of Hg from sediment into the water column influences transport, thus the spread of contamination, and methylation since only dissolved Hg species can be taken up by the methylating bacteria involved. A range of techniques is available for determination of Hg mobility. Extraction procedures are used to remove Hg bound to sediment phases into operationally defined groups of more, or less, soluble species (Bloom *et al.* 2003; Rodrigues *et al.* 2010; Wallschlager *et al.* 1998). Based on the stepwise use of increasingly harsh reagents to remove Hg from increasingly stronger complexes, sequential extraction gives an indication of Hg mobility, availability and bioaccumulation potential; Hg removed under less harsh conditions could be released more readily in the environment whereas those forms requiring harsh reagents for their removal are considered less mobile and not bioavailable (Wallschlager *et al.* 1998). Reviews on sequential extraction procedures have been presented by Issaro *et al.* (2009) and Bacon and Davidson (2008).

Thermal desorption (TD) techniques are increasingly used to provide information on total Hg content, on Hg species in soil and sediment samples (Bollen *et al.* 2008; Reis *et al.* 2012; Saniewska and Beldowska 2017) and more recently on Hg speciation in aquatic and atmospheric particulate samples (Beldowska *et al.* 2018). In TD speciation studies, Hg species adsorbed to solid particles are gradually removed by a stepwise increase in temperature, in a process analogous to sequential extraction where species are released by increasing harshness of extracting reagents. Individual Hg species are desorbed from the matrix within a characteristic temperature range. By comparing TD curves obtained from samples to TD curves of Hg standard materials, the Hg species present can be identified. The release of Hg species weakly associated with the sediment mineral matrix generally occurs at temperatures up to 250 °C, whilst higher desorption temperatures are required to release, for example, Hg species strongly associated with OM or present as HgS (Biester *et al.* 1999).

The Union Canal, Scotland, UK, has a history of Hg contamination arising from proximity to a munitions manufacturing site that produced detonators containing mercury fulminate for almost a century (Smith and Lassiere 2000). Following substantial redevelopment and regeneration in 2001–2002, which included dredging of sediment and soil excavation, the

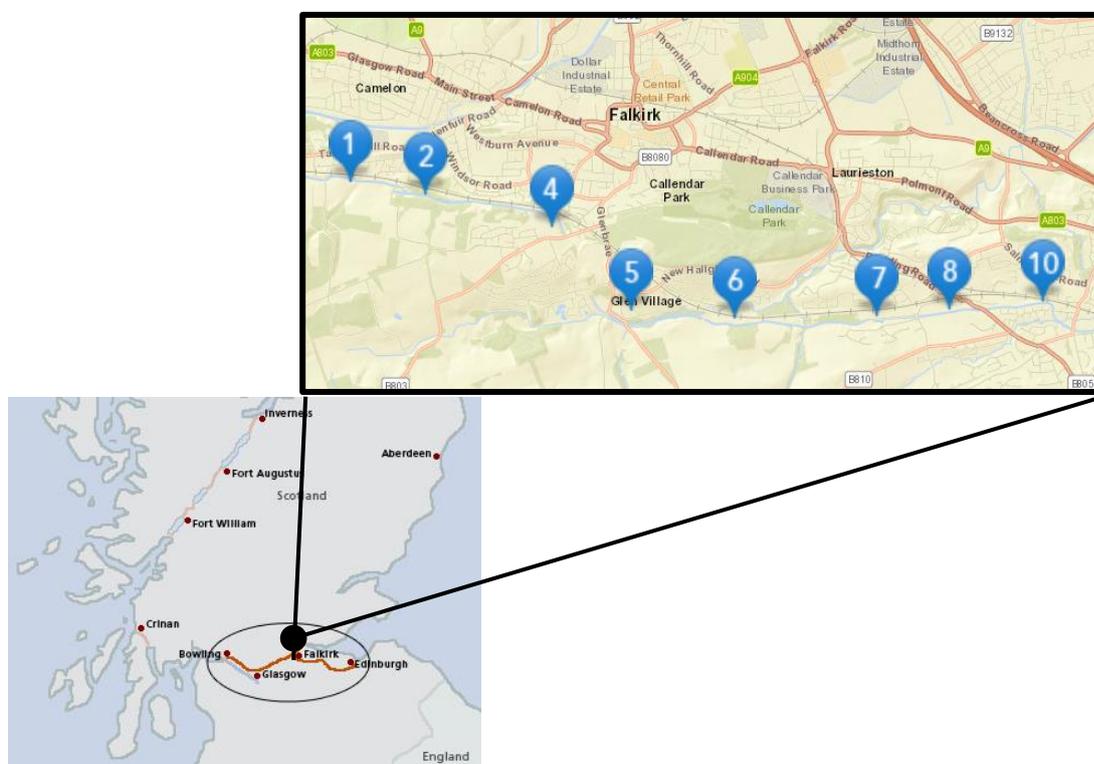
canal has become a major leisure facility used for boating and fishing. However, despite these remediation efforts, very high levels of Hg contamination persist in sediment close to the location of the former munitions factory (Cavoura et al. 2017). Methyl mercury levels in the canal sediments are currently low (Cavoura et al. 2017). However it is important that the mobility of Hg species present be determined to assess the likelihood of transport and potential for methylation.

The aim of this study was to determine the mobility of Hg species in sediment from the Union Canal, Scotland, UK using both sequential extraction followed by cold vapor atomic absorption spectrometry (CVAAS) and direct TDAAS techniques.

## 2. Materials and methods

### Sampling locations and method

Eight sampling locations were selected from the Falkirk area of the canal, between Tamfourhill (1) and Polmont (10) at approximately 2 km intervals (Figure 1). Location 1 was part of a canal extension added in 2000–2001 as part of the canal regeneration. Sediment samples were collected and processed as described in Cavoura et al. (2017) i.e. they were dried at 30 °C in a natural convection oven, sieved to <2 mm and stored in glass bottles at room temperature.



**Fig. 1** Location of the Union Canal running from Falkirk to Edinburgh, Scotland, UK and sediment sampling locations

## Reagents

Reagents used were of analytical grade or higher purity. A stock standard Hg solution (10 mg L<sup>-1</sup> in 10% (v/v) HNO<sub>3</sub>) prepared from a 1000 mg L<sup>-1</sup> Hg standard solution (Hg(NO<sub>3</sub>)<sub>2</sub>, Certipur, Merck, Leicester, UK) was stored at 4 °C and replaced monthly. Reagent-matched standard solutions with concentrations < 10 mg L<sup>-1</sup> were prepared daily as required. Sodium borohydride (NaBH<sub>4</sub>) reductant, a 3% solution in 1% NaOH, was prepared daily using NaOH pellets (AR, Mallinckrodt, Dublin, Ireland) and NaBH<sub>4</sub> powder (GR for analysis, Merck KGaA, Darmstadt, Germany) and filtered (glass fibre filters, Pall A/E Glass fibre filters 1.0 µm, 110 mm, Pall GmbH, Dreieich, Germany) before use. Tin chloride (SnCl<sub>2</sub>) reductant, 2% in 10% HCl, was prepared from SnCl<sub>2</sub>·2H<sub>2</sub>O (98%, Alfa Aesar, Heysham, UK). A 4 M HNO<sub>3</sub> solution for extraction of mobile Hg species was prepared by addition of 255 mL HNO<sub>3</sub> to approximately 250 mL deionized (DI) water and made up to 1000 mL with DI water. A 5.33 M HNO<sub>3</sub> solution for extraction of semi-mobile Hg species was prepared by combining 1 part HNO<sub>3</sub> with 2 parts DI water (1:2(v/v) HNO<sub>3</sub>:H<sub>2</sub>O). Standard materials for Hg desorption curves were prepared as described in Reis et al. (2015).

## Analytical procedures

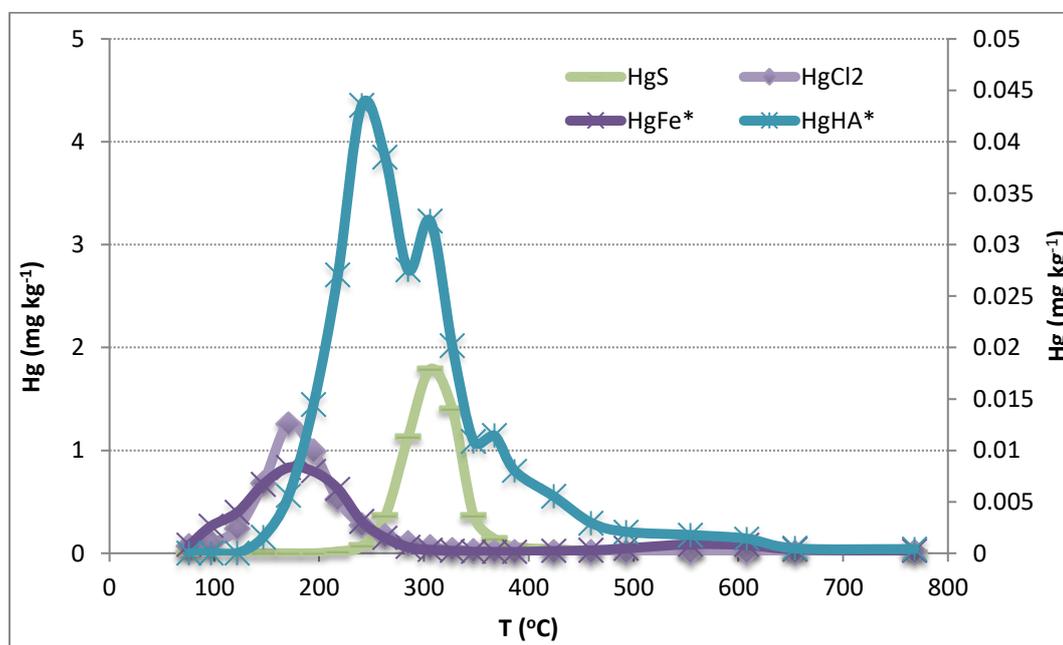
Glassware was soaked in 10% v/v HNO<sub>3</sub> overnight and rinsed with DI water before use. Glass containers were used for storing Hg samples, standard solutions and reagents. Moisture content was determined on dried, sieved, test portions (BS 2000) and OM content was estimated by loss on ignition (Schumacher 2002).

Determination of total Hg concentration was performed using CVAAS (PE 2006) after microwave assisted digestion of samples with HNO<sub>3</sub> (Berghoff Speedwave MWS-2 system). Analysis was performed following reduction with 3% NaBH<sub>4</sub> using a MHS-10 Hg/Hydride system (Perkin Elmer, Massachusetts, USA) operated in CV mode. Determinations were performed in triplicate after calibration of the instrument with reagent-matched standard solutions. Determination of total Hg concentration by TDAAS was carried out using a direct mercury analyser (LECO®, model AMA-254) with gold amalgamation and AAS detection system using a silicon diode detector at 253.6 nm. Further details can be found in Reis et al. (2013). Determinations were performed in triplicate.

Operationally-defined species mobility was determined using extractants of increasing acid strengths as recommended in USEPA Method 3200 (USEPA 2014). Extraction of mobile Hg species was achieved by microwave irradiation (Berghoff Speedwave MWS-2 microwave system, Berghof Products + Instruments GmbH, Eningen, Germany) with 4 M HNO<sub>3</sub> at 100 °C (Rahman and Kingston 2005). Extraction of semi-mobile species was achieved using 5.33 M HNO<sub>3</sub> extractant and a combination of vortex, heating (PD Group, Medingen, Dresden,

Germany) and centrifugation (Han 2003). Both extracts were analysed by CVAAS following reduction with 3% NaBH<sub>4</sub> as described for the determination of total Hg concentration. Non-mobile species such as HgS and HgSe were determined from the difference between total Hg concentration and the sum of the concentrations of mobile and semi-mobile species.

Species identification using TDAAS was carried out using a direct mercury analyser with gold amalgamation (LECO<sup>®</sup>, model AMA-254). Desorption curves were obtained for standard materials HgCl<sub>2</sub>, Hg associated with iron(III)oxide (HgFe), Hg-humic acid complex (HgHA), and HgS (Figure 2). As expected (Reis et al. 2015) lower desorption temperatures were observed for HgCl<sub>2</sub> and HgFe than for HgHA and HgS. The curves for HgFe and HgCl<sub>2</sub> showed peaks between 75 and 285 °C (maximum ~170 °C) and between 95 and 285 °C (maximum ~170 °C) respectively. The curve obtained for HgHA spanned the temperature range 125–655 °C (maximum ~240 °C) with three peaks corresponding to the release of Hg bound to S, O and N groups in OM (Reis et al. 2015). Desorption of HgS occurred over the temperature interval 240–370 °C, (maximum ~306 °C). The curves for HgCl<sub>2</sub> and HgFe overlapped preventing identification of these species individually from TD curves alone. While HgS was well separated from HgCl<sub>2</sub> and HgFe, there was overlap with desorption from Hg from S bonding sites in the HgHA standard. These limitations are considered further in Reis et al. (2015).



**Fig. 2** Thermal desorption curves for standard Hg materials

### Limits of detection and quality control

Limit of detection (LOD) for CVAAS was  $0.067 \text{ mg kg}^{-1}$ . Recovery of Hg from CRM BCR 320 R Channel Sediment containing  $0.85 \pm 0.09 \text{ mg kg}^{-1}$  Hg (Geel, Belgium) was  $116 \pm 20.3\%$  (n=3). For TDAAS, the LOD was  $0.020 \text{ mg kg}^{-1}$ . Recovery of Hg from CRM MESS-3 Marine Sediment containing  $0.091 \pm 0.009 \text{ mg kg}^{-1}$  Hg was  $107 \pm 2.05\%$  (n=6).

### 3. Results and discussion

Sampling locations, OM content and total Hg concentrations determined by both CVAAS and TDAAS are given in Table 1.

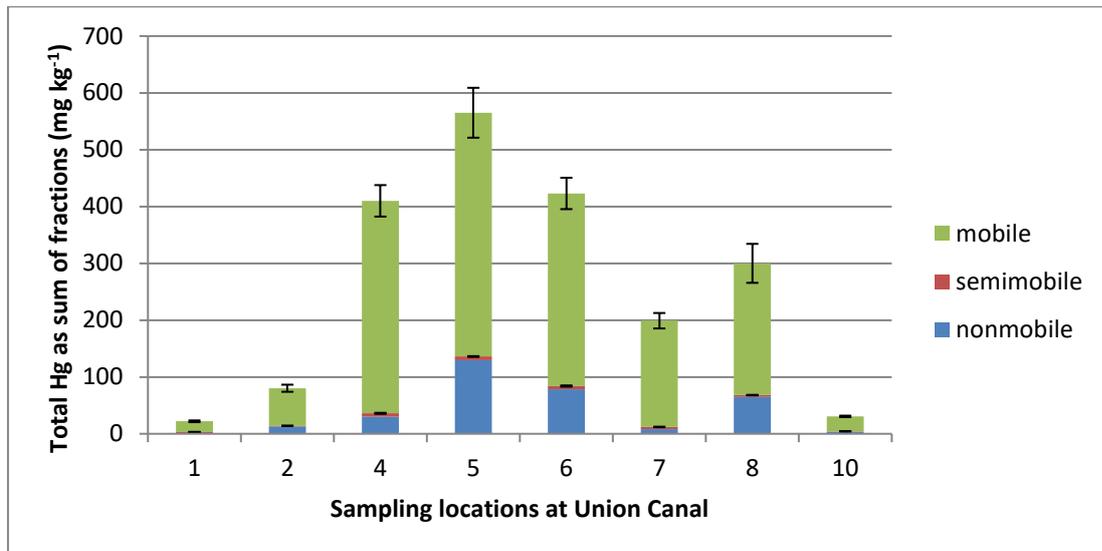
**Table 1** Location, characteristics and total mercury concentrations of sediment samples from the Union Canal, Scotland, UK

Location	Latitude Longitude	OM (%)	Hg (CVAAS) $\text{mg kg}^{-1}$	Hg (TDAAS) $\text{mg kg}^{-1}$
1	55.996° N, 3.830° W	6.84	$21.9 \pm 0.6$	$25.1 \pm 0.1$
2	55.994° N, 3.818° W	14.6	$80.2 \pm 6.1$	$100 \pm 5$
4	55.992° N, 3.795° W	18.1	$410 \pm 47$	$451 \pm 7$
5	55.984° N, 3.787° W	15.6	$565 \pm 48$	$542 \pm 27$
6	55.984° N, 3.774° W	10.9	$423 \pm 110$	$433 \pm 6$
7	55.983° N, 3.746° W	6.12	$199 \pm 23$	$189 \pm 2$
8	55.984° N, 3.735° W	13.7	$300 \pm 30$	$274 \pm 18$
10	55.983° N, 3.715° W	8.47	$21.9 \pm 0.6$	$31.3 \pm 1.9$

Sediment OM content ranged from  $6.12 \pm 1.4$  to  $18.1 \pm 1.1 \%$ . Total Hg concentrations as determined by CVAAS ranged from a minimum of  $22.0 \pm 0.6 \text{ mg kg}^{-1}$  at location 1, to a maximum of  $565 \pm 48 \text{ mg kg}^{-1}$  at location 5. No statistical difference was found between the results obtained by the CVAAS and TDAAS methods (non-parametric data, Wilcoxon matched pairs T-test,  $T_{\text{calc}} > T_{\text{crit}}$ , n=8,  $p < 0.05$ ). Despite the affinity of Hg for OM generally reported, the two parameters were not significantly correlated ( $r^2 = 0.376$ ,  $p > 0.05$ ). A previous study (Cavoura et al. 2017) also found no significant association between Hg and OM content ( $r^2 = 0.534$ ,  $p > 0.05$ ) in Union Canal sediment samples.

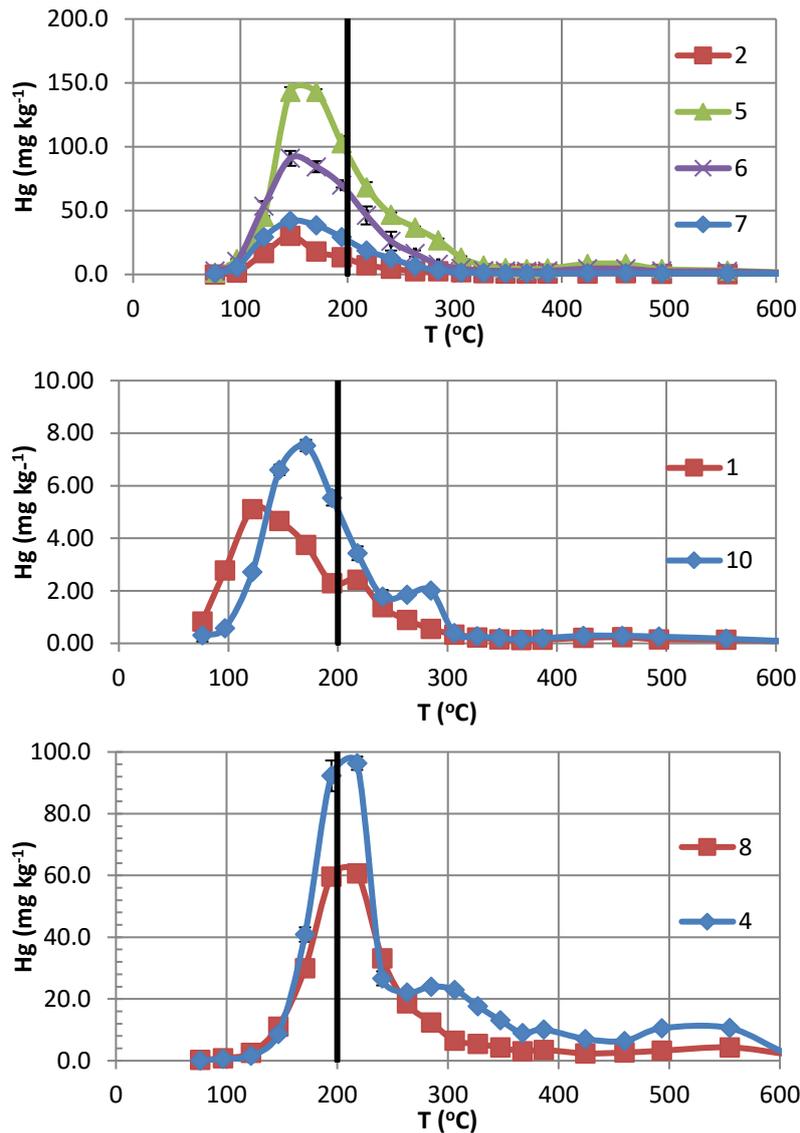
The sequential extraction results (Figure 3) indicated that over 75% of Hg species present were weakly bonded to the sediment. Specifically, between 75.9% of the total Hg content at location 5 (corresponding to  $429 \text{ mg kg}^{-1}$  of Hg) and 94.0% of the total content at location 7 ( $187 \text{ mg kg}^{-1}$  of Hg) was extracted in the first step (4 M  $\text{HNO}_3$ ). This fraction includes Hg species such as water soluble  $\text{HgCl}_2$ , weak acid soluble species and weakly bound organic

Hg species such as MeHg (Rahman and Kingston 2005). The majority of the remaining Hg was in non-mobile forms, with very little semi-mobile Hg present.



**Fig. 3** Total Hg concentration expressed as a sum of Hg in fractions in sediments of the Union Canal, Scotland, U.K. (mean  $\pm$  SD, n=3)

The TD results similarly indicated that the majority of Hg present was weakly bonded to the sediment. Desorption of >67% of Hg species in all samples occurred in the temperature range 100–250 °C coincident with HgFe and/or HgCl<sub>2</sub> TD curves. Samples 2, 5, 6 and 7 showed one major peak at approximately 160 °C consistent with HgFe and/or HgCl<sub>2</sub> but – in particular for samples 5 and 6 – with noticeable tailing into the temperature domain associated with HgHA (Figure 4). This is broadly consistent with the findings of the sequential extraction where samples 5 and 6 contained the highest proportions of Hg in forms released in later steps of the protocol. At sites 1 and 10 (the least contaminated sites) the speciation was similar though here there was a distinct second peak at a temperature consistent with one of the peaks observed for the HgHA standard (site 1) or with either HgHA or HgS (site 10) (Figure 4). In the TD curves for sediments from sites 4 and 8, the Hg release peaked at a higher temperature of around 200 °C (Figure 4).



**Fig. 4** Averaged thermal desorption curves for Hg in sediments from the Union Canal at locations 2,5,6,7 (upper), 1 and 10 (middle), 4 and 8 (lower)

This dominance of mobile, weakly associated Hg species in sediment is not common. Mobile species typically account for only a small proportion of the Hg content, with less mobile species strongly associated with S often the major forms (Oliveri et al. 2016; Beldowski and Pempkowiak 2003; Ram et al. 2009; Covelli et al. 2012; Frohne and Rinklebe 2013; Pinedo-Hernández et al. 2015; Garcia-Ordiales et al. 2018). The speciation of S is of course an important factor in such relationships (Liu et al. 2018). Only the reduced form is a strong Hg binder. Previous work in this study area (Cavoura et al. 2017) found no significant relationship between Hg and S content ( $r^2 = 0.140$ ,  $p > 0.05$ ). The fact that the sediment is present as a thin layer (<10 cm thick), typically overlain by <2 m of water, and frequently re-suspended by

passing boats, may mean that it is well-oxygenated with limited potential for the formation of reduced S species.

The nature of the dominant Hg species found in the current study cannot be determined with certainty. However, conclusions can be drawn about its likely identity. Sequential extraction indicates that the species is mobile, and the relatively low temperature at which it appears in the TD analysis is consistent with desorption mainly from the mineral matrix rather than association with OM (Biester et al. 1999). Such species could be  $\text{HgCl}_2$ , Hg associated with Fe, or another mineral-matrix bound Hg species released early in the extraction procedure and desorbed at a similar temperature to  $\text{HgCl}_2$  and  $\text{HgFe}$ . Due to its high solubility and stability in solution (Kim et al. 2004b),  $\text{HgCl}_2$  is not usually bound to sediment except in areas with high  $\text{HgCl}_2$  contamination for example from its use as a preservative in wood treatment (Bollen et al. 2008). While  $\text{HgO}$  would be released at the correct stage of the extraction, TD would occur at a higher temperature (Biester et al. 1999). Additionally,  $\text{HgO}$  is not widespread in the environment and is generally associated with mine tailings (Biester et al. 1999).

It is therefore suggested that the major form of Hg in Union Canal sediment is an Fe (hydr)oxide associated species. Extraction of such a species would occur in the first step of the sequential extraction scheme used (Rahman and Kingston 2005) and the dominant peak in the TD for the majority of samples occurred at a temperature consistent with the TD curve of the  $\text{HgFe}$  standard. Significant positive correlation between Hg concentration and Fe content has been previously reported in Union Canal sediments ( $r^2 = 0.670$ ,  $p < 0.05$ ) (Cavoura et al. 2017). Previous studies involving extended X-ray absorption fine structure (Kim et al. 2004a, 2004b) have confirmed that, in the absence of bonding with OM or reduced S species, adsorption of Hg to Fe (hydr)oxide surfaces can occur.

While mobile Hg species have been shown to be present, to what extent mobilization from the canal sediment in fact occurs depends on many factors. Zhu et al. (2018) recommended that changes in redox potential, Hg chemical speciation and the source and nature of OM all must be considered when assessing mobilization. Even following release from sediment, whether Hg will remain solvated, become associated with suspended particulate matter, or precipitate depends on numerous factors such as pH, composition and redox conditions of the water. However, some mobilization of Hg from contaminated sediment in the Union Canal (whether in solution or suspension) is strongly indicated by increased Hg levels in a connected waterway (Cavoura et al. 2017). Similarly, while mobility is used as an indicator of bioavailability, assimilation of Hg inside organisms depends not only on Hg speciation but also on physicochemical and physiological conditions. To assess whether biological uptake is occurring would require direct cellular analysis of relevant biota. In the

same way, any potential for biomagnification of Hg in the canal would require analysis of, for example, predatory fish.

## **Conclusions**

Sequential extraction followed by analysis of extracts by CVAAS and direct analysis by TDAAS both indicated that Hg in the sediment of the Union Canal in the vicinity of a former munitions factory was primarily in mobile forms, weakly associated with the mineral matrix. This unusually high mobility may be a consequence of limited association between Hg and OM or S. Results suggest that the dominant species present is Hg associated with iron (oxy)hydroxide. Shallow water depth and the fact that only a thin layer of sediment is present, which undergoes frequent re-suspension, may limit formation of the reduced S species usually responsible for binding the majority of Hg in sediment.

Further research to determine the redox status; Hg, Fe and S speciation; and the nature of OM present would be beneficial to improve understanding of the processes governing the binding of Hg in the canal sediment. Analysis of water and suspended sediment could help elucidate whether mobilization is taking place. Analysis of biota would be of interest to determine whether assimilation (potentially leading to the formation of methylmercury) and biomagnification are occurring and, if so, to what extent. Further studies are required to assess whether mobile Hg species are predominant in other shallow freshwater systems where limited sediment depth may preclude the formation of reduced binding sites.

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