



Mercury alkylation in freshwater sediments from Scottish canals



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HIGHLIGHTS

- High levels of Hg found in freshwater sediment from the Union Canal, Scotland, UK.
- Lower mercury concentrations in sediment from the Forth & Clyde Canal, Scotland, UK.
- Low methylmercury concentrations found in sediments from both canals.
- Significant inverse relationship between total Hg and %MeHg concentrations.
- Ethylmercury detected in sediment from the Union Canal.

GRAPHICAL ABSTRACT



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ABSTRACT

Mercury concentrations were investigated in freshwater sediment from two canals in Scotland, UK. High concentrations found in the Union Canal (35.3–1200 mg kg⁻¹) likely originate from historical munitions manufacture, with lower levels in the Forth & Clyde Canal (0.591–9.14 mg kg⁻¹). Concentrations of methylmercury (MeHg) were low – from 6.02 to 18.6 µg kg⁻¹ (0.001–0.023% of total Hg) in the Union Canal and from 3.44 to 14.1 µg kg⁻¹ (0.11–0.58% of total Hg) in the Forth & Clyde Canal – and there was a significant inverse relationship between total Hg concentration and %MeHg. Total Hg concentration was significantly negatively correlated with pH and positively correlated with Fe content (in the Union Canal only) but not with organic matter, S content or the proportion of clay present. The MeHg concentration was not correlated with any of the above sediment parameters. Ethylmercury was detected in the most highly contaminated sediments from the Union Canal.

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1. Introduction

In the aquatic environment sediments adsorb and store both inorganic Hg and MeHg. However, adsorption may not be permanent. Mercury can be released through the formation of soluble complexes with sulfide or organic matter (OM) (Merritt and

Amirbahman, 2007; Faganeli et al., 2003), or through the reduction of Fe^{III} and Mn^{IV} (oxy)hydroxide surfaces on which Hg species are adsorbed. The ease of Hg release from sediment varies depending on the species present, with inorganic Hg being released less readily than MeHg as a result of its stronger sorption. For example, Covelli et al. (1999) estimated that up to 25% of total sediment Hg content was released annually in sediments from the Gulf of Trieste, Italy, of which up to 23% could be in the form of MeHg.

Methylation is primarily an intracellular bacterial process, carried out mainly under anoxic conditions at the sediment-water interface where microbial activity is high, by certain species of sulfate- and iron-reducing bacteria (Compeau and Bartha, 1985; Fleming et al., 2006). It occurs only on dissolved inorganic Hg^{II} species since this is the form able to cross the cell membrane (Benoit et al., 1999; Mason et al., 1996). Bacteria either store the MeHg internally or excrete it into the water column. Potential exposure of other aquatic organisms to MeHg occurs mainly through direct uptake from sediment (Gagnon and Fisher, 1997) or the consumption of plankton by higher trophic level feeders. Bioaccumulation of MeHg increases with increasing trophic level (Mason et al., 1996; Watras et al., 1998; Campbell et al., 2005; Leopold et al., 2009). Consumption of high trophic-feeder fish is the main source of human exposure to Hg, with adverse neurological effects possible both in humans and the developing foetus above a reference dose of 0.1 µg kg⁻¹ body weight day⁻¹ (EPA, 2001).

The overall degree of Hg methylation is dependent not just on the rate of production but rather on the balance between rates of methylation and demethylation. Photodegradation is known to break down MeHg species (Sellers et al., 1996), as are two biotic processes: reductive demethylation and oxidative demethylation (Schaefer et al., 2004). Reductive demethylation is mediated by Hg-resistant bacteria as part of their mercury resistance (*mer*) system in both aerobic and anaerobic environments (Merritt and Amirbahman, 2009; Barkay et al., 2003). In the presence of Hg, these bacteria express *mer* genes that encode for enzymes to degrade MeHg to Hg⁰ which may then be lost to the atmosphere (Barkay et al., 2003). Oxidative demethylation, which is also carried out by both aerobic and anaerobic bacteria, is not considered a detoxification process since Hg^{II} is formed, which is still available to bacteria (Hintelmann, 2010).

Typically, the proportion of the total Hg content in sediment that is methylated (%MeHg) is around 0.5% (Hines et al., 2000; Zelewski et al., 2001). Lower %MeHg has been observed in freshwater with higher total Hg concentration (Schaefer et al., 2004). A decrease in net methylation may be a result of lower microbial activity at high Hg concentrations (Ullrich et al., 2001). It has also been proposed (Schaefer et al., 2004) that, in more contaminated environments, mercury-resistance (*mer*) genes are expressed which regulate reductive demethylation, while lower levels of Hg are insufficient to effectively induce expression of these genes. In addition to Hg content, sediment parameters such as the presence of OM; sulfur and iron content and speciation; pH, redox potential and texture all influence methylation (Frohne and Rinklebe, 2013; Frohne et al., 2012; Ullrich et al., 2001). Due to its affinity for sulfur, Hg^{II} in sediment can bind to reduced S groups in OM, limiting its mobility and potential for methylation (Ravichandran, 2004). However, OM can also stimulate microbial activity and, as a consequence, MeHg production (Drott et al., 2007). The ratio between dissolved organic carbon (DOC) and total dissolved Hg concentration has been shown (Frohne et al., 2012) to be a critical parameter influencing net Hg methylation in contaminated flood-plain soils. Sulfide concentration also affects Hg methylation rates. While sulfate-reducing bacteria promote methylation, sulfides, produced from sulfate reduction, inhibit methylation due to the

formation of insoluble HgS or soluble charged sulfide complexes such as HgS₂²⁻ and HgHS₂⁻ that cannot cross the cell membrane (Devai et al., 2005; Benoit et al., 1999). The influence of iron on methylation is also variable: while ferric iron is a substrate for iron-reducing bacteria and may enhance methylation, iron may also limit Hg solubility and availability through the formation of iron-Hg complexes (Behra et al., 2001; Jeong et al., 2007). Sediment pH affects mercury speciation and particle surface charge (Sarkar et al., 1999) thus indirectly affecting Hg adsorption, bioavailability and consequently methylation. Similarly, variations in redox potential may indirectly influence methylation by affecting OM and sulfur and iron speciation and hence the adsorption and release of Hg species (Frohne et al., 2012). Further discussion of factors affecting Hg methylation can be found in Frohne et al. (2012).

The Forth & Clyde Canal runs from Bowling on the River Clyde, Scotland, UK, through Falkirk, to Grangemouth on the Firth of Forth, whilst the Union Canal runs from Falkirk to Edinburgh (Fig. 1). Originally opened in 1790 and 1824, respectively, both canals were major routes for transport of goods before competition from the railways, beginning in the 1840's, led to their gradual decline and eventual closure in the 1960's (Haynes, 2015).

Substantial redevelopment and regeneration carried out under the Millennium Link Project saw both canals reopened as major leisure facilities in 2001–2002 and connected through a rotating boat lift, the Falkirk Wheel (Fig. 1). However, Central Scotland was formerly a major hub for heavy industry and 'legacy pollution' from this period is a major concern in the area. In particular, the Union Canal has a history of Hg contamination arising from proximity to a munitions factory that manufactured detonators from 1876 to 1968, the main constituent of which was mercury fulminate (Smith and Lassi re, 2000). Despite dredging from the most contaminated section of the waterway and soil remediation on the former factory grounds carried out between 2000 and 2006, very high levels of Hg contamination still persist in the canal sediment (Cavoura et al., 2013).

This study investigated Hg concentrations and speciation in sediments from the Forth & Clyde Canal, and the Union Canal. Relationships between Hg, MeHg, OM, S and Fe content, sediment pH and texture were explored to gain insight into the factors affecting the distribution and fate of Hg species in freshwater systems.

2. Materials and methods

2.1. Sampling locations and method

Sampling points 1–10 were on the Union Canal between Falkirk and Polmont, sampling points 12–14 were on the Glasgow branch of the Forth & Clyde Canal and sampling points 15–20 were between Kirkintilloch and Falkirk on the Forth & Clyde Canal (Fig. 1). The former munitions factory was located on both banks of the canal at site 7.

Sediment samples were collected by throwing a stainless-steel bucket attached to a rope across the width of the canal and slowly pulling it back along the canal bottom. This unconventional sampling method was adopted for several reasons. First, the canals are historic monuments and use of more conventional methods – grab samplers or corers – was not possible due to the risk of damaging the clay liner at the bottom of the canal. Second, the sediment layer is typically 10 cm in depth (overlain by ca. 2 m of water) and frequently re-suspended by passing boats. There is no long-term stratification or redox front present and so obtaining the entire sediment 'column' (as demonstrated by the presence of a minimal amount of clay liner on the lower edge of the bucket) was considered the most representative and reproducible sampling

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