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Temporal and spatial distributions of sediment mercury in restored coastal saltmarshes

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ABSTRACT

Saltmarsh restoration, through de-embankment, is implemented across Europe and North America with the aims of restoring habitat, sustainably protecting coastlines, and improving water quality. Yet, there is very little understanding of the effects of de-embankment on sediment physico-chemical characteristics and how these characteristics may influence the behaviour of redox-sensitive contaminant metals such as mercury (Hg). The overall aim of this study was to provide baseline data on Hg biogeochemistry in restored coastal saltmarshes and in particular: 1) to assess the spatial variability of sediment total mercury (THg) and methylmercury (MeHg) concentrations over three spatial scales, 2) to examine the association between Hg speciation and indicators of saltmarsh development (loss on ignition, sediment bulk density and moisture content) and 3) to explore how these sediment characteristics and Hg biogeochemistry change with time following de-embankment and hence saltmarsh development.

Total Hg and MeHg concentrations at all sites are moderate to high and THg variation is controlled by proximity to external Hg sources. MeHg concentrations and physico-chemical sediment characteristics are variable at different spatial scales in natural and restored sites. MeHg concentrations and physico-chemical parameters varied predominantly at the intermediate (~15–50 m) spatial scale in natural saltmarshes, whilst restored sites were less heterogeneous indicative of lower habitat and topographic heterogeneity suggesting that physico-chemical sediment characteristics exert a strong control on Hg methylation.

In restored sites, physico-chemical sediment characteristics and MeHg concentrations reflect saltmarsh development and MeHg concentrations increase with time following de-embankment. In the first few decades following de-embankment previous land-use has a significant impact on physical sediment characteristics and MeHg concentrations are lower in restored saltmarshes probably due to poor drainage and/or limited vegetation development. However, with time both physico-chemical characteristics and MeHg concentrations in the restored and natural sites converge, suggesting that it may take decades or even centuries before restored sites have similar physical and biogeochemical conditions to their natural counterparts.

1. Introduction

Saltmarshes are wetlands uniquely positioned at the land–sea interface (Craft et al., 2008) and though they occupy only 4% of the Earth's total land area, they have been valued at $15 trillion per year (Millennium Ecosystem Assessment, 2005). Historically many saltmarshes were embanked to prevent tidal inundation and drained for agriculture resulting in the loss of this important wetland habitat, whilst more recently they have been threatened by sea-level rise, as well as other aspects of climate change, changing land use and water quality deterioration (Kennish, 2002; Craft et al., 2008; FitzGerald et al., 2008). Restoration of these saltmarshes through de-embankment is increasingly being implemented within Europe and North America, predominantly driven by legislation to protect and recreate habitat, sustainably defend coastlines, and improve water quality (European Parliament and the Council of the European Union, 1992, 2009; National Research Council, 2001). De-embankment, also known as managed realignment or managed retreat, involves deliberately breaching an existing line of coastal defence to allow the tidal inundation of previously protected land (Blackwell et al., 2004; Andrews et al., 2006; Spencer et al., 2008). The restored saltmarshes have the potential to provide a range of ecosystem services including improvements to surface water quality through nutrient and pollutant uptake (Millennium Ecosystem Assessment, 2005). Yet there is poor understanding of biogeochemical processes in estuarine and coastal ecosystems compared with those in terrestrial and freshwater environments (Hammerschmidt et al., 2004; Sunderland et al., 2006; Mitchell and Gilmour, 2008) and there

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is even less understanding of biogeochemical processes in restored sites (Spencer and Harvey, 2012).

Saltmarsh restoration leads to a series of physical changes that may impact sediment biogeochemistry. Prior to restoration, the marsh elevation is low in comparison with the surrounding area. The sediment has higher bulk density and moisture content and lower organic matter content compared with sediment in natural saltmarshes (French, 2006) because of legacy effects of past land-use, agriculture and drainage, including compaction, carbon mineralisation and dewatering (Wolters et al., 2005) resulting in poorly drained sediments. Therefore, de-embankment and saline inundation can create waterlogged and anoxic sediments, which in turn can promote the development of reducing conditions and increased salinity and pH. These changes in sediment conditions can alter the mobility of contaminant metals (Emmerson et al., 2001; Speelmans et al., 2010; Teuchies et al., 2013). As sediment accumulates and the surface elevation increases within the tidal frame, drainage improves and saltmarsh plants will colonise (Garbutt and Wolters, 2008). However, restored saltmarshes have less topographic and microhabitat heterogeneity (Elsey-Quirk et al., 2009) and their vegetation is not equivalent to their natural counterparts (Garbutt and Wolters, 2008; Mossman et al., 2012).

Many coastal wetlands store Hg from past anthropogenic activity and atmospheric input due to their fine-grained and organic-rich sediments (Ullrich et al., 2001; Spencer et al., 2006). Wetlands can also be an important source of indirect Hg emissions and the formation of volatile Hg species can be on the same order of magnitude as industrial emissions (Wallschläger et al., 2000), whilst a large seasonal source of atmospheric Hg could come from agricultural land during tillage of embanked sites (Bash and Miller, 2007). A return to tidal inundation, cycles of wetting and drying, physical sediment reworking, and anoxia may all remobilise this legacy Hg, enhancing bioavailability and impacting biota (Marvin-DiPasquale and Cox, 2007). Yet, there is little understanding of how the restoration of these wetlands could impact Hg and its speciation.

Inorganic divalent mercury, Hg[II], is delivered to the saltmarsh surface via tidal inundation and/or atmospheric deposition where it is either reduced to Hg^0 or scavenged and buried with sediment. Consequently total Hg (THg) sediment concentrations are frequently elevated at depth reflecting past air and water quality, although profiles can vary significantly depending on sedimentation rates and post-depositional physical and chemical reworking (e.g. Hammerschmidt et al., 2004; Mitchell and Gilmour, 2008). In anaerobic sediments, Hg [II] is methylated in situ to methylmercury (MeHg), a potent neurotoxin (Compeau and Bartha, 1985; Bloom, 1992), by sulphate-reducing bacteria (SRB) (Benoit et al., 1999; Fitzgerald et al., 2007). MeHg has greater spatial, seasonal and vertical variability than THg in sediments (Choe et al., 2004) and methylation rates are often greatest at the anoxic/oxic boundary, usually within a few centimetres of the surface in saltmarsh sediments decreasing with depth (Fitzgerald et al., 2007; Choe et al., 2004). Bioturbation can increase Hg methylation at depth by removing toxic by-products of microbial respiration (e.g. S^{2-}) as well as providing labile organic substrates (Hammerschmidt et al., 2004). MeHg spatial variability is also controlled by vegetation with plants promoting SO_4^{2-} cycling (Yee et al., 2005) and exuding labile organic carbon in the rhizosphere which stimulates microbial activity and hence methylation (Windham-Myers et al., 2009).

Coastal wetlands can show high rates of methylmercury production (Krabbenhoft et al., 1999; Lacerda and Fitzgerald, 2001; Marvin-DiPasquale et al., 2003; Heim et al., 2007; Hall et al., 2008; Mitchell and Gilmour, 2008). Microbial Hg methylation could be promoted in restoration sites following de-embankment for the following reasons; 1) SRB thrive in anoxic sediments, 2) there will be an expansion of the root:soil interface (rhizosphere) and 3) fluctuations in redox conditions caused by wetting and drying during tidal cycles will cause the re-oxidation of sulphide and production of sulphate and increase carbon availability. Therefore, restoration sites could produce Hg methylation 'hotspots' (French, 2006; Hall et al., 2008). In contrast, sulphide, an end-product from sulphate reduction, can severely inhibit Hg methylation (Compeau and Bartha, 1984; Benoit et al., 1999, 2001) at concentrations higher than ~30 μM (Craig and Moreton, 1983; Morel et al., 1998) and in poorly drained sediments, such as those found in the early stages of de-embankment, sulphide may limit Hg methylation. Therefore, the implications of restoration on Hg methylation are uncertain. In addition, the zone of Hg methylation can vary by an order of magnitude depending on specific site characteristics (Choe et al., 2004; Bloom et al., 1999) and in these sites where physico-chemical sediment characteristics may vary significantly with depth, rates, patterns and controls on Hg methylation are unclear.

The overall aim of this paper is to provide baseline data on Hg biogeochemistry in restored coastal wetlands. The first objective is to assess the spatial variability of THg and MeHg concentrations in natural and de-embanked saltmarsh sediment over a range of spatial scales. It is hypothesised that THg and MeHg concentrations will show less variation at within-site scales (1 m to 50 m) in restored wetlands than in natural saltmarshes, because physical and biological factors (e.g., vegetation, topography) that indirectly influence Hg biogeochemistry are more spatially homogeneous in restored sites. The second objective is to examine the association between Hg speciation and indicators of saltmarsh development. It is hypothesised that THg concentrations will increase with % LOI because of the association between Hg and organic matter; MeHg concentrations will increase with THg concentration; and the proportion of MeHg as THg (% MeHg) will increase with moisture content because increased moisture content is indicative of anoxic sediments, conditions known to promote Hg methylation. The final objective is to explore how changes in these physico-chemical conditions and Hg biogeochemistry have changed with time since de-embankment and hence ecosystem development. It is hypothesised that recently-restored sites will have higher bulk density and lower LOI and moisture content than natural sites, but these properties will become more similar to those in natural sites with increasing time since de-embankment. It is expected that MeHg concentrations will be highest in recently-restored sites and decrease with time since de-embankment, as the sites drain and become less waterlogged and anoxic.

2. Methods

Sediment concentrations of THg and MeHg, as well as physical sediment properties indicative of saltmarsh development, were examined at three spatial scales (small scale, 1 m; intermediate, c. 15–50 m; and large scale, c. 15 km) across three paired de-embankment sites and adjacent natural saltmarshes in southeast England (Fig. 1). Orplands Farm (on the Blackwater Estuary) was artificially de-embanked through managed realignment in 1995, whereas Ferry Lane (Colne Estuary) and Northey Island (Blackwater Estuary) were inadvertently de-embanked in 1945 and 1897 respectively, during storm surges resulting in tidal inundation (Mossman et al., 2012). These three restored sites are therefore on a temporal gradient of 17 (Orplands), 67 (Ferry Lane) and 115 (Northey Island) years since inundation. Areas of natural saltmarsh occur adjacent to all three restored wetlands. Both restored and natural wetlands contain typical saltmarsh vegetation, although species richness, composition and structure differ (see Garbutt and Wolters, 2008 for full vegetation description). All three restored wetlands were previously used for agriculture, although practices would have differed significantly given the differences in age.

2.1. Field sampling

De-embanked and adjacent natural saltmarshes were sampled (six wetlands in total) in October 2012, with the natural saltmarshes serving as a control for between-site differences unrelated to time since breach. Samples were collected from vegetated saltmarsh in a hierarchical