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Tom Sizmur[a*], Adam Godfrey[a] and Nelson J. O'Driscoll[a]

[a]Department of Earth & Environmental Science, K.C. Irving Environmental Science Center, Acadia University, Wolfville, NS, B4P 2R6, Canada.

*Corresponding author

Present address: Soil Research Centre, Department of Geography and Environmental Science, Russell Building, University of Reading, Reading, RG6 6DW, UK

E-mail: t.sizmur@reading.ac.uk

Phone: +44(0)118 3788913

Abstract

We investigated the impact of managed retreat on mercury (Hg) biogeochemistry at a site subject to diffuse contamination with Hg. We collected sediment cores from an area of land behind a dyke one year before and one year after it was intentionally breached. These sediments were compared to those of an adjacent mudflat and a salt marsh. The concentration of total mercury (THg) in the sediment doubled after the dyke was breached due to the deposition of fresh sediment that had a smaller particle size, and higher pH. The concentration of methylmercury (MeHg) was 27% lower in the sediments after the dyke was breached. We conclude that coastal flooding during managed retreat of coastal flood defences at this site has not increased the risk of Hg methylation or bioavailability during the first year. As the sediment becomes vegetated, increased activity of Hg-methylating bacteria may accelerate Hg-methylation rate.

Keywords: Mercury, Methylmercury, Biogeochemistry, Sediment deposition, Coastal

Capsule: Mercury concentration doubled in sediments after coastal flooding but methylmercury concentration deceased

Introduction

Coastal wetlands have been subject to dramatic global declines in the past due to dyking and draining for agriculture. However, this practice is now being reversed in many countries because salt marshes are valued as habitats for wildlife and as natural defence against rising sea-levels (Singh et al., 2007). Managed retreat of coastal defences has led to an increase in the number of sites where dykes are breached, agricultural fields are inundated with seawater, sediment is deposited over soils, and new salt marshes are created. Inundation of previously dyked farmland leads to considerable biogeochemical changes, characterised by increased salinity, lower redox potential (Portnoy and Giblin, 1997) and a decaying mat of buried vegetation (Emmerson et al., 2000). There is concern that biogeochemical changes during managed retreat may alter the fate of redox-sensitive contaminants such as mercury (Hg) (Morris et al., 2014).

The Bay of Fundy in Southeastern Canada is renowned for having the largest tidal amplitude in the world, which gives rise to expansive intertidal mudflats and vast areas of salt marsh (Crowell et al., 2011; Desplanque and Mossman, 2004). For centuries the Bay's coastline has been extensively dyked to use the land for agriculture (Wynn, 1979). The land surrounding the Bay of Fundy is designated a ‘biological mercury hotspot’ due to elevated concentrations of Hg in biota (Evers et al., 2007). The Bay of Fundy itself has been identified as an area of special concern for Hg contamination because the Bay’s ecosystem may be critical to concentrations of Hg found in fish, birds and wildlife (Hung and Chmura, 2006).

Mercury enters the Bay of Fundy through seawater inflow and atmospheric deposition (Sunderland et al., 2012). The Hg present in sediments of the Bay of Fundy is strongly associated with organic matter and fine textured sediments (O'Driscoll et al., 2011; Sizmur et al., 2013b). Inorganic Hg in sediments can be converted to methylmercury (MeHg) under anoxic conditions by sulphate-reducing bacteria (Compeau and Bartha, 1985). Methylmercury can biomagnify through food webs (Lavoie et al., 2010) and is a potent neurotoxin affecting higher trophic level animals and humans (Rasmussen et al., 2005).

Increases in MeHg concentrations in sediments and biota have been observed during the decades that follow terrestrial freshwater flooding for dam construction or wetland creation (Kelly et al., 1997; Sinclair et al., 2012). However, little research has been done to assess changes in Hg biogeochemistry after coastal wetland flooding. Terrestrial flooding events, like reservoir or wetland creation, entail a permanent change in sediment redox from oxic to anoxic conditions because the sediments are constantly flooded. However, coastal flooding events subject the land to fluctuating oxic/anoxic conditions due to the tidal cycle. These fluctuations generate an oxic-anoxic interface in the sediment. The temporal fluctuations in redox conditions increases the volume of sediment where sulphate reduction and mercury methylation may occur (Heim et al., 2007; Sizmur et al., 2013a). However, there is also frequent tidal flushing of inundated areas which acts as a significant means of removing MeHg from the surface of coastal sediments (Guédron et al., 2012). Therefore, it is not clear if managed retreat will increase or decrease Hg and MeHg concentrations in sediments.

We investigated the effects of managed retreat on mercury biogeochemistry at Beaubassin Research Station where a dyke has recently been breached, allowing the seawater to inundate land previously drained for agriculture.

Materials and Methods

Site Description

Beaubassin Research Station (Latitude: 45.852195 Longitude: -64.279631) is located on the Chignecto Isthmus between Nova Scotia and New Brunswick, Canada (Figure 1a). It lies along the Cumberland Basin, a branch of Chignecto Bay, in the Bay of Fundy which is sourced from the Gulf of Maine. The average tidal amplitude at Beaubassin is 11 m (Gordon Jr and Baretta, 1982). Recently, an eroding 150-year-old dyke was replaced with a new dyke built approximately 90 m back from the pre-existing coastline in order to protect transport infrastructure and the historic site of Fort Beausejour from tidal surges. The 40 ha of low lying land between the old dyke and the new dyke (Latitude: 45.851595 Longitude: -64.294379) was flooded in October 2010. Flooding occurred when the old dyke was deliberately breached so that sediment could accumulate to protect the new dyke before the old dyke completely failed (Ollerhead et al., 2011). Tidal re-entry has resulted in the rapid deposition of fresh sediment over the top of the agricultural soil, burying a mat of terrestrial vegetation. At the time of sampling, new salt marsh vegetation was yet to establish.

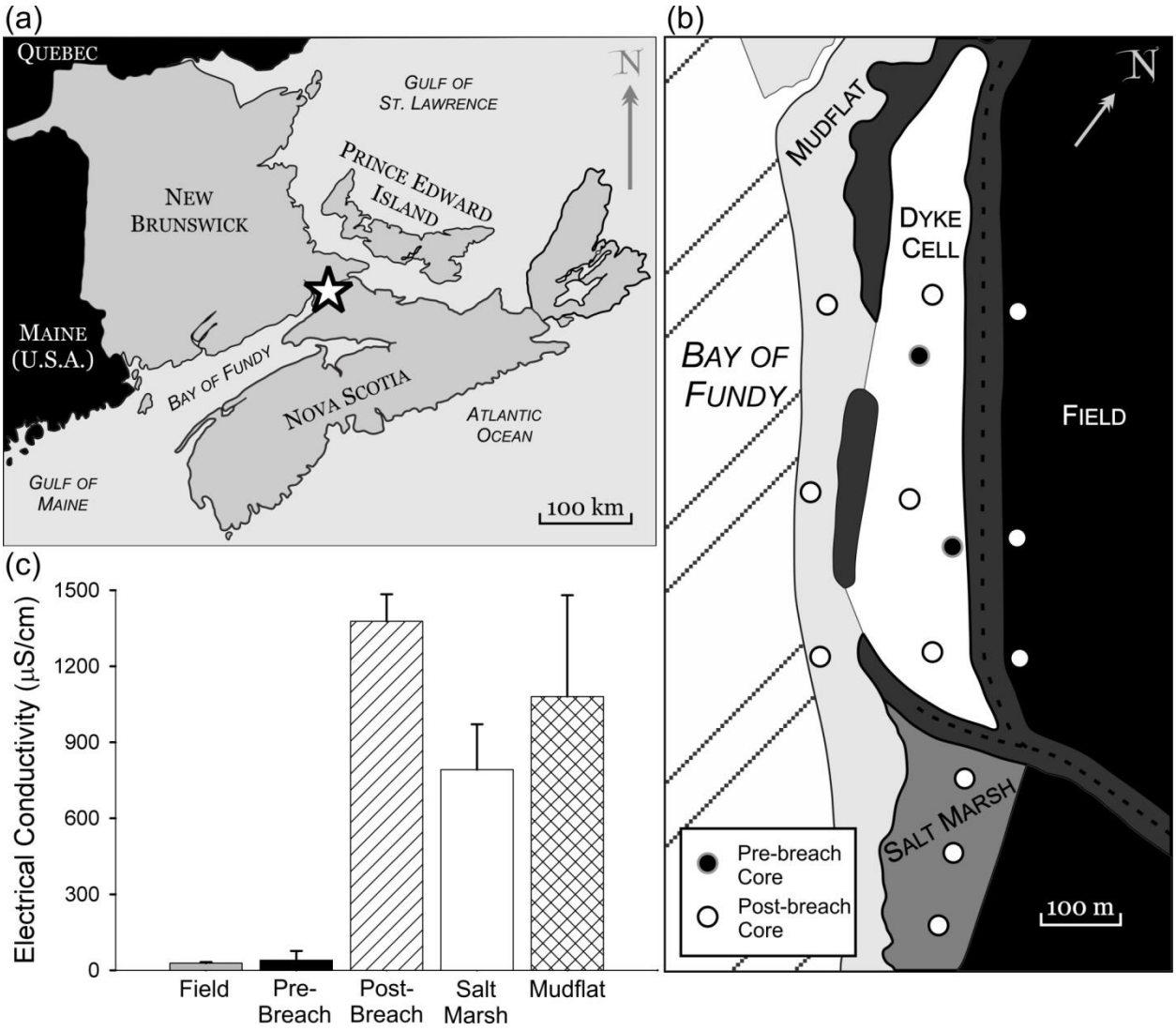

Figure 1. (a) Site location at Beaubassin, New Brunswick, Canada; (b) Location of all cores sampled from the dyke cell (pre-breach and post-breach) along with adjacent sites (mudflat, salt marsh and field). The location of two gaps in the wall of the dyke cell represent where they were deliberately breached in 2010; (c) Electrical conductivity of sediment cores sampled (averaged 0-15 cm) shown here to demonstrate the influence of seawater on the dyke cell pre-breach and post-breach.

Sample Collection and Preparation

Two 16 cm deep cores were taken in the dyke cell (Figure 1b) between the new and the old dykes (hereafter referred to as the pre-breach cores) in summer 2009 (before the old dyke was breached in 2010). We returned to the site in summer 2011 to collect cores one year after the old dyke was breached. Three 15 cm deep cores were sampled at four locations: (i) The area previously sampled in the dyke cell between the new and old dykes (hereafter referred to as the post-breach cores), (ii) the mudflat seaward of the dyke cell, (iii) a pre-existing salt marsh adjacent to the dyke cell, and (iv) the field landward of the dyke cell (Figure 1b). All cores were sampled at low tide using polyvinyl chloride (PVC) cores (10 cm internal diameter) that were dug out with a stainless steel spade.

Pre-breach cores were sliced in 2 cm intervals to a depth of 16 cm, producing a total of eight slices per core. Each of the post-breach, mudflat, salt marsh, and field cores were sliced at 1 cm intervals for the upper 5 cm of sediment and then at 2 cm intervals for the remaining 10 cm, producing a total of 10 core slices per core. Core slices were individually sealed in Ziploc bags at the research station and placed in a dark cooler with ice packs for transport back to the laboratory.

At the laboratory each sediment slice was thoroughly homogenised by hand in the Ziploc bag and frozen as a wet homogenate at -20 ˚C. Sediment samples were later thawed and a subsample dried at 60 ^{o}C for 24 hours. Dried sediment samples were ground with a pestle and mortar and sieved to < 2 mm. A subsample of wet sediment was analysed for electrical conductivity (EC)

using a VWR Symphony SP90M5 meter and Orion electrical conductivity probe. The field was only sampled to demonstrate that the pre-breach sediments had not been inundated by seawater prior to the breach. Since the EC of the pre-breach and field cores (Figure 1c) revealed no significant difference ($p > 0.05$), further analysis of the field cores was deemed unnecessary. Each slice of the remaining cores was analysed for total mercury (THg), MeHg, percentage organic matter (%OM), particle size distribution, water-extractable organic carbon (WEOC) and pH.

Analytical Procedures

Total mercury in sediment was determined using thermal degradation – gold amalgamation atomic absorbance spectroscopy as outlined in EPA Method 7473 (1998) using a Nippon MA-2000 non-dispersive double-beam cold-vapor atomic absorption Hg analyzer. Methylmercury was determined in sediments by alkaline digestion, ethylation purge and trap Gas Chromatography - Cold Vapour Atomic Fluorescence Spectrometry (GC-CVAFS) following Sizmur et al (2013b). A 100 mg sample of sediment was digested in 2.5 ml of basic methanol (25 % KOH/MeOH) by shaking on a reciprocal shaker for 1 hour and then heating for 1 hour at 90 ^{o}C. Within 24 hours of digestion, a 60 µl aliquot was transferred to a glass reaction bubbler, ethylated with $NaB(C_2H_5)_4$, purged with argon, collected on a Tenax trap and analysed for MeHg using GC-AFS (Brooks Rand Model III).

Organic matter in sediment was determined by loss on ignition at 500 ^{o}C (Byers et al., 1978) and particle size distribution by the micro-pipette method (Miller and Miller, 1987). Sand was

142 calculated as particles 2000-63 µm, silt as 63-2 µm, and clay as < 2 µm in diameter. Water-
143 extractable organic carbon was determined following Sizmur et al (2011) by shaking 1 g of
144 sediment with 40 ml of Milli Q water for 2 hours on a reciprocal shaker at 120 shakes min^{-1},
145 followed by centrifuging at 4000 rpm (2647 G) for 20 min and filtering to < 0.45 µm with
146 polypropylene membrane filters, before TOC/TIC analysis with a Shimadzu TOC-V CPH Total
147 Organic Carbon Analyzer. Sediment pH was analysed in WEOC vials prior to centrifuging.

148

149 *Quality control*

150 Sediments were analysed in triplicate alongside certified reference materials MESS-3 (National
151 Research Council Canada) and SQC-1238 (Sigma Aldrich RTC) for THg and MeHg
152 respectively. Mean recovery of THg from MESS-3 was 102.2 % (SD = 1.4 %). Mean recovery of
153 MeHg from SQC-1238 was 94.4 % (SD = 12.0 %). Detection limits for MeHg and THg were
154 0.65 and 1.21 pmol g^{-1}, respectively. Both samples and reference materials during Hg analysis
155 were corrected for background by subtracting averaged method blanks from the analysed
156 samples.

157 *Statistical Analysis*

158 Statistical analysis was carried out using Genstat version 16. Normality and homoscedasticity
159 was assessed by inspecting residual plots. Two-way analysis of variance was carried out on all
160 data (MeHg, THg, pH, clay, %OM, WEOC and EC) using 'site' and 'depth' as the factors and
161 allowing for interactions. Fisher's least significant difference was used to identify differences
162 between individual treatments. Multiple linear regression was carried out by forward selection;
163 first the variable that resulted in the highest R^2 values was included in the model, then variables

that resulted in the greatest increase were added. Data presented in text as average values at each site are calculated from the concentrations in cores averaged across all depths. All the raw data is provided in the supporting information.

Results

Mercury and Methylmercury

The average concentration of THg in the post-breach cores was 85.1 pmol g^{-1} (SD = 15.6) which was approximately double the concentration in the pre-breach cores (41.1 pmol g^{-1}, SD = 9.52). THg decreased significantly ($p < 0.001$) with depth (Table 1) in the post-breach and mudflat cores but this decrease was not observed in the pre-breach or the salt marsh cores (Figure 2). The THg concentration in the salt marsh cores was significantly ($p < 0.05$) greater than the mudflat or the dyke cell pre- or post-breach. The post-breach cores had significantly ($p < 0.05$) greater Hg concentrations than the pre-breach cores.

Table 1 Analysis of variance from physiochemical sediment variables; Water Extractable Organic Carbon (WEOC), pH, Electrical Conductivity (EC), Clay content and Organic Matter (OM).

Variable	Site F value	Depth F value	Site-depth interaction F value
THg	62.19***	2.34*	0.41
MeHg	12.83***	2.06*	0.55
% MeHg	31.41***	0.95*	0.62
% OM	15.03***	0.29	0.93
pH	16.87***	0.97*	0.79
% Clay	24.93***	1.74	0.38
WEOC	32.14***	1.68	1.36
EC	69.15***	0.82	1.23

* = $p < 0.05$, *** = $p < 0.001$

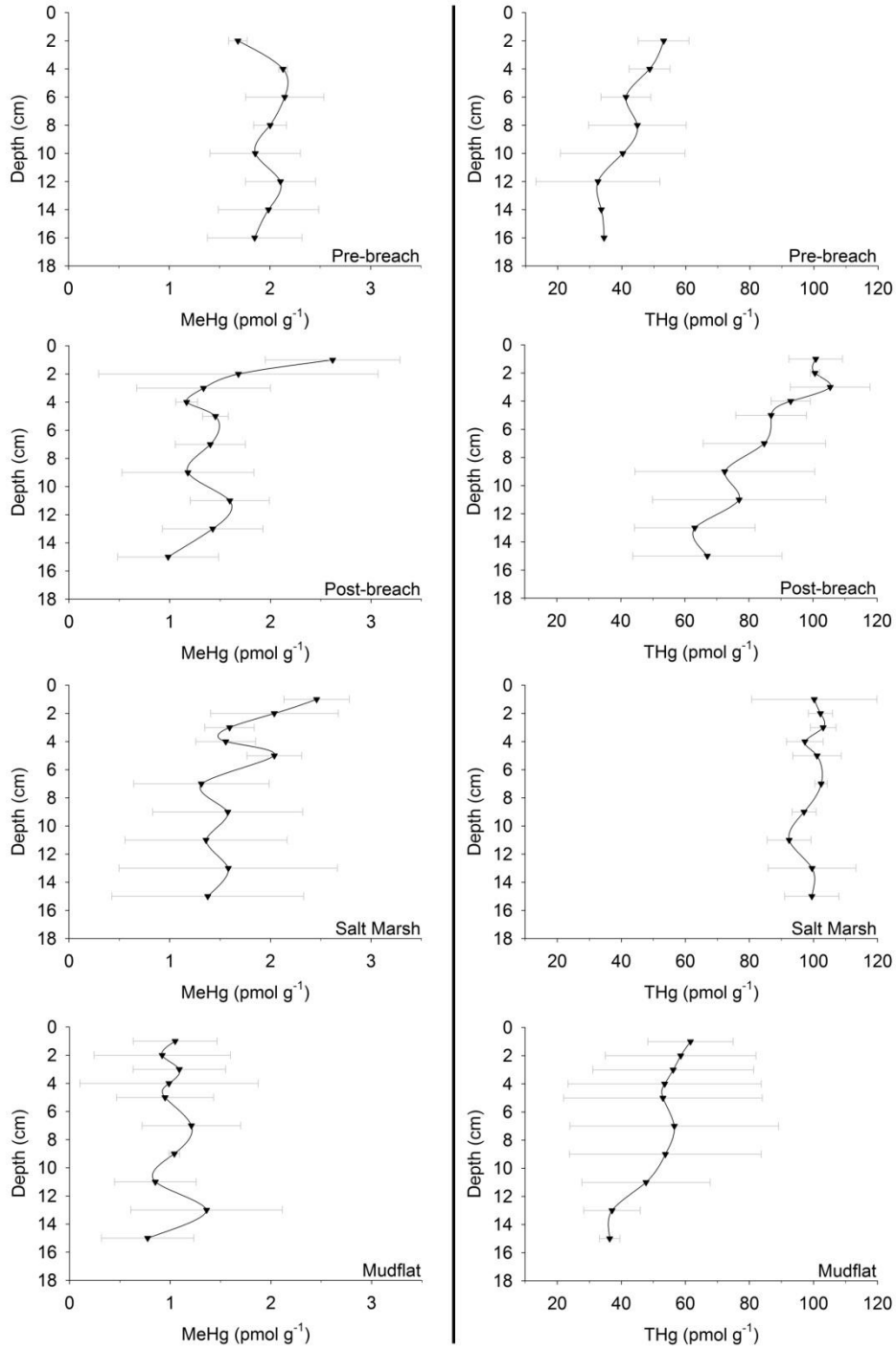

Figure 2. Total mercury (THg) and methylmercury (MeHg) concentrations of sediment slices of cores sampled from the dyke cell (pre-breach and post-breach) along with adjacent sites (mudflat and salt marsh). The error bars represent the standard deviation of three replicate cores (n = 2 for the pre-breach cores).

MeHg significantly ($p < 0.05$) decreased with depth (Table 1) in the post-breach and salt marsh cores (Figure 2). Although THg was greater after inundation, MeHg concentration was significantly ($p < 0.05$) lower in post-breach sediments (Figure 2). Methylmercury concentrations were 27% lower in the post-breach cores (1.48 pmol g^{-1}, SD = 0.54) compared to the pre-breach cores (1.97 pmol g^{-1}, SD = 0.31). However, we did measure 36% higher MeHg concentrations in the upper 2 cm of the post-breach sediment than in the top 2 cm of the pre-breach cores (Figure 2). The post-breach MeHg concentration was not significantly ($p > 0.05$) different than that measured in the salt marsh (1.69 pmol g^{-1}, SD = 0.60) but was significantly ($p > 0.05$) greater than MeHg in the mudflat (1.02 pmol g^{-1}, SD = 0.51). The percentage of MeHg as a proportion of the THg (%MeHg) was significantly ($p < 0.05$) greater in the pre-breach cores (5.97%, SD = 2.99) than the post-breach cores (2.02%, SD = 0.58). %MeHg in the post-breach sediment was not significantly ($p > 0.05$) different from the mudflat (2.34%) or salt marsh (1.84%) sediments.

Physiochemical variables

The EC of the pre-breach cores was not significantly different to the samples taken from the field behind the new dyke. EC was significantly increased ($p < 0.05$) by periodic tidal inundation of the dyke cell, increasing over 2000% from pre- to post-breach (Figure 1c). Post-breach sediment EC was also significantly ($p < 0.05$) greater than the salt marsh and mudflat but the magnitude of the difference was much smaller.

Sediment pH was significantly ($p < 0.001$) greater after inundation of the dyke cell, rising from 5. 08 (SD = 1.2) in the pre-breach cores to 7.43 (SD = 0.6) in the post-breach cores (Figure 3).

209 There was no significant ($p > 0.05$) pH difference between the post-breach cores and the salt
210 marsh or mudflat cores.

211

212 The texture of the sediment in the top 15 cm of the dyke cell significantly ($p < 0.001$) changed
213 during salt marsh restoration as fresh sediment with a smaller particle size distribution was
214 deposited over the top of the drained agricultural field (Figure 3). Percentage clay was
215 significantly ($p < 0.05$) greater and sand significantly ($p < 0.05$) lower in the sediment after the
216 inundation. Percentage clay in the post-breach cores (29.8%, SD = 1.52) was nearly double that
217 in the pre-breach cores (16.6%, SD = 13.8). The proportions of sand, silt and clay in the post-
218 breach cores were not significantly ($p > 0.05$) different to the sediments sampled from the
219 mudflat (Figure 3) but clay content was significantly ($p < 0.05$) greater than sediments sampled
220 from the salt marsh.

221

222 The post-breach sediments had significantly ($p < 0.05$) higher organic matter (%OM) and WEOC
223 than the pre-breach cores (Table 1 and Figure 3). There was no significant ($p > 0.05$) difference
224 between the post-breach cores and the salt marsh and mudflat cores, for either %OM or WEOC.
225 The concentration of both WEOC (44.9 mmol kg^{-1}, SD = 4.64) and %OM (6.3%, SD = 0.8) in
226 the post-breach cores was greater than the mudflat cores (32.1 mmol kg^{-1}, SD = 8.87 and 5.8%,
227 SD = 1.2) but lower than the salt marsh cores (47.9mmol kg^{-1}, SD = 7.17 and 6.7%, SD = 0.7).

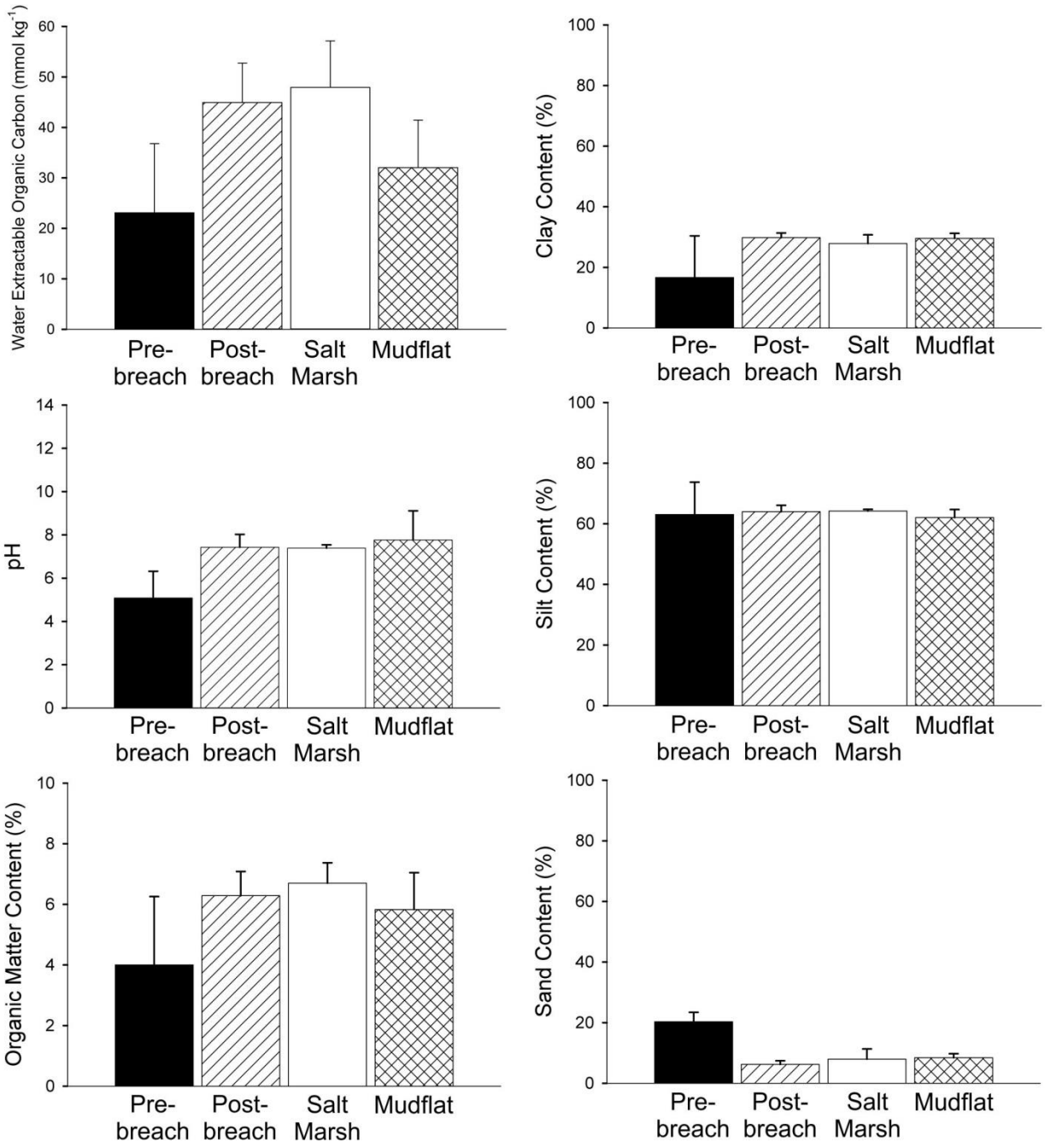

Figure 3. Physiochemical variables measured in cores (averaged 0-15 cm) sampled from the dyke cell (pre-breach and post-breach) along with adjacent sites (mudflat and salt marsh). The error bars represent standard deviation of three replicate cores (n = 2 for the pre-breach cores).

Multiple linear regressions

The correlation between the best multiple linear regression model and the THg concentrations measured in the sediments (Figure 4) yielded an R^2 value of 0.524 and a p value < 0.001 (Table 2). The explanatory variables in order of decreasing importance were WEOC, pH, EC and %Clay. Adding the next most important variable (%OM) decreased the R^2 value to 0.519. WEOC alone explained 36.7% of the variation in the observed data.

Table 2 Significance and correlation results of forward multiple linear regression models for the prediction of THg and MeHg from physiochemical sediment variables; Water Extractable Organic Carbon (WEOC), pH, Electrical Conductivity (EC), Clay content and Organic Matter (OM).

Response variable	Fitted terms	F value	R^2
THg	WEOC	61.8***	0.367
	WEOC+pH	48.6***	0.476
	WEOC+pH+EC	35.5***	0.496
	WEOC+pH+EC+Clay	29.9***	0.524
MeHg	EC	7.02**	0.54
	EC+THg	8.36***	0.123
	EC+THg+pH	7.07***	0.148
	EC+THg+pH+Clay	6.05***	0.161
	EC+THg+pH+Clay+WEOC	5.50***	0.176
	EC+THg+pH+Clay+WEOC+OM	6.56***	0.241

** = p < 0.01, *** = p < 0.001

The variability in MeHg concentrations was more difficult to explain than the THg concentrations using the physiochemical variables measured. The multiple linear regression model for MeHg (Figure 4) had a lower R^2 value than the model for THg. The fit which included EC, THg, pH, %Clay, WEOC and %OM (in order of decreasing importance) had an R^2 value of 0.241 and a p value of < 0.001. Although EC accounted for the greatest extent of the variability in the MeHg dataset, when considered on its own EC accounted for only 5.4% of the variation. This indicates that variables that we measured could not adequately explain the concentration of MeHg in the sediments.

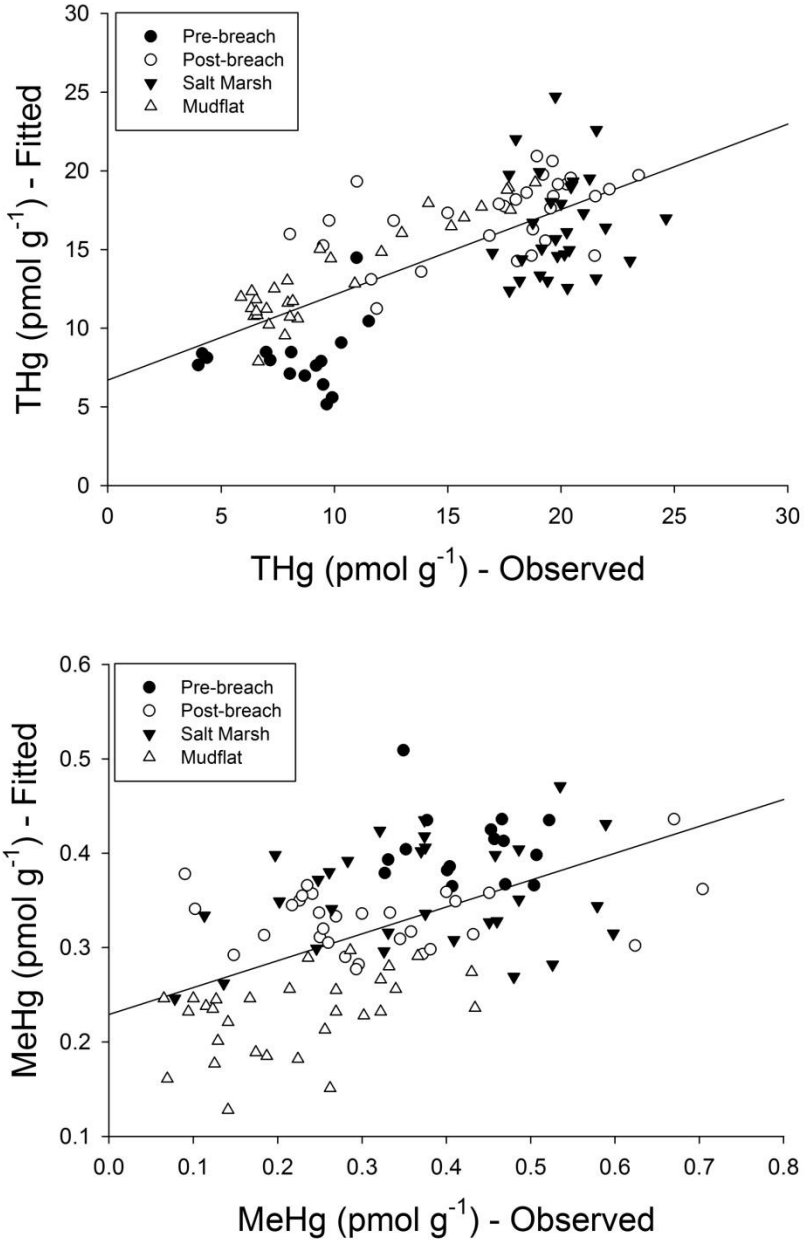

Figure 4. Total mercury (THg) and methylmercury (MeHg) concentrations observed in cores sampled from the dyke cell (pre-breach and post-breach) along with adjacent sites (mudflat and salt marsh) plotted against fitted THg and MeHg concentrations that were predicted using multiple linear regression models (Table 2) created with the same data. The THg model included WEOC, pH, EC, and %Clay as explanatory variables, explaining 51.9% of the variability. The MeHg model included EC, THg, pH, %Clay, WEOC and %OM as explanatory variables, explaining 24.1% of the variability.

Discussion

Post-breach sediments are chemically more similar to the salt marsh and mudflat than pre-breach sediments

The breaching of the dyke and inundation of the dyke cell deposited a large quantity of fresh sediment over the top of the pre-existing soil. This event changed the biogeochemistry of the system by increasing the EC, pH, %OM and WEOC. The impact of this change is best demonstrated by the considerable increase in the EC observed (Figure 1c) as the dyke cell changed from a terrestrial environment to a coastal environment due to inundation with saline water. While the topography of the mudflat and the salt marsh gently slopes down towards the sea, the soil in the dyke cell was relatively flat prior to breaching and inundation. The deposition of fresh sediment in the dyke cell was unevenly distributed leaving puddles of seawater which we observed in depressed areas at low tide. Evaporation of water and precipitation of salts in these depressed areas (Mouneimne and Price, 2007) has resulted in the EC of the post-breach sediments being elevated above levels measured in the mudflat or the salt marsh (Figure 1c).

The objective of the managed retreat is for salt marsh vegetation to colonise the freshly deposited sediment once the depth of the sediment raises the wetland to an elevation high enough for vegetation to survive (Williams and Orr, 2002). During the post-breach sampling in 2011 the dyke cell was still unvegetated and looked more similar to a mudflat than a salt marsh. This observation is supported by the textural analysis of the sediment deposited in the dyke cell (post-breach) which was similar to the sediment sampled from the mudflat (Figure 3). The chemistry of the post-breach sediments (WEOC, pH and %OM) was more similar to the salt marsh and

mudflat sediments than the samples collected pre-breach. However, this data must be interpreted with caution since only two cores were collected prior to the dyke being breached.

Post-breach sediments have greater total Hg but lower MeHg concentrations

The total Hg concentrations in the reclaimed region were similar to those found in other studies of non-vegetated intertidal mudflats (O'Driscoll et al., 2011; Sizmur et al., 2013b) and salt marshes (Hung and Chmura, 2006; Sunderland et al., 2004) in the Bay of Fundy. Over a period of two years (and only one year after the dyke was breached) the concentration of total Hg in the dyke cell was considerably greater (Figure 2). We acknowledge, however, that this dataset has limitations since there were only two replicate cores collected prior to the dyke being breached. Despite this apparent increase, the concentration of Hg in the post-breach sediments had not yet reached that of the salt marsh, which is the target ecosystem. There was a clear decrease in Hg concentration with sediment depth in both the mudflat and the post-breach sediments but not in the salt marsh sediments which is a further indication that the sediment characteristics more closely match the mudflat at this stage of restoration.

While the total Hg concentrations were greater in the dyke cell after inundation, and the MeHg concentrations were greater at the surface of the sediment, MeHg was observed to be lower overall in the post-breach cores (Figure 2). This lower MeHg concentration was reflected by %MeHg in the sediments of the dyke cell decreasing from 6% pre-breach to 2% post-breach when averaged over all the depths. This observation indicates that methylation has not rapidly

occurred in the newly deposited Hg(II) species in the sediment. If the lower MeHg in the post-breach sediments was due to greater export of MeHg from the sediments by tidal flushing then we would have expected to see MeHg depleted in the top few cm of sediment. However, MeHg concentrations were greatest in the top few cm (Figure 2). Therefore, tidal flushing is probably not the reason for the lower MeHg in the post-breach sediments.

Because total Hg concentrations are greater post-breach and MeHg concentrations are lower, Hg methylation cannot be limited by the supply of total Hg. Hg methylation is rather limited by the bioavailability of Hg to Hg methylating bacteria or the activity of these bacteria (Sunderland et al., 2006). Canário et al. (2007) showed that %MeHg in unvegetated coastal wetland sediments were only 0.6%, while vegetated sediments had up to 18% MeHg. The authors explained that this discrepancy is likely to occur because the presence of vegetation increases microbial activity and favours Hg methylation. Colonisation of the dyke cell by benthic invertebrates (e.g. polychaete worms) may also increase the sediment-water interface and the concentration of MeHg in their burrows (Sizmur et al., 2013a). Therefore, the MeHg concentrations in the dyke cell may increase as the restoration progresses and the dyke cell becomes colonised by vegetation and fauna. This prediction must be contrasted with the observation by Morris et al. (2014) that restored salt marshes have lower MeHg concentrations several decades after inundation when compared to adjacent natural salt marshes. It is therefore unclear whether the MeHg concentration in the dyke cell sediments will increase beyond the concentrations in the adjacent natural salt marsh in the long term.

THg concentrations are influenced by soluble carbon, particle size, pH, and salinity but MeHg concentrations are poorly predicted

Water-extractable organic carbon, pH, EC, and clay content of sediments all contributed to the multiple linear regression models that explained 52.4% of the variability associated with the concentration of THg, but only 24% of the variability associated with MeHg concentrations in the sediments (Table 2 and Figure 4). Clay content was positively correlated with THg sediment concentration. A reduction in sediment particle size (here observed by an increase in clay content) increases the surface-area-to-volume ratio of particulates in a system. The high surface area and cation exchange capacity of clays results in the adsorption of Hg to fine particles (Bengtsson and Picado, 2008). Suspension of fine sediments in the tidal water increases the likelihood of sediments to scavenge Hg from the water column by settling and retaining Hg in the accumulating sediment (Covelli et al., 2009; Hung and Chmura, 2006; Sunderland et al., 2006). Sediments comprised of fine particles also increase the proportion of particle-bound Hg (Bengtsson and Picado, 2008) and may thus reduce the bioavailability of Hg to methylating bacteria.

Dissolved organic matter (DOM) is a major binding phase for Hg in aquatic environments (Haitzer et al., 2002; Haverstock et al., 2012; Le Faucheur et al., 2014; O'Driscoll and Evans, 2000; Ravichandran, 2004). Here we use WEOC as a proxy for DOM in the sediments following Sizmur et al (2013b). Although we found a positive correlation between THg and both %OM and WEOC, the WEOC explains the THg concentration in the sediments better (Table 2). This observation indicates that the changes in Hg in the sediments are due to a greater fraction that is bound to soluble carbon complexes. The concentration of WEOC in the post-breach sediments

(Figure 3) was higher than the mudflat and (unlike the salt marsh) was not associated with vegetation growing in situ. It is therefore likely that the cause of higher concentrations of WEOC (and THg) in the post-breach sediments, compared to the mudflat, is the decaying mat of terrestrial vegetation underneath the freshly deposited sediment. Hg complexation with DOM reduces the bioavailability of Hg to methylating bacteria because the complexes are generally too large to penetrate their biological membranes (Le Faucheur et al., 2014; Ravichandran, 2004). However, soluble organic matter also provides an energy source for methylating bacteria and may increase their activity resulting in greater methylation rates (Ullrich et al., 2001). Further increases in DOM (and microbial activity) are likely to occur as the dyke cell becomes vegetated (Canário et al., 2007) which may increase methylation rates in the future. The deposition of plankton is likely to increase the %MeHg in the fresh sediment as they contain approximately 6% to 15% MeHg in the Northwest Atlantic Ocean (Hammerschmidt et al., 2013).

The solubility and speciation of Hg and the binding of dissolved Hg species to DOM or sediment particles is pH dependent (Gabriel and Williamson, 2004). At low pH, H^+ competes with Hg for binding sites on DOM or the surface of sediment particles, which releases Hg into solution but they also both compete for uptake by negatively charged bacterial cells. In this study pH correlated positively with Hg but negatively with MeHg. This contrast indicates that the greater pH of the mudflat, salt marsh, and post-breach sediments, compared to pre-breach sediments (Figure 3) resulted in greater Hg retention (Hung and Chmura, 2006) but may have reduced Hg bioavailability to methylating bacteria (Barkay et al., 1997; Gilmour and Henry, 1991; Le Faucheur et al., 2014).

373 The increase in EC that resulted from the inundation of the dyke cell with sea water (Figure 1c)
374 is due to the high salinity of the seawater (Mouneimne and Price, 2007). The high salinity of the
375 sediment deposited after the dyke cell was inundated with seawater created an environment with
376 a higher ionic strength. As ionic strength increases, the concentration of Hg desorbed into
377 solution decreases (Duarte et al., 1991) resulting in greater Hg retention in sediments and a
378 decrease in the bioavailability of Hg to methylating bacteria (Barkay et al., 1997). Seawater
379 contains high concentrations of chloride ions which can form strong ($\log_{10} K_1° = 7.31$)
380 complexes with mercury species (Powell et al., 2005). The greater the concentration of chloride,
381 the more negatively charged mercuric chloride ions ($HgCl_3^-$ and $HgCl_4^{2-}$) will be present in
382 solution and these negative ions also have a lower bioavailability (Barkay et al., 1997) to
383 methylating bacteria with negatively charged cell walls. Therefore, the increase in ionic strength
384 and formation of trivalent or tetravalent mercuric chloride species in the high EC sediments of
385 the post-breach sediments may have reduced their bioavailability to mercury methylating
386 bacteria. These Hg-chloride complexes may also be less susceptible to photoreduction and loss to
387 the atmosphere (Qureshi et al., 2009).

388

389 In summary, the chemical changes that occur in the sediment after inundation may have
390 impacted on the bioavailability of Hg to methylating bacteria. The decrease in particle size
391 distribution and subsequent increase in sediment surface area may have increased sorption of Hg
392 out of the water column but lowered its bioavailability. Higher organic matter levels may provide
393 a food source for methylating bacteria and increase their activity. Greater soluble organic carbon
394 may mobilise Hg from the surface of sediments but also complex it in a form that is unavailable
395 to methylating bacteria. An increase in sediment pH increases the concentration that can be

adsorbed from the solution phase and reduces the bioavailability. Finally, the higher ionic strength leads to a greater proportion of inorganic complexes and a lower bioavailability of Hg. This final conclusion assumes that the uptake of Hg by methylating bacteria occurs by passive diffusion of neural or ionic lipophilic Hg species but there is now a considerable body of evidence to suggest that uptake may occur by facilitated diffusion or active transportation by protein pumps (Hsu-Kim et al., 2013).

Conclusions and Implications for Coastal Managed Retreat

Despite a doubling of Hg concentration within the dyke cell after the dyke was breached, Hg concentrations are still below the Canadian Sediment Quality Guidelines (CCME, 2002). The reason for the Hg increase in this study was the fresh deposition of sediments with a smaller particle size distribution that are able to scavenge and retain Hg due to their higher surface area, negative charge, and higher pH. This site can therefore be considered a net sink for mercury during the first year after the dyke was breached. The more sediment that is deposited, the larger the sink will become. In contrast to considerable increases in mercury methylation observed during freshwater wetland creation (Kelly et al., 1997; Sinclair et al., 2012), we observed a 27% decrease in MeHg concentrations in the dyke cell after the dyke was breached. This decrease may have been due to greater Hg retention and lower Hg bioavailability to methylating bacteria but ultimately cannot be fully explained with the available data and is limited by the low number of replicate cores collected. Further work will be required to explain the precise mechanisms for this decrease.

Our data provides no evidence for a flush of Hg methylation during the first year of managed retreat. As the restoration progresses and vegetation colonises, the soluble carbon concentration and microbial activity may increase and the rate of Hg methylation may also increase. However, contradictory data from other studies indicate that it is unclear whether MeHg will be elevated beyond the concentration found in natural wetlands (Canário et al., 2007; Kelly et al., 1997; Morris et al., 2014; Sinclair et al., 2012). We conclude that coastal flooding of sediments subject to diffuse Hg contamination during managed retreat of coastal flood defences does not pose a significant risk of increasing Hg methylation or bioavailability during the first year.

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