Sea level rise produces abundant organobromines in salt-affected coastal wetlands

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Abstract

Global sea level rise exposes terrestrial natural organic matter to elevated salinities, which may alter the complex biogeochemical cycling of halogens in coastal wetland sediments. Here we show that sea level rise increases the natural production of organobromines in submerged soils and wetland sediments. We compared the concentrations and speciation of sedimentary chlorine and bromine along a salinity gradient in low-lying forested wetlands in Winyah Bay (South Carolina, United States). Sorption differences between chloride and bromide were not observed, but up to 80\% of total retained bromine is organically bound, with the highest fraction of organically bound bromine found in formerly freshwater wetlands inundated by seawater. Wet/dry cycling of soils and the abundance of aromatic-rich natural organic matter in these salt-affected dieback forested wetlands promote bromination of organic matter, as demonstrated by laboratory simulations. Bromination of soil organic matter caused by continued sea level rise thus may be a major source of organobromines in coastal environments and possibly volatile halomethanes.

Introduction

Global warming and associated rises in sea level threaten to alter the biogeochemistry of coastal ecosystems. Flooding of coastal freshwater wetlands exposes their vegetation and soil-bound natural organic matter (NOM) to seawater and ultimately results in conversion to salt marshes (Doyle et al., 2007; Hilton et al., 2008; Krauss et al., 2009). The increased salinity alters the abundance and composition of NOM in salt-affected wetlands (Goñi and Thomas, 2000; Neubauer, 2013), due to changes in vegetal inputs (Tuxen et al., 2011) and microbial activity (Morrissey et al., 2014). Conversely, reactions with previously inaccessible terrestrial NOM may also alter the biogeochemical cycling of halogens.

Both chlorine (Cl) and bromine (Br) undergo complex biogeochemical cycling in marine and soil systems. During NOM decomposition, inorganic Cl and Br react with NOM both abiotically and biotically to form halogenated organic compounds (organochlorines and organobromines, respectively) (Leri and Myneni, 2010, 2012). Understanding the natural formation of organohalogens is important in order to evaluate the stability of these compounds and their potential breakdown and release as volatile halomethanes. Many halomethanes are known to catalytically destroy stratospheric ozone (Molina and Rowland, 1974), and coastal ecosystems such as salt marshes contribute as much as 10\% of halomethane emissions in the atmosphere (Rhew et al., 2000). It is thus crucial to determine how global sea level rise may affect the biogeochemistry of halogen cycling in coastal ecosystems.

In this study, we evaluate the impacts of seawater intrusion on the production of organohalogens in wetland sediments as a first step towards predicting future halomethane emissions. The study site is located on the southeastern coast of the United States (Winyah Bay, South Carolina, United States) (Fig. S-1) (Titus and Richman, 2001). Winyah Bay is a tidally influenced forest-marsh, backwater-dominated, low-lying wetland ecosystem that has experienced severe saltwater intrusion, successively converting forested freshwater wetland to a salt-affected wetland and salt marsh over a short distance (~5 km) (Krauss et al., 2009). The freshwater and salt-affected wetlands experience seasonal wet and dry cycles based on precipitation. In contrast, the salt marsh is always saturated, although water depth varies with daily tidal cycles. Vegetation varies significantly with salinity (Krauss et al., 2009; Chow et al., 2013). To assess the importance of NOM origin and composition, we compared the effects of increased salinity on freshwater wetland soils from Winyah Bay and on temperate forest soils from pine lands in New Jersey.

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Methods

Methodological details are available in the Supplementary Information. In brief, three sites at Winyah Bay spanning a range of salinities were sampled along a transect from the freshwater wetland to the salt-affected wetland and the salt marsh (Fig. S-1). 18-24 cm soil cores were collected between July 2012 and December 2016. At least two cores were taken at each site to assess variability. Additionally, a 30 cm soil core was collected from the Pine Barrens in New Jersey to determine whether halogenation reactions occur in other ecosystems.

The functional group composition of organic carbon was assessed using Fourier transform infrared (FTIR) spectroscopy and solid state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. Cl and Br concentrations and speciation were determined using X-ray fluorescence (XRF) and synchrotron-based 1s X-ray absorption near edge structure (XANES) spectroscopy respectively.

Results and Discussion

Both the concentrations and the speciation of sediment-bound Cl and Br vary between the different sites, as expected. The average concentration of Cl ($\text{Cl}_{\text{total}}$) increases linearly with salinity: from 0.14 (±0.07) g.kg$^{-1}$ in freshwater wetland sediments to 6 (±1) and 27 (±2) g.kg$^{-1}$ in the salt-affected wetland and salt marsh, respectively (Table S-1). The variability shown in the parentheses arises from differences between the two sampled cores, which were minimal, and between different depths and seasons. Cl concentrations decrease with depth in the freshwater and salt-affected wetlands, consistent with soil studies where Cl concentrations are reported to decrease sharply below the top organic-rich horizons (Leri and Myneni, 2010; Krzmarzick et al., 2012). The absence of such a trend with depth in the salt marsh may be caused by homogenisation via tidal action. The speciation of Cl also varies with salinity, as shown by Cl XANES spectroscopy (Fig. 1). Most Cl in the top layers of freshwater sediments is organically bound ($\text{Cl}_{\text{org}}$), although Cl speciation in the lower layers (>~14 cm) could not be determined due to the low concentration of Cl. In contrast, salt-affected wetland and salt marsh samples at all depths show predominantly inorganic Cl ($\text{Cl}_{\text{org}}$) (Fig. 1). The presence of $\text{Cl}_{\text{org}}$ cannot be ruled out in the latter samples but is expected to be less than 6 % of $\text{Cl}_{\text{total}}$ (Leri et al., 2006). Variability in Cl speciation between the two cores collected at each site was also minimal.

The abundance and speciation of Br significantly differ from the behaviour of Cl. Total Br concentrations ($\text{Br}_{\text{total}}$) averaged over depth and between two separately collected cores increase from 13 (±10) mg.kg$^{-1}$ in the freshwater wetland to 120 (±50) in the salt-affected wetland but increase only marginally to 160 (±40) mg.kg$^{-1}$ in the salt marsh despite the roughly threefold increase in water salinity. Similar to Cl, most Br in the freshwater sediments is in the form of organically bound Br ($\text{Br}_{\text{org}}$) (Fig. 2, Table S-1), although variations between wet and dry seasons are observed (Fig. S-3), which may be due to both temporal and spatial heterogeneity. More than 80 % of Br in the salt-affected wetland and 50 % of Br in the salt marsh is present as $\text{Br}_{\text{org}}$, in contrast to the predominance of inorganic Cl at these two sites.

The large difference in Br:Cl ratios for seawater and sediments is striking. Br:Cl ratios in all sediments are greater than the Br:Cl ratio in seawater by a factor ranging from a maximum of 26.5 in the freshwater wetland to a minimum of 1.5 in the salt marsh. Cl and Br ions are considered inert and

![Figure 1](https://example.com/fig1.png)

**Figure 1** (a) Cl and (b) Br XANES spectra of top layer of sediments (~0-4 cm) on top (black) and standards (grey) at the bottom. Cl standards are chlorophenol red, chlorodecane, and NaCl (aq) for aromatic, aliphatic, and inorganic Cl respectively. Br standards are bromophenol blue, 1-bromoeicosane, and KBr for aromatic, aliphatic, and inorganic Br respectively. Grey dotted and dashed lines show the spectral maxima for aliphatic and aromatic organohalogen standards respectively.

![Figure 2](https://example.com/fig2.png)

**Figure 2** The concentration and speciation of Br (left, blue y axis) and Cl (right, black y axis) in sediments as a function of salinity (x axis) in Winyah Bay, South Carolina. All concentrations are the average of samples from different depths and two cores. Vertical error bars show the standard error and are in some cases smaller than the points.
The concentration and speciation of sediment-bound Cl and Br differ significantly along the salinity gradient due to the geochemical differences between the halides and between these sites. In general, bromination of organic matter greatly exceeds chlorination. At all sites and all depths, the fraction of organically bound Br (Br$_{org}$/Br$_{total}$) is greater than the fraction of organically bound Cl (Cl$_{org}$/Cl$_{total}$) (Table S-1). This is likely because Br is both more polarisable and less electronegative than Cl, aiding organic molecule halogenation reactions, which are commonly electrophilic addition reactions (Butler and Walker, 1993; Leri and Myneni, 2012).

In addition, the high abundance of NOM (Table S-2) and its high aromaticity (Figs. S-5–S-7) likely support preferential bromination of NOM in the salt-affected wetland, even though the salinity at that site is much less than in the salt marsh. In the salt-affected wetland, salt water intrusion and increases in halide concentrations stress the freshwater plants, such as bald cypresses, and reduce their productivity, ultimately leading to forest dieback and conversion to salt marsh (Munns and Walker, 1993; Leri and Myneni, 2012). The salt-affected wetlands also experience wet/dry conditions with seasons and thus promote extensive redox cycling of reactive Fe and Mn oxides, which are known in turn to promote halogenation reactions (Comba et al., 2015; Leri and Ravel, 2015; Lin et al., 2016). The loss of plant cover in these salt-affected wetlands may also promote photolytic reactions. In contrast to salt-affected wetlands, Br$_{org}$ production is limited in freshwater wetlands by access to Br and in salt marshes by the low abundance of reactive NOM and permanent water-saturated conditions.

Laboratory experiments conducted on freshwater wetland sediments to simulate geochemical conditions in salt-affected wetlands (wet/dry cycles, relatively low salinity) and salt marshes (saturated conditions, relatively high salinity) reproduced the field observations and trends (Fig. 3). Br$_{total}$ retained by sediments increased with exposure to elevated Br concentrations in all samples rapidly (within hours). However, the samples exposed to wet/dry conditions, mimicking salt-affected wetland conditions, in general retained more Br$_{total}$ and produced more Br$_{org}$ than the samples exposed to saturated conditions, mimicking salt marsh conditions (Fig. 3). No consistent trend with depth is apparent, and elevated levels of Cl$^{-}$ and sample pH did not influence Br$_{org}$ production significantly (Fig. S-8). Reactions of New Jersey soils with organic matter with Br also produced extensive Br$_{org}$ (Fig S-9). Organic matter in the New Jersey soils is derived from pine, maple, and oak, so its functional group composition is expected to differ from the Winyah Bay sediments, whose organic matter exhibit similar weak sorption onto sediments, so the disproportionate retention of Br compared to Cl cannot be explained by differences in partition coefficients between sediment and water (Kd(Cl) > Kd(Br)). The measured Kd(Cl) is small and varies between 0.2 and 1.8 with the lowest values in the freshwater wetland (Table S-1). These differences in Kd values are likely caused by differences in sediment characteristics (e.g., mineralogy, particle size, organic matter content) and depth averaged salinity values. However, the amounts of sorbed Br predicted using Kd(Cl) are much smaller than the observed levels of Br$_{total}$. The excess Br is likely retained in the sediment as Br$_{org}$, and the abundance of Br$_{org}$ determined spectroscopically matches well with this calculated excess (measured Br$_{total}$ – calculated sorbed Br) (Figs. 2 and S-4).

Figure 3  (a) Total Br and (b) organically bound Br produced in Br-reacted soil samples as a function of increasing aqueous Br concentrations. Filled shapes (●) represent saturated conditions (mimicking salt marsh conditions) and open shapes (○) represent wet/dry conditions (mimicking salt-affected wetland conditions). Vertical gray dotted line shows Br concentration in seawater in both panels. Error bars are based on replicate XRF analyses (total Br and organic Br) and error from XANES linear combination fitting for organic Br.
The preferential production of \( \text{Br}_3 \) in the New Jersey soil is greater in the soil O-horizon, where the reactive NOM is more abundant, than in mineral-rich lower horizons. These results suggest that the extensive bromination observed in the Winyah Bay salt-affected wetland sediments is not unique to this site but rather may occur in many types of soils and sediments with varying sources of organic matter if they are affected by saltwater intrusion.

Both field and laboratory studies indicate that sedimentary NOM can be brominated when exposed to seawater. Bromination of NOM is consistently favoured over chlorination, resulting in the accumulation of organobromines in sediments. Intrusion of salt water in coastal regions caused by sea level rise and extensive pumping of ground water exposes freshwater sediments and surface and subsurface soils to elevated salt levels (Fig. 4). This exposes \( \text{Br}_3 \) to aromatic-rich terrestrial NOM, and \( \text{Br}_3 \) production is likely to increase in all these environments (Fig. 4). The lability of this \( \text{Br}_3 \) is unclear. Increased flooding of salt-affected wetlands by seawater increases sulphate concentrations, which stimulates microbial sulphate reduction and accelerates organic carbon decomposition and the microbially mediated reductive debromination of \( \text{Br}_3 \) (Berg and Solomon, 2016). Thus, salt-affected wetlands are not a net source of methyl bromide (Wang et al., 2016). However, salt marshes are a net source of methyl bromide (Wang et al., 2016; Jiao et al., 2018), and in the long term, the conversion of salt-affected wetlands into salt marshes with further sea level rise is ultimately likely to release \( \text{Br}_3 \) retained in soil to the atmosphere as halomethanes. More work is needed to evaluate the timescale and extent of increased halomethane emissions due to sea level rise.

Our study documents for the first time that a large repository of \( \text{Br}_3 \) forms from the reactions of seawater with terrestrial NOM and that the reactions are rapid, on the order of hours to days. Facilitated by changes in water salinity and fluctuating wet/dry seasonal cycles in coastal wetlands, bromination of NOM creates a potentially labile pool of organohalogenes. Further biotic and abiotic decomposition of NOM may break down these sediment-bound organohalogenes into either \( \text{Br}_3 \) (Jeong et al., 2011; Krzmarzick et al., 2012) or volatile halomethanes (Huber et al., 2009). The preferential production of organohalogenes is particularly problematic because \( \text{Br}_3 \) radicals are an order of magnitude more efficient at destroying stratospheric ozone than Cl radicals (Daniel et al., 1999). As sea levels continue to rise, understanding both the formation and the breakdown of sediment-bound organohalogenes may be crucial for predicting future changes in water quality in salt-affected wetlands and stratospheric ozone.

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**Author Contributions**

Joe-Wong and Schlesinger contributed equally to the design and execution of experiments, analysis of the data, and to writing the manuscript and supplementary information. Myneni supervised the project and provided manuscript revisions and feedback. Chow assisted in monitoring of the field site and sample collection and provided input on the manuscript.

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**Additional Information**

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1911.
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