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Organic matter drives high interannual variability in methylmercury concentrations in a subarctic coastal sea☆

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ABSTRACT

Levels of neurotoxic methylmercury (MeHg) in phytoplankton are strongly associated with water MeHg concentrations. Because uptake by phytoplankton is the first and largest step of bioaccumulation in aquatic food webs many studies have investigated factors driving seasonal changes in water MeHg concentrations. Organic matter (OM) is widely accepted as an important driver of MeHg production and uptake by phytoplankton but is also known for strong interannual variability in concentration and composition within systems. In this study, we explore the role of OM on spatial and interannual variability of MeHg in a subarctic coastal sea, the northern Baltic Sea. Using MeHg (2014: 80 ± 25 fM; 2015: <LOD; 2016: 21 ± 9 fM) and OM measurements during late summer/early fall, we find that dissolved organic carbon (DOC) and humic matter content explain 60% of MeHg variability. We find that while labile DOC increases MeHg levels in the water, humic content reduces it. We propose that the positive association between MeHg and labile DOC shows that labile DOC is a proxy for OM remineralization rate in nearshore and offshore waters. This is consistent with other studies finding that *in situ* MeHg production in the water column occurs during OM remineralization. The negative association between water humic content and MeHg concentration is most likely due to humic matter decreasing inorganic mercury (Hg^{II}) bioavailability to methylating microbes. With these relationships, we develop a statistical model and use it to calculate MeHg concentrations in late summer nearshore and offshore waters between 2006 and 2016 using measured values for water DOC and humic matter content. We find that MeHg concentrations can vary by up to an order of magnitude between years, highlighting the importance of considering interannual variability in water column MeHg concentrations when interpreting both short and long term MeHg trends in biota.

1. Introduction

Methylmercury (MeHg) is a neurotoxin that bioaccumulates in aquatic food webs and can adversely affect wildlife and human health (Mahaffey et al., 2011; Scheuhammer et al., 2007). Microbes produce MeHg from inorganic mercury (Hg^{II}), thus factors controlling microbial activity and Hg^{II} bioavailability affect ambient MeHg concentrations. One well known driver of Hg^{II} methylation is organic matter (OM), which can contain metabolic substrate molecules essential for heterotrophic microbes (Münster and Chróst, 1990) and strong ligands that bind Hg^{II} (Ravichandran, 2004). The importance of OM concentration and composition on MeHg levels have been shown in laboratory (Chiasson-Gould et al., 2014; Graham et al., 2013) and field studies (Bravo et al., 2017; Drott et al., 2007; Kim et al., 2011; Schartup et al., 2015a), but the implications of OM's strong interannual variability in concentration and composition within systems have not been explored. Here we use mercury (Hg) and OM measurements from a subarctic coastal sea to explore how OM concentration and composition influences aqueous MeHg concentrations from 2006 to 2016, and discuss implications for future MeHg concentrations.

The Northern Baltic Sea is composed of two basins separated by a sill: Bothnian Bay and Bothnian Sea (Fig. 1). Most freshwater enters through the Bothnian Bay (~5% of the basin volume each year versus 1.5% of the volume in the Bothnian Sea), creating north-south gradients of salinity and ratios of allochthonous

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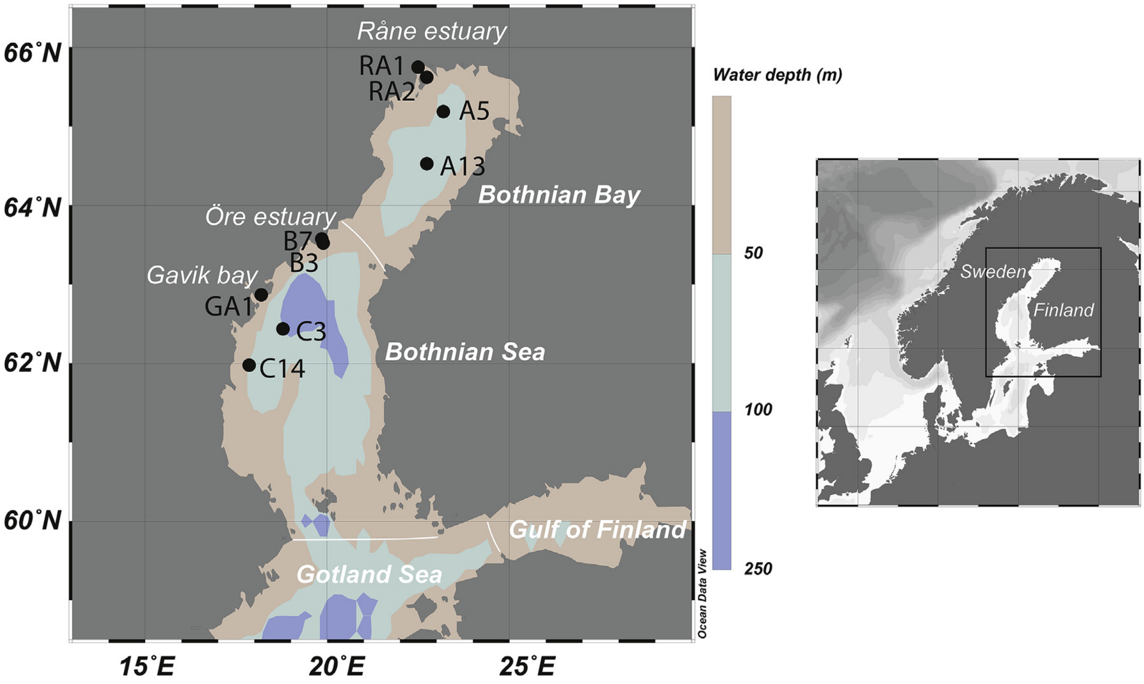

Fig. 1. The location of stations sampled during the 2014–2016 cruise campaigns.

(transported from the terrestrial environment) to autochthonous (produced locally) dissolved organic matter (DOM; OM that passes through a 0.2 μm filter) (Deutsch et al., 2012; Ripszam et al., 2015). The total DOM concentration remains relatively constant across the offshore northern Baltic Sea but the fraction of allochthonous DOM rich in aromatic functional groups (Hoikkala et al., 2015; Ripszam et al., 2015) decreases from the coastal Bothnian Bay (83%), to the offshore Bothnian Bay (70%) and Bothnian Sea (55%) (Deutsch et al., 2012).

In the offshore northern Baltic Sea, about 80–90% of DOM is not a preferred microbial substrate (refractory) and forms a baseline refractory dissolved organic carbon (DOC) concentration of ~300 μM in offshore water (Hoikkala et al., 2015; Zweifel et al., 1995). In estuarine and nearshore sites high river discharge in the spring and fall increases inputs of allochthonous DOM (Hoikkala et al., 2012; Zweifel et al., 1995), and the supply of new DOM therefore outpaces remineralization and builds up a reservoir of microbially available (labile) DOM. In offshore waters, labile DOM accumulates in summer and fall (Hoikkala et al., 2012; Zweifel et al., 1995) when autochthonous DOM is produced during the decomposition of marine plankton. In the Baltic Sea, >50% of the primary production can be released as autochthonous DOM and represents ~44% and ~88% of the yearly DOM input to the Bothnian Bay and Sea, respectively (Hoikkala et al., 2015). Labile DOM therefore reflects the potential for remineralization within the offshore water column (Hoikkala et al., 2012).

Inorganic mercury (Hg^{II}) can be converted to MeHg by a range of identified heterotrophic microbes (e.g. iron and sulphur reducers, methanogens, and nitrite oxidizers) (Gionfriddo et al., 2016; Parks et al., 2013; Podar et al., 2015). Hg^{II} methylation in the water column can occur in the dissolved phase in oxic water (Monperrus et al., 2007; Schartup et al., 2015b), and in low oxygen conditions found inside particulate organic matter (POM; OM that does not pass through a 0.2 μm filter) aggregates (Gascon Diez et al., 2016). The microbes break down OM for energy and Hg^{II} methylation can occur during this OM remineralization in the water column (Heimburger et al., 2010; Sunderland et al., 2009). Fresh and energy rich (labile) OM results in higher Hg^{II} methylation rates than more degraded (refractory) OM both in sinking particles and sediment (Bravo et al., 2017; Drott et al., 2007; Gascon Diez et al., 2016). Bravo et al. (2017) recently characterized the molecular composition of OM in boreal lake sediment and demonstrated that compounds originating from fresh chlorophylls, proteins and phytoplankton-derived cell wall lipids enhance Hg^{II} methylation.

Most Hg^{II} and MeHg present in the environment is complexed by OM (Ravichandran, 2004), the largest fraction of which is in the dissolved form (DOM) in offshore water (Hammerschmidt et al., 2013). DOM composition is source dependant and differs considerably between that of allochthonous or autochthonous origin (Baldock et al., 2004; Osburn and Stedmon, 2011). Allochthonous DOM for example have a higher content of humic substances than autochthonous DOM (Ravichandran, 2004) and humic matter content is therefore a good proxy for allochthonous DOM. DOM has been shown to affect the availability of Hg^{II} to microbes and thereby exert a strong control on Hg^{II} methylation fluxes (Mazrui et al., 2016; Schartup et al., 2015a).

The main objective of this study is to explore how interannual variability in concentration and composition of OM impacts water column MeHg concentration. To do this, we measured the concentrations of total Hg (Hg^{II}+MeHg), MeHg, DOC and dissolved humic matter content in the subarctic northern Baltic Sea during three years in summer/fall. We use the data to construct a statistical model and estimate interannual variability in MeHg concentrations in this subarctic coastal sea between 2006 and 2016.

2. Methods

2.1. Field sampling

Fig. 1 shows sampling locations in the northern Baltic Sea. Data are from three cruises: 8th-11th of September 2014, 3rd-6th of August 2015 and 15th-18th of August 2016 (Table 1). We group sampling locations into two categories: nearshore and offshore. The four nearshore sites (RA1, RA2, B3, B7) are shallow (<25 m) and within

Table 1

Offshore mercury concentrations during the three sampling campaigns (numerical average ± stdv). Individual station data from the sampling campaigns are available in the SI Table S2.

	Bothnian Bay			Bothnian Sea		
	2014 10-11 Sep	2015 5-6 Aug	2016 17-18 Aug	2014 8-9 Sep	2015 3-4 Aug	2016 15-16 Aug
Total Hg (pM)			1.24 ± 0.30			0.84 ± 0.24
MeHg (fM)	69 ± 23	15 ± 16	26 ± 7	103 ± 12	<LOD	18 ± 9

5 km of the coast, located near major rivers (the Råne river and the Öre river; Fig. 1) and present strong estuarine characteristics (Figueroa et al., 2016; Malmgren and Brydsten, 1992). The remaining five sampling locations are labeled offshore (A5, A13, C3, C14, GA1). All offshore sites are located more than 30 km away from the coast with the exception of GA1. GA1 is located in a bay near the coast (<3 km) but away from large riverine inputs and its deep water column (85 m) is replenished with offshore water and thus presents the characteristics of offshore sites (Albertsson, 2013).

Water samples were collected with 2 L Niskin bottles or 5 L Teflon-lined GO-FLO (General Oceanics) bottles attached individually to a clean line following trace-metal clean protocols. Subsamples were collected into 125 mL Teflon bottles for total Hg and 125/250 mL Teflon or HDPE bottles for MeHg. To clean total Hg bottles they were filled with 0.5% bromine monochloride (BrCl) and held overnight, then filled with 10% trace metal grade hydrochloric acid (Suprapure HCl) and kept at 65 °C overnight. Finally, the bottles were filled with 2% trace metal grade HCl until use. MeHg bottles were filled with 10% volume of 10% trace metal grade HCl before leaving for the field campaigns, which was left until use. Samples for total Hg were not acidified and analyzed within a month of sampling. Samples for MeHg analysis were acidified with 0.1 M Suprapure HCl and spiked with $Me^{200}Hg$ internal standard on the ship or in the lab (Supplementary data (SI) Table S1). All samples were stored at 4 °C on the ship and in the lab until analysis.

2.2. Total Hg analyses

Water total Hg was measured at the Swedish Environmental Research Institute following USEPA 1631, revisions E 2002 (USEPA, 2002). All Hg species were oxidized to Hg^{II} with BrCl, followed by tin(II) chloride ($SnCl_2$) to reduce Hg^{II} to volatile elemental Hg (Hg^0). Hg^0 was then purged into a gold trap and thermally desorbed into a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection. The method detection limit was 0.2 pM and the measurement uncertainty was 14% for concentrations <1.25 pM and 7% for >1.25 pM.

2.3. Methylmercury analysis

MeHg samples were prepared based on the methods described in Munson et al. (2014) and Lambertsson and Björn (2004) and analyzed by isotope dilution following the procedure in Lambertsson and Björn (2004). Ascorbic acid (2.5% wt:vol) was added to the samples (Munson et al., 2014) and the pH adjusted to 4.8 using a 2 M acetic acid/acetate buffer and natriumhydroxide (NaOH). After pH adjustment, Hg species were ethylated to form volatile Hg species using sodium tetraethylborate (NaTEB) and purged onto Tenax traps. The traps were thermally desorbed onto a gas chromatography column coupled to an inductively coupled plasma mass spectrometer (TDGC-ICPMS, Agilent 6890 GC and 7700 ICPMS). This method does not distinguish between monomethylmercury and dimethylmercury, therefore in this study MeHg refers to total methylated mercury species present. Samples were blank corrected with 10 fM (difference between field blanks and laboratory MQ water) (Soerensen et al., 2016). The detection limit (LOD) was 13 fM based on three times standard deviation of replicate field blanks ($n = 12$) and the relative standard deviation of replicate samples was 25%. Concentrations below detection were set to 50% of the LOD value.

2.4. DOC, humic matter content and ancillary data

Temperature, salinity, and concentrations of oxygen, sulfide, phosphorous, nitrate, ammonium, silicate, chlorophyll a, humic matter content, and DOC are measured during monthly cruises as part of the Swedish National Monitoring Program. Samples are analyzed according to HELCOM guidelines (HELCOM Combine, 2014) and quality controlled data is available for download from the Swedish Meteorological and Hydrological Institute's website (SMHI, 2015). Humic matter content is measured by fluorescence spectroscopy at 350/450 nm excitation/emission wavelength, fluorescence was calibrated and quantified using quinine sulfate (HELCOM Combine, 2014). Temperature, salinity, oxygen, sulfide, phosphorous, nitrate, ammonium, silicate, and Chl A a were available for all our cruises. DOC and humic matter content have been measured monthly at the nearshore stations and bi-monthly at offshore stations in the northern Baltic Sea since 2000. For comparison of DOC and humic matter content to our Hg data, we use the closest available data to our sampling periods. DOC is the carbon fraction of DOM while the humic matter content is the most light absorbing fraction of DOM.

2.5. Statistical models

To examine the association between MeHg concentrations and other environmental variables in the dataset, we use simple and multiple linear regressions analyses. All statistical analyses were conducted using SAS/STAT® software.

3. Results and discussion

3.1. Water mercury concentrations

Fig. 2A shows how total Hg concentration declined with salinity from 5.95 pM (salinity 0.7) in the inner Råne river estuary (RA1) to 2.00 pM (salinity 1.5) in the outer Råne river estuary (RA2), 1.24 ± 0.30 pM ($n = 6$, salinity 2.0–3.6) in the Bothnian Bay offshore water (A5, A13) and 0.84 ± 0.24 pM ($n = 9$, salinity 3.7–6.1) in Bothnian Sea offshore water in 2016 (C3, C14, GA1; Table 1). There is a small but significant decrease in total Hg from Bothnian Bay to Bothnian Sea offshore water (Wilcoxon two sample *t*-test, $P < 0.05$, $n = 15$).

Fig. 2B shows that MeHg concentrations ranged from a maximum of 306 fM in the inner estuary (RA1) in 2015 to offshore averages of 80 ± 25 fM in 2014, <LOD in 2015 and 21 ± 9 fM in 2016 (stations included: A5, A13, C3, C14, GA1; Table 1). MeHg decreased with increasing salinity in both basins but showed a different

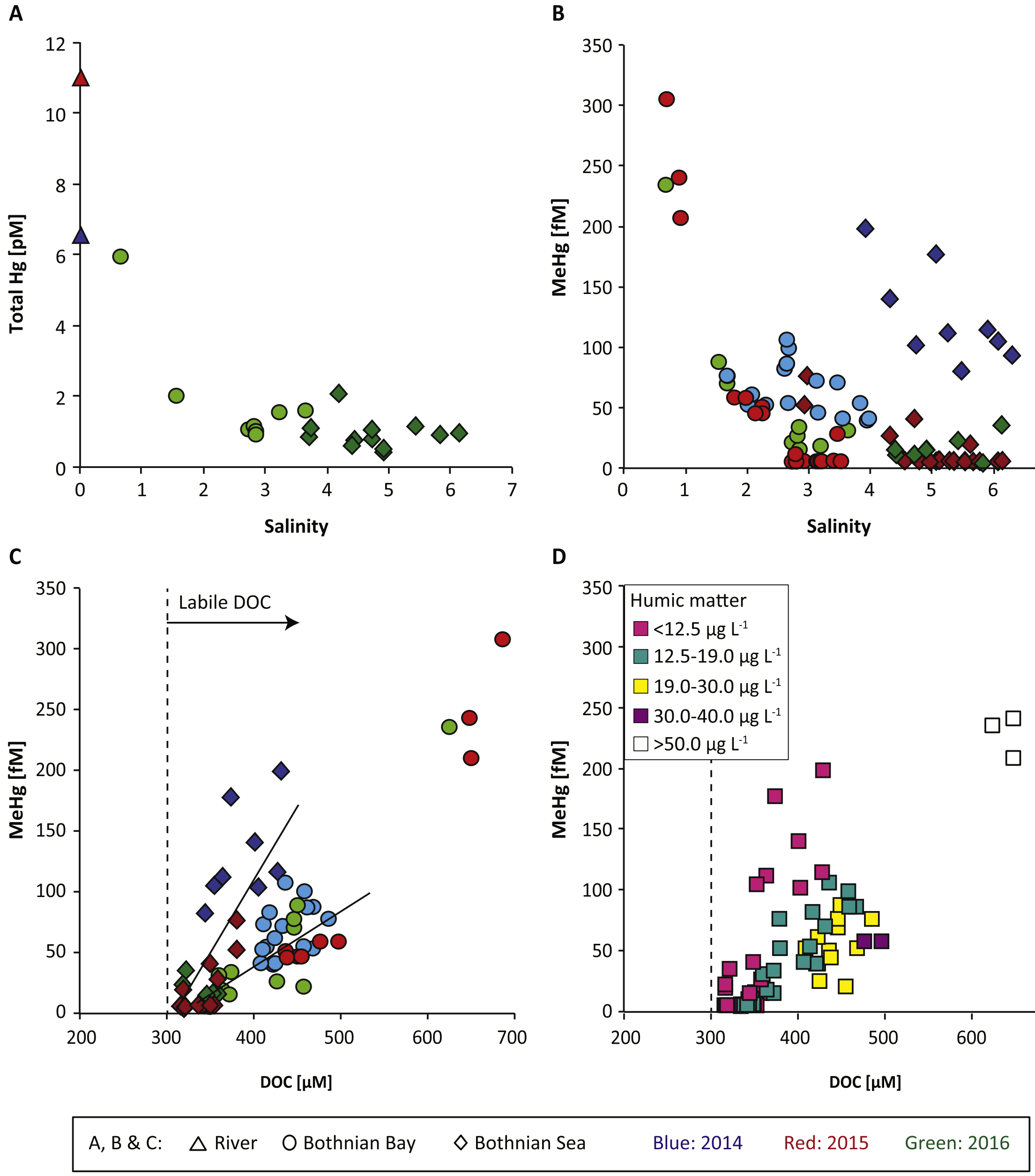

Fig. 2. A) Water total Hg concentration and salinity; B) water MeHg concentration and salinity; C) water MeHg concentration and DOC (solid lines indicate significant linear regressions for the Bothnian Bay and Bothnian Sea separately); D) water MeHg concentration and DOC (where the color of the squares indicates the concentration of humic matter content). For A, B, and C two different shades of blue, red, and green are used for the Bothnian Bay and Bothnian Sea to make it easier to distinguish between the two basins. Total Hg concentrations in the Råne river (salinity of 0) are from 14th September 2014 and 15th August 2015 (SLU, 2016). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

MeHg:salinity ratio each year. Offshore MeHg concentrations showed large interannual variability of up to a factor of three in the Bothnian Bay and a factor of eight in the Bothnian Sea. Average concentrations, however, remained within a factor of two between the two basins (Bothnian Bay and Bothnian Sea) in any given year (Table 1). Total Hg, MeHg and ancillary data from individual stations are available in the SI Table S2.

3.2. Mercury losses in the Råne river estuary

Mercury can be removed from the estuarine water column during transport through evasion and settling. Northern rivers are rich in DOC and tend to have lower POC content than temperate rivers (Ludwig et al., 1996; McClelland et al., 2016). This results in considerable losses of DOC through flocculation and settling when river waters encounter higher salinities in estuaries. For example, Asmala et al. (2014) found that 10–15% of riverine DOC is lost in northern estuaries before salinity reaches 2. Because a large fraction of Hg is bound to DOM, we expect that removal of Hg through flocculation and settling is a significant loss mechanism in the Råne river estuary.

Fig. 2A shows the association between total Hg and salinity across the northern Baltic Sea. We pool data into salinity ranges of one salinity unit bins and use the averages to calculate the deviation from conservative mixing along the salinity gradient (Fig. S1). We find that total Hg deviates by 2 pM, corresponding to a 49% loss of total Hg, from conservative mixing between salinities 1 to 2 while the deviation at higher salinities is < 0.5 pM (Fig. 2A; Fig. S1). If there is considerable input from atmospheric deposition during the transport through the estuary, the loss could be even higher.

In the Bothnian Bay the overall organic carbon load is estimated to contain 7% POC (Strååt, 2017). For the Råne estuary (stations RA1 and RA2) we calculate a 11% POC fraction using DOC and suspended particulate matter (SPM) data from Figueroa et al. (2016) and assuming that all SPM is organic and that carbon makes up half of the OM mass (text S1). Using a particle partitioning coefficient (log K_p) of 4–5 for Hg in the subarctic river and estuary (Schartup et al., 2015b) we calculate that 1–13% of total Hg is associated with particles (text S1). If we posit that 85% of particles are lost during transport through the estuary (Soerensen et al., 2016), then 1–11% of Hg is lost in the Råne estuary during settling of particles.

To quantify the loss of Hg through DOM flocculation and settling, we first estimate losses of DOC and humic matter content by calculating their deviations from conservative mixing in the Råne estuary between salinities 1–2 (using 2014–2016 data, Fig. S2). We find a loss of 9% and 17% for DOC and humic matter content respectively, consistent with Asmala et al. (2014). High molecular weight, humic-like DOM, most susceptible to flocculation (Asmala et al., 2014), preferentially mobilizes and binds Hg in the terrestrial landscape (Eklöf et al., 2012; Waples et al., 2005). If dissolved Hg (87–99% of the total Hg pool) is mostly associated with humic substances we expect that 8% to 17% of dissolved Hg to be lost through flocculation and settling. This accounts for 16–35% of the total Hg lost in the estuary and is equal to or higher than the predicted loss through particle settling (2–22% of the total loss). We suggest that Hg^0 evasion accounts for the remaining loss of total Hg from the Råne estuary (43–82%). Our result suggests that even in rivers with low POC content, flocculation of DOM in estuaries allows for a substantial fraction of Hg to be removed through settling.

Similarly to total Hg, MeHg declines with increasing salinity (Fig. 2B), however the fraction of MeHg removed through the water column processes differs from total Hg. The MeHg to total Hg ratio is 4.0–4.5% in the estuarine flocculation zone (salinity <2) and decreases to 2.1 ± 1.0% (1.3%–3.7%; $n = 15$) in the offshore water (Fig. S1). While some MeHg is removed through particle and flocculated DOM settling similarly to Hg^{II}, other competing processes, such as methylation and demethylation, are likely contributing to the differences in MeHg:total Hg ratio between estuarine and offshore waters.

3.3. *Drivers of methylmercury variability in the northern Baltic Sea*

Fig 2C and D shows the association between concentrations of MeHg and DOC, Fig. 2D also presents the water humic matter content. We use simple linear regression analysis and find that DOC is a strong predictor of MeHg concentrations within each basin (Bothnian Bay: $R^2 = 0.6, P < 0.01, n = 40$; Bothnian Sea: $R^2 = 0.6, P < 0.01, n = 31$) when samples in the low salinity (<1) zone are excluded, but not when the basins are combined ($R^2 = 0.3, P < 0.01, n = 71$). We use multiple regression analysis and find that of the variables tested (DOC, humic matter content, temperature, salinity, chlorophyll a, total nitrogen, ammonium, phosphorous), MeHg concentrations across the entire dataset are best predicted by concentrations of DOC and humic matter content ($R^2 = 0.5, P < 0.01, n = 62$; MeHg [fM] = DOC [μM] × 0.91 − Humic [μg L^{-1}] × 4.8 − 227). The model improves when sampling stations with strong riverine influence in the Bothnian Sea (<4 km from river mouths – B3 and B7) are excluded ($R^2 = 0.6$, $P < 0.01$, $n = 55$; MeHg [fM] = DOC [μM] × 0.73 − Humic [μg L^{-1}] × 3.16 − 192). We also find that only the labile DOC reservoir (>300 μM) correlates with MeHg concentrations (Fig. 2C and D).

The positive association between MeHg and labile DOC (Fig. 2C and D) suggests that labile DOC is a proxy for the remineralisation rate (Hoikkala et al., 2015) and Hg^{II} methylation potential within nearshore and offshore water columns. Hg^{II} and MeHg preferentially bind to DOM over inorganic particles, which depending on DOM quality can affect bioavailability (Mazrui et al., 2016; Schartup et al., 2015a). DOM can also decrease light attenuation reducing MeHg photodemethylation, or increase MeHg photodemethylation by forming reactive oxygen species (Fernandez-Gomez et al., 2013). If the primary effect of DOM was to decrease Hg^{II} availability or increase MeHg photodemethylation, then we would expect a negative relationship between MeHg and DOC. Furthermore, if the observed positive relationship between MeHg and DOC was driven by the formation of strong and stable MeHg-DOM complexes or by an increase in MeHg lifetime due to decreased light attenuation, the association would extend to the refractory pool of DOC. On the contrary, we find that MeHg concentration approaches 0 (by extrapolation) when the labile DOC reservoir is exhausted i.e. when the DOC concentration reaches the refractory “baseline” level of 300 μM (Fig. 2D) where the remineralization rate is expected to approach zero. We propose that below this labile DOC “baseline” level MeHg demethylation outcompetes the MeHg production resulting in net water column demethylation and a depletion of the MeHg reservoir.

Humic matter content (a good proxy for allochthnous DOM) decreases from the Bothnian Bay to the Bothnian Sea, where it remains constant around 10 μg L^{-1}. The multiple linear regression model suggests that the humic matter content negatively affects MeHg concentrations (Fig. 2D). Humic content can reduce microbial MeHg degradation by decreasing its bioavailability and reduce photodemethylation of MeHg by increasing light attenuation (Fernandez-Gomez et al., 2013). These processes would enhance the MeHg concentrations. Humic substances are also known to bind Hg^{II} and the humic matter content has been shown to correlate more strongly than DOC with Hg^{II} concentration in streams (Dittman et al., 2009; Mierle and Ingram, 1991). Previous studies suggest that binding to humic substances could make Hg^{II} less prone to microbial reduction and methylation (Schartup et al., 2015a). In addition, as humic substances are not easily remineralized, an increased proportion of humic matter can decrease the activity of Hg^{II} reducing and methylating microorganisms, and thus further decrease the rates for microbial mediated Hg transformation reactions. Humic substances have also been shown to abiotically reduce Hg^{II} to Hg^0 (Chakraborty et al., 2015; Skogerboe and Wilson, 1981). Our data suggests that in the northern Baltic Sea humic substances most likely decrease Hg^{II} availability for methylation, either by forming stable complexes with Hg^{II} or by converting Hg^{II} to Hg^0.

We propose that the variability in MeHg concentrations, explained by DOC and humic content is linked to the effect of net Hg^{II} methylation in the northern Baltic Sea water column. Furthermore, we suggest that this effect is controlled by OM remineralization rate (with labile DOC as a proxy) and Hg^{II} availability (through the effect of humic matter content). This is consistent with recent studies on lake water column and sediment that show that Hg^{II} methylation rates are lower in sediment dominated by refractory terrigenous (largely humic) OM than in sediment or sinking particles with a larger proportion of phytoplankton-derived organic matter (Bravo et al., 2017; Gascon Diez et al., 2016).

3.4. Interannual variability of methylmercury in the northern Baltic Sea

We use our statistical multiple regression model, and DOC and humic matter content measured between July and September to calculate interannual variability in water MeHg concentrations for the northern Baltic Sea in the summer/fall period between 2006 and 2016 (Fig. S3). We chose this period, as other principle factors controlling MeHg levels (like atmospheric Hg deposition (Amos et al., 2013) and Hg input from runoff (Soerensen et al., 2013)) are not likely to have changed considerably. Fig. 3A shows a comparison between our observed and modelled MeHg concentrations (2014–2016) in the nearshore Bothnian Bay (station RA2) and offshore Bothnian Bay and Sea. The statistical model is able to estimate main features of the MeHg variability (nearshore to offshore water differences in individual years and differences between years; $R^2 = 0.6$, $P < 0.05$) and the estimated concentrations are within 16 ± 14 fM of observations.

Fig. 3B shows estimated nearshore and offshore MeHg concentrations between 2006 and 2016. We estimate an interannual variability in the seawater concentration of MeHg by one order of magnitude and with a 105–140 fM difference between highest and lowest value within the 11-year span for the three locations. This is consistent with the high interannual variability measured between our three years of observations (factor of 3–8; 54–85 fM). Few previous studies have measured the interannual variability of MeHg in the water column and the ranges in other marine systems are largely unknown. Studies in the offshore waters of the Mediterranean and the New England Shelf found an interannual MeHg variability of up to a factor of two (Heimburger et al., 2010; Schartup et al., 2015a). These studies were, however, limited to two consecutive years and may not have fully captured the magnitude of the interannual shifts in MeHg.

Long term changes in regional and global emissions of Hg are likely to drive decadal trends in water column MeHg concentrations (Amos et al., 2013), and some interannual MeHg variability will be controlled by terrestrial input of Hg (Soerensen et al., 2013). Our results suggest that variability in terrestrial input of humic substances and internal production of labile OM are also important drivers of large interannual variability in water column MeHg concentrations. An implication of this result is that we cannot rely on one to two years' measurements of MeHg concentrations in coastal systems like the Baltic Sea to understand MeHg levels and variability in biota whose lifespans usually exceed two years. Interannual variability in water column MeHg concentrations should be considered when interpreting both short and long term trends in fish and other aquatic animals.

3.5. Northern Baltic Sea methylmercury concentrations in a changing environment

Anthropogenic activity is altering the organic carbon cycle in coastal and marine systems worldwide (Regnier et al., 2013; Vonk et al., 2012). In the northern Baltic Sea, a 10–30% increase in precipitation and river water discharge is anticipated over the next 50–90 years (IPCC, 2013; Meier et al., 2012). The higher freshwater inputs are predicted to increase allochthonous OM (which includes humic substances) inputs by ~15% (Stråât, 2017). The composition of OM impacts future MeHg production and we use our statistical model to propose a range of possible MeHg concentrations in the northern Baltic Sea using expected ranges in humic matter content and DOC levels. Here we assume that external inputs of MeHg and Hg^{II} remain at current levels although we recognise that Hg^{II} and MeHg inputs are likely to increase with increasing freshwater inputs. Fig. 4 shows that an increase in allochthnous OM, and thus larger humic substances fraction of OM, will suppress MeHg production and keep MeHg water concentrations at or below current level. However, higher freshwater inputs can also increase the nutrient supply to the northern Baltic Sea increasing primary production and autochthonous OM, resulting in elevated water MeHg

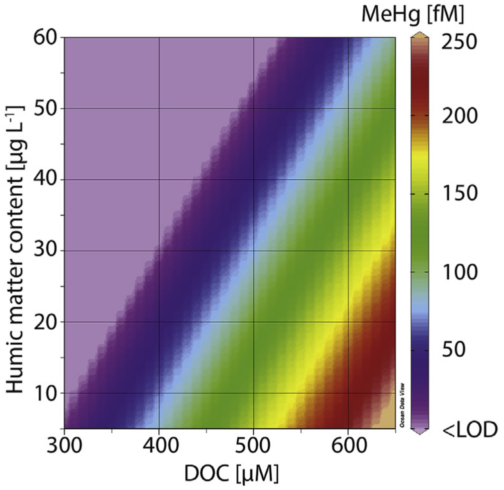

Fig. 4. Predicted water column MeHg concentration at different DOC and humic matter concentrations.

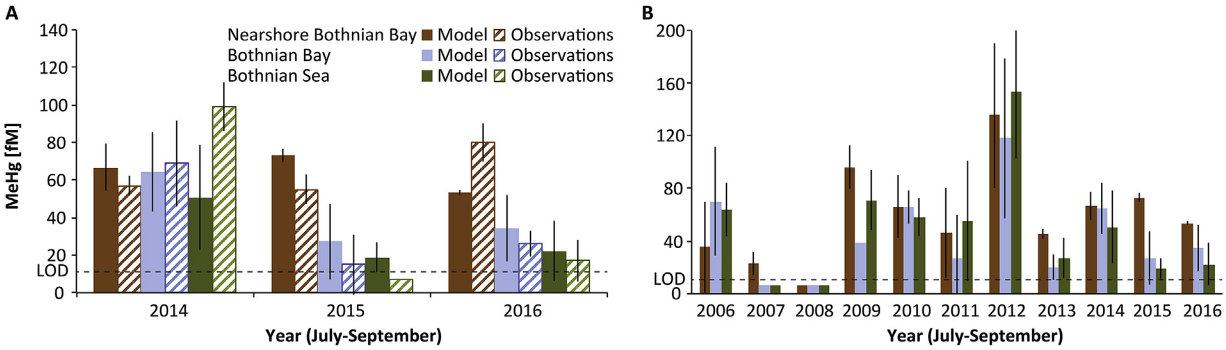

Fig. 3. A) Observed and modeled interannual variability in water MeHg concentrations in July to September 2014–2016. B) Calculated MeHg concentrations in July to September for 2006–2016. MeHg concentrations are estimated using the linear regression model (MeHg [fM] = DOC [µM] × 0.73–Humic [µg L^{-1}] × 3.16–192) and measured DOC and humic content in the Bothnian Bay outer estuary (station RA2, Fig. 1) and offshore water in the Bothnian Bay (stations A5, A13) and Bothnian Sea (stations C3, C14) (SMHI, 2015). For the multiple linear regression the variance inflation factor is < 3. Error bars indicating standard deviations for observations and model estimates are indicated on the figures.

concentrations. Climate's impact on the relative contribution of different components of OM to total OM are currently unknown making it difficult to predict whether OM will have an overall positive or negative impact on future MeHg concentrations. This manuscript highlights the need to understand future changes in OM cycling and consider these changes in order to better predict future Hg^{II} and MeHg concentrations in coastal ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.06.008.

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