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Mercury bioaccumulation in aquatic biota along a salinity gradient in the Saint John River estuary

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ABSTRACT

Although estuaries are critical habitats for many aquatic species, the spatial trends of toxic methylmercury (MeHg) in biota from fresh to marine waters are poorly understood. Our objective was to determine if MeHg concentrations in biota changed along a salinity gradient in an estuary. Fourspine Stickleback (*Apeltes quadracus*), invertebrates (snails, amphipods, and chironomids), sediments, and water were collected from ten sites along the Saint John River estuary, New Brunswick, Canada in 2015 and 2016, with salinities ranging from 0.06 to 6.96. Total mercury (proxy for MeHg) was measured in whole fish and MeHg was measured in a subset of fish, pooled invertebrates, sediments, and water. Stable sulfur ($\delta^{34}S$), carbon ($\delta^{13}C$), and nitrogen ($\delta^{15}N$) isotope values were measured to assess energy sources (S, C) and relative trophic level (N). There were increases in biotic $\delta^{13}C$ and $\delta^{34}S$ from fresh to more saline sites and these measures were correlated with salinity. Though aqueous MeHg was higher at the freshwater than more saline sites, only chironomid MeHg increased significantly with salinity. In the Saint John River estuary, there was little evidence that MeHg and its associated risks increased along a salinity gradient.

Introduction

While methylmercury (MeHg) is often found at high concentrations in fish, concentrations are typically lower in marine than freshwater species of similar trophic levels (Zitko et al., 1971; Luten et al., 1980). However, MeHg in estuarine environments has been less studied. Previous work on MeHg in estuarine food webs include broader spatial studies on fish (van der Velden et al., 2013; Fry and Chumchal, 2012; Evans and Crumley, 2005), and intensive sampling in Arctic through sub-tropical estuaries (Buckman et al., 2017; Taylor et al., 2012; Farmer et al., 2010). There have been equivocal patterns in MeHg in biota along estuarine salinity gradients, but total mercury (THg) concentrations in fish (a proxy for MeHg) can be lower in individuals from higher salinity habitats (Fry and Chumchal, 2012; van der Velden et al., 2013; Smylie et al., 2016). In addition, sediments from lower salinity sites have higher mercury (Hg) methylation rates (Compeau and Bartha, 1984, 1987; Blum and Bartha, 1980). Much of the existing literature supports this negative trend between MeHg and salinity, which could be due to increased sulfide in saline waters binding inorganic mercury (Hg (II)), making it less available for methylation within this environment (Compeau and Bartha, 1984). Also, the decreased deposition/increased

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dilution of Hg in marine waters compared to terrestrial environments (Mason et al., 1994) would likely contribute to lower MeHg concentrations in marine habitats and organisms. Studies have also found no relationship between THg in wild fish and salinity (Evans and Crumley, 2005) or that their THg increases with salinity (Dutton and Fisher, 2011; Farmer et al., 2010). The mixed results most probably reflect the complex relationships between estuarine environmental factors (*e.g.*, salinity, percent forest cover, level of human development, total suspended solids, dissolved organic carbon) and MeHg production or availability to biota (Buckman et al., 2017).

Stable isotopes can be used to identify diet and to trace MeHg biomagnification through food webs (Clayden et al., 2017; Kidd et al., 2012). Nitrogen isotope ratios ($^{15}N/^{14}N$; expressed as $\delta^{15}N$) assess relative trophic level of consumers because they retain more of the heavier isotope, and it is generally accepted that this ratio increases by 3.4 ± 0.98‰ (average ± SD) with each trophic level (Post, 2002). Because MeHg also increases with trophic level, $\delta^{15}N$ can be used to quantify and contrast its biomagnification in aquatic food webs (Kidd et al., 2012; Clayden et al., 2017). Beyond identifying primary production fueling food webs (Fry, 2006; Svensson et al., 2007), carbon isotopes ($\delta^{13}C$; $^{13}C/^{12}C$) can measure how much feeding takes place in freshwater or marine environments for biota as $\delta^{13}C$ values increase with salinity, reflecting the enriched $\delta^{13}C$ of marine CO_2 (Fry, 2002, 2006). In addition, $\delta^{13}C$ increases by 0.39 ± 1.3‰ in consumers compared to their food (Post, 2002). Marine sulfur has higher isotope values ($\delta^{34}S$; $^{34}S/^{32}S$) compared to freshwater sources and, thus, can distinguish whether animals have been feeding on marine or freshwater food sources (Fry, 2002) because their values will be similar to those of their diet, *i.e.*, little fractionation occurs (McCutchan et al., 2003; Fry, 2013; Fry and Chumchal, 2011).

This study investigated concentrations of Hg, measured as THg, MeHg and Hg (II), in fish and invertebrates along a salinity gradient in an estuary. We hypothesized that Hg bioaccumulation in estuarine food webs was regulated by the degree of marine influence. We predicted a negative correlation between salinity and MeHg in biota based on marine dilution of Hg inputs to aquatic systems and evidence of decreasing concentrations of MeHg from freshwater to marine environments commonly seen in the literature (Compeau and Bartha, 1984, 1987; Blum and Bartha, 1980; van der Velden et al., 2013; Evers et al., 2005; Fry and Chumchal, 2012; Farmer et al., 2010; Smylie et al., 2016). If this prediction is true, then marine influence could mitigate the risk of MeHg toxicity that exists for fishes found in estuarine environments.

1. Methods

1.1. Study area

The Saint John River has a drainage area > 55,000 km^2 and flows into the Bay of Fundy at the City of Saint John, New Brunswick, Canada (Kidd et al., 2011; Metcalfe et al., 1976). The Bay of Fundy exhibits high tides up to 8 m in the Saint John Harbour, and the head of the tide occurs 135 km upstream (Kidd et al., 2011). The saline waters extend as far as 60 km upstream of the river mouth, creating a continuous salinity gradient from freshwater to the harbor (Metcalfe et al., 1976). The Saint John River estuary is a nursery ground for fish and hosts 35 species (Department of Fisheries and Oceans Canada, 2009). THg concentrations in sediments and large-bodied fishes were measured in the 1970s, but no studies have assessed MeHg in the estuary (Dadswell, 1975; Travers, 1976).

1.2. Field collections

Ten sites within the Saint John River estuary were selected along the salinity gradient ranging from freshwater to brackish water near the mouth of the river (Fig. 1; see also Table 1). The sites had shallow beaches conducive to seining (Curry et al., 2009). Site physico-chemical characteristics were sampled within a three-hour window after the high tide measured at Saint John. Dissolved oxygen (DO) was measured at 0.75 m below the surface using a calibrated YSI Multi-Meter Model 85 (2015 and 2016). From July 26 to September 4, 2016, HOBO Conductivity Data Loggers were deployed at each site recording conductivity (0.1 μS/cm) and temperature (0.01°C) every 5 min for roughly 24 hr for two neap tide and three spring tide cycles (n = 5 data sets with n = 283, 5-minute samples). The loggers were deployed 50 cm above the substrate at a total depth of 0.5–1.5 m (depending on the tide's height). Salinity (Practical Salinity Scale) was used as a proxy of marine influence. It was calculated from each conductivity and temperature reading (Weinkauf, 2015) based on algorithms outlined by UNESCO/ICES/SCOR/IAPSO (1981) and assuming a pressure of 1 standard atmosphere. For each site, the average of the salinity data between the 10th and 90th percentiles was used for all subsequent analysis to remove data extremes. These averages were also used to represent salinity at the sites for both years because only point measures of salinity were collected in 2015. The average absolute difference between one-time YSI probe salinity measures in 2015 and the average of continuous HOBO measures in 2016 from the same site was 1.42 ± 1.56 (average ± SD will be reported throughout text).

Seine nets were used to collect fish from each site (Curry et al., 2009). Fourspine Stickleback (*Apeltes quadracus*) occurred at all sites and thus was selected for Hg analyses. At each site, 7–10 fish were weighed (0.01 g), measured for total length (0.1 cm), euthanized using MS-222 and sacrificed using spinal severance according the University of New Brunswick's Animal Care protocol (2016-1S-01), and frozen within a few hours of collection. We analyzed MS-222, and no THg was found at a detection limit of 3.75 μg/kg. Fish collections were completed within a three-hour window after high tide (Saint John) between August and October 2015 and in August 2016. Clips were taken from the caudal fin of each fish and stored in 95% ethanol in a freezer for subsequent genetic analysis.

Invertebrate collections were done at each site using sweep nets, kick nets, and rock-picking. Snails (genera *Physa*, *Fossaria*, and *Viviparus*) and amphipods (*Gammarus*) were the common invertebrates found during collections in August 2015 (n = 1 sample per site in 2015, except no snails were present at site 9 in 2015). We pooled all individuals to make one pooled sample per site for both amphipods and snails to obtain sufficient mass for all chemical analyses (>30 mg dry weight (dw)). In 2016, snails and amphipods were collected on

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