Distribution of mercury and trace metals in shellfish and sediments in the Gulf of Maine

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The use and disposal of toxic chemicals contributes to the degradation of environmental quality in marine and estuarine ecosystems. Monitoring programs in the Gulf of Maine (GoM) have databases for contaminants that can reveal useful information on the status and trends of contaminants. Information on mercury distribution within Gulf of Maine sediments and shellfish from regional monitoring programs is presented here to illustrate the potential utility of regional synthesis from separate but appropriately-scaled monitoring efforts in shellfish safety assessment and environmental management. Mercury is highlighted because the high level of public awareness of environmental and human health risks and its continued release to the environment. These data show trace metals are present across a broad range of concentrations in sediments and blue mussels in the GoM. Between 2000 and 2006, the highest mercury concentrations observed in GoM sediments and blue mussel tissue occurred within urbanized or industrialized estuaries: Boston Harbor, Great Bay Estuary and Casco Bay, but also in Penobscot Bay where a chlor-alkali plant had been in operation. Trace metal concentrations in GoM blue mussel tissue has generally remained unchanged. Mercury and lead are of concern because they are present in some GoM areas at levels considered as “elevated” when compared to USA national averages (i.e., NOAA-Mussel Watch Program) . This study draws attention to the data available in two important environmental matrices (sediment and shellfish tissue), notes the need for evaluating and integrating information of additional matrices (e.g., water column, other biota) and lays a foundation for gaining a better understanding of shellfish safety and potential human exposure to trace metals from coastal marine ecosystems.

Keywords: mercury, trace metals, Mytilus edulis, sediments, integrated database assessments

Introduction

The widespread use and release of trace metals and other toxic chemicals by industrialized societies contribute significantly to the degradation of environmental condition and quality (Sanudo-Wilhelmy et al. 2004). Estuarine and coastal environments

are important areas for trace metal accumulation, and the biological communities in these areas can be adversely impacted by these contaminants, despite recent advances in pollution prevention and treatment (Appleton et al. 2006). Many priority pollutants, including mercury, have been observed at concentrations elevated well above natural background levels in higher trophic organisms throughout the global oceans (Harding et al. 1997; Campbell et al. 2005; Hammerschmidt & Fitzgerald 2006). Chemical contaminants present at toxic concentrations adversely affect processes essential for growth, reproduction, and survival (Kawaguchi et al. 1999). These processes are often used to reflect ecosystem condition. Moreover, human health is often linked with the quality of food and the environment (Dolan at al. 2005).

Mercury, more often in inorganic forms, has been released to the marine environment from many sources, most notably from fossil fuel combustion via atmospheric transport from terrestrial sources (Sunderland and Mason 2007). Ecosystem and human health concerns are heightened where inorganic mercury is microbiologically transformed to methylmercury, a neurotoxin that can have adverse effects on higher trophic level organisms as a result of bioaccumulation and biomagnification through aquatic food webs. In the US, there are consumption warnings due to elevated mercury levels in fish for most of the coastal states (US EPA 2007) and Health Canada issues similar warnings for Canadian waters (http://www.hc-sc.gc.ca/fn-an/securit/chem-chim/contaminants-guidelines-directives-eng.php).

Three monitoring programs that monitor for mercury and trace metals and include sites throughout the Gulf of Maine (GoM) are explored for their utility to present a regional perspective on trace metal levels in sediments and bioexposure to resident organisms in the GoM ecosystem. For example, bivalves, such as *Mytilus edulis* (blue mussel), are successfully used as an indicator organism for contaminant exposure in environmental settings throughout the world (Cantillo 1997; Monirith et al. 2003; Gil et al. 2006; Kljakovic-Gaspic et al. 2006). Here we explore the information available from various databases and monitoring programs (Chase et al. 2001; US EPA, 2004; Kimbrough et al. 2008) to describe the distribution of mercury and to a lesser extent, selected trace metals in the GoM to obtain a more integrated regional assessment. Comparison of metal concentrations to published public health and biological effects levels have been made to assess shellfish quality in the GoM. A basic descriptive approach is taken here because more complex analysis of combined data from the three programs presents some limitations due, in part, to differing monitoring purposes, program design, and analytical and sampling methods. The results of this cross-program analysis serve to evaluate the existing monitoring efforts, and to highlight aspects necessary for more detailed and comprehensive monitoring programs (Evers et al. 2008) that may contribute to improved local and regional environmental management in the GoM.

1. Materials and methods

1.1 Sources of Information

The monitoring programs featured for this analysis include the US Environmental Protection Agency's (EPA) National Coastal Assessment (NCA) Program, the Gulf of Maine Council's Gulfwatch Program and the US National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program (Table 1). Each program has unique criteria for site selection and measurement logistics (timing, frequency, replication, etc.), and within program spatial and annual variability. The focus here is on eight trace metals (Table 2) considered of environmental concern and common to all three programs, with specific attention given to mercury.

Table 1. Description of GoM monitoring program for metals and organic contaminants. Bolded information is covered in this study.

	EPA-NCA	**Gulf of Maine Council Gulfwatch**	**NOAA Mussel Watch**
Geographic area	US-wide	Gulf of Maine: US & Canada	US-wide
Sites in Gulf of Maine	422	58	14
Time period	2000-2006	1993-2008	1986-2008
Sediments	**YES**	no	no
Finfish species	YES	no	no
Bivalve species	no	**YES**	**YES**

Table 2. Range of trace metal concentrations for mussel tissues (Gulfwatch) and sediments (NCA) in the GoM

METAL	**Gulfwatch (µg g^{-1} DW)**				**NCA (µg g^{-1} DW)**			
	MDL	**Low**	**High**	**% Sites >FDA level**	**MDL**	**Low**	**High**	**% Sites >PEL**
Hg	0.0065	0.04	0.6	0	0.01	0.03	2.2	1.3
Ag	0.004	0.01	3.3	NA†	0.01	0.02	9.3	1.3
Cd	0.002	0.35	4.0	0	0.05	0.02	9.8	0.6
Cr	0.04	0.4	65	0	5.0*	0.49	489	3.6
Cu	0.04	2.6	43	NA	5.0*	0.46	331	1.1
Ni	2.6	0.05	8.2	0	1.0*	0.4	64	1.5
Pb	0.004	0.02	38	8.9	1.0	2.2	410	1.5
Zn	0.07	24	430	NA	2.0	3	1030	0.6

*Some contract analytical laboratories exceeded target method detection limits (Heitmuller 2001)
†NA: No FDA level available

The NCA program (http://www.epa.gov/emap/nca/html/regions/northeast.html) is designed to provide an assessment of conditions in estuaries at the national (USA) scale. Sampling is based on a stratified probabilistic design. Thus NCA data are interpreted to represent areas rather than specific locations. The NCA program is the most intensive spatial sampling program undertaken for trace metals, although of more brief duration, in the GoM region. Field and laboratory procedures are specified in Heitmuller (2001).

The Gulfwatch Program (http://www.gulfofmaine.org/gulfwatch/) is intended to provide information on the status and trends for chemical contaminants specifically to inform environmental and resource management in the GoM. Gulfwatch is the only trace metal monitoring program that spans the entire GoM, covering both US and Canada territories, and is modeled after the NOAA Mussel Watch Program (MW). As such, Gulfwatch uses *M. edulis* as an indicator of habitat exposure to a similar suite of organic and inorganic contaminants but is unique from the MW program in terms of the timing of collection and analytical details. Samples are collected during autumn and represent a composite of mussel tissues from each of the 64 sampling sites. Gulfwatch samples were analyzed for trace metals before 2003 at the Maine Health and Environmental Testing Laboratory (HETL, Augusta ME) and thereafter at the Battelle Marine Sciences Laboratory (MSL, Sequim, WA).

The US-wide NOAA MW Program (http://www8.nos.noaa.gov/cit/nsandt/download/mwmonitoring.aspx) is designed to provide information on the extent and temporal trends of chemical contamination in blue mussels and other shellfish in coastal waters for the purpose of identifying coastal areas at risk from the perspective of environmental quality (Kimbrough et al. 2008). In the GoM, 14 MW sites are sampled every two years. Trace metal analysis methods are described in Kimbrough and Lauenstein (2006).

In order to relate the observations of GW and MW to human exposure, FDA levels are used since they form the basis for Canadian and US assessments of shellfish consumption safety (USFDA 2001). Probable effects levels (PEL) are used to assess the effects of trace metals on resident biota in GoM coastal sediments (Buchman 2001, MacDonald et al., 1996).

1.2 Data Analysis

Annual means of Gulfwatch data were calculated from each replicate for each year and site combination. Site medians were used when aggregating results across sampling years in order to determine significant differences ($p \leq 0.05$). Descriptive statistics were obtained using S-Plus 7.0® (Insightful Corp., 2006) and Microsoft Excel (2008). Significant trends ($p \leq 0.05$) were evaluated using Spearman's rho computed as Pearson's correlation on ranked expression measurements according to Sokal and Rohlf (1995). The 85th percentile of GoM trace metal concentration values are used as a measure for identifying sites with 'high' metal concentrations. This is consistent with the approach used by the NOAA Mussel Watch Program as an index of high contaminant levels and serves as a means for comparisons between the two programs (O'Connor and Lauenstein 2005; Lauenstein et al., 2002, O'Connor 2002) . Spatial gradients of NCA sediment concentrations were estimated using the Kriging interpolation of the random NCA samples within targeted ecosystems in the GoM (e.g., Great Bay Estuary, NH & Cape Cod Bay, MA) using Surfer (Golden Software, Inc., CO).

2. Results

Trace metals in blue mussel tissue (Gulfwatch) and in sediments (NCA) were present at a wide range of concentrations in the GoM (Table 2), from near detection limits to relatively elevated concentrations (≥ 85th GoM percentile) at sites located in more urban or industrial settings. Lead had the widest-ranging concentrations in both mussel tissue and sediments. Lead and other chemicals that correlate with human populations tend to have wide ranging concentrations (O'Connor 2002). The FDA guidance level for lead in shellfish was exceeded at nearly 9% of the sites. No samples exceeded the FDA guidance levels for mercury, cadmium, chromium or nickel. PEL levels for all eight metals in sediments were exceeded at a low percentage of sites (0.6 to 3.6%).

Median mussel tissue Hg and Pb concentrations were relatively higher in the GoM (Gulfwatch) compared to the median US value (Mussel Watch,) (Fig. 1).

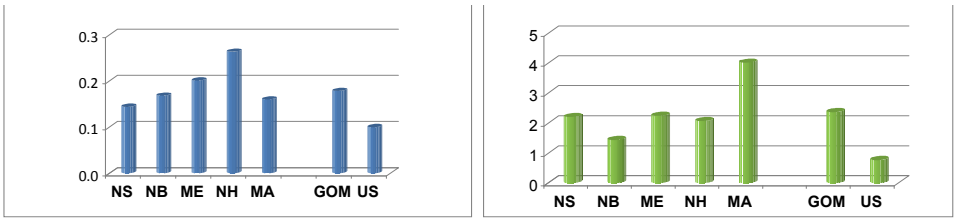

Fig. 1. Median concentrations (µg/g DW) of Hg (left panel) and Pb (right panel) in blue mussels for the five GoM jurisdictions (Gulfwatch) and for the continental US (Mussel Watch).

Other trace metal comparisons not presented here either showed little difference or the US median mussel concentrations were slightly higher than for mussels collected by

Gulfwatch. Median mercury and lead mussel concentrations also differed among the GoM jurisdictions; mercury was significantly highest ($p<0.05$) in New Hampshire, and lead was significantly highest ($p<0.05$) in Massachusetts compared to the other four jurisdictions.

Mercury distribution at all sites in the GoM shows areas where concentrations are elevated in both sediments and mussels (Fig. 2). The 85th GoM concentration percentile (0.296 µg g^{-1} DW) for Hg in sediments was exceeded in four distinct coastal areas of the Gulf of Maine: Penobscot Bay, Casco Bay, Great Bay Estuary and in and near Boston Harbor (Fig. 2B). The latter three areas are more urbanized, while Penobscot Bay has an industrial legacy that contributes to its elevated Hg levels. In Penobscot Bay, 21% of the sediment samples were above the 85th percentile, second only to 32% of the samples from Great Bay Estuary. The highest Hg concentration, (2.2 µg g^{-1} DW), was detected in Boston Harbor sediments. Three of the same areas, Penobscot Bay, Casco Bay and Great Bay, and two sites in New Brunswick had elevated Hg levels in mussel tissue (Fig. 2A).

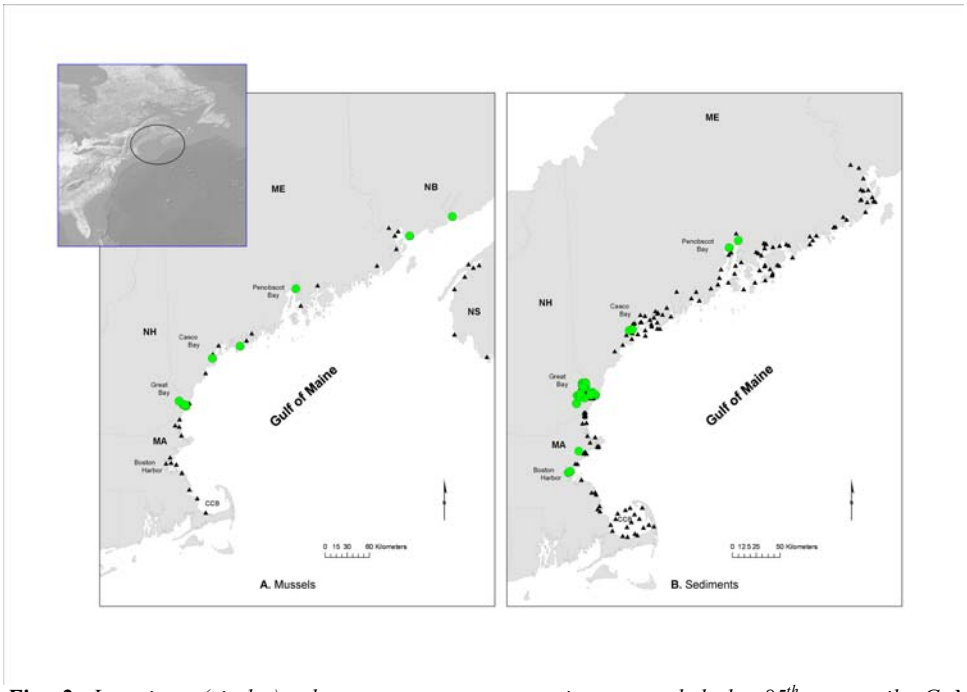

Fig. 2*. Locations (circles) where mercury concentrations exceeded the 85th percentile GoM concentrations in blue mussels (left panel-A) and sediments (right panel-B). Triangles represent sites with lower mercury concentrations.*

Temporal trends for metals at GW sites with more than five years of available data generally show no change in concentration over time, though a few significantly decreasing trends were found (Jones et al. 2010). The Mussel Watch program also reported few trends for similar metals that included sites in northeastern US (O'Connor & Lauenstein, 2006).

The extensive NCA sediment database for trace metals allows concentration distributions to be shown across a range of spatial scales. The most intensive survey available is for the Great Bay Estuary in New Hampshire, where the fine scale concentration gradients are consistent with known historical pollution sources (Fig. 3).

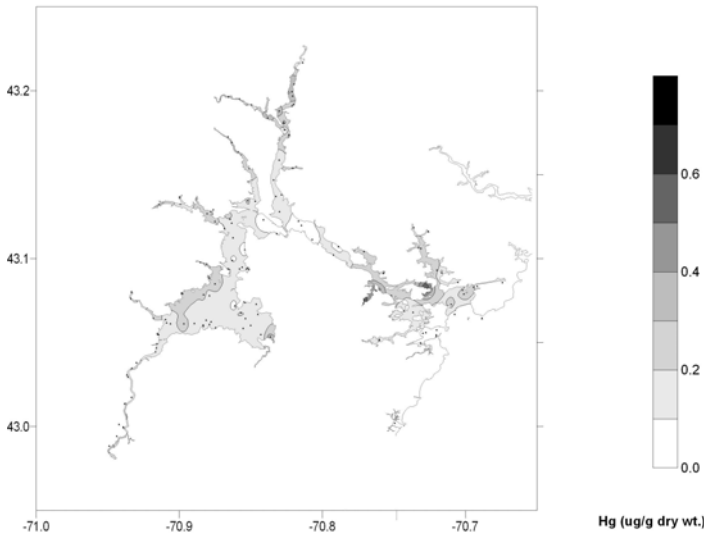

Fig. 3.Distribution of mercury in the sediments of the Great Bay Estuary, New Hampshire/Maine. Hg concentrations (µg g-1 DW) in 0.1 increments. Black dots indicate sample locations used in generation the spatial concentration gradient

Mercury concentrations in Cape Cod Bay, where sampling was less spatially intensive than Great Bay of New Hampshire, show a non-random distribution, with higher Hg concentrations present in a depositional area located near the center of the bay (Fig. 4).

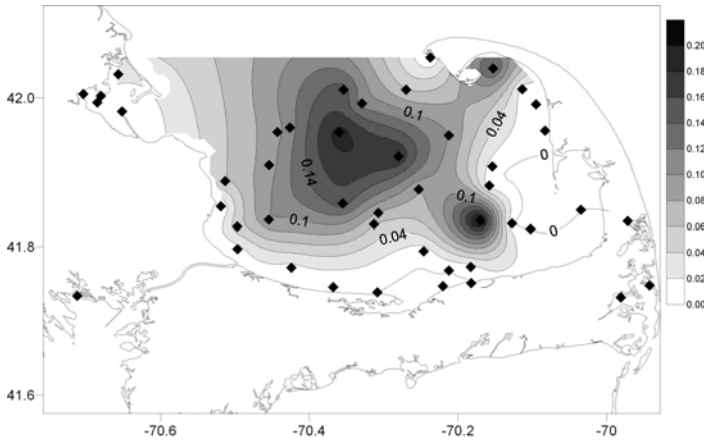

Fig. 4.Distribution of mercury in the sediments of Cape Cod Bay, Massachusetts. Hg concentration (µg g-1 DW) in 0.02 increments. Black diamonds indicate sample locations used in generation thethe spatial concentration gradientt

3. Discussion

The consistent occurrence of high mercury levels in sediment and blue mussel tissues in urbanized and industrially impacted coastal areas of the GoM suggest a linkage between these matrices and the importance of known local sources. It is clear that both historic and present-day pollution sources affect the degree to which sediments and bivalves are contaminated and by extension, human health risks for shellfish consumption.

The combined results of the MW and GW programs help evaluate which trace metals may be of more importance with respect to human and ecosystem health in the GoM. The elevated GoM median concentrations for both mercury and lead and the Gulfwatch sites where samples that exceeded the national criteria (MW 85th percentile) for lead and mercury lend support for heightened concern for these two contaminants. Equally important is evaluating temporal trends for contaminant levels. The Gulfwatch Program has recently compiled enough annual data (1993-2008) to evaluate temporal trends. The general observation of little or no changes in trace metal concentrations with time is similar to USA national trends (O'Connor and Lauenstein 2006) is significant because all the metals have been subject to management actions to reduce their discharge into the marine environment.

Significant management action may have contributed to discernable changes in spatial patterns for some trace metals with time. The impacts of these management actions, like the relocation of the Boston municipal outfall from Boston Harbor to Massachusetts Bay, need to be further evaluated. The accumulation of mercury in Cape Cod Bay is complex and includes aspects of transport from urban point sources, atmospheric deposition from local and distant sources, prevailing currents, equilibrium processes between overlying water and the quality of sediments-such as is indicated by contaminant accumulation in the deeper, organic–rich areas of Cape Cod Bay. The fine scale spatial mapping illustrated here shows that the fate of contaminants can be either immediate to areas adjacent to sources or distant to more removed areas where transport by currents, atmospheric deposition, and sediment-water equilibria may affect trace metal fate. The NCA program information for sediment trace metals and other contaminants is extensive, though few if any studies have incorporated the information for GoM-wide assessments.

Assessing contaminant exposure and impacts on an ecosystem basis remains a significant challenge. Comparison of trace metal levels with FDA and PEL values are means that relate impacts to humans and resident biota of the region. This initial attempt to analyze a few relevant monitoring program databases in space and time illustrates the potential for synthesizing information on GoM-wide contamination, exposure and trends for two important environmental matrices. Nevertheless, many questions remain unanswered. Further support of similar efforts that focus on the interpretation of existing data with exploratory analyses for the purpose of generating ecosystem-scale information may be one approach to advance current, more narrowly-focused monitoring efforts into a broader understanding of contaminant exposure in the GoM ecosystem.

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