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Covariance of Copper Concentrations in Lobsters and Seawater

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Lobsters (*Homarus americanus*) are an important commercial fishery resource in the Maritime provinces of Canada. They inhabit, and are fished in, the waters of numerous harbours and estuaries, many of which are subject to substantial contaminant inputs. It is well known that lobsters accumulate very high concentrations of metals from their environments (Uthe et al. 1982, Chou et al. 1998. According to Cooper and Uzmann (1980) adult lobsters from inshore populations are rather sedentary animals generally not ranging far from their home shelters. A tagging study in Belledune Harbour (Uthe et al. 1982) confirmed that movement of contaminated harbour lobsters was limited. Thus, the majority of lobsters caught in any location will have been exposed to contaminants in the immediate vicinity, and measures of biological effects or contaminant burdens should reflect this exposure.

In this study we investigated whether levels of copper in lobster digestive gland reflect average levels in water or sediment in the area where the lobsters were captured. Water or sediment concentrations represent two chemical measures of the environmental quality that the lobsters are exposed to, rather than a direct source of contaminants to the lobsters. Food is expected to be the main vector for contaminant uptake by lobsters, but ultimately the food sources will reflect water and/or sediment exposure.

Copper was chosen as a target contaminant for several reasons. First, it has a relatively high biological concentration factor for many marine organisms including crustaceans. It is also relatively easy to measure in water, sediment and biota and as a result there is a more extensive data set for copper than for most other contaminants. Its marine geochemistry is well understood, and we have observed a large range in the copper concentrations in lobster digestive gland samples collected arround the Maritime provinces. Finally, copper is a toxic metal that appears on most lists of priority environmental contaminants.

MATERIALS AND METHODS

Most of the lobsters used in this study were collected during a recent project to assess levels of contaminants in inshore lobsters from Nova Scotia and New

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Brunswick. In this study market-sized lobsters (generally 450-900 g) were collected in the intermolt period by commercial fishermen. Digestive gland copper analyses were conducted by inductively coupled plasma mass spectrometry (ICPMS) or atomic absorption spectrophotometry (AAS) on pooled samples prepared from 30 lobsters (15 male and 15 female) from each site. The methods are described in more detail in Chou et al. (1998). Analytical results for metallic contaminants from this project are reported in Chou et al. (1998, 2000). Additional measurements of copper in digestive gland generated in our labs and elsewhere have been taken from the literature (Uthe et al. 1989; NOAA 1994; Brunswick Mining & Smelting, Belledune, NB unpublished data).

Most of the sediment values for Cu used in this paper were generated either as a part of the surveys of metals in lobsters in harbours (Chou et al. 2000) or in earlier surveys of metallic contaminants in Nova Scotia and New Brunswick embayments (Dalziel et al. 1993; Loring et al. 1996, 1998). Measurements reported in the literature were also used (Buckley and Winters 1992). In these studies sediment samples were collected using either van Veen grabs or short, diver-collected sediment cores. Only results for analyses of total copper, conducted by AAS or ICPMS methods after total sediment digestion (HF/HNO_3), were used in this investigation.

Water column measurements for dissolved copper have been taken from reports of several surveys of metals in coastal inlets that we have conducted (Uthe et al. 1986; Dalziel et al. 1991, 1993) as well as unpublished data contained in the Bedford Institute of Oceanography (BIO) chemical oceanographic database. Additional estimates of copper concentrations in harbours have been made by adjusting observed measurements of long-term average copper concentrations in rivers (Dalziel et al. 1998) for dilution with seawater based on observations of salinity in the appropriate harbours using either published reports (Keizer and Gordon 1985; Keizer et al. 1996) or salinity data in the BIO Ocean Sciences climate database. Coastal water copper distributions have been generated by projecting copper concentrations onto an optimally estimated description of long-term averaged salinity distributions for the Scotian Shelf/Gulf of Maine using observed copper-salinity relationships for these waters. The estuarine copper concentration at any salinity (Cu_s) can be estimated from the average river concentration (Cu_r, from Dalziel et al. 1998), the average offshore copper concentration (Cu_o), and the offshore salinty (S_o) according to:

$$Cu_s = (Cu_o - Cu_r)(S/S_o) + Cu_r.$$

RESULTS AND DISCUSSION

The validity of the prediction of representative estuarine/coastal copper concentrations from river values depends on the linearity of the relationship between salinity and copper. The general linearity in the copper-salinity mixing relationship for these waters has been shown in a number of investigations (Yeats and Loring 1991; Dalziel et al. 1991; Yeats 1993 and references therein). Deviations from linearity are observed on occasion (e.g. Dalziel et al. 1993), but, clearly, linear relationships are a good description of the average picture.

The offshore copper distribution developed using optimal estimation techniques is a climatological average combining observations made over many years. It is important to use an average picture of the water column copper concentrations in this study because both the lobster and sediment concentrations will be integrators of their respective exposures. Spot measurements of dissolved copper may or may not give a good representation of this long-term exposure/input. Measurements that are averages of measurements taken at different times and over an area that represents the lobster's range will be preferable. In this respect, the concentrations calculated from river inputs are good in that they are based on numerous measurements of both the river concentrations and the harbour salinity. The offshore distributions are also good long-term averages. The numbers based on direct measurements in Halifax Harbour are fairly robust as they are based on seven surveys plus some additional spot measurements. The water column numbers for Pictou Harbour and Belledune Harbour are less robust being based on only two surveys in each of the harbours. The Ship Harbour value is based on three surveys and the Passamaquoddy value on only one survey.

All the results used in this study are listed in Table 1. Sampling locations in Maritime provinces of Canada are illustrated in Figure 1. Overall, the sediment and water concentrations in Table 1 are not significantly correlated (Figure 2). High sediment concentrations in Dartmouth Cove in Halifax Harbour, however, are associated with high dissolved copper concentrations and there is a covariance of water and sediment copper concentrations for the four Halifax Harbour samples. Buckley and Winters (1992) have shown a strong dependance of the sedimentary copper distribution on the sewage inputs, and Petrie and Yeats (1990), the importance of sewage inputs on the water column concentrations. The plot of lobster vs sediment concentrations (Figure 2) shows a similar pattern. There is a general lack of correlation except for the Halifax Harbour samples where high concentrations in sediments are associated with higher lobster digestive gland concentrations.

The plot of lobster digestive gland vs water concentrations (Figure 2) does show a significant correlation. The equation that describes the relationship is:

$$\text{Digestive gland } (\mu g/g) = 735 \text{ water } (\mu g/L) - 218 \qquad n = 17 \quad r = 0.722.$$

The quoted correlation coefficient ($P<0.01$) is based on a Spearman correlation to avoid any bias caused by the unsymmetrical nature of the distribution. The strength of this relationship (and the lack of a significant correlation with sediments) indicates that copper concentrations in lobster digestive gland are reflecting exposure to copper in the water column rather than levels in the sediments. The slope of the regression line implies a biological concentration factor for lobster digestive gland of 8 x10^5. This factor is higher than most reported for copper in marine biological tissues (eg. Fisher 1986), but perhaps not surprising as the lobster digestive gland is a known concentrator of metals.

Table 1. Copper concentrations in lobster digestive gland, sediment and water.

location	digestive gland µg/g	sediment µg/g	calc. water[1] µg/l	obs. water µg/l
Annapolis Basin (AB)	70.5[2]	11.8[3]	0.29[4]	
Ship Harbour (SP)		23.5[3]	0.40[4]	0.27[5]
Country Harbour (CH)	50.8[2]	18.1[3]	0.40[6]	
St. Marys Estuary (SM)	44.4[2]	9.6[3]	0.42[6]	
Petpeswick Inlet (PI)	12.3[2]	15.7[3]	0.36[6]	
Lunenburg Harb. (LH)	28.8[2]	58.2[3]		
Shelburne Harb. (SH)	18.5[2]	15.8[3]	0.34[6]	
Pubnico Harb. (PH)	10.4[2]	8.9[3]	0.37[6]	
Lahave Estuary (LE)	42.6[2]	31.2[3]	0.43[6]	
Cumberland Basin (CU)	836[7]	16.8[7]	1.36[8]	
Shepody Bay (SB)	636[7]	15.0[7]	1.18[8]	
Cobequid Bay (CB)	856[7]	17.0[7]		
Minas Basin (MB)	405[7]	9.3[7]		
St. John Harbour (SJ)	317[7]	19.2[7]	0.55[6]	
Dartmouth Cove (DC)	199[9]	250[10]		0.58[11]
Bedford Basin (BB)	70[9]	125[10]		0.35[11]
Northwest Arm (NA)	36[9]	100[10]		0.38[11]
Fergusons Cove (FC)		40[10]		0.24[11]
Pictou Harbour (PC)	53.5[12]	32[13]		0.53[13]
Belledune (BH)	93[14]			0.53[15]
Passamaquoddy (PB)	40.7[16]	14[17]	0.25[6]	0.24[5]
Lidonia Canyon (LC)	18.3[18]			0.2[19]

1. Calculated water column concentrations are based on river water concentrations from Dalziel et al. 1998 and estimates of salinity based on refs. indicated in the table. 2. Chou et al. 1998. 3. Loring et al. 1996. 4. Keizer et al. 1996. 5. Yeats unpublished data. 6. BIO Ocean Sciences Climate database. 7. Chou et al. 2000. 8. Keizer and Gordon 1985. 9. Uthe et al. 1989. 10. Buckley and Winters 1992. 11. Dalziel et al. 1991. 12. W. Fairchild unpublished data. 13. Dalziel et al. 1993. 14. BM&S unpublished data. 15. Uthe et al. 1986. 16. Chou unpublished data. 17. Loring et al. 1998. 18. NOAA 1994. 19. From optimally estimated copper distribution.

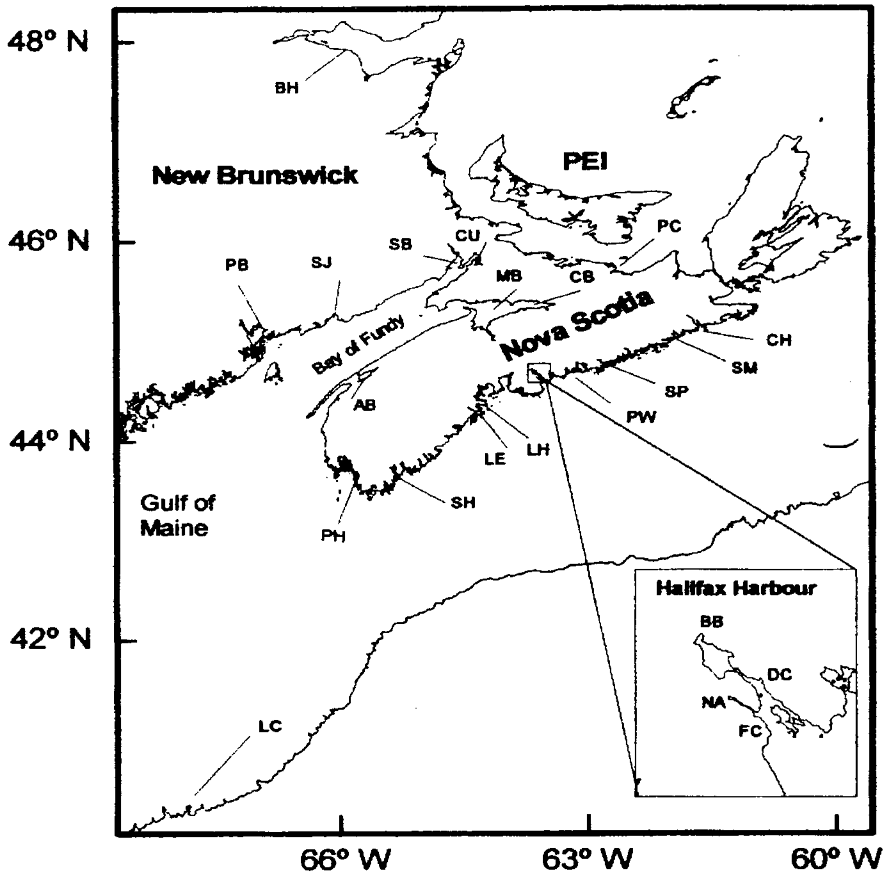

Figure 1. Sampling locations (location abbreviations are explained in Table 1).

High levels of copper in digestive glands of lobsters collected in Dartmouth Cove and elsewhere in Halifax Harbour likely result from municipal and industrial inputs, and shipping activities in the Harbour. High levels have been observed in other industrialized harbours (e.g. Boston Harbour; NOAA 1994). Industrial or shipping inputs may also explain the high level seen for the sample from Saint John Harbour. The highest levels in our study were found in the inner part of the Bay of Fundy, far from these industrialized harbours. The inlets at the head of the Bay of Fundy where these samples where collected (Cumberland Basin, Shepody Bay, Minas Basin, Cobequid Bay) are all highly turbid environments, but not

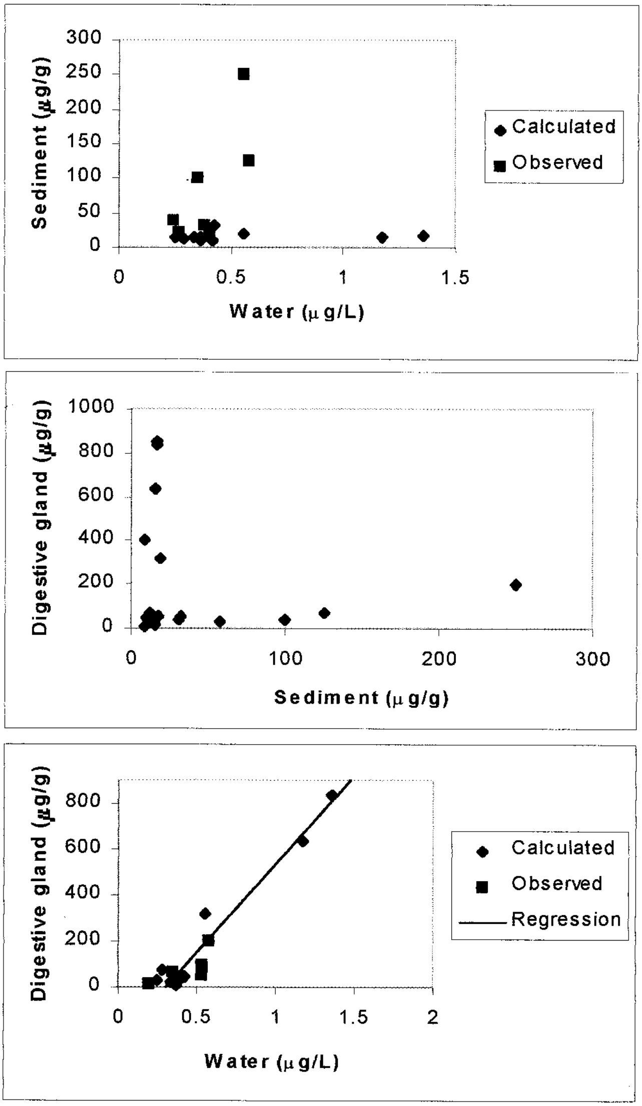

Figure 2. Plots of copper concentrations in (top) sediment vs. water; (middle) lobster vs. sediment; and (bottom) lobster vs. water.

highly industrialized. There are, however, several large communities on the rivers draining into these bays/basins including Moncton and Sackville NB and Windsor and Truro NS. These rivers also drain an environment with a more carboniferous sedimentary surface geology than seen for most of the other drainage basins included in this study. An analysis of the river data in Dalziel et al. (1998) shows that the two rivers draining the more sedimentary regimes around the upper Bay of Fundy have higher average copper concentration than those on the Atlantic coast of Nova Scotia which drain more igneous rocks (5.3 vs 2.5 μg/l). Data on the rivers draining into Minas Basin would be useful. Unfortunately, they were not sampled in the Dalziel et al. study.

Osmoregulation and changes in copper speciation may affect uptake of copper in lower salinity estuarine waters (Brown and Depledge 1998). Our samples, however, were all collected in the higher salinity outer reaches of estuaries (salinities from approximately 27 to 31), open coastal waters (salinity approximately 30 to 32), and in one case, the offshore (salinity approximately 35). Limited data on copper uptake by decapods at constant salinity suggests that regulation may occur at low concentrations, but at higher concentrations body burdens increase with increasing exposure (Rainbow 1998).

There are no human health guidelines for copper levels in fishery products in Canada. Concentrations of approximately 800 μg/g in lobster digestive gland, however, are very high, 30 to 100 times levels found in unindustrialized locations elsewhere. A study to investigate the possible sources of the high copper concentrations in inner Bay of Fundy lobsters, and the potential for biological effects on these lobsters is needed.

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