

Distribution, transport, and sources of metals in marine sediments near a coastal lead smelter in northern New Brunswick

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Abstract: Significant variations in metal concentrations occur in marine sediments collected from Chaleur Bay, an estuary located between northern New Brunswick and Quebec's Gaspésie. The bay receives metals from many sources including a lead smelter, a mercury-cell chlor-alkali plant, and numerous mined and unmined base-metal deposits. This study examines the dispersal patterns of metals released to the bay from natural and anthropogenic sources, and the processes that collect and redistribute these elements in the marine environment. Bottom sediments were collected from 124 sites in the bay, at distances up to 100 km away from the smelter. The ranges in metal and metalloid concentrations of 918 sediment subsamples are as follows, in mg/kg: As, 2.8 to 74; Cd, 0.02 to 69; Cu, 3.4 to 200; Hg, <0.01 to 2.4; Pb, 0.3 to 2000; and Zn, 22 to 3200. Dispersion of smelter effluents and atmospheric emissions by wind and/or nearshore currents has resulted in an area of elevated As, Cd, Cu, Hg, Pb, and Zn concentrations in surficial sediments within approximately 10 to 20 km of the smelter. The concentrations of most metals decrease sharply with increasing distance from the smelter; however, Pb concentrations exceed background levels in surface sediments throughout the bay. In sediments adjacent to the smelter, metal levels are highest at approximately 5 to 10 cm depth and decrease toward the sediment surface, which may reflect the significant reduction in smelter emissions since the mid-1970s. Lead isotope ratios suggest that the surface enrichment of Pb throughout the bay is mainly derived from smelter emissions and historical leaded gasoline combustion.

Résumé : Les concentrations de métaux varient significativement dans les sédiments marins prélevés dans la baie des Chaleurs, qui s'ouvre entre le nord du Nouveau-Brunswick et la Gaspésie (Québec). Les métaux rejetés dans cette baie sont issus de nombreuses sources, y compris une fonderie de plomb, une usine de chlore et de soude caustique à cellules d'électrolyse à cathode de mercure, de même que de nombreux gisements de métaux communs exploités ou non. La présente étude porte sur la répartition des métaux rejetés dans la baie depuis des sources naturelles et anthropiques, ainsi que sur les processus qui régissent leur dépôt et leur redistribution dans un milieu marin. Des sédiments de fond ont été prélevés dans 124 sites situés dans la baie, à des distances de la fonderie qui peuvent atteindre 100 km. Les concentrations de métaux et de métalloïdes relevées dans 918 sous-échantillons de sédiments sont les suivantes (mg/kg) : arsenic, de 2,8 à 74; cadmium, de 0,02 à 69; cuivre, de 3,4 à 200; mercure, de moins de 0,01 à 2,4; plomb, de 0,3 à 2000; et zinc, de 22 à 3200. La dispersion des effluents et des émissions atmosphériques de la fonderie par le vent ou les courants littoraux a entraîné la formation d'une zone de fortes concentrations en arsenic, en cadmium, en cuivre, en mercure, en plomb et en zinc dans les sédiments de surface qui reposent à environ 10 à 20 km de la fonderie. La plupart des concentrations de métaux diminuent rapidement en s'éloignant de la fonderie, mais celles du plomb dépassent les concentrations de fond dans les sédiments de surface de l'ensemble de la baie. Dans les sédiments au voisinage de la fonderie, les concentrations de métaux sont davantage élevées à une profondeur allant de 5 à 10 cm, tandis qu'elles diminuent vers la surface, ce qui pourrait refléter l'importante réduction qui touche les émissions de la fonderie depuis le milieu des années 1970. Les rapports isotopiques du plomb laissent supposer que l'enrichissement du plomb dans les sédiments de surface de l'ensemble de la baie résulte principalement des émissions de la fonderie et de la combustion, par le passé, de l'essence au plomb.

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INTRODUCTION

Emissions of metals, metalloids, and sulphur dioxide from base-metal smelters have caused extensive contamination of local environments since ancient times (Nriagu, 1990, 1996; Shotyk et al., 1998; Brännvall et al., 1999). Before the advent of modern pollution control devices, smelter emissions commonly resulted in vast tracts of barren land, and many studies have documented widespread contamination of air, water, soil, vegetation, and sediments in downwind receiving environments (e.g. Davies, 1983; Nriagu, 1984; Winterhalder, 1996; de Caritat et al., 1997; McMartin et al., 1999; Eckel et al., 2002; Lukin et al., 2003). However, the extent to which smelters have contributed to metal contamination of remote environments (i.e. >100–200 km from the point source) is not well understood, and there is much debate over the relative contributions of natural (geogenic) and anthropogenic sources of metals in such settings (Hong et al., 1994, 1996; Rasmussen, 1996; Garrett, 2000). In Canada, recent studies have focused on characterizing the fluxes, transport properties, environmental cycling, and fate of metals emitted from base-metal smelters to provide a sound scientific basis for ecological risk assessment and risk management decisions (Chapman and Wang, 2000; Conard, 2001; Newhook et al., 2003).

Many historical and modern base-metal smelting sites are located near the coast to facilitate shipping of raw materials and smelter products. Metal emissions from coastal smelters, through liquid effluents, atmospheric releases, and/or concentrate spillage, have caused significant contamination of the marine environment near most of these facilities (e.g. Crecelius et al., 1975; Dossis and Warren, 1981; Ward et al., 1984; Norrish et al., 1986; Ward and Hutchings, 1996; Nicolaidou and Nott, 1998; Schintu and Degetto, 1999). Unlike landlocked smelters, the dispersion of metals around coastal operations is controlled by both airborne transport and oceanographic processes. Once metals enter the marine environment they rapidly partition between various compartments: a portion will become associated with dissolved inorganic and organic ligands in solution, and another fraction will become associated with particulate matter following sorption, precipitation, and/or uptake by planktonic organisms (Tessier and Campbell, 1988). Transport of dissolved and particulate-bound metals by tides and currents can extend the influence of smelter emissions well beyond the main area of atmospheric fallout (Tiller et al., 1989). Ultimately, bottom sediments serve as a sink (and sometimes a source) for many of these metals and can provide a record of historical metal loading in the absence of significant postdepositional remobilization (Farmer, 1991).

The present study was undertaken in order to provide a marine component to the Point Sources project of the Geological Survey of Canada's Metals in the Environment (MITE) initiative (1997–2002). This paper examines the distribution and fate of metals emitted to the marine environment from Noranda, Inc.'s Brunswick smelter, a primary lead smelter located on the south shore of Chaleur Bay in Belledune, New Brunswick (Fig. 1). Chaleur Bay makes up half the surface area within 25 km of the smelter and receives a large part of the airborne particulate emissions and all the

hydrological release. The main objectives of this study are (1) to assess the origin and dispersal patterns of metals and metalloids released to the bay from natural and anthropogenic sources over time; (2) to evaluate the reliability of historical metal records in marine sediment cores; and (3) to characterize the chemical and physical processes that collect and redistribute these elements in the marine environment. This investigation examines the sources, transport, and fate of metals in marine sediments in order to provide scientific input for ecological risk-management decisions; however, direct assessments of the biological impacts of these contaminants are beyond the scope of this study.

REGIONAL SETTING

Chaleur Bay is located between northern New Brunswick and the south shore of Quebec's Gaspésie; it is one of several large estuaries draining into the Gulf of St. Lawrence (Fig. 1). It is approximately 180 km long and up to 38 km wide and deepens gradually eastward of Dalhousie, New Brunswick, to maximum depths of about 135 m. It receives an average annual freshwater discharge of 26 km³, with the largest contribution from the Restigouche River (7.2 km³/a) west of Dalhousie. Surface circulation in the bay is dominated by a 2 to 3 m tidal variation, which results in a net movement of water out of the bay, with stronger currents along the southern shore (Syvitski, 1992). Superimposed on this tidal regime is an inflow of water westward along the Gaspésie shore and an outflow of water from river discharge moving eastward along the New Brunswick coast (Legendre and Watt, 1970). Near Belledune, these currents follow the coastline and transport materials toward the east and southeast (Loring et al., 1980). Longshore currents arising from wave activity also play an important role in sediment transport near Belledune. The long easterly fetch results in heavy wave action on the east side of Belledune Point and gives rise to a net littoral drift of material to the west (Reddy, 1968). Therefore, transport of coastal marine sediments and suspended material by oceanographic processes in the Belledune region may vary from east to west depending on wave conditions and freshwater discharge at a given time of year.

The interplay of waves, tides, river discharge, and water depth controls the texture of recent bottom sediments in Chaleur Bay, which range from gravelly sands to silty clays. The textural characteristics of modern marine sediments throughout the bay shown in the GIS MITE database are based on an analysis of 250 surface sediment samples by Schafer (1977). In general, fine-grained sediments are restricted to deeper waters along the central axis of the bay and to sheltered nearshore areas such as Belledune and Dalhousie harbours (Loring et al., 1980). Gravelly sands characterize the margins of the bay, reflecting the effective wave action in these shallower waters. Further details of the marine geology of the bay are presented by Schafer (1977) and Syvitski (1992).

Chaleur Bay drains a hinterland basin of about 25 800 km² with a complex bedrock and surficial geology (Alcock, 1943). The bedrock data (*see* /Data directory on this CD)

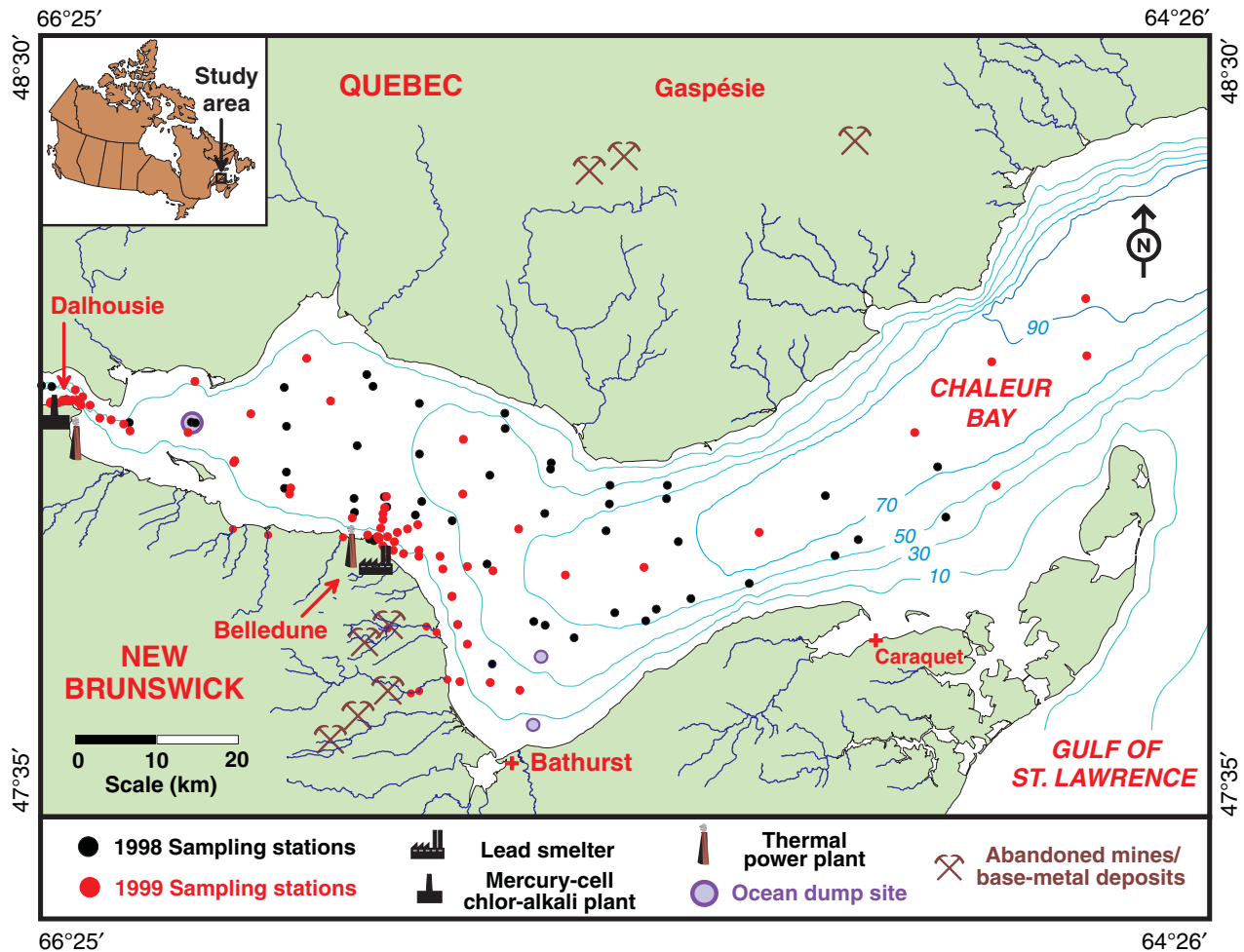


Figure 1. Chaleur Bay location map showing sediment sampling sites and point sources of metal emissions. Bathymetry contours are given in metres below lowest normal tides (after Canadian Hydrographic Service, 1982).

for northern New Brunswick and the southern Gaspésie are based on information from Potter et al. (1979), the Ministère de l'Énergie et des Ressources du Québec (1987), and Wheeler et al. (1997). In the low-lying Maritime Plain physiographic region, which extends from Bathurst, New Brunswick, east to the Gulf of St. Lawrence, the bedrock consists mainly of Pennsylvanian or younger sandstone, conglomerate, and siltstone. The New Brunswick Highlands region, which runs from Bathurst westward to Heron Island (just east of Dalhousie), is underlain by folded and faulted Ordovician, Silurian, and Devonian sedimentary and volcanic rocks, at least five Devonian felsic intrusions, and an Ordovician ophiolite suite (van Staal and Fyffe, 1995). In the Chaleur Uplands region, which extends from Heron Island around to southern Gaspésie, the bedrock geology is dominated by two main units. In southernmost Gaspésie where the land is relatively flat, middle Paleozoic bedrock is unconformably overlain by Carboniferous sandstone and conglomerate (van de Poll, 1995). The rugged interior is dominated by Late Ordovician to Middle Devonian sedimentary and volcanic rocks of the Gaspé Belt (Bourque et al., 1995); in eastern Gaspésie, a Cambro-Ordovician inlier is composed

of a greenschist facies volcanic-sedimentary sequence (De Broucker, 1987). Extensive glaciation of the entire study area occurred during the Quaternary, leaving behind thin, locally derived basal till, ablation till, glaciofluvial and alluvial deposits, erratics, and weathered bedrock over much of the region (Grant, 1989). The spatial distribution of these surficial deposits in New Brunswick and Gaspésie have been mapped in detail and compiled by Rampton (1984) and Veillette and Cloutier (1993), respectively.

METAL SOURCES AND PREVIOUS WORK

Chaleur Bay receives metals from a wide variety of natural and anthropogenic sources. Hildebrand (1984) presented a comprehensive overview of pollution sources and ecosystem impacts in the Chaleur Bay region as of the early 1980s; some significant reductions in metal emissions have occurred since that time. This section describes some of the main sources of metals in the Chaleur Bay drainage basin and presents results from previous studies at these sites.

Brunswick smelter

Noranda, Inc.'s Brunswick Smelting Division operates a primary lead smelter and refinery on the coast at Belledune (Fig. 1; lat. 47°53'57" N; long. 065°50'04" W). The smelter began production in September 1966 processing bulk lead-zinc concentrates, but was modified in 1972 to produce refined lead and associated byproducts by traditional lead-smelting methods (Dugdale and Hummel, 1977). Significant feed supplies have included lead concentrates from the Brunswick No. 6 and No. 12 mines and the Heath Steele mine, Cottrell precipitator dusts from other smelters (e.g. Noranda's Horne smelter in Quebec), and recycled lead batteries from a variety of sources. A description of the lead-smelting process at Belledune is provided in Bonham-Carter (2005). Additional details of the smelter operation and metal emissions can be found in Sergeant and Westlake (1980), Bowers et al. (1987), and Environment Canada (1998).

The principal environmental concerns associated with the smelter operations are the presence of potentially toxic elements, especially cadmium, in waste water and surface runoff, and air emissions of SO₂, lead, zinc, cadmium, arsenic, copper, and mercury. Noranda currently employs various pollution control technologies to reduce emissions including baghouses, electrostatic precipitators, scrubbers, a sulphuric acid plant, and a waste-water treatment plant (Bonham-Carter, 2005, Fig. B1). Prior to November 1980, surface-water runoff, process water, and slag-pond effluent were discharged directly to the sea from several points along the property, resulting in significant contamination of the marine environment, especially Belledune Harbour (Hildebrand, 1984; Bowers et al., 1987). Since that time, all liquid effluent from the smelter site has been collected and monitored by Noranda, Inc. and directed to an on-site water treatment plant if metal levels exceeded specified limits (Environment Canada, 1998).

Atmospheric emissions of metals have varied considerably over time in response to changes in smelting procedures, total production, and installation of pollution control devices. Figure 2 shows the variations in atmospheric emissions of Pb, Zn, Cd, and As from the Brunswick smelter between 1975 and 2001, and releases of Cu and Hg in 2001. Emission data from 1966 to 1974 are not available. The main sources of particulate and gaseous metal emissions to the atmosphere are the stacks associated with the sinter plant, blast furnace, acid plant, and the lead and silver refineries (P. Deveau, Noranda, Inc., pers. comm., 2003). Analyses of electrostatic precipitator dust and stack samples from the sinter plant and blast furnace baghouses show that these sources emit distinctly different particulates (Fig. 3). Dusts from the sinter plant baghouse consist mainly of angular sulphides (e.g. pyrite, chalcopryrite, sphalerite, galena), oxides, and Pb-Zn-Cd-rich agglomerates and spheres. Blast-furnace baghouse dusts and stack samples

consist primarily of metal-rich spheres containing up to 90 weight per cent Pb and rounded particles of metallurgical coke (Fig. 3). As shown in Figure 4, the prevailing winds at Belledune blow from west to east, transporting most of these atmospheric emissions into Chaleur Bay.

The relative contributions of metals through air and water emissions from the Brunswick smelter since 1981 were calculated using the historical data shown in Bonham-Carter (2005, Tables B3, B4). The results of this comparison are summarized in Table 1. Since 1981, atmospheric releases of Pb, Zn, Cd, and As have outweighed emissions to water by average factors of 342, 23, 44, and 23 times, respectively. However, these ratios have varied considerably over time, and average emissions of As were actually slightly higher to water than to air from 1983 to 1984. The data in Table 1 indicate that both atmospheric and waterborne emissions have contributed significant quantities of metals to the bay over time.

There have been many previous studies of the environmental impacts of metals emitted from the Brunswick smelter. Noranda, Inc. has conducted routine environmental monitoring in the Belledune region since the early 1970s and analyzed metal concentrations in soils, groundwater, forage crops, garden produce, marine sediments, mussels, and lobster. The company also operates high-volume air samplers and SO₂ analyzers at various locations around the smelter facility and monitors workplace contaminant levels and worker exposures to arsenic, cadmium, lead, and other contaminants (Environment Canada, 1998; Fleming et al., 1998). Detailed scientific studies of cadmium pollution in the marine environment took place in the early 1980s after high levels of Cd in sediments and biota near the smelter were detected during monitoring studies by Noranda, Inc. in the late 1970s (Dugdale and Hummel, 1977). In 1980, Fisheries and Oceans Canada closed the lobster fishery in Belledune Harbour and installed a controlled lobster fishery zone around

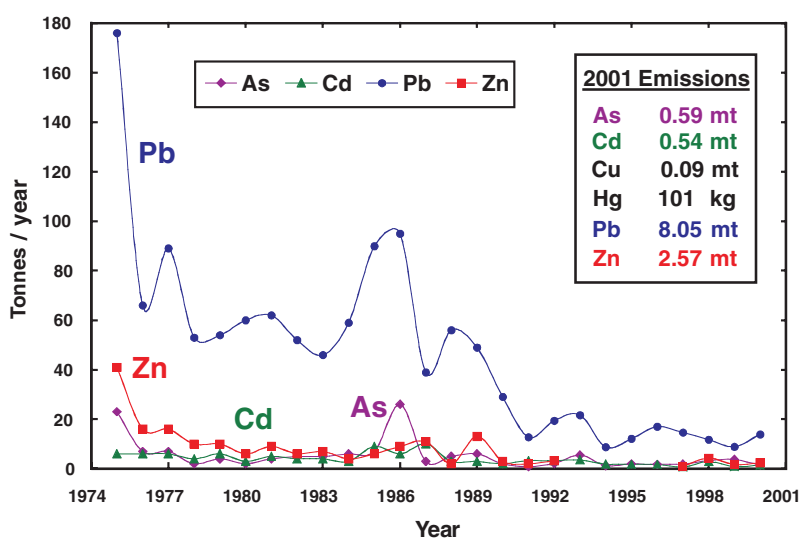


Figure 2. Atmospheric emissions of As, Cd, Pb, and Zn from the Brunswick Smelter between 1975 and 2000 (data supplied by Noranda, Inc.). Inset shows metal emissions in 2001, including Cu and Hg (Environment Canada, 2003).

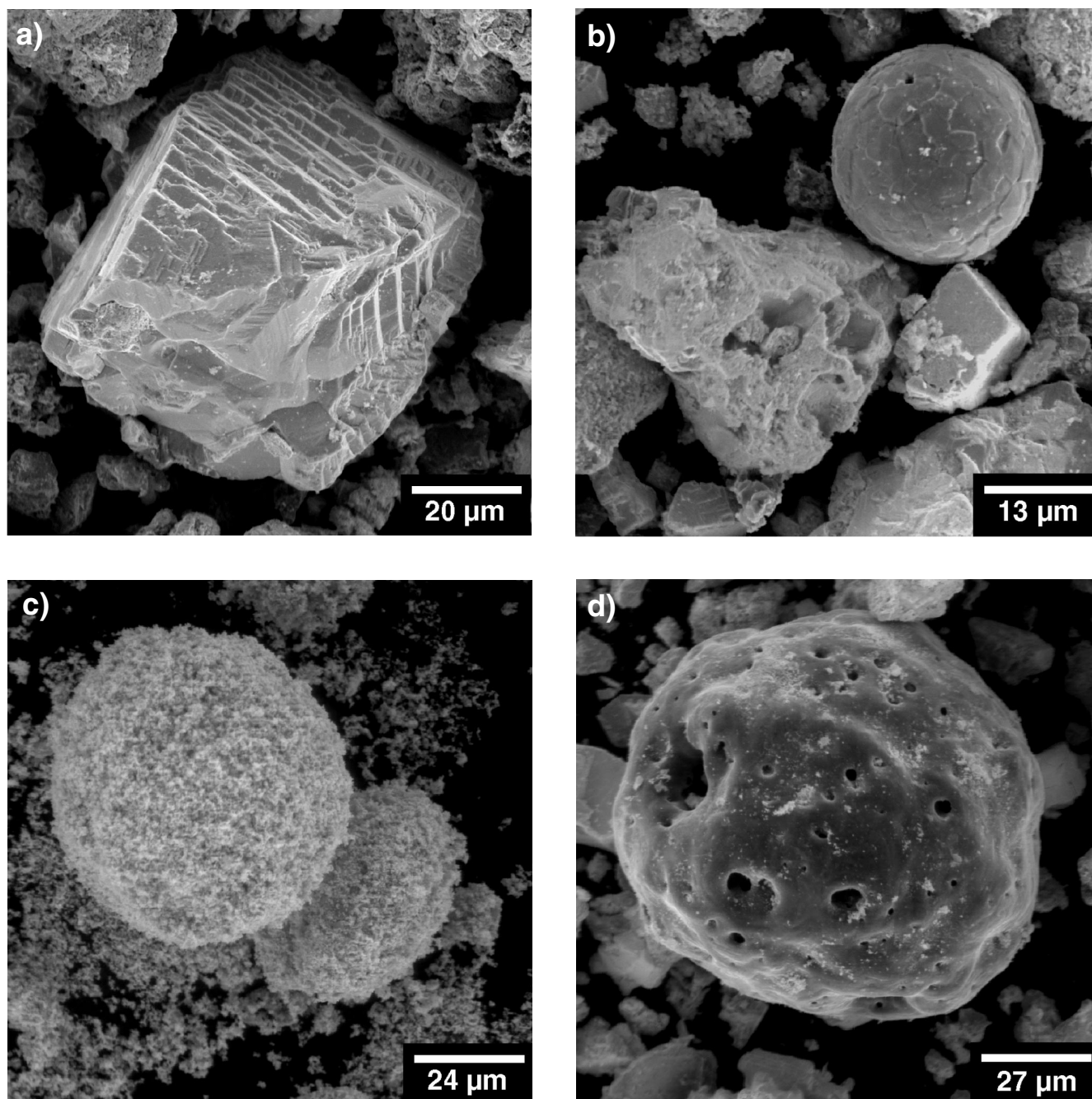
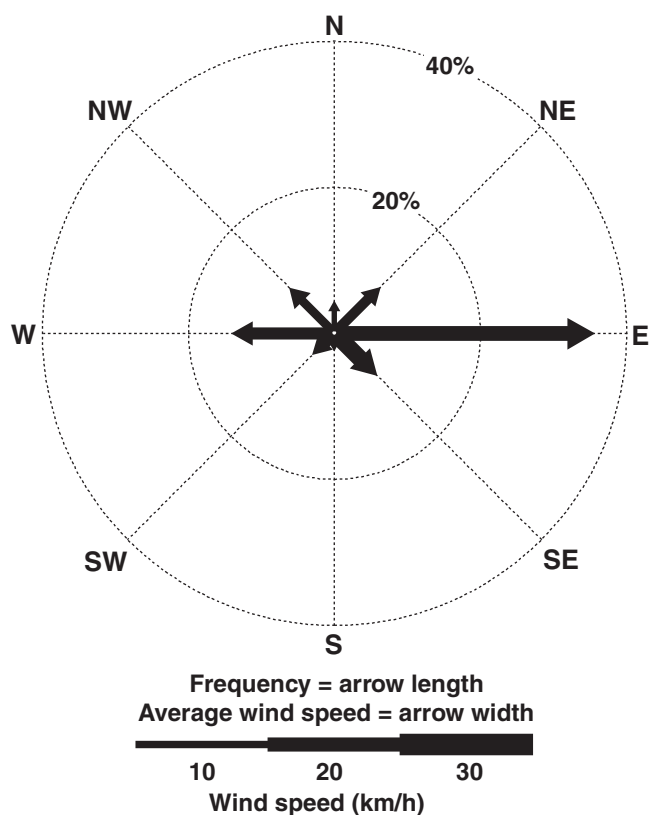


Figure 3. Secondary electron images of baghouse dusts and stack samples collected from the Brunswick smelter. **a)** Terraced sphalerite (ZnS) grain from the sinter plant baghouse; **b)** metal-rich sphere (upper right) and agglomerated particle (lower left) in stack samples from the sinter plant baghouse. Qualitative energy-dispersive spectrometry (EDS) analyses show that both particles are composed primarily of Pb, O, Fe, S, and Zn; **c)** dust-covered spherical particles from the blast-furnace baghouse. Qualitative EDS analyses indicate that these spheres consist mainly of Pb, with minor amounts of Zn, Cd, As, and Sb; **d)** metallurgical coke particle in a stack sample from the blast-furnace baghouse (all samples provided by P. Deveau, Noranda, Inc.).

**Figure 4.**

Wind rose diagram for Belledune, New Brunswick, for all months from 1978 to 1990. The frequency and average wind speed for eight principal wind directions are represented by the length and width of the arrows, respectively. This Figure is based on monthly records of meteorological observations in Canada published by Environment Canada's Atmospheric Environment Service, 1978–1990.

Table 1. Comparison of atmospheric and waterborne metal emissions from the Brunswick smelter, 1975 to 2000 (data supplied by Noranda, Inc.)

Year	Atmospheric metal emissions				Metal emissions in treated liquid effluent				Releases to air / Releases to water			
	Pb	Zn (tonnes/year)	Cd	As	Pb	Zn (tonnes/year)	Cd	As	Pb	Zn	Cd	As
1975	176	41	6	23	nd	nd	nd	nd	—	—	—	—
1976	66	16	6	7	nd	nd	nd	nd	—	—	—	—
1977	89	16	6	7	nd	nd	nd	nd	—	—	—	—
1978	53	10	4	2	nd	nd	nd	nd	—	—	—	—
1979	54	10	6	4	nd	nd	nd	nd	—	—	—	—
1980	60	6	3	2	nd	nd	nd	nd	—	—	—	—
1981	62	9	5	4	0.18	1.88	0.36	2.93	352	5	14	1.4
1982	52	6	4	5	0.13	1.26	0.62	4.93	401	5	6	1.0
1983	46	7	4	5	0.12	1.41	0.86	10.96	371	5	5	0.5
1984	59	4	3	6	0.12	0.61	0.21	7.58	505	7	15	0.8
1985	90	6	9	7	0.30	0.34	0.14	2.40	301	18	65	3
1986	95	9	6	26	0.66	0.66	0.87	2.42	144	14	7	11
1987	39	11	10	3	0.15	0.54	0.42	0.49	259	20	24	6
1988	56	2	3	5	0.09	0.14	0.14	0.24	601	15	22	21
1989	49	13	3	6	0.11	0.07	0.03	0.38	438	180	91	16
1990	29	3	2	2	0.08	0.09	0.05	0.81	360	32	43	2
1991	13	2	3.2	0.9	0.05	0.10	0.10	0.22	247	19	31	4
1992	19	3.2	3.2	2.1	0.07	0.18	0.31	0.10	292	18	10	20
1993	22	nd	3.6	5.5	0.05	0.22	0.09	0.07	460	nd	42	78
1994	9	nd	1.9	1.3	0.09	0.23	0.04	0.05	94	nd	53	26
1995	12	nd	1.7	2.0	0.04	0.17	0.02	0.06	291	nd	81	36
1996	17	nd	1.7	1.7	0.03	0.14	0.02	0.04	519	nd	104	42
1997	15	1.0	0.7	1.9	0.03	0.16	0.02	0.06	446	6	32	32
1998	12	4.3	2.9	3.2	0.06	0.36	0.03	<0.04	190	12	112	—
1999	9	1.8	0.9	3.8	0.04	0.26	0.02	0.05	205	7	43	69
2000	14	2.4	1.4	1.5	0.04	0.29	0.02	0.02	365	9	76	64
Totals	1216	184	101	138	2.45	9.11	4.36	33.82				
nd = no data												

the harbour when it was found that Cd concentrations in lobsters had reached a level considered unsafe for human consumption (Ray et al., 1981a; Hildebrand, 1984). Emergency procedures were instituted to study the situation and the results of these investigations are reported in Uthe and Zitko (1980). Rapid action by Noranda, Inc. reduced cadmium levels in the effluent by 97%, resulting in a reopening of the lobster fishery under controlled conditions in 1985 (Uthe et al., 1986). Since that time, numerous studies have documented the geochemical partitioning and bioavailability of metals in Belledune Harbour sediments and the uptake of these elements by marine biota (e.g. Bewers et al., 1987; Uthe et al., 1987; Samant et al., 1990; Bourgoïn et al., 1991; Chou and Uthe, 1993, 1995; Hansen et al., 1996).

Concentrations of Pb, Cd, As, and Zn in the terrestrial environment within 40 km of the Brunswick smelter have been reported by Pilgrim and Hughes (1994), who found that trace-element concentrations were highest within 2.2 and 3.0 km of the smelter in grass and snow, respectively. The results of their snowpack survey conducted in 1992 show that the maximum dispersion distances of these elements around the smelter (i.e. distance to background concentrations) are approximately 3.0 km for As, 3.0 km for Cd, 5.0 km for Zn, and 10 km for Pb. Given that the prevailing winds at Belledune blow toward the east (offshore) more than 50% of the time from December to February, these results suggest that eolian transport of smelter emissions over Chaleur Bay could extend to greater distances than suggested by the snowpack data.

Metallic mineral deposits

The varied geology of the Chaleur Bay drainage basin plays a major role in controlling the chemistry and mineralogy of the marine sediments. Mineral deposits of various types occur throughout the region, and elevated levels of metals have been reported for soils and stream sediments in many watersheds (e.g. Boyle et al., 1966; Presant, 1971; Choinière, 1982; Friske and Hornbrook, 1989; Pronk et al., 1998). The most extensive mineralization occurs in the Bathurst–Newcastle district in northern New Brunswick, which contains about 100 known base-metal occurrences, including 37 deposits with defined tonnages. Most of these are Zn-Pb-Cu massive sulphide deposits including the ‘super-giant’ Brunswick No. 12 deposit (located 60 km south of Belledune), which is the primary source of lead feed for the Brunswick smelter (McCutcheon, 1992; Goodfellow et al., 2003). In the past, acid mine drainage from some of these sites resulted in extensive contamination and fish kills in several rivers that enter Chaleur Bay near Bathurst (Fig. 1). However, studies have shown that Bathurst Harbour acts as an efficient trap for these metals through flocculation and sedimentation processes, and significant quantities of metals from these mines are unlikely to be transported into the open Chaleur Bay (Ray and White, 1977). Prior to 1975, dredged material from Bathurst Harbour was dumped at two sites just north of the harbour (Fig. 1), but previous studies of these disposal sites did not indicate significantly elevated levels of metals in the sediments (Hildebrand, 1984).

A number of smaller Pb-Zn-Cu massive, vein, and disseminated sulphide deposits also occur along several rivers within a 20 km radius of Belledune (Fig. 1; Davies et al., 1969). Acidic, metal-rich runoff from both mined and unmined deposits has contaminated local drainages near some of these sites (e.g. Appt, 1995), but stream-sediment surveys show that elevated metal levels are generally restricted to within 1 or 2 km of the deposits. One exception is the Elmtree River, 8 km south of Belledune, which contains high concentrations of metals in sediments derived from an abandoned Pb-Cu-Zn mine and numerous sulphide veins that cross the river bed (Boyle et al., 1966). This river, like many others along the New Brunswick and Gaspésie coasts, drains directly into a sheltered lagoonal estuary that most likely acts as a settling pond for metals in a manner similar to Bathurst Harbour. Mining activity in southern Gaspésie has not been as extensive as in New Brunswick, although a variety of mineral deposits occur in this region including polymetallic Cu-Zn-Pb-Ag-Au skarn occurrences, gold-bearing veins, and serpentinite-hosted Ni-Cr deposits (Dugas et al., 1969; Moritz and Malo, 1996). Stream-sediment surveys in southern Gaspésie indicate that these mineral deposits are not a significant source of metals to Chaleur Bay (Choinière, 1982).

Concentrate loading facilities

Noranda, Inc. operated an ore concentrate storage and shiploading facility in Dalhousie from the late 1960s until 1996, when they commissioned a new concentrate handling facility and consolidated port operations at Belledune (L. Surges, Noranda, Inc., pers. comm., 1998). High concentrations of metals (primarily Pb, Zn, Cd, and Cu) in Dalhousie Harbour sediments adjacent to the former Noranda facility are attributed to surficial runoff, wind-blown dust, and accidental spillage during ship loading (MacKnight, 1985). Several studies of the geochemical partitioning and bioaccumulation of these metals have shown that they are less bioavailable to marine invertebrates than those found in the Belledune Harbour sediments (e.g. Ray et al., 1981b; Samant et al., 1990; Bourgoïn et al., 1991). The low bioavailability of metals in the Dalhousie Harbour sediments reflects the extremely anoxic conditions created and maintained by large volumes of organic debris from an adjacent pulp and paper mill (MacKnight, 1985). Dredging of Dalhousie Harbour has occurred for many years to maintain adequate depths at the wharves. Before 1972, this material was dumped at any convenient location, but from 1972 to 1978 the Canadian Environmental Protection Service required disposal at a 25 m deep ocean dump site located 15 km east of the harbour in Chaleur Bay (Fig. 1). From 1978 to 1980, disposal was relocated to an intertidal location in Dalhousie Harbour and since 1981, dredge spoils have been placed in land containment cells (MacKnight, 1985). Several studies have examined the recovery of the ocean dump site since that time. Chemical analysis of surface sediments collected in 1988 showed that Cd, Pb, and Zn concentrations were significantly lower than in previous surveys in 1981 (Lee et al., 1990). The spatial distribution of metals suggests that metal-contaminated sediments had been

transported back toward Dalhousie by the predominately westward bottom currents, as previously suggested by MacKnight (1985).

Chlor-alkali plant

The only remaining mercury-cell chlor-alkali plant in Canada is operated by PCI Chemicals Canada Inc. in Dalhousie (Fig. 1). This plant, in operation since 1963, produces chlorine and caustic soda for the pulp and paper industry by passing a brine solution over mercury cells. Monitoring data from 1993 to 1997 showed average annual mercury releases to air and liquid effluents of 51 kg and 4.4 kg, respectively (Doiron et al., 1998; Environment Canada, 2003). However, mercury releases to air and water during the 1970s and 1980s were considerably higher and may have exceeded 2000 kg/a during the first decade of operations (Hildebrand, 1984). Sediments in the vicinity of the outfall of the plant and out into Chaleur Bay were found to have elevated Hg levels (up to 8.1 mg/kg) in studies conducted in 1974 and 1976 (Cranston et al., 1974). Clams collected in the intertidal zone near the outfall were also found to contain elevated levels of Hg in 1971 (Hildebrand, 1984). Recent studies of epiphytic lichens in the Dalhousie region indicate that the terrestrial area of influence of the mercury emissions extends 2.4 to 3.4 km from the chlor-alkali plant (Sensen and Richardson, 2002).

Thermal generating stations

New Brunswick Power Corporation operates thermal generating plants in both Dalhousie and Belledune (Fig. 1). The Dalhousie generating station (320 MW) started operations in 1969 as an oil-fired unit, and a second oil-coal unit came online in 1979. In 1994, both units were converted to Orimulsion® (an emulsion containing 70% bitumen in 30% water) firing in an effort to reduce SO₂ emissions. The Belledune generating station (480 MW) was constructed in 1993 approximately 2 km west of the Brunswick smelter and is currently fueled by pulverized coal and petroleum coke. Both stations employ flue gas desulphurization systems and electrostatic precipitators to reduce SO₂ and particulate emissions, respectively (Rivenbark and Moulard, 1995). Emissions of SO₂ are the primary environmental concern at these stations; however, fossil-fuel burning is a well known source of metal emissions. Bitumen combustion at Dalhousie is a significant source of vanadium and nickel to the atmosphere, and coal combustion at Belledune releases significant quantities of trace elements including arsenic, chromium, copper, mercury, nickel, and zinc (Environment Canada, 2003). A comparison of emission data (Environment Canada, 2003) for industrial sources in Belledune shows that the annual releases (1997–2001) of all reported metals except mercury are at least seven to eight times greater from the smelter than from the generating station. Atmospheric releases of mercury from the smelter in 2000 and 2001 were 76 kg and 101 kg, respectively, whereas stack emissions of mercury from the power plant were 110 kg and 111 kg for the same two years.

In summary, many different sources of metals exist in the Chaleur Bay region. In addition to the point sources described in this section, other metal sources (e.g. a decommissioned fertilizer plant at Belledune; municipal waste waters) have contaminated local environments (Hildebrand, 1984). Long-distance transport of certain elements (e.g. Hg, Pb) may also contribute to the overall metal budget of the bay. The results of previous work clearly show that high concentrations of metals exist near certain point sources and have occasionally resulted in adverse biological impacts. However, no studies have assessed the spatial extent of the Brunswick smelter footprint or the relative magnitudes of natural and anthropogenic metal emissions. The sampling and analytical methods employed during this study were chosen to help discriminate among metals from these various sources.

METHODOLOGY

Field sampling

Marine sediment samples were collected throughout Chaleur Bay during field expeditions in 1998 and 1999. The first sampling campaign was carried out from May 20 to 27, 1998, aboard the CCGS *Navicula* (Cruise 98012), collecting 37 cores and 15 surface-sediment samples from the study area (Fig. 1). Sediment cores were collected using a 1.5 m long gravity corer (10 cm internal diameter) and surface sediment samples were obtained with a Van Veen grab sampler (0.1 m², ~15 cm penetration). Sampling sites were originally located close to known point sources of pollution, near the mouths of most major rivers, and in a grid-like pattern throughout the remainder of the bay. However, the abundance of relatively coarse gravelly sand near both the north and south shores of the bay resulted in poor sample recoveries, and some sites had to be relocated closer to the finer grained sediments along the central axis of the bay. The second sampling program was conducted from September 20 to October 1, 1999, aboard the CCGS *Opilio* (Cruise 99046), collecting 39 cores and 33 surface-sediment samples on three radial transects near Belledune and at other sites up to 100 km away from the smelter. Stream sediments were also collected from four rivers in northern New Brunswick in 1999 (Fig. 1); however, the metal concentrations in these samples were in close agreement with the results of previous surveys (e.g. Boyle et al., 1966) and are not discussed further in this paper.

During both cruises, gravity cores were examined immediately upon retrieval in order to determine the depth of corer penetration and assess the nature of the sediment–water interface. In general, the top few centimetres of most cores consisted of light yellowish-brown sediments, reflecting the presence of oxidized iron and manganese minerals in the oxic surface layer. If the sediment surface appeared to be missing or had been disrupted by the coring process, or if corer penetration was insufficient, additional attempts were made to recover an undisturbed sediment sample. Once a satisfactory core had been collected, the core liner was immediately capped and kept upright in a cool area of the ship, then

transported to a makeshift laboratory at Belledune for processing within 24 hours of collection. Cores were subsampled at 2.5 cm intervals down to 10 cm depth, and then at 10 cm intervals down to the bottom of the core. Approximately 20 cm³ of wet sediment from each depth interval were placed into 25 mL polystyrene vials, and pore waters were separated using centrifugation. Grab samples were subsampled from 0 to 5 cm depth with a plastic spatula and all subsamples were frozen on the ship. Additional details of the sampling procedures are summarized in Cranston (2000) and Cranston and Parsons (2001).

Analytical methods

Sediment pore waters from all cores were filtered through 1 µm pore-diameter filters and analyzed in the field for ammonium, sulphate, and salinity. These pore-water data were used to evaluate sediment redox conditions and to estimate present-day sediment accumulation rates (Cranston, 1999). Dissolved ammonium was measured using a standard phenol-hypochlorite colourimetric technique modified from Solarzano (1969). Dissolved sulphate was determined by a turbidimetric method that uses barium to precipitate the available sulphate. Pore-water salinity was quantified by diluting 100 µL of sample with 6.5 mL of distilled, deionized water and measuring the sample conductivity. Precision and accuracy of the ammonium, sulphate, and salinity analyses were approximately ±0.2 mM, ±2 mM, and ±0.2 ppt, respectively. Detailed descriptions of these methods are presented in Cranston (2000) and Cranston and Parsons (2001).

Sediment subsamples for organic carbon and metal analyses were freeze dried. Organic carbon was determined in 0.5 g of sediment using a high-temperature combustion method following removal of the inorganic carbon using 1 M HCl. Precision and accuracy were estimated to be ± 0.03 weight per cent on the basis of replicate analyses of calibration standards. Subsamples for metal (Cd, Cu, Fe, Mn, Ni, Pb, Zn) analysis were prepared by digesting 1.000 g of freeze-dried sediment in 5.0 mL of concentrated HNO₃ for 24 hours at 60°C. This method results in a partial digestion of the sediment samples, but generally recovers between 50 and 90% of the total concentrations of the metals considered in this study (Parsons and Cranston, unpub. data, 2003). Arsenic concentrations were measured following a reverse aqua regia (3 mL HNO₃ + 1 mL HCl) digestion of 1.0 g of freeze-dried sediment for 3 h at 90°C. One-gram subsamples for mercury analyses were digested for 1.5 h at 80°C in a mixture of 0.1 g KMnO₄, 5 mL HNO₃, 5 mL H₂SO₄, and 5 mL of 5% K₂S₂O₈. The digestion procedures used for both the As and Hg analyses provide 'nearly total' concentration values for these elements. Element concentrations were measured using flame (Cu, Fe, Mn, Ni, Zn), graphite furnace (Cd, Pb), hydride-generation (As), and cold-vapour (Hg) atomic absorption spectroscopy (AAS). Analysis of duplicate samples and certified reference materials was used to monitor analytical accuracy and precision, which were generally ±5 to 10% for most elements (Cranston and Parsons, 2001). Scanning electron microscopy and energy dispersive

spectrometry were used to characterize selected sediment subsamples, as well as particulate samples collected from the smelter baghouses.

A subset of 20 gravity-core subsamples was analyzed in detail by quadrupole inductively coupled plasma mass spectrometry (ICP-MS) in order to measure the isotopic composition of Pb (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb). Wet sediment samples were taken from the archived sections of gravity cores, which had been stored at 4°C in air-tight liners for 16 months prior to subsampling. Lead isotope ratios and element concentrations were measured in leachates from two sequential extractions on 1 g of each sediment sample: 0.25 M NH₂OH•HCl (20 mL at 60°C for 2 h), followed by aqua regia (6 mL HCl + 2 mL HNO₃ in a 40–90°C water bath for 3 h (1 h at 90°C)). Leach solutions were diluted with 1% Seastar Baseline HNO₃ to yield Pb concentrations in the 5 to 10 µg/L concentration range. The proportions of each Pb isotope were determined by measuring the ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb intensities with dwell times of 100, 20, 25, and 10 ms, respectively. Thirty measurements of 60 s duration were completed on each sample. The intensity of ²⁰²Hg was measured to correct for any ²⁰⁴Hg signal contribution to the ²⁰⁴Pb intensity, and matrix blanks were analyzed to correct for any trace blank contribution (minimal). Instrumental drift and mass bias were corrected offline using NIST 981 Common Lead Isotope Standard diluted in the same matrix as the samples. The NIST standard was analyzed every eight samples. Analytical precision averaged 0.51% RSD for the ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios, and 0.55 % RSD for the ²⁰⁶Pb/²⁰⁷Pb ratio.

RESULTS AND DISCUSSION

Gravity-core concentration profiles

Most previous investigations of metals in sediments from Chaleur Bay have been based on analyses of surface samples collected using various types of grab samplers. These surveys are useful for mapping out the horizontal distribution of metals in recent sediments, but they do not provide much information on the vertical distribution of metals in the sediment column. In this study, 76 gravity cores were collected at various locations throughout the bay, in addition to 58 grab samples. Vertical metal profiles in gravity cores can potentially be used to infer changes in metal fluxes over time and, with sufficient corer penetration, may indicate background levels of metals in pre-industrial sediments. However, many chemical and physical processes can distort elemental profiles in sediment cores (e.g. sampling artifacts, bioturbation, diffusion, diagenetic remobilization), and the effects of these processes must be carefully considered before interpreting vertical metal records (e.g. Ridgway and Price, 1987; Farmer, 1991; Gobeil et al., 1999; Alpay et al., 2005).

Figure 5 shows vertical concentration profiles for gravity cores collected from Belledune Harbour, 1 km north of the Brunswick smelter, and the open Chaleur Bay, 34 km east-southeast of Belledune. Similar data for all gravity cores collected in 1998 and 1999 are tabulated in Cranston (2000)

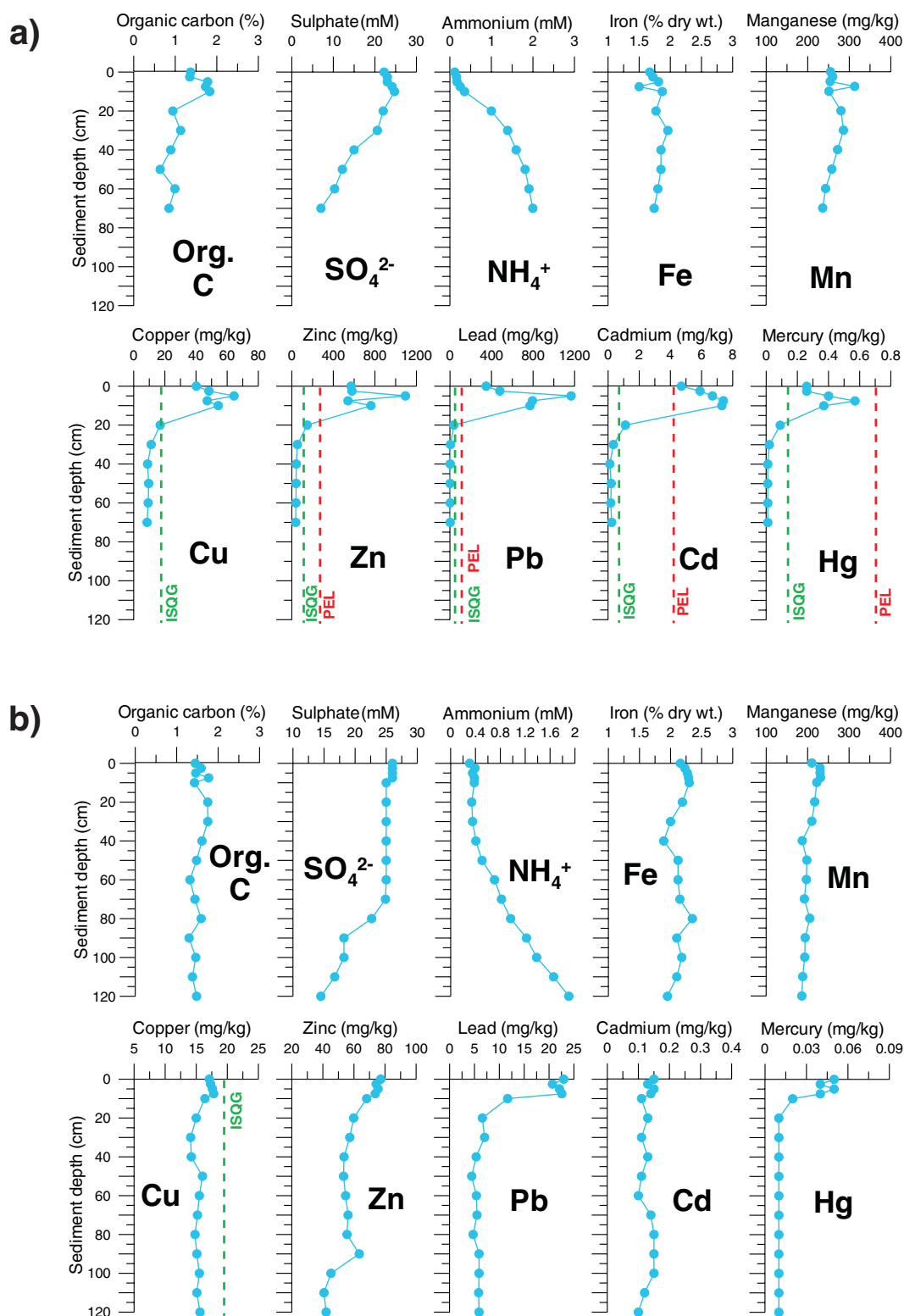


Figure 5. Vertical concentration profiles in sediment cores collected from **a)** Belledune Harbour, 1 km north of the Brunswick smelter, and **b)** the open Chaleur Bay, 34 km east-southeast of Belledune. Data for organic carbon (Org. C) and all metals are solid-phase concentrations, whereas the sulphate and ammonium profiles represent dissolved concentrations in the pore waters. The green and red vertical dashed lines on some plots show the Canadian interim sediment quality guideline (ISQG) and the probable effect level (PEL), respectively, for metals in marine sediments (Canadian Council of Ministers of the Environment, 1999).

and Cranston and Parsons (2001), respectively. The vertical distributions of metals in the core from Belledune Harbour (Fig. 5a) are typical of profiles observed in most cores collected within several kilometres of the smelter, with the exception of those disturbed by dredging activities. In general, the concentrations of most elements emitted from the smelter (As, Cd, Cu, Hg, Pb, Zn) rise above background levels at depths of 15 to 30 cm below the sediment surface (depth varies with sedimentation rate) and reach maximum values at 5 to 10 cm depth before decreasing toward the sediment–water interface. Most cores collected from the open Chaleur Bay away from point sources of metal emissions display concentration profiles similar to those shown in Figure 5b. In these cores, the concentrations of most metals are relatively constant in the deeper, pre-industrial sediments, with the exception of fluctuations caused by changes in sediment grain size or mineralogy. Near-surface enrichment of some metals (e.g. Hg, Pb, Zn) is observed in the top 10 to 15 cm of many cores, and is especially pronounced in cores from the western half of the bay and in cores collected within a 20 km radius of Belledune. Sediment cores near Dalhousie commonly contain elevated levels of Cd, Cu, Hg, Pb, and Zn down to depths of 50 cm or more, reflecting the long history of industrial activities in this area and the high sedimentation rates in the Restigouche Estuary.

A detailed analysis of concentration profiles in all the cores collected for this study suggests that, in general, the surface enrichment of metals observed in many cores is not caused by sampling artifacts or diagenetic remobilization. In the field, sampling artifacts were minimized by carefully controlling the descent rate of the gravity corer, thoroughly examining the sediment–water interface upon retrieval, and subsampling from the central portion of the cores in order to avoid contamination from smeared sediment along the core liner. The effects of sediment diagenesis on metal profiles are somewhat difficult to ascertain without detailed pore-water chemistry, but several lines of evidence suggest that extensive remobilization of metals has not occurred in most cores. Redox-controlled cycling of metals may be an important process in organic-rich sediments (up to 4.9 weight per cent total organic carbon (TOC)) in the immediate vicinity of Dalhousie; however, diagenetic remobilization does not seem to be a major factor in most other parts of the bay where TOC values in the sediments are usually less than 2.0 weight per cent. As shown in Figure 5, the peaks in Cd, Cu, Hg, Pb, and Zn levels are generally not accompanied by significant increases in solid phase Fe and Mn concentrations, which suggests that co-precipitation and/or adsorption of metals onto iron and manganese oxides in the oxic surface layer are not responsible for the profiles observed in these cores (cf. Farmer, 1991). Likewise, most metals do not show a strong correlation with organic carbon in these sediments, suggesting that scavenging and redistribution of metals during organic matter diagenesis is not a key control on the shapes of these vertical metal profiles (cf. Ridgway and Price, 1987). Arsenic is one element that may be affected by diagenetic remobilization, as evidenced by local peaks in As concentrations in deep, pre-industrial sediments in some core bottoms. The one process that clearly has a significant impact on the vertical metal records in some cores is bioturbation, which

tends to ‘straighten out’ the metal profiles in the top 5 to 10 cm of some cores (e.g. Fig. 5b). The extent of bioturbation varies throughout the bay, but is only prominent in less than 10% of all cores.

Overall, the concentration profiles in most cores collected during this study seem to provide a relatively reliable historical record of changes in metal fluxes to Chaleur Bay. Metal profiles in sediment cores collected within 2 to 3 km of the Brunswick smelter (e.g. Fig. 5a) all show a pronounced peak in metal concentrations at 5 to 10 cm depth followed by a decrease toward the surface, which probably reflects the significant reduction in smelter emissions since the early 1980s (Fig. 2). Close correspondence between the Cd, Cu, Hg, Pb, and Zn profiles in cores from the Belledune region suggests that most of the Hg in these sediments can be attributed to historical emissions from the Brunswick smelter; however, Hg levels in the uppermost sediment layers (1–2 cm) most likely include contributions from the adjacent coal-fired Belledune thermal generating station, which commenced operations in 1993.

Sediment accumulation rates in Chaleur Bay

Sedimentation rates were measured during this study to provide a better understanding of sediment transport processes in Chaleur Bay, to help identify potential sinks for metals released to the bay, and to estimate the approximate age of sediments in gravity cores. The GSC Atlantic Geochemistry Laboratory has studied roughly 40 field sites since 1984 where sediment cores were collected, pore water was removed from various sediment depths, and ammonium and sulphate concentrations were measured in the pore water (Cranston, 1999). In general, dissolved ammonium concentrations increase with depth downcore as a result of bacterial oxidation of organic matter in the sediment. Dissolved sulphate concentrations in pore water are usually about 28 mM (full seawater) at the sediment–water interface and decrease with depth as sulphate is reduced to sulphide downcore. The rate at which the ammonium concentration increases and the sulphate concentration decreases depends on the supply of organic matter to the seafloor (Berner, 1980). The organic carbon burial rate is the product of the organic carbon concentration in the sediment and the sediment accumulation rate. On the basis of results from various studies, a predictive relationship between organic carbon burial rates and ammonium and sulphate gradients has been established (Cranston, 1999). The correlation is highly significant and the relationship can be applied to conditions that range from deep, unproductive, mid-ocean sites to highly enriched zones near fin-fish aquaculture cages. In practice, the ammonium and sulphate gradients are determined for each core using the pore-water data, and once the organic carbon content of the sediment is known, an estimate of the sedimentation rate is made. By using this method, immediate and inexpensive estimates of present-day sediment accumulation rates can be obtained that are accurate to within one order of magnitude or better. Other methods to determine sedimentation rates are available, including radionuclide dating (e.g. ^{210}Pb , ^{137}Cs , ^{14}C), sediment traps, and micropaleontology studies; however,

these methods are slow to carry out, expensive, and sensitive to bioturbation in the sediment column, and each method is applicable only to a limited range of sediment accumulation rates (Cranston, 1999).

In the present study, sediment cores from 76 sites in Chaleur Bay were processed using the pore-water gradient approach (Cranston, 2000; Cranston and Parsons, 2001). Figure 5 shows examples of ammonium and sulphate depth profiles in two cores. In the core from Belledune Harbour (Fig. 5a), the concentrations of dissolved sulphate and ammonium in the sediment pore waters are relatively uniform in the top 5 to 10 cm, indicating that the sediments are moderately oxidized to this depth. The decrease in sulphate and increase in ammonium below this depth reflect the microbial oxidation of organic-rich sediment in this sheltered harbour. The present-day sedimentation rate for this location is estimated to be approximately 500 cm/ka (centimetres per thousand years), or 0.5 cm/a. Assuming the sedimentation rates at this site have not changed dramatically since the construction of the Belledune Harbour breakwater in the late 1960s, the top 15 to 20 cm of sediment represent deposition over the past 30 to 40 years. Allowing for some vertical movement of metals through diffusion and bioturbation, this estimate correlates reasonably well with the metal profiles shown in Figure 5a, which all show a substantial increase in concentrations at about 20 cm depth. By comparison, sediment pore waters in the core from the open Chaleur Bay (Fig. 5b) do not show a pronounced decrease in sulphate or increase in ammonium concentrations until approximately 70 cm and 30 cm depth, respectively. At this location, the sulphate and ammonium gradients are lower than those in Belledune Harbour, reflecting the lower sedimentation rate in this area (approximately 150 cm/ka).

The ammonium and sulphate gradients in cores collected during this study provide estimates of sediment accumulation rates ranging from <10 to about 600 cm/ka. Figure 6 shows a contour map of the results. Accumulation rates are highest near Dalhousie, exceeding 200 cm/ka, which reflects the abundant sediment supply from the Restigouche River and the high organic carbon flux from a local pulp and paper mill. Present-day sedimentation rates also exceed 200 cm/ka in some parts of Belledune Harbour. In general, sedimentation rates in most other areas of the bay are <100 cm/ka, with the exception of one area centred approximately 34 km east of Belledune. The higher sedimentation rates in this region are most likely related to changes in seafloor bathymetry (water depths increase significantly in this area, Fig. 1), or they may reflect the presence of a cyclonic gyre near this location, which results in higher primary productivity in the water column (Legendre and Watt, 1970). This apparent depocentre lies downwind of the Brunswick smelter and may serve as a sink for metal emissions.

Regional distribution of metals in sediments

Chemical analyses of 918 sediment subsamples from Chaleur Bay show the following ranges in elemental concentrations: As, 2.8 to 74 mg/kg; Cd, 0.02 to 69 mg/kg; Cu, 3.4 to 200 mg/kg; Fe, 0.72 to 3.80 dry weight per cent; Hg, <0.01 to 2.4

mg/kg; Mn, 100 to 750 mg/kg; Ni, 8.4 to 68 mg/kg; Pb, 0.3 to 2000 mg/kg; and Zn, 22 to 3200 mg/kg (Table 2; Cranston, 2000; Cranston and Parsons, 2001). The highest concentrations of metals occur in surficial sediments within 1 to 2 km of the Brunswick smelter in Belledune, and in sediments near the former concentrate loading facility and mercury-cell chlor-alkali plant in Dalhousie. The spatial distributions of As, Cd, Cu, Fe, Hg, Ni, Pb, and Zn are shown in a series of proportional dot maps (*see* /Data directory on this CD); these illustrate the average concentration of each element in the 'post-industrial' surface sediments (core tops and grab samples) and in the deeper 'pre-industrial' sediments (core bottoms). The boundary between the pre- and post-industrial sediments in each core was estimated by carefully examining the vertical profiles to determine the depth at which metal concentrations (especially Pb) begin to rise above background levels. On these maps, the metal concentrations have been separated into six classes using a percentile breakdown and colour scheme that is consistent with other studies in the MITE Point Sources project (percentile range (colour)): minimum to 25th (blue), 25th to 50th (cyan), 50th to 75th (green), 75th to 90th (yellow), 90th to 95th (orange), and 95th to maximum (red). These percentile ranges were calculated using the entire data set for each element (i.e. concentrations in all subsamples from both core tops and core bottoms); therefore, some maps do not contain samples that fall into all six percentile classes. Table 2 provides summary statistics for metal and metalloid concentrations in all sediments analyzed during this study.

These proportional dot maps are useful for depicting the overall metal contents of sediments throughout Chaleur Bay (as defined by the sediment digestion methods) and for comparing metal levels in pre- and post-industrial sediments. In general, metal concentrations in the core bottoms are higher in fine-grained sediments along the central axis of the bay, which have more surface area per unit mass than coarse-grained sediments in shallower waters. In most cores, metal concentrations in the surface sediments tend to be higher than concentrations in the core bottoms, especially near point sources of metal emissions. Some notable exceptions to this general trend do occur, however, especially in the easternmost core collected during this study, which displays increasing concentrations of As, Cu, Fe, Mn, and Zn below 50 cm. Significant variations in element concentrations in deeper, pre-industrial sediments are most likely caused by changes in sediment grain size and/or mineralogy over time (Loring, 1991).

The concentrations of As, Cd, Hg, and Pb in bottom sediments of the bay are plotted versus longitude in Figure 7. These graphs demonstrate the high concentrations of metals in sediments near Belledune and Dalhousie compared to other parts of Chaleur Bay. The estimated background level for each element is also shown on these plots by a black, horizontal dashed line labeled 'BKGD'. For each of these elements, the upper limit of background values is arbitrarily defined as the 95th percentile of the concentrations of each element in the pre-industrial sediments in the core bottoms. Using this definition, the background values for As, Cd, Hg, and Pb in marine sediments from the bay are 19, 0.26, 0.04,

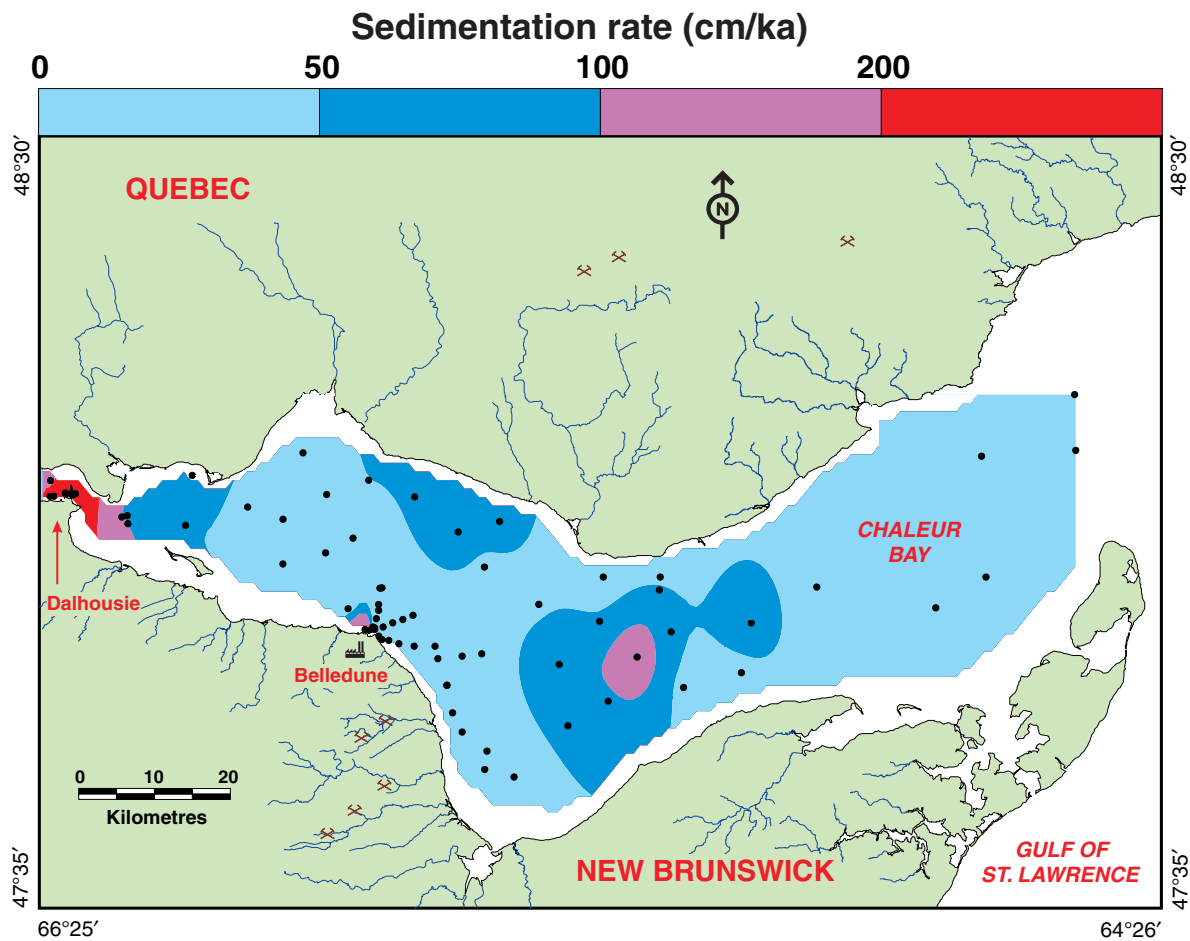


Figure 6. Present-day sediment accumulation rates throughout Chaleur Bay, estimated from sulphate and ammonium gradients in the sediment pore waters.

Table 2. Metal and metalloid concentrations in sediments from Chaleur Bay.

Element	As ^b	Cd ^b	Cu ^b	Fe ^c	Hg ^b	Mn ^b	Ni ^b	Pb ^b	Zn ^b
Minimum	2.8	0.02	3.4	0.72	<0.01	100	8.4	0.3	22
Maximum	74	69	200	3.80	2.40	750	68	2000	3200
Average	11	0.72	17	2.20	0.08	220	41	38	100
n ^a	321	918	918	918	918	918	918	918	918
Percentiles									
95 th	21	2.00	33	2.90	0.33	360	56	100	250
90 th	17	0.68	23	2.80	0.16	300	52	25	130
75 th	12	0.22	18	2.50	0.05	230	47	14	73
50 th	9.0	0.14	15	2.20	0.02	200	42	6.2	62
25 th	7.1	0.11	12	1.90	0.01	180	36	4.6	54

^a n = number of analyses
^b in mg/kg
^c in dry weight per cent

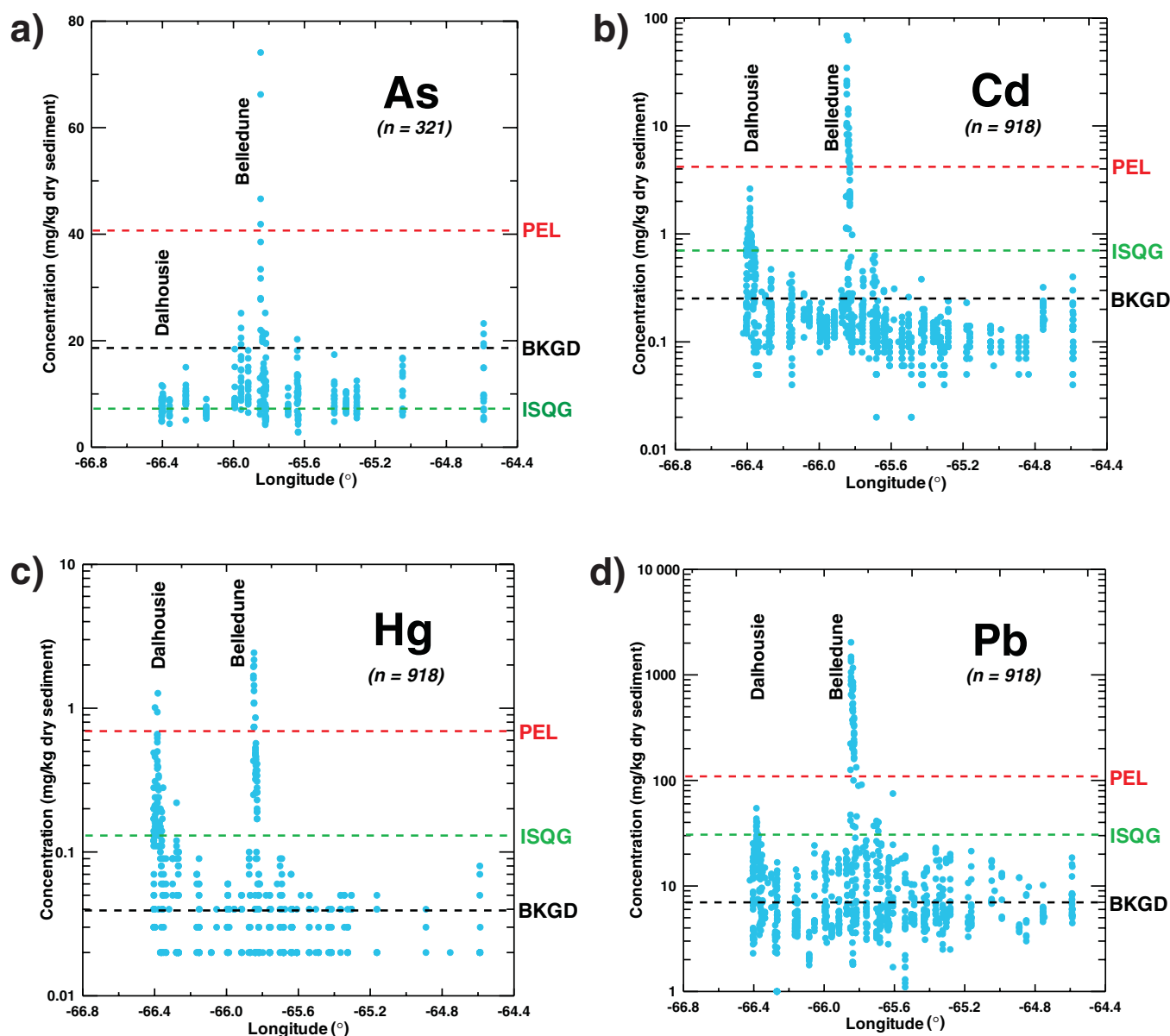


Figure 7. Concentrations of **a)** As, **b)** Cd, **c)** Hg, and **d)** Pb in bottom sediments of Chaleur Bay, plotted versus longitude. The green and red horizontal dashed lines on each plot show the Canadian interim sediment quality guideline (ISQG) and the probable effect level (PEL), respectively, for that element in marine sediments (Canadian Council of Ministers of the Environment, 1999). The black horizontal dashed line on each graph represents the upper limit (95th percentile) of background concentrations for that element in the pre-industrial sediments.

and 7.3 mg/kg, respectively. As shown in Figure 7, the concentrations of As are generally close to background values in most parts of the bay and are only significantly elevated near Belledune. The concentrations of Cd and Hg in the surface sediments are significantly higher than background levels near both Belledune and Dalhousie and in a number of other locations in the western half of the bay. Lead concentrations in surface sediments are higher than background levels throughout the entire Chaleur Bay and are especially high near Belledune and, to a lesser degree, near Dalhousie.

The Canadian interim sediment quality guideline (ISQG) and the probable effect level (PEL) for each of these elements in marine sediments have been plotted in Figures 5 and 7 in order to provide a rough indication of the level of contamination in Chaleur Bay (Canadian Council of Ministers of the Environment, 1999). These numerical guidelines have been developed to help assess sediment quality and provide rough guidelines for protecting ecosystem health. The ISQG and the PEL define three ranges of total concentrations for a particular element: those that are rarely (\leq ISQG), occasionally (between the ISQG and the PEL), and frequently (\geq PEL) associated with adverse biological effects (Canadian Council

of Ministers of the Environment, 1999). However, the ISQG and PEL are based on total dry-weight concentrations of various elements and do not consider many factors that influence the bioavailability and toxicity of metals and metalloids to biota (e.g. Chapman et al., 1999; Chapman and Wang, 2000; O'Connor and Paul, 2000). As shown in Figure 7, the concentration of Hg exceeds the ISQG and PEL for this metal in both Belledune and Dalhousie harbours, whereas the concentrations of As, Cd, and Pb exceed the PEL for these elements only in Belledune Harbour. Given that the Cd and Pb levels in Figure 7 are based on a partial sediment digestion, the total concentrations of these metals likely also exceed the PEL in Dalhousie Harbour. This comparison shows that the concentrations of potentially toxic elements in these harbours exceed recommended levels for the protection of aquatic life, but is not necessarily indicative of adverse biological effects (Canadian Council of Ministers of the Environment, 1999; Chapman et al., 1999; O'Connor and Paul, 2000).

The need for site-specific environmental quality guidelines is evident in the plot of sediment As concentrations (Fig. 7a), where the ISQG (7.2 mg/kg) is approximately 2.5 times lower than the background As concentrations (19 mg/kg) in this area. The relatively high As background values in sediments from Chaleur Bay probably result from postdepositional diagenetic remobilization of arsenic. Upward migration of arsenic in sediment pore waters following the reductive dissolution of iron and/or manganese oxides during early diagenesis is well documented (e.g. Farmer, 1991). Subsequent coprecipitation of arsenic with authigenic iron sulphides or adsorption to iron and/or manganese oxides could explain the local enrichment of As observed in pre-industrial sediments from the bottoms of some cores (Farmer and Lovell, 1986; Mucci et al., 2003).

Identification of metal-contaminated surface sediments

A detailed interpretation of element distributions based on the proportional dot maps discussed above is complicated, because the concentrations of some metals are strongly controlled by natural variations in sediment grain size and/or mineralogy. In general, metal concentrations tend to increase with decreasing sediment grain size because of the higher specific surface areas of fine-grained sediments. Various methods have been used to compensate for the natural variability of metals in marine sediments so that anthropogenic metal contributions can be detected and quantified (e.g., Loring, 1991; Daskalakis and O'Connor, 1995; Matthai and Birch, 2001). In this study, iron was used as a proxy for sediment grain size because it is a common constituent of clay minerals and other phases (e.g. iron (oxy)hydroxides) that can act as metal carriers in marine environments. As shown in Figure 8, the concentrations of Fe are higher in fine-grained sediments along the central axis of Chaleur Bay and in Belledune and Dalhousie harbours, compared to higher energy locations along the margins of the bay. In the absence of detailed grain-size information, it is assumed that variations in Fe concentrations in most pre-industrial sediments collected during this study are primarily related to changes in

sediment grain size and mineralogy, and not to diagenetic remobilization. Detailed analyses of Fe profiles in sediment cores suggest that this assumption is reasonable for most sites, with the possible exception of some locations near Dalhousie that consist of relatively organic-rich sediments.

Table 3 shows correlation coefficients for the relationships between organic carbon, As, and metals in pre-industrial sediments in core bottoms throughout Chaleur Bay. With the exception of Cu, Ni, and Zn, most elements do not show strong correlations with Fe, and no elements seem to co-vary appreciably with changes in organic carbon concentrations. These results suggest that changes in sediment grain size and/or mineralogy exert a significant control on the concentrations of Cu, Ni, and Zn, but are not a major factor in controlling the distributions of most other elements. Therefore, the background concentrations of Cd, Hg, and Pb in marine sediments collected during this study are considered to be less than or equal to the 95th percentile of concentrations in the core bottoms (0.26, 0.04, and 7.3 mg/kg, respectively). Excess concentrations of Cd, Hg, and Pb in surface sediments from the bay were calculated by subtracting these background values from the measured concentrations in each sample. In the following discussion, the term 'contaminated' is used to refer to sediments containing metal concentrations that exceed the estimated background values.

The background levels of Cu, Ni, and Zn vary substantially throughout the bay as a result of changes in sediment grain size and/or mineralogy. The concentrations of all three of these metals are notably higher in fine-grained, iron-rich sediments than in coarse-grained, iron-poor sediments. Figure 9 shows the concentrations of Ni and Cu plotted versus Fe for all sediment subsamples collected from Chaleur Bay. The solid green line on each of these plots represents the linear regression for the relationship between the concentrations of each metal and Fe in pre-industrial sediments in the core bottoms. The dashed black lines represent the upper and lower limits of the 95% prediction interval for the regression, i.e. the area where 95% of all data points are expected to fall if grain-size variations are the dominant control on changes in metal concentrations. For Cu, Ni, and Zn, the upper limit of background values (M_{bkgd}) in the sediments is taken as the upper limit of the 95% prediction interval, given by

$$M_{bkgd} = m_{reg} [Fe] + b_{reg} + (SE_{reg}) (1.96) \quad (1)$$

where m_{reg} , b_{reg} , and SE_{reg} are the slope, intercept, and standard error, respectively, of the linear regression line for the relationship between the concentration of each metal and Fe in the core bottoms, [Fe] is the concentration of Fe in a given sample, and 1.96 is a statistical parameter (t) for the 95% confidence level of the two-tailed Student's t -distribution (Fisher and Yates, 1963). Excess concentrations of Cu, Ni, and Zn in surface sediments from the bay were calculated by subtracting the solution to equation (1) (using appropriate regression parameters for each metal) from the measured metal concentration (M_{obs}) in each sample. Sediment subsamples with metal concentrations higher than the upper limit of the 95% prediction interval (i.e. background values) are shown in red on Figure 9, and are considered to be contaminated with metals.

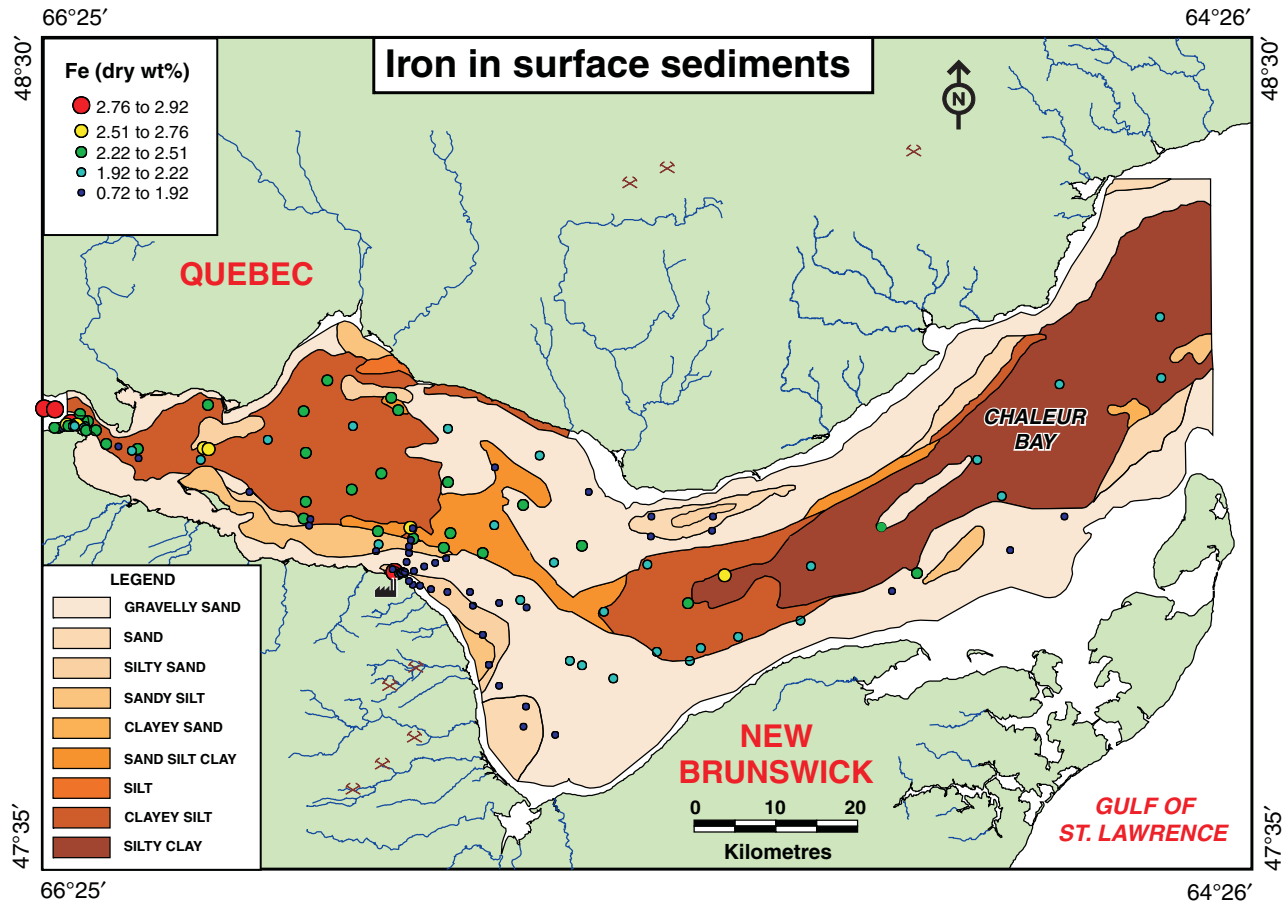


Figure 8. Concentrations of iron in surface sediments throughout Chaleur Bay, superimposed on a map of surface sediment textures (modified from Schafer, 1977, Fig. 4).

Table 3. Correlation coefficient (*r*) between organic carbon, arsenic, and metals in pre-industrial sediments from Chaleur Bay.

	OC	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Zn
OC	1.00									
As	<i>0.06^a</i>	1.00								
Cd	0.14	-0.16	1.00							
Cu	0.26	<i>0.03</i>	<i>0.06</i>	1.00						
Fe	0.34	-0.08	0.12	0.57^b	1.00					
Hg	0.19	-0.26	0.11	<i>0.01</i>	0.24	1.00				
Mn	-0.18	-0.37	-0.04	0.50	0.47	<i>0.05</i>	1.00			
Ni	0.19	-0.09	0.11	0.49	0.69	0.22	0.30	1.00		
Pb	0.21	<i>0.05</i>	-0.07	0.37	0.13	0.16	0.16	<i>0.08</i>	1.00	
Zn	0.27	-0.02	<i>0.04</i>	0.77	0.73	0.18	0.41	0.69	0.33	1.00

n (number of analyses) = 514 for all variables except As, for which n = 188.

oc = organic carbon

^a All correlations are statistically significant at >95% confidence level except for those shown in italics.

^b Correlation coefficients greater than 0.5 are shown in bold-face type.

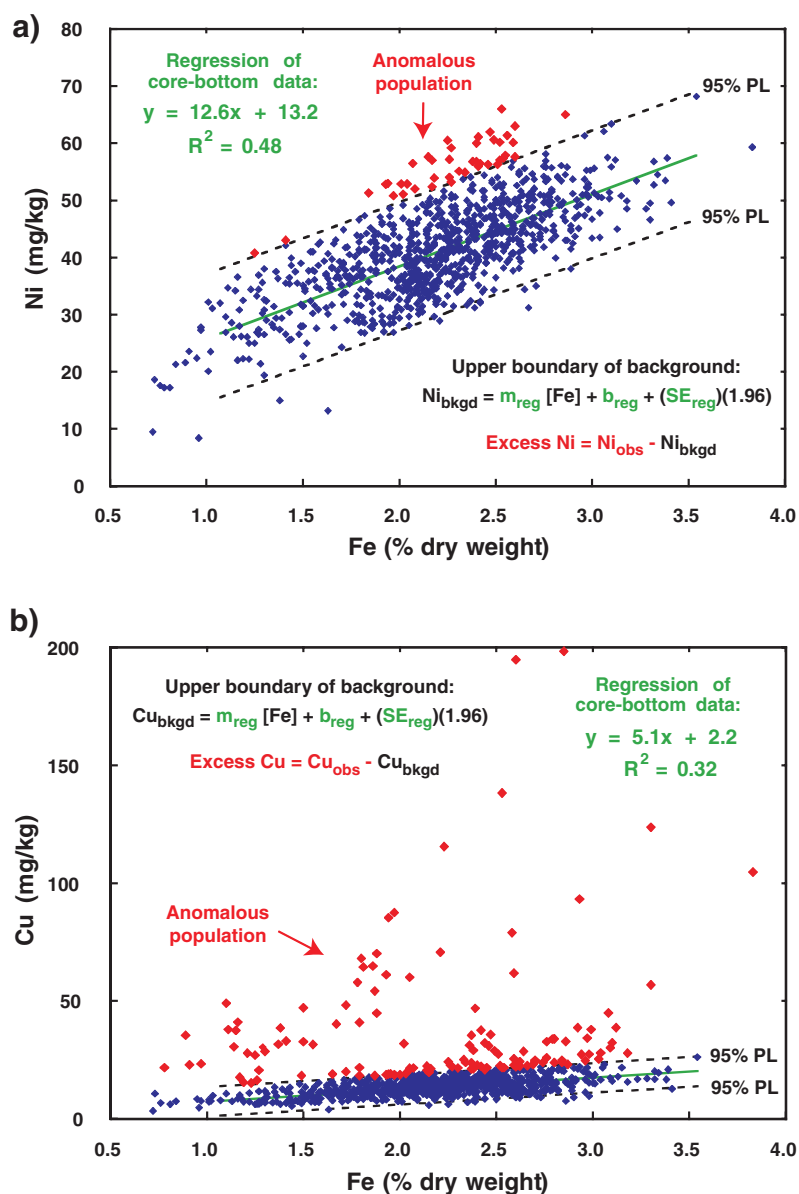


Figure 9. Concentrations of **a)** Ni and **b)** Cu plotted versus Fe in sediments from Chaleur Bay. The solid green line on each plot represents the best-fit linear regression line for the relationship between the concentrations of each metal and Fe in the uncontaminated core bottoms. The dashed black lines represent the upper and lower limits of the 95% prediction interval for the regression line. See text for further explanation.

Spatial extent of contaminated surface sediments

The spatial distribution of surface sediments containing concentrations of Cd, Cu, Hg, Ni, Pb, and Zn higher than background values is shown on proportional dot maps in Figure 10. The metal concentrations on these plots represent average values for excess metal levels in the contaminated surface layer at each site. The data are presented using the same percentile breakdown and colour scheme discussed previously; however, the percentile values on these maps were

calculated using only the excess metal concentrations. Sample locations that do not appear on these maps contain metal concentrations at or below background levels.

These maps show that surface sediments in Belledune and Dalhousie harbours are contaminated with all metals except Ni, concentrations of which are only slightly higher than background levels near Dalhousie and in one site near the Gaspésie coast (Fig. 10d). Copper-contaminated sediments (Fig. 10b) are restricted to within 1 to 2 km of Belledune and Dalhousie, although a few sites in the open bay have Cu values slightly above background levels. Figure 10a shows that surface sediments between Dalhousie and Heron Island are somewhat contaminated with Cd, which most likely reflects sediment transport from Dalhousie Harbour and/or reworking of dredge spoils from the former ocean dump site in this area (Fig. 1; MacKnight, 1985; Lee et al., 1990). Cadmium levels near the Brunswick smelter drop off sharply outside of Belledune Harbour, reflecting dilution by relatively clean sediments. This observation is similar to observations made during previous studies in the early 1980s, which showed that Cd levels in sediments reached background levels within 2 to 3 km of Belledune Harbour (e.g. Loring et al., 1980; Bowers et al., 1987). Elevated Cd concentrations also occur in surface sediments at two sites 12 to 15 km southeast of Belledune (Fig. 10a). Sediments in this area are somewhat finer-grained than those just outside of Belledune Harbour (Fig. 8), and they may act as a sink for metals transported from the smelter by wind and nearshore currents. Previous studies of metal levels in mussels and scallops from this area also showed elevated concentrations of Cd and Pb up to 29 km southeast of the smelter in the early 1980s; however, metal concentrations have decreased significantly since that time (Uthe and Zitko, 1980; Hildebrand, 1984; Ray et al., 1984).

Sediments containing excess Hg, Pb, and Zn are much more widely distributed than sediments contaminated with Cd, Cu, and Ni. As shown in Figure 10c, mercury-contaminated sediments near Belledune and Dalhousie show a spatial distribution similar to that described for Cd; however, many open-water sites in the western half of the bay also show excess Hg. The origin of Hg at sites in the central part of the bay cannot be determined unequivocally on the basis of results from this study. However, excess Hg at sites west of Belledune is likely derived mainly from the chlor-alkali plant in Dalhousie, whereas mercury-contaminated sediments east of Belledune probably include contributions from the coal-fired Belledune generating station and the Brunswick smelter. Long-range atmospheric transport likely contributes

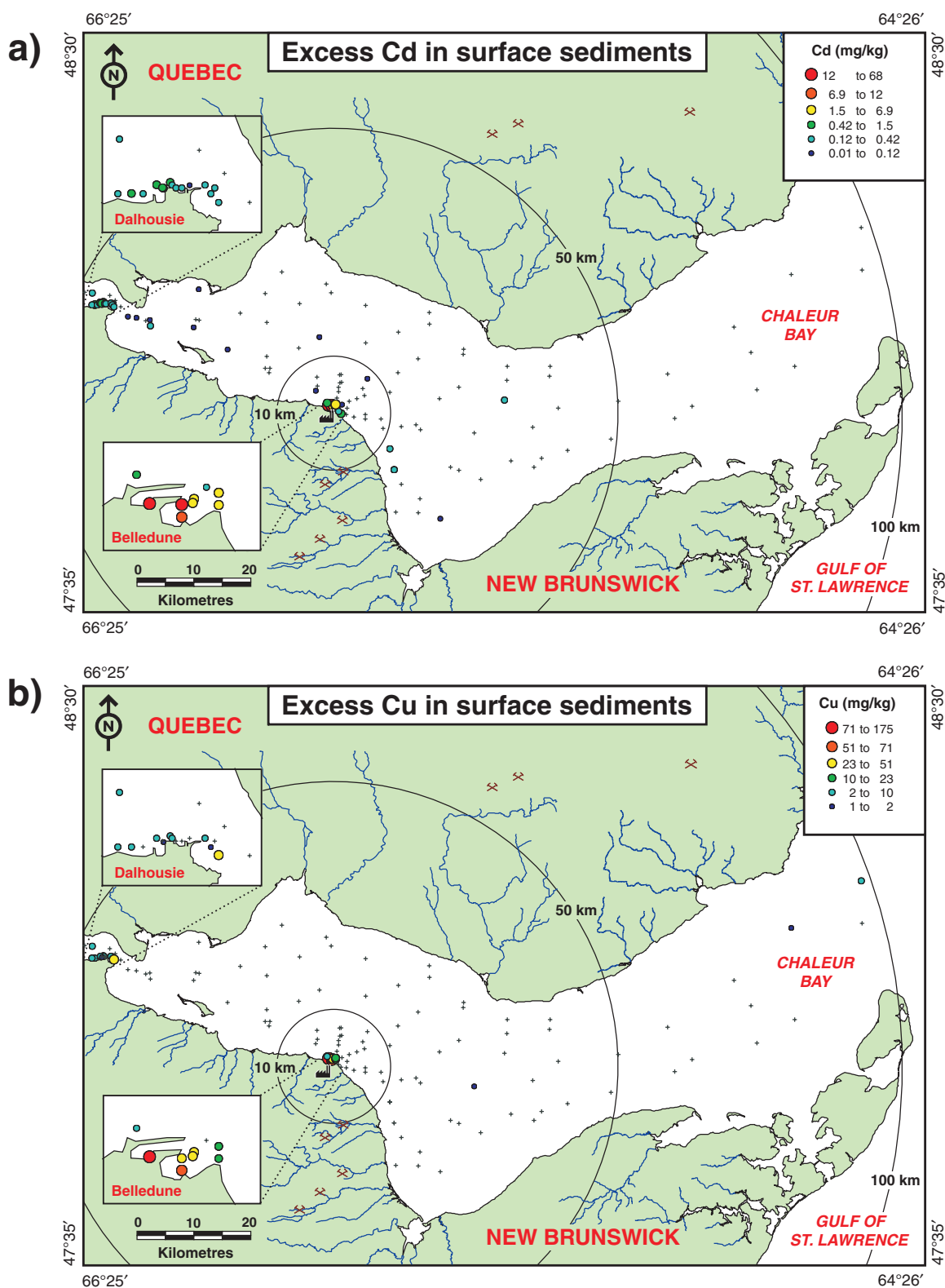


Figure 10. Spatial distribution of 'excess' **a)** Cd, **b)** Cu, **c)** Hg, **d)** Ni, **e)** Pb, and **f)** Zn concentrations (i.e. measured concentrations minus background values) in surface sediments from Chaleur Bay. The data shown on these maps represent sample locations where metal concentrations in the surface sediments exceed the estimated background values. The small grey crosses on each map show the locations of all sediment sampling sites.

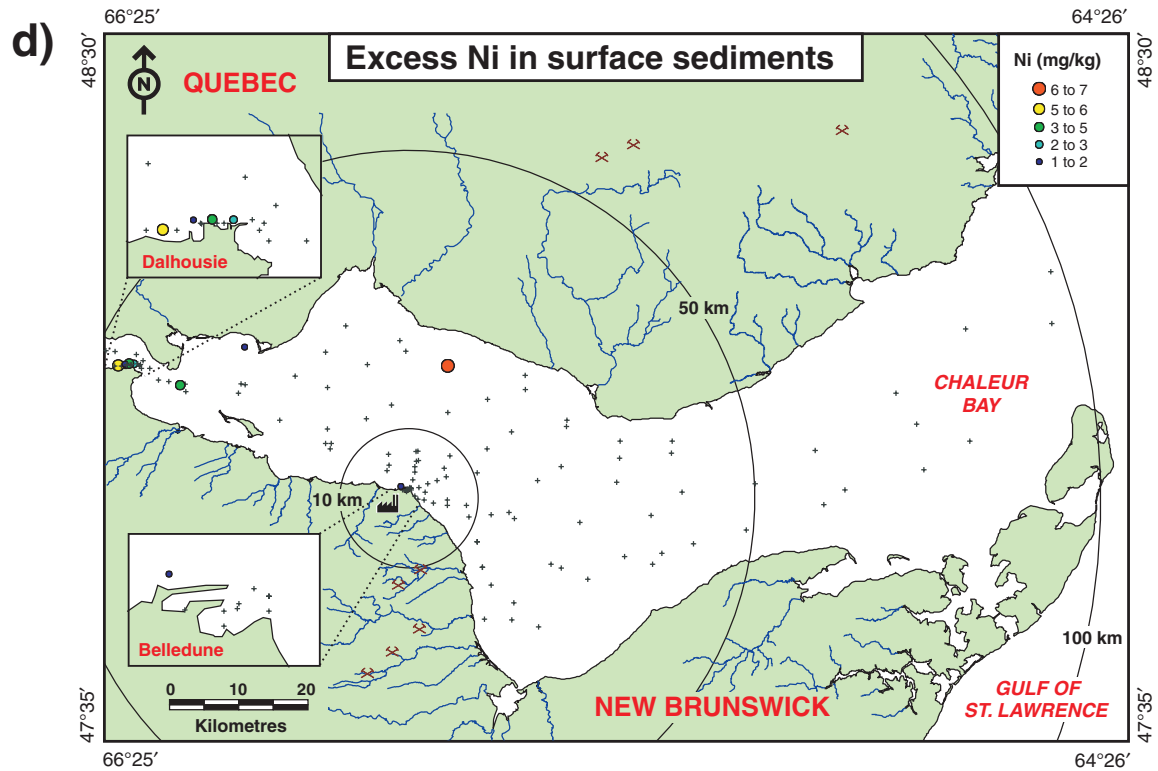
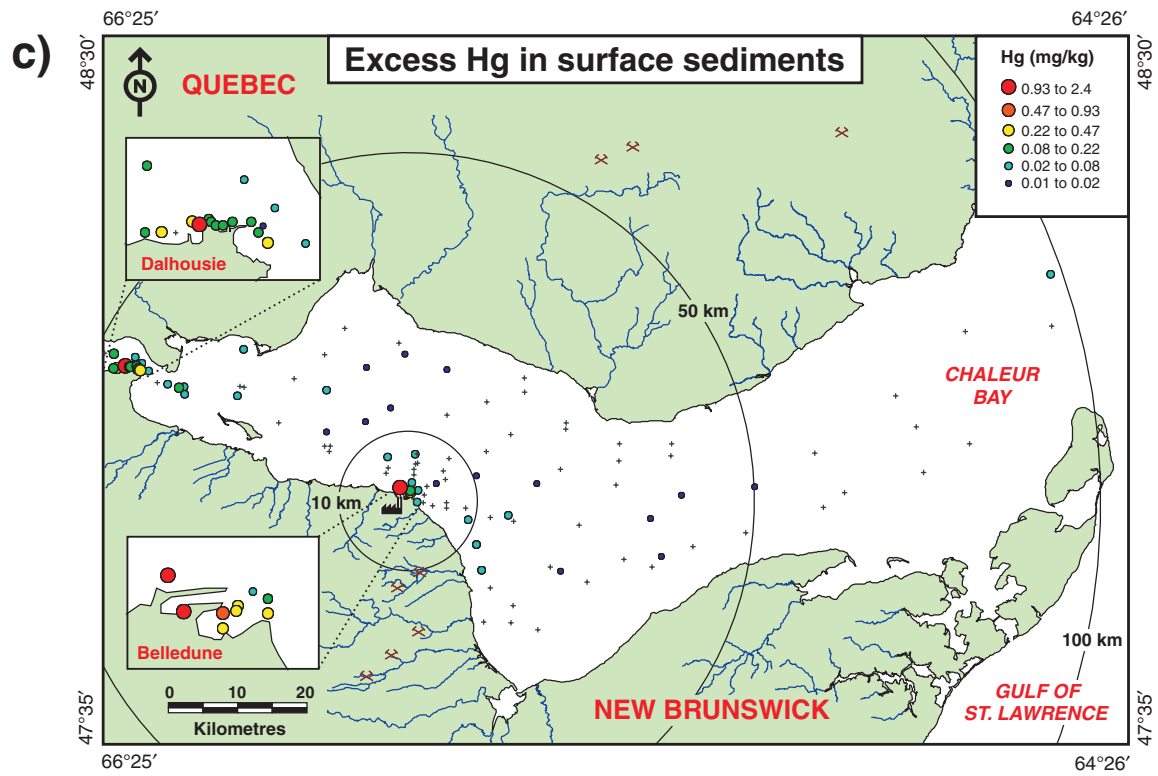


Figure 10. (Cont.)

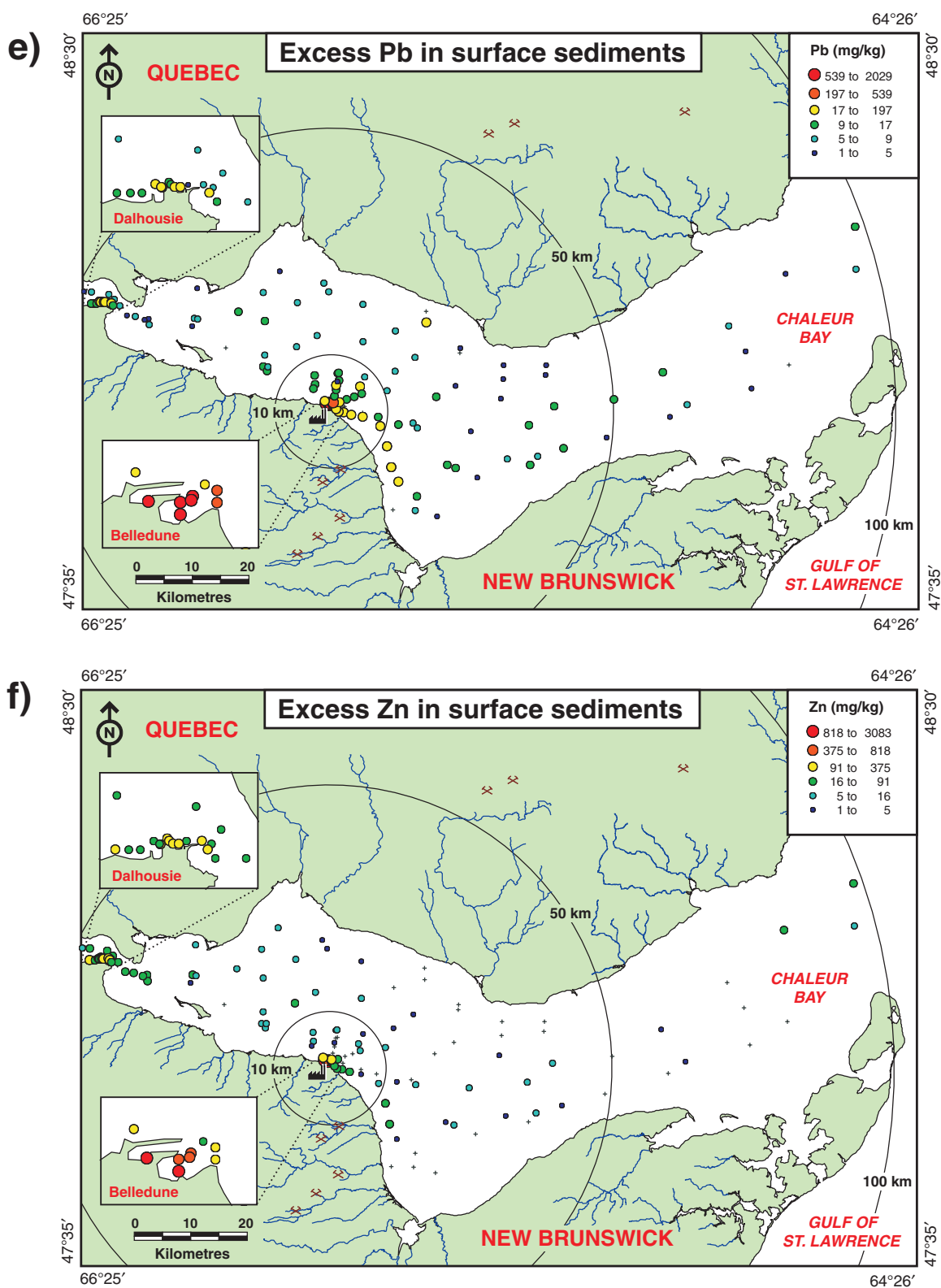


Figure 10. (Cont.)

some Hg to sediments in Chaleur Bay (e.g. Fitzgerald et al., 1998), but this does not appear to be a major source as Hg levels in surface sediments from many sites are close to background levels (Fig. 10c). Most surface sediments in the western part of the bay also contain excess concentrations of Zn (Fig. 10f). Zinc contamination within 20 km of Belledune and Dalhousie is most likely dominated by emissions from the Brunswick smelter and the former concentrate loading facility, respectively. Sediments at open-water sites in the western half of the bay are probably affected by other sources of Zn as well, including the former ocean dump site (MacKnight, 1985) and sewage from municipalities in the Restigouche watershed (Hildebrand, 1984). The origin of excess zinc levels measured at three sites near the mouth of Chaleur Bay (Fig. 10f) is uncertain, but the significant increase in water depths in this area (Fig. 1) may promote sedimentation of metal-enriched particles transported from other parts of the bay.

Almost all surface sediments throughout Chaleur Bay contain elevated Pb concentrations (Fig. 10e). The distribution of excess Pb at nearshore sites southeast of Belledune clearly shows that emissions from the Brunswick smelter have contaminated sediments to distances of at least 20 km. Slight modifications in the percentile ranges used in Figure 10e (i.e. changing the lower limit of the yellow dots to the 60th percentile (11 mg/kg) instead of the 75th percentile (17 mg/kg)) show that all but three of the surface sediment samples collected within a 10 km radius of Belledune contain Pb concentrations that are at least twice the background values. Anomalously high Pb concentrations (21 mg/kg, or roughly three times background values) are also present at one site 34 km east-southeast of Belledune, near the centre of the sediment depocentre shown on Figure 6. However, identifying the source(s) of excess Pb in sediments at open-water sites throughout the bay is not straightforward. Long-range transport of Pb is a well known source of global metal pollution (e.g. Nriagu, 1990), and historical combustion of leaded gasoline has caused significant contamination of most environments in North America (e.g. Sturges and Barrie, 1987; Véron et al., 1993; Rosman et al., 1994; Callender and van Metre, 1997). Lead isotope ratios were measured in selected sediment cores in an effort to identify the predominant sources of Pb to Chaleur Bay.

Source apportionment using lead isotope ratios

Naturally occurring variations in stable lead isotope abundances provide a fingerprinting tool for estimating the relative contributions of Pb (and associated metals) from many different natural and anthropogenic sources. The lead isotopes used for this purpose are ²⁰⁴Pb, which is nonradiogenic, and ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb produced by the radioactive decay of ²³⁸U, ²³⁵U, and ²³²Th with half-lives of 4.5, 0.7, and 14 billion years, respectively. The abundances of ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb have all been increasing at known independent rates throughout Earth's history relative to that of ²⁰⁴Pb. Thus, observed isotope ratios in contaminated sediments reflect the age of the lead-bearing materials used in the various emission sources. Distinguishing between natural and anthropogenic

sources of Pb in sediments should be possible if Pb isotopic signatures of the different sources (both proximal and distal) can be well constrained, since Pb isotopes are not measurably fractionated by recent industrial or biogeochemical processes (Rasmussen, 1996). For further details about this method, see Kersten et al. (1992) and Sangster et al. (2000).

Lead isotope signatures are available for a number of natural and anthropogenic metal sources in the Chaleur Bay region (Fig. 11). In pre-industrial times, weathering and erosion of lead-bearing minerals (e.g. K-feldspar, biotite, apatite) in bedrock and surficial deposits in the Chaleur Bay drainage basin were most likely the dominant source of Pb to the marine environment. Recent studies of lead isotope ratios in till and bedrock from northern New Brunswick provide data for natural sources that should be representative of many parts of the drainage basin (Ayuso and Bevier, 1991; Hussein, 1996). The most probable sources of Pb to surface sediments at open-water sites throughout the bay are the Brunswick smelter and long-range transport of emissions from historical leaded gasoline combustion. The isotopic compositions of emissions from the smelter are dominated by galena concentrates from the Bathurst Mining Camp, which constituted more than 95% of the lead feed prior to 1990 (Fig. 11). Sources of lead concentrate have been more varied since that time, but at least 65% of the lead feed has come from the Brunswick No. 12 mine (P. Deveau, Noranda, Inc., pers. comm., 1999). Ore sources used in the production of North American leaded gasoline have changed considerably over time, but detailed studies of gasoline, aerosols, and epiphytic lichens collected in the eastern United States and Canada have shown that the lead isotopic composition of U.S. and Canadian anthropogenic emissions are distinct and generally fall within the ranges shown on Figure 11 (Sturges and Barrie, 1987; Véron et al., 1993; Rosman et al., 1994; Carignan and Gariépy, 1995).

Table 4 summarizes the sequential extraction results on 20 sediment subsamples from various parts of Chaleur Bay, including the Pb concentrations and isotopic ratios measured in the NH₂OH·HCl and aqua regia leachates. The sequential extraction analyses indicate that metals in the contaminated surface sediments are present in relatively extractable forms (i.e. absorbed to mineral surfaces, or associated with carbonates or amorphous Fe/Mn oxyhydroxides (Hall and Pelchat, 1999)), compared to metals in deeper sediments. Lead isotope ratios measured in the tops and bottoms of cores from the bay show that in general, Pb in the contaminated surface sediments is significantly less radiogenic than the natural background Pb. As shown in Figure 11, the ²⁰⁶Pb/²⁰⁷Pb ratio in polluted surface sediments from Belledune Harbour is approximately 1.16, which matches the lead isotope composition of the Brunswick No. 12 mine (Ostic et al., 1967; R. Thorpe, Geological Survey of Canada, unpub. data, 1992). As the lead content of the surface sediments decreases, the ²⁰⁶Pb/²⁰⁷Pb ratio increases. This most likely reflects dilution by relatively uncontaminated sediments. The more radiogenic lead isotope values measured in the core bottoms are similar to lead isotope ratios measured in till and plutons from

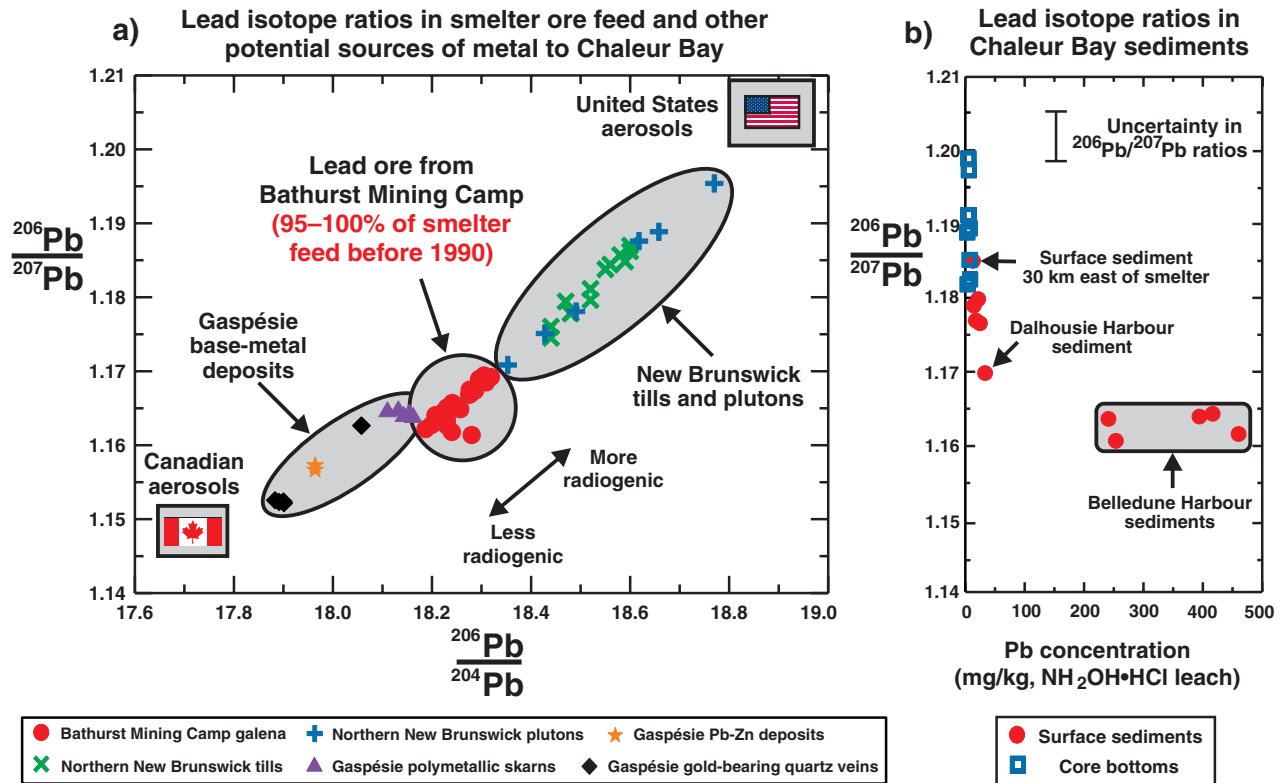


Figure 11. Lead isotope ratios in **a)** natural and anthropogenic metal sources and **b)** marine sediments collected during this study. Isotopic data plotted on the left side of this Figure were taken from a variety of sources: Bathurst Mining Camp galena (Ostic et al., 1967; Stacey et al., 1969; R. Thorpe, Geological Survey of Canada, unpub. data, 1992), northern New Brunswick plutons (Ayuso and Bevier, 1991), northern New Brunswick tills (Hussein, 1996), Gaspésie mineral deposits (Moritz and Malo, 1996), Canadian aerosols (Sturges and Barrie, 1987; Carignan and Gariépy, 1995), and United States aerosols (Véron et al., 1993; Rosman et al., 1994).

Table 4. Lead concentrations and lead isotope ratios measured in two sequential leachates on marine sediment core subsamples from Chaleur Bay.

Location	Sediment depth (cm)	Pb concentration (mg/kg)		$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$		$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$		$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$		$\frac{^{206}\text{Pb}}{^{207}\text{Pb}}$	
		HH	AR	HH	AR	HH	AR	HH	AR	HH	AR
Belledune Harbour, 1 km N of smelter	1	253	27	18.22	18.11	15.70	15.57	38.33	37.96	1.160	1.160
	5	417	53	18.34	18.17	15.75	15.61	38.58	38.17	1.160	1.160
	10	460	48	18.33	18.19	15.78	15.60	38.58	38.13	1.160	1.170
	15	394	62	18.39	18.25	15.80	15.65	38.62	38.23	1.160	1.170
	20	241	23	18.23	18.10	15.66	15.47	38.24	37.70	1.160	1.170
	45	3	3	18.58	18.47	15.63	15.40	38.53	38.07	1.190	1.200
	70	4	4	18.47	18.60	15.63	15.72	38.42	38.93	1.180	1.180
7.5 km N of smelter	2	25	6	18.56	18.61	15.78	15.70	38.98	39.08	1.180	1.190
	120	7	3	18.58	18.65	15.62	15.53	38.82	38.99	1.190	1.200
10 km ENE of smelter	2	14	4	18.53	18.51	15.72	15.52	38.90	38.54	1.180	1.190
	50	5	3	18.58	18.56	15.60	15.48	38.73	38.66	1.190	1.200
20 km N of smelter	1	18	5	18.59	18.46	15.80	15.56	39.02	38.56	1.180	1.190
	80	8	4	18.52	18.42	15.66	15.45	38.64	38.46	1.180	1.190
30 km E of smelter	1	13	5	18.64	18.69	15.73	15.72	38.83	39.17	1.180	1.190
	140	5	4	18.70	18.70	15.60	15.65	38.74	39.21	1.200	1.190
60 km E of smelter	2	22	6	18.66	18.53	15.82	15.52	39.07	38.61	1.180	1.190
	100	6	5	18.77	18.58	15.68	15.49	39.10	38.61	1.200	1.200
2 km NW of Dalhousie	2	33	6	18.30	18.32	15.64	15.57	38.30	38.36	1.170	1.180
	70	7	3	18.53	18.56	15.63	15.51	38.72	38.89	1.190	1.200
	120	6	2	18.65	18.81	15.65	15.52	38.87	39.62	1.190	1.210

All sediments were extracted with 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (HH), followed by concentrated aqua regia (AR; 3:1, $\text{HCl}:\text{HNO}_3$).

northern New Brunswick (Fig. 11), suggesting that Pb in the pre-industrial sediments originated from weathering of these parent materials.

The relatively small range in lead isotope signatures for the various metal sources shown in Figure 11 makes it difficult to identify the dominant sources of Pb to surface sediments at open-water sites throughout Chaleur Bay. None of the surface sediments have $^{206}\text{Pb}/^{207}\text{Pb}$ ratios less than 1.16, which suggests that extensive contamination from Canadian leaded gasoline combustion is unlikely. However, Pb from the Brunswick No. 6 and No. 12 mines was used in the production of gasoline additives by the Canadian petrochemical industry in the past (Sturges and Barrie, 1987), and it may not be possible to separate this source from the smelter emissions using lead isotopes. The increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios with decreasing Pb concentrations in the surface sediments may also reflect contributions from relatively radiogenic U.S. leaded gasoline emissions (cf. Weiss et al., 2002), but the lead isotope ratios measured in this study are all less than the reported isotopic signatures of this source (Fig. 11). In summary, the surface enrichment of Pb observed at many open-water sites throughout the bay most likely results from historical combustion of Canadian and U.S. leaded gasoline and from Brunswick smelter emissions, especially at sites downwind of Belledune. However, it is not possible to determine the relative importance of these sources using the lead isotope data from this study.

CONCLUSIONS

The results of this study demonstrate that the flux of metals to marine sediments in many areas of Chaleur Bay has increased in recent years relative to pre-industrial times. The spatial distribution of metals in surface sediments is controlled mainly by proximity to point sources of metal emissions, transport by wind and/or ocean currents, and natural variations in sediment grain size and/or mineralogy. Background concentrations of Cd, Hg, and Pb do not vary significantly throughout the bay and are estimated to be 0.26, 0.04, and 7.3 mg/kg, respectively, on the basis of the 95th percentile of their concentrations in pre-industrial sediments from gravity cores. The concentrations of Cu, Ni, and Zn are strongly controlled by changes in sediment grain size and/or mineralogy, as indicated by their significant correlations with Fe levels in the sediments. The ranges in background concentrations of Cu, Ni, and Zn in sediments from the bay are 6 to 26 mg/kg, 10 to 68 mg/kg, and 28 to 83 mg/kg, respectively. Note that the concentrations of all elements reported in this paper are based on a partial chemical extraction of the sediments using HNO_3 , with the exception of As and Hg concentrations, which are 'nearly total' values. Analyses of ammonium and sulphate gradients in the sediment pore waters, vertical profiles of Fe, Mn, and organic carbon in the solid phase, and grain-size variations indicate that the profiles of most elements (except As) are not strongly affected by sampling artifacts or diagenetic remobilization. The presence of random

peaks in As concentrations in pre-industrial sediments from some cores suggests that the distribution of this element is influenced by diagenetic processes.

The dispersion of Brunswick smelter emissions by wind and ocean currents has resulted in an area of elevated metal concentrations in surficial sediments within approximately 10 to 20 km of Belledune. A detailed analysis of background-corrected metal distributions suggests that the dispersion of smelter-emitted elements is least for As and Cu (1–2 km), intermediate for Cd and Hg (12–15 km), and greatest for Pb and Zn (at least 20 km). In general, the concentrations of most metals in the surface sediments decrease rapidly with increasing distance from the smelter; however, Pb is enriched in surface sediments throughout most of the bay. In harbour sediments adjacent to the smelter, As, Cd, Cu, Hg, Pb, and Zn concentrations decrease toward the sediment surface from maximum values at about 5 to 10 cm depth, reflecting reductions in smelter emissions since the mid-1970s. Concentrations of Hg and Cd, Cu, Pb, and Zn exceeding background levels are also found within 10 km of the chlor-alkali plant and the abandoned Cu-Zn concentrate loading facility, respectively. A comparison of lead isotope ratios measured in the tops and bottoms of cores and published isotopic data for geogenic and anthropogenic sources suggests that the surface enrichment in Pb throughout most of the bay is derived mainly from smelter emissions and historical combustion of leaded gasoline. It is not possible to ascertain the relative contributions of Pb from these sources using the lead isotope data from this study. In summary, the results of this investigation show that sediments within 10 to 20 km of Belledune and Dalhousie are significantly contaminated with metals but that overall, the metal concentrations in most other areas of Chaleur Bay are relatively close to background levels.

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