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THE DISTRIBUTION AND COMPARATIVE BIOGEOCHEMISTRY OF SILVER
WITH OTHER SELECTED TRACE METALS IN COASTAL WATERS NEAR
MASSACHUSETTS, USA.

A Dissertation Presented

by

CHRISTIAN F. KRAHFORST

Submitted to the Office of Graduate Studies,
University of Massachusetts Boston,
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2010

Environmental, Earth, and Ocean Sciences Program

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ABSTRACT

THE DISTRIBUTION AND COMPARATIVE BIOGEOCHEMISTRY OF SILVER WITH OTHER SELECTED TRACE METALS IN COASTAL WATERS NEAR MASSACHUSETTS, USA.

December 2010

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Water samples and hydrologic data were collected during 1994-1996 in New England coastal waters near Massachusetts, USA to examine the distribution of silver and other trace metals (Cu, Pb, Cd, Zn, and Fe) in the coastal systems of Massachusetts and Cape Cod Bays. These investigations were designed to test the hypothesis that silver could serve as a tracer of dispersion of municipal wastewater in Boston Harbor into Massachusetts and Cape Cod Bays and estimate the relative contribution of wastewater discharge to the overall silver budget of the Massachusetts Bays system. Silver concentrations in both particulate and filtered ($<0.4\ \mu\text{m}$) fractions averaged 103 and 117 pmol kg^{-1} for Boston Harbor, 34 and 10 pmol kg^{-1} in western Massachusetts Bay, and 11 and 7 pmol kg^{-1} in the central portion of Massachusetts Bay, respectively. Average Ag concentrations in southern Gulf of Maine coastal waters were 10 and 2 pmol kg^{-1} for filtered and particulate fractions, respectively. While nearly half of the silver existed in

particulate form in Boston Harbor, nearly 80% of the silver in Massachusetts and Cape Cod Bays occurred in the filterable fraction. Coastal water surveys revealed non-conservative Ag behavior and probably the result of incomplete mixing of three or more water masses with unique Ag signatures (e.g., Merrimack River, Boston Harbor, surface and intermediate Gulf of Maine waters). Quasi-steady state mass balance approaches estimate most of the silver entering into the Massachusetts Bays system during the study period was the result of municipal wastewater discharge to Boston Harbor (84-93%).

Multivariate analyses were conducted to evaluate fundamental controls on the distribution and fate of Ag in Massachusetts coastal waters. The results of observations from water samples collected during surveys in Massachusetts Bays and the near coastal region of southwestern Gulf of Maine show that Ag is intermediate with respect to particulate reactivity when compared to the metals observed for this study and consistent with observations of Ag speciation in other coastal and open ocean systems. Exploratory factor analysis revealed behavior of Ag similar to that of Cu and Zn, and may reflect similar complexation potential with and preference for common ligand classes in the water column.

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To my parents, Siegfried and Marianne, I am grateful for your support and for providing me with at least three of the most interesting people I have ever met: my brother Benedict, and sisters, Susanna and Anna. Thank you all for encouragement, occasional refuge, and rescues.

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CHAPTER 1

THE USE OF SILVER IN TRACING URBAN COASTAL POLLUTION IN THE MASSACHUSETTS BAYS

1.1 Introduction

Estuaries and embayments are often the first among coastal systems to exhibit symptoms of impairment due, in part, to activities associated with exponential human population growth and our propensity to live near coastal areas (Bricker et al., 1999; Rabalais and Turner, 2001). Much of the recent pollution-driven management actions in marine systems (e.g., contaminant monitoring, ecosystem assessment, pollution mitigation practices) are focused in coastal and estuarine waters. This is due in part to the near-coastal marine environment's proximity to sources of land-based pollution. Nearly 80% of marine pollutants are derived from land-based activities; primarily those associated with agriculture, industry, and household waste (Karau, 1992). Much of the coastal monitoring and research is in response to needs for a better understanding of the extent of these anthropogenic impacts, as well as for measuring the effect of best management practices once improved pollution controls are put into practice.

In many instances, coastal urban areas use their immediate coastal waters as a repository for wastewater and other sources of pollution, oftentimes without an adequate understanding of subsequent environmental impacts. The disposal of wastewater is a long standing problem. For

metropolitan Boston by the 1990's, this problem had been exacerbated as antiquated and poorly maintained sewage treatment plants were outpaced by human population growth. Untreated or partially treated sewage was discharged into Boston Harbor when these facilities became overwhelmed (Dolan, 2004).

Litigation over pollution in Boston Harbor culminated in 1985 when the United States Attorney filed suit on behalf of the Environmental Protection Agency against the Commonwealth of Massachusetts for violations of the Federal Clean Water Act (Dolan, 2004). As a result, the Massachusetts Water Resources Authority (MWRA) was created to oversee multi-billion dollar projects designed to repair and upgrade Metropolitan Boston's sewage treatment facility and mitigate its impact to coastal waters. Two of the major steps in this process were the discontinuation of sludge discharge to Boston Harbor (1991) and the relocation of wastewater discharge from within the confines of Boston Harbor to a new location 16 km offshore in Massachusetts Bay (September 2000).

The impacts of wastewater discharge in Massachusetts' coastal waters continue to be evaluated in light of programs intended to improve the quality of Boston Harbor and protect Massachusetts and Cape Cod Bay. These efforts — improved wastewater treatment and the extension of the outfall to a new site in Massachusetts Bay — have provided added incentive for a better understanding of the sources of contaminants, their relative contributions to the degradation of coastal systems, and the effectiveness of management measures to improve coastal water quality.

Wastewater discharges are important sources of contaminants to Massachusetts and Cape Cod Bays (Werme and Menzie, 1991). A total of 30 major municipal discharges ($> 3.8 \times 10^3 \text{ m}^3$ daily), which are regulated through the National Pollution Elimination Discharge

System, were identified as emptying directly into the Bays (Massachusetts Bays Program, 2004). The composition of these discharges varies greatly and is dependent on the type of communities they serve and on the amount and character of industrial waste that are added to the domestic sewage. Sewage treatment is designed to remove biological oxygen demand, solids, and pathogens from wastewater. Advance treatment or source reduction to the treatment facilities are often needed to reach regulatory-mandated effluent targets for chemicals of environmental concern.

Understanding wastewater dispersion and fate in natural waters is therefore important because of the known and unknown impairments imposed by contaminants associated with the discharge of effluents from municipal treatment facilities. Wastewater dispersion in coastal systems has been studied using silver as a tracer (Rutherford and Church, 1975; Martin et al., 1988; Sañudo-Wilhelmy and Flegal, 1992). Silver concentrations in municipal wastewater are often elevated by 100 – 1000 times above those occurring naturally in seawater (Smith and Flegal, 1994; Rivera-Duarte and Flegal, 1997, Adams and Kramer, 1999). In relatively unperturbed marine waters, silver occurs at levels from less than 1 to 10 pM (Murozumi, 1981; Martin et al., 1983; Bloom and Creclius, 1984; Flegal et al. 1995). This characteristic ultralow background and relatively high source strengths renders silver as a potentially effective tracer for evaluating the dispersion and fate of wastewater effluent in the coastal waters of Massachusetts.

Purcell and Peters (1998) summarized that most of the silver makes its way to municipal treatment facilities primarily in waste streams from industrial use. In the U.S during the 1990's, when this study was initiated, slightly more than 50% of the industrial use of silver was through the production of photographic materials and processing and about 15% was in the

manufacturing of circuit boards, electrical contacts and conductors. Silver discharges by photographic processing facilities to municipal waste treatment facilities were essentially as silver thiosulfate, typically as the complexes $\text{Ag}(\text{S}_2\text{O}_3)_2^{-3}$ and $\text{Ag}(\text{S}_2\text{O}_3)_3^{-5}$ (Newbrough and Kinch, 1981). Most of the silver thiosulfate is converted to silver sulfide within secondary sewage treatment plants and incorporated into sewage sludge. Silver entering the aquatic environment appears to be mainly in the form of silver sulfide (as particles or colloids), silver chloride, or soluble organic complexes (Smith and Carson, 1977). By 2003, much of the World's silver use and by extension- its waste- was from industrial applications, particularly in the manufacturing of electronic components (see Chapter 2).

Silver is highly particle-reactive. Partition coefficients, used to describe the distribution among solid and liquid phases (expressed as $\log K_D$'s), based on silver concentrations in filtered natural waters and measured on particles range from 4.5-6 (Kramer et al., 2002). Because of its high affinity for particles, most of the silver discharged in Boston Harbor would be expected to be associated with colloids or particles and most likely deposited near the mixing zone of the discharge or transported as fine particles into Massachusetts and Cape Cod Bays. However, a portion of the silver will be kept in solution either as chloride complexes, or, more likely, associated with sulfide or reduced sulfur complexes (Adams and Kramer, 1998) and dispersed by currents and tides. For coastal waters impacted by municipal wastewater discharges, ambient silver concentrations are most likely a function of solids management by local wastewater treatment facilities. Inorganic ligands in wastewater, which contain metal sulfide moieties, can be stable for hours and days in oxic waters (Adams & Kramer, 1999a). Kramer and Adams (1999b) found Ag concentrations in the dissolved state to be relatively constant in

wastewater effluent and receiving waters, intimating that silver is strongly complexed by ligands that are not significantly affected by oxidative changes after discharge.

The silver ion is one of the most toxic of the heavy metal ions and is in the highest toxicity class that includes mercury, chromium (VI), copper, and cadmium (Ratte, 1999). It is commonly held that the apparent toxicity is related to the free metal ion activity (Morel and Hering, 1993), or more recently, to bio-available forms of metal-ligand complexes – where metal interaction with cations at the site of toxicity is significant. Because of the advances in measurements of reduced sulfur in oxic natural waters (Cutter and Krahforst, 1987; Luther and Tsamakis, 1989, Radford-Knoery and Cutter, 1994), observations that reactive sulfide concentrations typically exceed silver concentrations in natural waters, and the high formation constants ($\log K = 12-21$) for silver-sulfide complexes (Cloke, 1963; Adams and Kramer, 1998), silver complexation with sulfide or reduced sulfur compounds may be more likely rather than with chloride as previously believed for marine waters. The activity of free silver in natural waters is currently considered to be extremely low and an environmentally inconsequential species when considering aquatic toxicity and the biogeochemical cycling of silver in the marine environment (Al-Farawati and van den Berg, 1999; Kramer et al., 2002).

However, even in the absence of any biologically significant free metal ion activity, silver concentrations and bioconcentration factors have been observed in aquatic organisms (see Ratte, 1999, for an extensive review). Adams and Kramer (1998) observed very rapid kinetics of ligand exchange with silver and demonstrated thiols were capable of mobilizing silver from inorganic sulfides.

During the 1990's, when the reported field studies here were conducted, between 3-10 kg (28 - 93 moles) of silver were discharged daily into the waters of Massachusetts Bay from

Metropolitan Boston's wastewater discharge (Delaney and Rex, 2007). This relatively high source strength serves as the starting point for the investigation of silver fate and transport in the coastal waters of eastern Massachusetts and serves as the basis of research reported here.

1.2 Research objectives

The main objectives of this dissertation are to demonstrate the use of silver as a tracer of wastewater effluent dispersion and fate in Massachusetts and Cape Cod Bays and provide additional information on the geochemical behavior of silver in coastal marine waters. The coastal waters of the southwestern portion of the Gulf of Maine, especially Massachusetts and Cape Cod Bays, serve as the study area for this work. Specific questions addressed in this work were:

What are the predominant forms of silver and their concentrations in the waters of Massachusetts and Cape Cod Bays?

What are the important sources of silver to the Bays?

How effective is silver as a tracer for wastewater effluent dispersion and fate in Massachusetts Bay?

What important factors control the biogeochemical fate of silver in the coastal waters of Massachusetts?

A review of the technical literature on the environmental fate, transport, and effects of silver in the marine environment is presented in Chapter 2. The distribution of silver and other selected trace metals in coastal waters of Massachusetts and estimates of sources to the

Massachusetts Bays are presented in Chapter 3. Chapter 4 focuses on the marine geochemistry of silver in near coastal waters. The comparative biogeochemistry of silver is examined through comparative multivariate analysis with other measured metals and selected water quality parameters. Chapter 5 presents the analytical methods used to determine the concentration of silver and selected metals in marine water. Certified reference water for selected metals (which do not include silver) were also analyzed and silver concentrations for these materials are reported there. Detailed descriptions of all other analytical methodologies used for this work are also presented. Finally, an overall summary is provided in Chapter 6.

CHAPTER 2

TRANSPORT, FATE AND EFFECTS OF SILVER IN THE MARINE ENVIRONMENT: A REVIEW

2.1 Introduction

Since the mid-1970's, knowledge about trace metal distributions in the marine environment and its biogeochemistry has been significantly advanced by improvements in sampling and analytical methodologies (Patterson et al., 1976). Prior to the development of sensitive instrumental techniques and controls for contamination during sample collection, storage and analysis, reliable trace metal data of the marine environment were restricted to sediment contamination studies where trace metal concentrations occurred at levels well above most sampling artifacts, provided reasonable sampling precautions were followed. Along with ultra-clean sampling methods and the development of highly sensitive analytical instrumentation and methodologies, the determination of many trace metals in many of the components (e.g., sediment, water, biota) of the ecosystem have been reported (Cai and Braids, 2002). Despite these advancements however, most of the information on the distribution and biogeochemistry of Ag in the marine environment have only recently been reported. This chapter presents a review of the current literature of the marine biogeochemistry of silver, including a synopsis of distribution in compartments of the marine environment as well as speciation, fate, and transport.

2.2 Silver use and environmental fluxes

Taylor and McLennan (1985) report that the average abundance of silver in the earth's crust is about $0.7 \mu\text{mol kg}^{-1}$. However, silver concentrations are elevated by about an order of magnitude in sediments and rocks containing sulfidic matter (Gorsuch and Klaine, 1998). Soil concentrations in natural mineral deposits where silver is mined may reach as high as 10 mmol kg^{-1} . Silver occurs in elemental form and in ores such as argentite (Ag_2S) and horn silver (AgCl). Silver is predominantly mined as a by-product of important primary ores of lead, lead-zinc, copper, gold, and copper-nickel. In 2007, most of the silver was mined from Peru, Mexico, and China; these three contributed just over 90% of the $19 \times 10^6 \text{ kg}$ mined in 2007. Approximately $1.1 \times 10^6 \text{ kg}$ (5.6 %) was mined in the United States (The Silver Institute, 2008).

Other important silver deposits occur as a result of activities associated with anthropogenic uses of silver, such as landfills (especially those receiving sludge materials from waste water treatment facilities). Atmospheric emissions resulting from ore processing (smelting) and coal burning activities (Scow et al., 1981), and discharges to the aquatic environment from mining, industrial, and waste water treatment are significant.

Some of the major uses of silver include the fabrication of electrical contacts and conductors, photographic materials, brazing alloys and solders, catalysts, batteries, and jewelry. According to the Silver Institute's World Silver Survey for 2003, nearly 96% of silver was used in jewelry and silverware fabrication, the production of photographic material and other industrial applications, (Fig. 2.1). In the US and during this study period (1994-1996), the production of photographic material accounted for more than half of the industrial demand in the late 1990s (CPM Group, 2001). Most of the photographic processing facilities

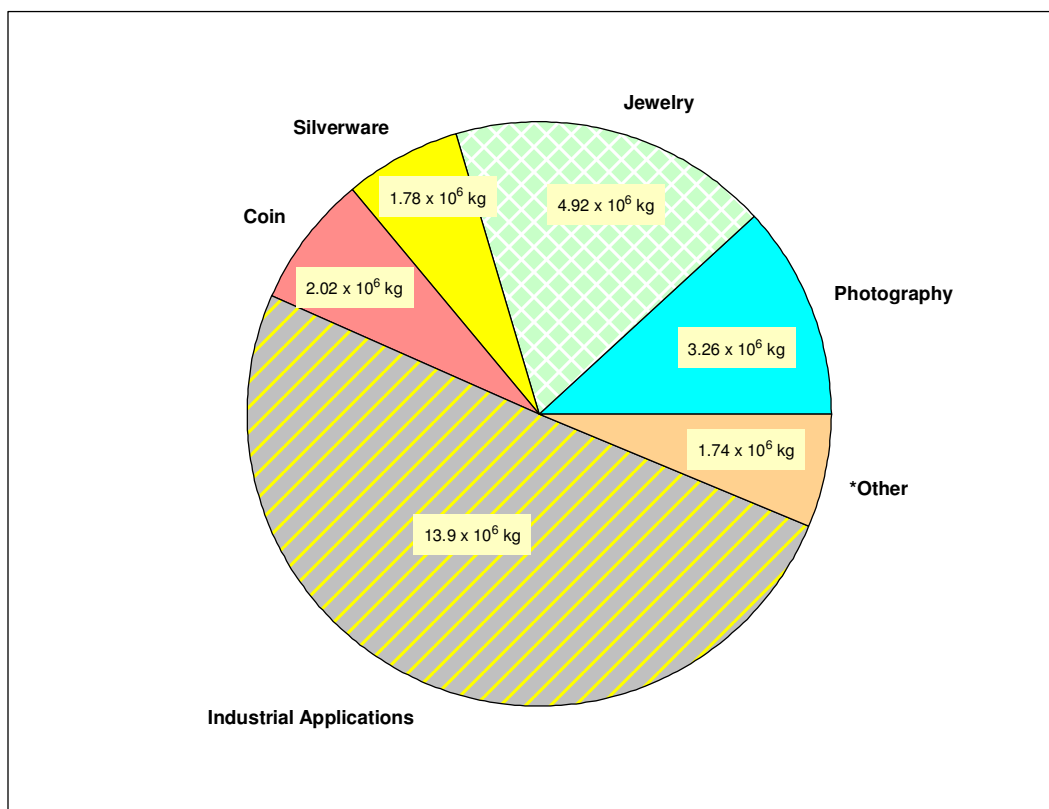


Figure 2.1. 2008 World Silver demand. Industrial applications, which include the manufacture of electrical contacts and circuit boards, represented slightly more than 50% of the world use of silver. Brazing alloys, catalysts, batteries, coatings (mirrors), silver bearings, dental and medical products are some of the industrial applications. De-hedging and global investment practices are represented in by “other” demands (6.3%). Data from annual summaries provided by the Silver Institute.

have been shown to discharge their wastewaters to publicly owned wastewater treatment facilities (Newbrough and Kinch. 1981). For this reason, silver could served as a potentially useful tracer during the study period for tracking the transport and fate of wastewater effluent in Massachusetts coastal marine waters. It is important to note that by 2008, the percentage of silver used in the photographic sector dropped to below 12% (Silver Institute, 2009) due, in part, to increased use of digital solutions for image storage. Most of the silver use (50%) for 2008 was in industrial applications (e.g., bearing production, electronics, manufacturing of batteries, etc.).

The overall amount of silver input into the environment was estimated to be on the order of 10^6 kg yr^{-1} in the late 1970's (Smith and Carson, 1977; Scow et al., 1981). The relative amounts of silver released to various environmental reservoirs were estimated by Scow et al. (1981) as 53% to the atmosphere, 12% to the aquatic environment, and 35% to the land. However, estimates of atmospheric fluxes of silver based on inventories of industrial loss (Silver Institute and GFMS, Limited; 2005) do not include contributions from aeolian weathering of crustal material. To date, very little reliable data exist for estimating atmospheric deposition of Ag. Measured atmospheric deposition of silver has been reported for remote areas of the South Pacific and yield an estimated atmospheric flux (corrected for recycled sea spray) of $0.8 \text{ nmol m}^{-2} \text{ d}^{-1}$ (Arimoto et al., 1987). This translates to a global atmospheric flux of silver to the World's oceans of approximately $3 \times 10^6 \text{ kg yr}^{-1}$ (Table 2.1); two orders of magnitude greater than estimates based solely on industrial losses to the atmosphere (Scow et al., 1981). Elevated concentrations of silver in surface sediments (Chapter 3; Galloway and Likens, 1979; Heiss et al., 1996; Gobeil, 1999; and others), surface ice and snow (Van de Velde et al., 2000), and from peat bog cores (Shotyk and Krachler, 2004) not only provide multiple lines of evidence of atmospheric enrichment due to global industrialization, but also illustrate the importance of local and varying atmospheric source strengths to understanding regional deposition of silver to the environment.

While there are no recent estimates of silver losses to the environment, worldwide silver discharge should to some extent follow consumption trends despite improvements in reclamation of silver from industrial waste streams. The annual world production and United States (U.S.) consumption trends (Figure 2.2) were derived from refinery data compiled by Porter and Hilliard in Kelly et al. (2007) from mineral statistics reported to the U.S. Bureau of Mines and the U.S. Geological Survey. By the 1942, annual U.S. consumption exceeded

Table 2.1. Estimate of Global Silver Fluxes in the environment. Estimates are based primarily on 1978 data reported from Scow et al. (1981). The atmospheric estimate is derived from Arimoto et al. (1987).

Source	Estimated Global Flux (10^6 kg yr^{-1})
Atmosphere (Total)	2.6
Industrial loss to atmosphere	0.09
Water (not including atm. dep.)	0.6
Natural sources	0.44
Stormwater	0.07
Sewage Treatment Plants	0.07
Land (not including atm. dep.)	1.7
Photographic industrial waste	0.63
Sewage Treatment Plants	0.22
Urban Refuse	0.45
Other	0.37
TOTAL:	4.9

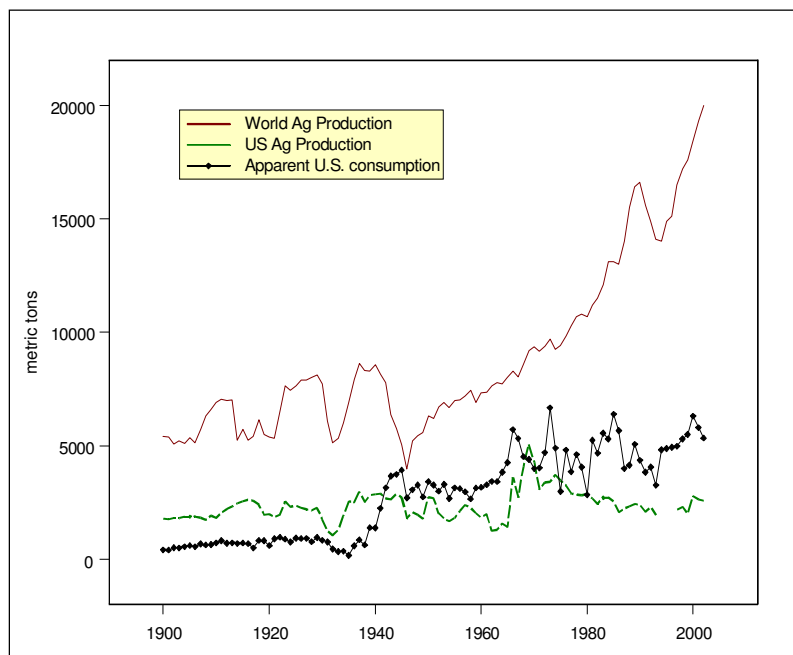


Figure 2.2. Annual silver production, 1900-2003. Data from the U.S. Geological Survey (primarily Porter and Hilliard, 2004).

US production. During the two most recent decades on record, the U.S. annually consumed nearly twice the amount of silver it produced.

The estimate of $4.9 \times 10^6 \text{ kg yr}^{-1}$ for a global silver flux is most likely an upper limit because (1) estimates reported by members of the silver industry may, in part, be also included in flux estimates attributed to the sewage treatment plants, and (2) estimates which include fluxes from rivers also include a portion of the atmospheric deposition. Atmospheric sources of silver have been shown to be highly variable over time (Van de Velde et al., 2000) and are not that well understood. Based on the estimates in Table 2.1, atmospheric deposition is the dominant flux of silver to the environment, particularly to the World's oceans. The estimated Ag flux to the environment represents less than $1/5^{\text{th}}$ of the recent increased annual global production reflecting added production from new participants in global commerce (Silver Institute, 2009).

2.3 Silver marine chemistry

Silver is one of the main transition elements and has the highest electrical and thermal conductivity of any of the metals. It is slightly harder than gold and is second only to gold in malleability and ductility. It can be beaten into silver leaf as fine as $0.25 \mu\text{m}$ in thickness. Silver can exist in 0, 1+, 2+, and 3+ oxidation states, but is almost entirely found in its most stable oxidation state as 1^+ . The electron configuration of Ag ($[\text{Kr}]4d^{10}5s^1$) is uniquely different from "true" transition elements (like Fe, Cu). True transition elements are traditionally considered as having incompletely filled outer d orbitals. Silver, in its neutral and ionic state, has a full complement of electrons in its $4d$ orbital. Another important characteristic of transition metals (including Ag) is that the outer most s orbital is filled before the nearest inner d orbital.

Silver is classified as a B-type cation (i.e., a soft metal) and coordinates preferentially with bases containing I, S, or N as donor atoms (Pearson, 1963). Silver, in particular, forms strong

complexes with reduced sulfur, or S(II)-containing ligands, and to much lesser extents with N, I, and Cl⁻ (Kramer et al., 2002). In oxic marine waters, Ag complexation was thought to be almost entirely by the Cl⁻ ion (Turner et al., 1981, Miller and Bruland, 1995) primarily as AgCl²⁻₃, AgCl⁻₂, and AgCl³⁻₄ (Byrne et al., 1988). These earlier models did not include sulfide complexation reactions because of the instability of reduced sulfur in the presence of molecular oxygen (Stumm and Morgan, 1996) and a perceived absence in oxic aquatic systems. However, reduced sulfur compounds are now known to be fairly ubiquitous and meta-stable in oxic marine waters at nanomolar levels (Krahforst, 1987; Cutter and Krahforst, 1988; Luther and Tsamakis, 1989; Radford-Knoery and Cutter, 1994; Theberge et al., 1997; Tang et al., 2000, Vachet and Callaway, 2003, Dupont et al., 2004). Where these sulfide levels do occur, thermodynamic equilibrium calculations predict virtually all of the silver in the water column should be complexed with reduced sulfur species (Bianchini and Bowles, 2002).

Bell and Kramer (1999) predict the complexation of Ag(I) in natural waters to be very rapid with both inorganic and organic forms of S(II). The rapid formation kinetics is further supported and inferred for Ag and Hg by observations of the rapid formation ($K_f > 10^8 \text{ M s}^{-1}$) of intermediate, meta-stable sulfide clusters with zinc (Luther et al., 1999). Studies designed to evaluate silver sulfide species in natural waters are limited analytically, in part, by ultra low levels predicted for these species. However, soluble zinc sulfide clusters observed in the laboratory suggest that these meta stable intermediates would be available for replacement by silver in natural waters, given log Ks for AgS⁻ and ZnS of 22.8 (Rozen and Luther, 2002) and 11.7 (Luther et al., 1996) respectively. The replacement of zinc by silver should be rapid, since sulfur in these clusters are 2-coordinate—that is they have linear geometry (Bell and Kramer, 1999)—and thus not hindered by steric factors.

Phytoplankton have been shown to produce thiols (organic compounds containing sulfhydryl moieties) which participate in a number of functions necessary for growth and survival.

Most notably, thiols play a role in metal detoxification (Ahner et al., 2002; Dupont et al., 2004), regulation of intercellular redox reactions (Marrs, 1996), and intercellular nitrogen storage (Dupont et al., 2004). Thiols and other reduced sulfur compounds in natural waters are important ligands for trace metal speciation and biogeochemistry (Adams and Kramer, 1998; Bianchini and Bowles, 2002; Laglera and van den Berg, 2003; Vachet and Callaway, 2003; Hand and Honek, 2005). Smith et al. (2002) present an excellent review on the importance of reduced sulfur complexation in natural waters; evaluate natural organic matter as an important general ligand, and model chemical equilibrium of Cu and Ag. Model runs that varied concentrations of class ligands (e.g., carboxyl, amino, and reduced sulfur sites on a generalized natural organic ligand) and metal concentrations yielded clusters of formation constants of ligand class in the following order of strength: $-SR > -NH_3^+ > -OOC$ and $-SR > -NH_3^+ \sim -OOC$ for Cu and Ag, respectively. Less scatter associated with the distribution of $\log K^*$ for Ag suggests more constrained binding (selective) when compared with Cu conditional constants.

The conditional stability constants (K^*) of some important Ag compounds found in marine waters illustrates the potential importance of sulfur in silver complexation among organic and inorganic ligands (L) in natural waters (Table 2.2). Adams and Kramer (1998) predict chloro complexes dominate marine waters only when total sulfide $< 10^{-9}$ M. Thiols, as an example, have been determined in coastal and estuarine waters at nM levels (Tang et al., 2000; Laglera and van den Berg, 2003) and contribute to physical speciation and long-term fate of silver in these environments.

Table 2.2. Selected conditional stability constants ($\log K^*$) for important silver-ligand complexes commonly found in marine waters.

Compound	Log K^*_{AgL}	Reference
Important Inorganic species		
$AgCl_3^{2-}$	5.9	Stumm and Morgan, 1996
$AgCl_2^{1-}$	5.2	Stumm and Morgan
AgS^- complexation	22.8	Rozan and Luther, 2001
Important organic species		
Ag-sulfide complexes, (-SR, predominantly organic, operationally defined)	11.6	Al-Farawati and van den Berg, 1999
	12.1	in Smith et al., 2002
Ag-2-Mercaptoethanol complex	13.2	Bell and Kramer, 1999
Ag-Glutathione complex	12.3	Adams and Kramer, 1999
Ag-Cysteine complex	11.9	Bell and Kramer, 1999
Carboxyl binding sites on natural organic matter (-OOC)	~2	Smith et al., 2002
Natural organic matter amino sites ($-NH_3^+$)	3.4	Smith et al., 2002
Natural marsh DOC	~9	James and Playle, 1995

K^* represents the “conditional” equilibrium constant reported and cover a range of pH (6-8.5) and ionic strengths.

2.4 Physical speciation of Ag

The fate and transport of trace metals in marine surface waters are controlled by many factors such as riverine input, atmospheric deposition (including solubilization in seawater), upwelling, removal by biological uptake and/or particle scavenging, sinking, and regeneration with depth. The types of transformations that occur as these elements move through the environment affect their reactivity, bioavailability, toxicity, and fate. As with other trace elements, silver can exist in the water column in various physicochemical forms, either as free hydrated ions, associated with organic or inorganic complexes, or adsorbed onto colloids and particles.

In the open ocean, silver is most likely introduced to the surface ocean associated with marine aerosols. As has been shown with iron (Zhuang and Duce, 1993), silver most likely exists as

the Ag^+ species in the acidic media associated with the aerosol. Silver is subsequently removed from solution by incorporation or association with colloids and/or particles. Colloids may enhance the residence time of silver in the ocean or enhance its removal via coagulation to produce larger particles (Honeyman and Santschi, 1992). As these particles settle out, silver is then remobilized into the dissolved phase coincident with the regeneration of the sinking organic carrier phase. Martin et al. (1983) observed regeneration rates for dissolved silver to mimic organic carbon regeneration in the Pacific open ocean. Here, particulate Ag was found to be strongly bound with particulate matter. Correlation of silver with silicate in the open ocean (Flegal et al., 1995; Ranville and Flegal, 2005) suggests that silver, to some extent, may have a diatom-mediated component to its biogeochemical cycling in the marine environment. The co-variance of silicate with other trace elements in the ocean water column has been observed. For instance, Ge is very similar to silica and can occupy the place where silica exists in the structure of diatom tests (Froelich et al., 1989). Zn, Ni and Se also show a similar combination of deep and shallow regeneration behavior typical of silicate in open ocean waters (Millero, 2006, and references therein).

There is little reliable data on the geochemistry of silver in rivers and estuaries. Silver enters an estuary largely associated with particles (Sanders and Abbe, 1987) and desorbs from the particle as it encounters greater salinity levels, becoming stabilized through complexation with soft B-type ions. Silver is a B-type metal, and thus has easily deformed (i.e., “soft”) outer electron shells (Stumm and Morgan, 1995). B-type metals interact well with “soft” anions (e.g., S^{2-} , Cl^-). Consequently, silver is either removed by advection out of the estuary as dissolved, colloidal and fine particulate moieties or may be transported to the sediments through association with rapidly settling larger particles.

Tanizaki et al., (1992) examined the distribution of silver among the dissolved, colloidal and particulate states in river water and observed silver to be largely associated with particles (55-77%).

The remaining silver fraction in the filtrate was found to be associated with larger colloids (apparent spherical diameter of 1 -450 nm as determined by ultrafiltration). However, the data is suspect due to large losses of silver and other metals attributed to adsorption to the apparatus walls (up to 50%) during ultrafiltration. Benoit et al. (1994) observed about 50% of the silver in Texas estuaries was associated with particulates ($> 0.4 \mu\text{m}$). Pham and Garnier (1998) found that 95-99% of the silver in fresh water passing through a $0.45 \mu\text{m}$ filter was associated with colloids ranging in size from 1 – 100 kDa. Colloidal silver determined in filtered estuarine and marine samples ranged from 15 - 90% (Wen et al., 1997). Colloids clearly play an important role in the fate and transport of silver in natural waters. Whether colloids increase the solubility of silver (and other metals) through complexation or enhance its removal through colloidal aggregation, particle formation and eventual deposition to the sediments remains uncertain (Wells et al., 2000).

Smith and Flegal (1994) identify estuarine sediments as a potentially significant source of silver to the overlying water column. Principal component analysis of total suspended solids (TSS), salinity, dissolved Ag, Cd, Hg, Pb and dissolved nutrients in the San Francisco Bay Estuary indicated dissolved silver was most closely associated with dissolved Si concentrations. They observed that benthic fluxes of silicate become a more important source of silicate to the water column in this region during periods of low flow.

Smith and Flegal (1994) also observed relatively consistent conditional distribution coefficients (K_D 's) for silver throughout the San Francisco Bay Estuary at low to moderate TSS concentrations ($K_D = 10^5$). The observed decrease of K_D 's in water samples with TSS above 40 mg kg^{-1} may be the result of simple dilution by refractory, low silver inorganic crustal material or the greater significance of colloidal species present. Benoit et al. (1994) investigated the role of colloids in the partitioning of silver in selected estuarine waters along the Texas coast. They attribute observed decreases in K_D 's in water samples containing high suspended matter to typical sample

processing artifacts; a greater portion of colloidal species contributing to the total silver in the water column was included in the “dissolved” (filtered) pool. Colloidal forms of Ag have been shown to be a significant component the total Ag present in natural waters (Wen et al., 1997 and 1999; Ndung’u et al., 2006) and thus important to long-term transport and ultimate fate of Ag in the marine environment.

Sanders and Abbe (1987) investigated sorptive and desorptive properties of silver as a function of salinity (0, 15 and 23 psu) and particle type (phytoplankton and sterilized suspended sediment). In this laboratory study, silver uptake by live phytoplankton and sediments decreased with increasing salinity but not in proportion to the estimated free ion activity, illustrating the importance of chemical and physical speciation changes as fresh water mixes with marine water. Further, silver displayed a greater tendency to desorb from non-living particles (resuspended sediments) relative to live phytoplankton cells. Accordingly, biological uptake may be important to the retention of silver in estuaries as it enters the food chain and recycled within the estuary. The importance of zooplankton in the repackaging of selected elements was investigated by Reinfelder and Fisher (1991). The degree to which elements are assimilated can affect the residence times of these elements in the water column. The assimilation efficiency of silver by zooplankton feeding on phytoplankton (defined by the amount retained by zooplankton after gut evacuation divided by the amount ingested) exposed to ^{110m}Ag and axenically grown in filtered seawater media was one of the lowest (~17%) among the transition elements studied (compared to 27-48% and 97% for Zn and Se, respectively). The lower silver retention by zooplankton is attributed to its non-essential role in growth and survival.

Much of the data generated to demonstrate the utility of silver concentrations in coastal environmental media for understanding the fate of wastewater discharge have been conducted on heavily impacted urban estuarine sediments and coastal waters. Silver and other sewage indicators

were used to study the impact of municipal sewage sludge disposal to offshore sediments (Rutherford and Church, 1975; Bothner et al., 1994) and the impact of wastewater discharge in the coastal waters of Massachusetts (Bothner et al., 2002). Sañudo-Wilhelmy and Flegal (1992) estimate 95% of the anthropogenic silver in the water column of the Southern California Bight originate from coastal wastewater discharges (point sources). The San Francisco Bay estuary is heavily impacted from municipal wastewater discharges either through direct discharge or from the legacy of polluted sediments. Though direct discharge of waste water is generally considered the primary source of Ag to the water column in San Francisco Bay, flux from contaminated sediments can be a significant source for water column Ag (Smith and Flegal, 1994). Changes in silver sediment concentration, along with *Clostridium perfringens* (a bacterial spore associated with sewage), were used to evaluate sewage-contaminated sediment transport by major coastal storms in Massachusetts Bay (Bothner et al., 2002) further illustrating the potential for silver as a tracer of wastewater transport and fate in coastal waters.

2.5 Environmental distributions

The earliest investigations of silver in the marine environment were limited to tracer studies of sewage-derived particle dispersion in coastal waters (Rutherford and Church, 1975) and as a measure of anthropogenic contamination in sediments (Greig et al., 1977). Municipal wastewater is enriched in silver from industrial waste streams (Bothner et al., 2002; Smith and Flegal, 1994, Sigovia-Zavala et al., 2004). Silver distributions in marine waters remained relatively uncharacterized until the early 1980's when reliable oceanic distributions of silver were first reported (Murozumi, 1981; Martin et al., 1983). Murozumi's (1981) observations consisted of 5 data points taken from samples collected in the mid-South Pacific (20°S, 160°W) and show a roughly linear increase in Ag concentration with depth, ranging from about 0.5 pmol kg⁻¹ in the

surface water to 34 pmol kg^{-1} at 3,500 m. Because of the high analytical detection limits of the instrumental analysis of the period, a preconcentration step was needed in order to quantify ultra-low levels of metals typical of natural waters. Preconcentration is often performed by using a strong chelating agent to produce an insoluble complex and subsequent use of liquid-liquid extraction techniques. Murozumi's data from these first samples included an acid-leachable portion of the total Ag because these samples were not filtered and contained particles. A portion of the particle-bound Ag may not have been captured during the preconcentration procedure, and thus these data may slightly underestimate the total amount of silver present in the surface waters of the southern Pacific.

Martin et al. (1983) determined Ag concentrations in unfiltered samples and filtered samples collected along the eastern north Pacific, observing similar levels ($\sim 1 \text{ pmol kg}^{-1}$) in surface waters to a maximum of 24 pmol kg^{-1} at 2,440 m. These data agreed well with the observations of Murozumi (1981) and also were analytically similar in that they used a liquid/liquid preconcentration step prior to instrumental analysis. In addition, Martin et al. (1983) showed that Ag retained on $0.4\text{-}\mu\text{m}$ filters from samples was typically less than 10% of the total, with exceptions occurring in the photosynthetically active region near the pycnocline corresponding to the depth of a dissolved Ag minimum where the particulate fraction approached nearly 30% of the total.

Close correlations between water column dissolved Ag and silica have been noted (Martin et al., 1983; Flegal et al., 1995; Rivera-Duarte et al., 1999; Ndung'u et al., 2001; Sañudo-Wilhelmy et al., 2002; Ranville and Flegal, 2005). Silver nutrient-like profiles low surface water concentrations and increasingly greater concentrations with depth, are consistent with removal by particle scavenging or biological uptake in the surface waters and subsequent regeneration back into non-particulate forms with depth (Fig. 2.3). Fisher and Went (1993) demonstrated greater Ag uptake in cultures of diatoms relative to cultures of coccolithophoridae, inferring a possible uptake mechanism

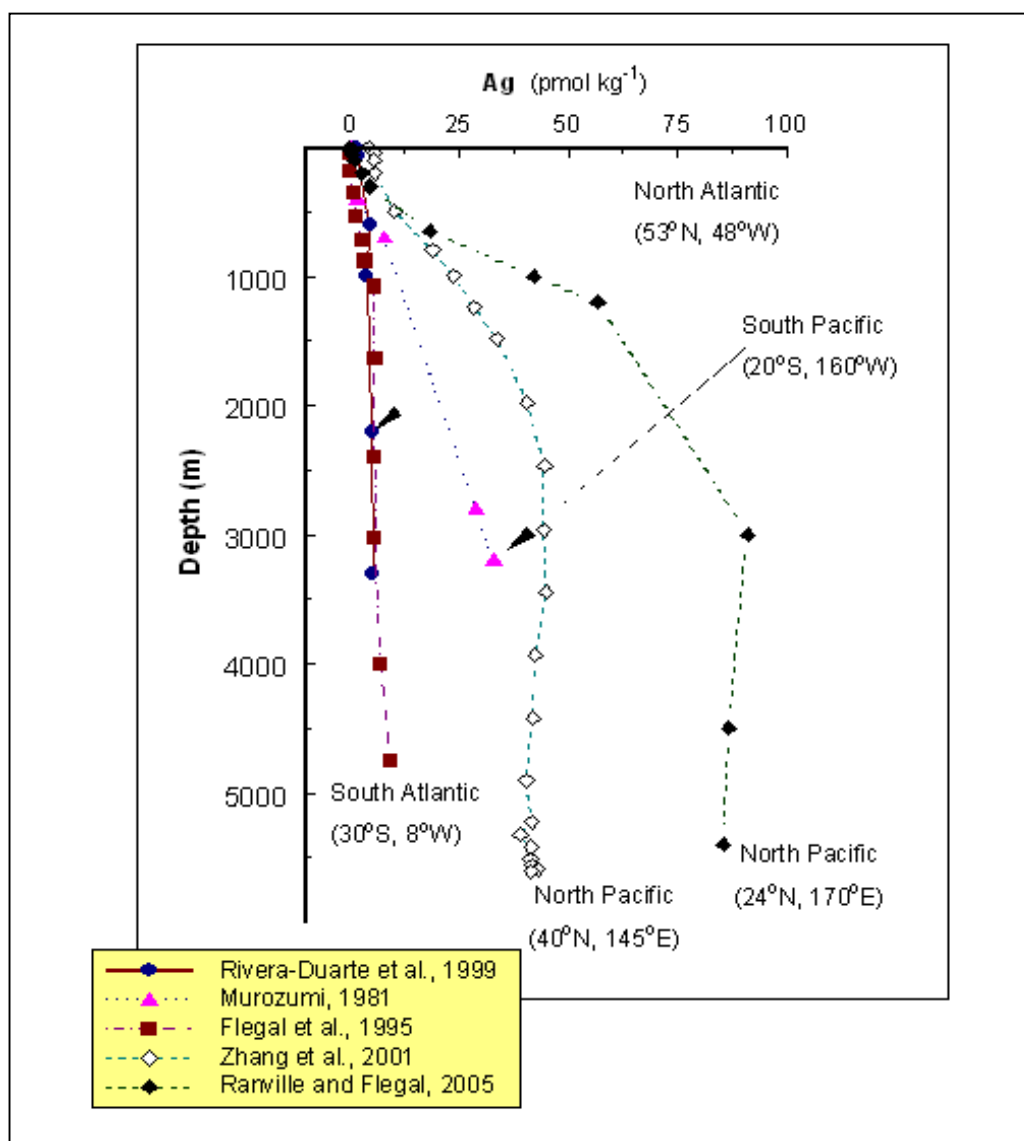


Figure 2.3. Vertical distribution of Ag at selected stations in the World's oceans.

associated with silicate uptake and diatom growth. Biologically-mediated particle scavenging is thought to account for most of the silver concentrations in the deep ocean sediments in the North Pacific (Morford et al., 2008).

Over the last two decades, investigations of the distribution of silver in the world's oceanic waters have been conducted (Sañudo-Wilhelmy and Flegal, 1992 ; Flegal et al., 1995; Rivera-Duarte et al., 1999; Zhang et al., 2001; Sañudo-Wilhelmy et al., 2002; Ranville and Flegal, 2005;), including embayments and estuaries (e.g.: Benoit et al., 1994; Smith and Flegal, 1994, Wen et al., 1997 and 1999; Barriada et al., 2007; Cozic et al., 2008; Lares et al., 2008 Valverde et al., 2009; Beck et al., 2009), and have contributed significantly to describing silver distribution of the world's ocean. The spatial extent of a number of these surveys is illustrated in Figure 2.4. Silver's nutrient-like distribution in the oceans shows considerable variability both geographically and with depth (Fig. 2.3). Silver is enriched in both surface and deep Pacific waters relative to the surface and deep waters of the Atlantic. Silver concentrations increase as oceanic waters move from the North Atlantic, through the Atlantic and ultimately into the Pacific; similar to concentration distributions observed for nutrients (i.e., reactive nitrate, phosphate and silicate) and consistent with the thermohaline circulation of the world oceans (e.g., Broecker and Peng, 1982). To date, no measurements have been made in the Indian Ocean.

Surface ocean samples to date have generally shown Ag concentrations to be less than 1 pmol kg⁻¹ (Table 2.3). Exceptions to this have been observed in coastal areas where anthropogenic input or upwelling of deep water is significant. Sañudo-Wilhelmy and Flegal (1992) observed elevated Ag concentrations in surface water along the Southern California Bight and demonstrated the effective use of silver in these waters as a tracer of wastewater originating over 100 km to the north from San Diego's municipal wastewater treatment facility. Similar elevated surface water concentrations (4 – 8 pmol kg⁻¹) in filtered seawater were observed off the coast of Japan (Zhang et

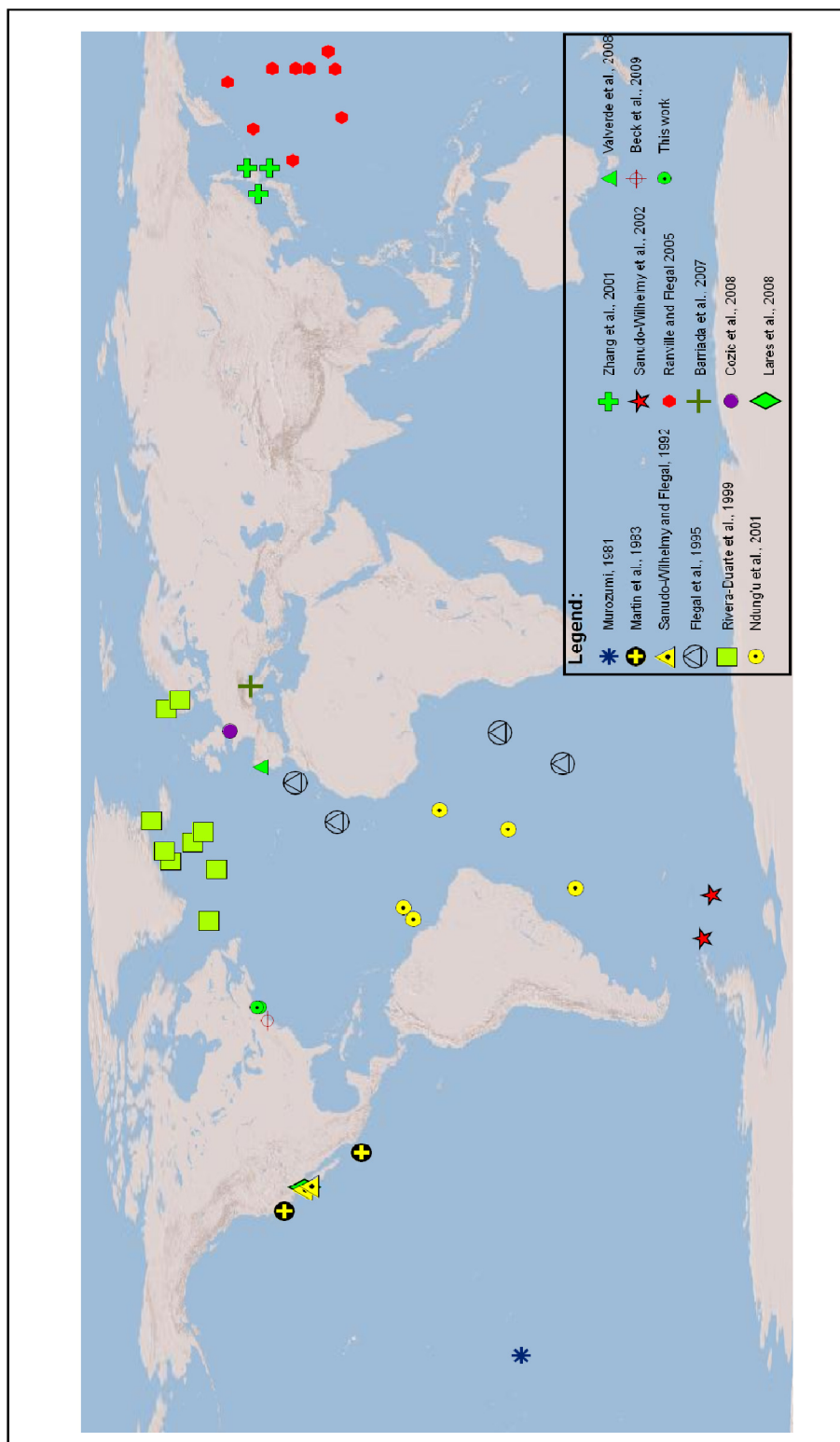


Figure 2.4. Summary of marine stations with reliable silver data, World's oceans, 1981 – 2009.

Table 2.3. Ranges of Ag concentrations in the world's oceans

Reference:	Location	pmol kg ⁻¹
Murozumi, (1981)	Central S. Pacific	< 1 – 30 (unfiltered)
Martin et al., (1983)	Eastern N. Pacific (near coastal)	0.4 – 22.8 (0.45 µm-filtered) 0.07 – 0.65 (particulate)
Sañudo-Wilhelmy and Flegal, 1992	Eastern N. Pacific (near coastal)	4 – 17 (unfiltered <i>and</i> 0.4 µm-filtered)
Flegal et al., 1995	Eastern Atlantic	<0.2 – 9.6 (unfiltered, pH=1)
Rivera-Duarte et al., 1999	Northern N. Atlantic	0.7 – 6.9 (unfiltered, pH<2)
Zhang et al., 2001	Western N. Pacific (near coastal)	4.4 – 46.8 (0.04 µm-filtered)
Ndung'u et al., 2001	Western equatorial and South Atlantic Ocean	1.3 – 11.3 (0.22 µm-filtered) 1.6 – 31.7 (0.22 µm-filtered)
Sañudo-Wilhelmy et al., 2002	Southern Ocean (Weddell Sea)	8.9 – 22.4 (0.45 µm-filtered)
Ranville and Flegal, 2005	North Pacific Ocean	– 87.7 (unfiltered, pH<2)
Barriada et al., 2007	Adriatic Sea	13 – 28 (0.2 µm-filtered)

al., 2001). The authors observed the elements Y and Ag to co-vary ($r^2 > 0.9$) and show similar nutrient-like behavior. Corresponding dissolved Y concentrations were used as a non-anthropogenic river-borne tracer in these waters. By extension, and assuming negligible other sources (e.g., atmospheric deposition, upwelling), silver in the waters near Japan was viewed to be largely from natural weathering processes. However, as the authors point out, samples with the lowest observed Ag concentrations and lower salinities (i.e., most “coastal” samples), were significantly enriched in Ag relative to corresponding Y concentrations and possibly reflect a relatively greater influence from anthropogenic sources in these samples.

Sañudo-Wilhelmy et al. (2002) investigated the distribution of trace metals, including Ag, in the Weddell Sea of the Southern Ocean to better understand natural processes controlling the distribution of trace metals in marine waters. They considered the Weddell Sea to be an ideal

setting for studying natural processes because of the undeveloped coastal margin and wind patterns and surface currents that isolates this system from distant anthropogenic influences. Observations of very low concentrations of Pb and Al are consistent with this isolation paradigm. However, Ag (along with Cu, Cd, Zn, Fe, and measured dissolved nutrients) is enriched in the Weddell Sea relative to observations of other ocean systems. This enrichment is attributed, in part, to weathering products delivered by glacial processes from land to the open ocean. However, metal-salinity plots show most of the measured metal concentrations increase with salinity, in contrast to the reverse observed for most estuaries where metal loading to coastal waters is strongly associated with riverine input. Silver concentrations in samples collected in open water beyond the ice sheet are consistent with linear mixing along the salinity gradient (Fig.2.5); possibly the result of elevated ocean end-member concentrations mixing with the surface waters of the Weddell Sea. The relatively older, higher salinity waters are associated with recirculated deep water of the Antarctic Ocean. Silver concentrations in the Weddell Sea were significantly higher than neighboring surface waters of the Atlantic and are more typical of concentrations found in the south Pacific (Murozumi, 1981).

The oceanic data reported above lends to a broader global perspective of the marine biogeochemistry of silver. Oceanic residence times of silver have been reported to be as short as 350 years (Broecker and Peng, 1982). The fate and transport of silver is similar to essential nutrients (where their distributions appear to co-vary), especially in pelagic systems. Data in Fig. 2.3 can be used to determine the oceanic residence time of silver is probably less than a few thousands of years, at least on the time scale of oceanic mixing (1000 yrs consistent with the conveyor belt ocean circulation model where traveling deep water becomes increasingly enriched by decomposition of organic material and cumulative loadings, ending up in the N. Pacific as older deeper water before upwelling and returning as surface flow to the N. Atlantic.

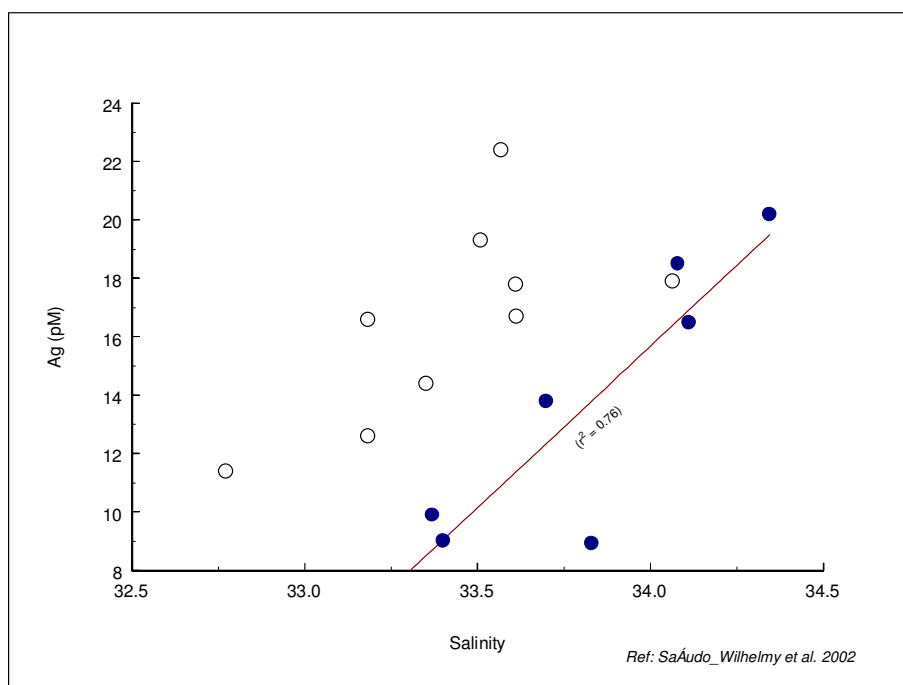


Figure 2.5. Distribution of Ag in the Weddell Sea plotted against salinity. Solid circles represent samples collected outside the ice cover ($r^2=0.76$). Open circles represent samples collected from leads within the ice cover. (Recreated from data provided in Sañudo-Wilhelmy et al., 2002).

Assuming a simple steady-state box model of the world's oceans (i.e., fluxes to and from the ocean are in balance), using the non-anthropogenic global silver fluxes listed in Table 2.1 (3.3×10^6 kg y^{-1}), and estimates of Ag mass in various oceanic reservoirs derived from studies that contributed to Fig. 2.3, an estimate for a global ocean residence time for Ag is ~ 1027 y (Fig. 2.6) and most of the oceans' silver ($\sim 65\%$) is located in the North Pacific middle and deep waters.

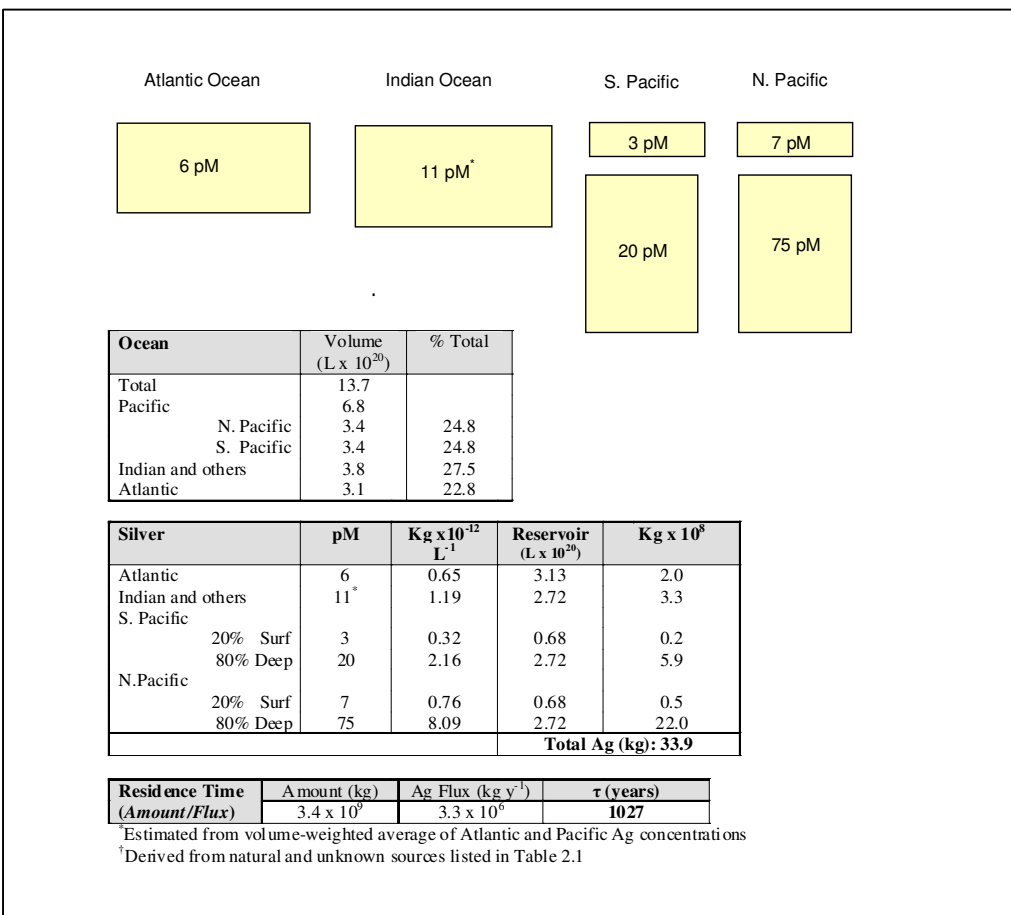


Figure 2.6. Estimated residence time (τ) for Ag in ocean waters (τ = amount in oceans/amount delivered to the oceans). Reservoir concentration values estimated from investigations captured in Fig. 2.3. Flux estimates from “natural or unknown” sources (land, atmosphere, and fresh water) listed in Table 2.1.

2.6 Silver accumulations in marine biota

Silver is thought to be non-essential to organism growth and provides no known benefit to biological processes for health and growth. However, silver is found to be bioaccumulated in many marine organisms (Eisler, 2000). The liver of marine animals is often a site of trace metal accumulation (Braune et al., 1991; Szefer et al., 1994; Becker et al., 1995; Saeki et al., 2001; Ikemoto et al., 2004). Evidence presented earlier suggests that Ag distribution in the marine environment is influenced by biological processes, most notably in diatom productivity (Fisher and Went, 1993). Because silver occurs only at trace levels, even in urban coastal waters where levels

are elevated by several orders of magnitude above background, heterotrophic microbial productivity is an important gateway to food chain bioaccumulation of Ag. Eisler (2000) compiled a compendium of silver concentrations reported in plants and animals.

Except for acute exposure found in human skin, the highest biological tissue concentrations reported in Eisler (2000) were in the soft tissue of the american oysters, *Crassostrea virginica*, from Georgia, USA (28-82 mg kg⁻¹ dry wt.); the baltic clam, *Macoma balthica*, collected near a sewage outfall in San Francisco Bay (32-133 mg kg⁻¹ dry wt.); common eider liver (44 mg kg⁻¹ dry wt.); up to 320 mg kg⁻¹ dry wt. in the mud sail, (*Nassarius obsoletus*) from San Francisco Bay; and 59 -113 mg kg⁻¹ dry wt. in mussels exposed to wastewater in San Diego Bay and in New Zealand (respectively). Algae have also been shown to accumulate significant levels of silver, exhibiting high bioconcentration factors (often expressed as the ratio of chemical concentration in the organism to that of the surrounding medium or food) ranging from 20,000 – 200,000 (e.g., Ratte, 1999; Eisler, 2000).

In general, metal uptake in organisms requires interaction, whether passive or active, and exposure to bioavailable forms of metal complexes. In addition to direct uptake from the environment, Ag is also accumulated in organisms from food ingestion. The quality and quantity of food sources can be important in bioaccumulation and food web transport (Fisher and Wang, 1999). Twinning and Fisher (2004) observed greater assimilation efficiencies of silver (60-80%) in copepods feeding on herbivorous protozoans when compared to those that fed directly on phytoplankton (10-20%). Though Sorption, ingestion, and assimilation are important bioaccumulation mechanisms, as is the chemical form, the importance of bacterioplankton productivity as a pathway for Ag transport through the food web is implicated. While carbon-based microbial production is very efficient in general (Fenchel, 1982), it may be the leaky process of

ubiquitous heterotrophs (Jumars et al., 1989) that render forms of some contaminants more bioavailable to other consumers (e.g., Ag and Cd, see Twining and Fisher, 2004).

The bioavailable forms include the free metal ion and dissolved, colloidal, and particulate metal-ligand complexes. The biotic ligand model (BLM) has been developed for describing the interaction (either as a biological response or by contaminant accumulation) of the organism to contaminant exposure (Campbell, 1995). As noted earlier, sulfur (especially sulfides) is of particular importance for Ag complexation and recent efforts have been made to adopt aquatic Ag-sulfide speciation to the BLM (Bianchini and Bowles, 2002). Ag uptake in phytoplankton is thought to occur as incidental transport across cellular membranes (Campbell, 1995) and/or absorption processes associated with ambient exposure. Silver uptake by algae appears to be enhanced by the presence of thiosulfate, which complexes Ag and is transported across the plasma membrane (Fortin and Campbell, 2001). This process may also be important in bacteria and other organisms that have cellular sulfate/thiosulfate transport systems. In addition, chloro-complexed Ag exhibit high membrane permeability (Fisher and Wang, 1999) and may be more toxic than free silver (Erickson et al., 1998) and thus important species in Ag uptake mechanisms for marine organisms.

The gills of fish (Wood et al., 1996; Ferguson and Hogstrand, 1998) and other aquatic organisms (Bury et al., 2002) have known active Ag complexation sites. These Ag-active sites have been modeled using the BLM to predict metal toxicity to marine organisms (Paquin et al., 2000). BLM models are chemical equilibrium models for contaminant speciation in aqueous systems which include, along with important inorganic and organic ligands, the binding sites on biotic surfaces (e.g., gills in fish, phytoplankton cell walls, etc.).

2.7 Toxicology

The free ion, Ag^+ , has been shown to be toxic to many aquatic organisms at low levels (Calabrese et al., 1973; Coglianese and Martin, 1981; Ghosh et al., 1990; Hook and Fisher, 2001; Davies et al., 1978). Aquatic chemical speciation models of natural systems predict Ag^+ concentrations $<10^{-13}$ - 10^{-15} (for Cl dominated models: Reinfelder and Chang, 1999; Ward and Kramer, 2002) and $< 10^{-17}$ when sulfur complexation is considered (Bell and Kramer, 1999). While Ag^+ is considered readily bio-available and highly toxic, neutrally complexed Ag^+ has been recognized as a more probable toxic agent (Webb and Wood, 2000). The dynamic aspects of speciation in natural systems is often neglected when equilibrium models such as the BLM and free ion activity models are used to assess bioavailability and toxicity in aquatic systems. More sophisticated approaches to understanding the role of chemical speciation in bioaccumulation and toxicology of aquatic organisms recognize the importance of the dynamic nature of speciation and are sensitive to kinetic aspects associated with fluxes and reactivity among a constantly changing milieu of compounds in solution. Thus, a more comprehensive assessment of bioavailability considers chemical kinetic of complex formation/dissociation and local diffusion-controlled exchanges (Pineiro et al., 2006). Dynamic speciation assessments of trace elements in aquatic systems have identified important trace metal species in biouptake and bioaccumulation (van Leeuwen et al., 2005).

A good portion of soluble Ag is thought to be bioavailable in order to support levels accumulated in marine organisms (e.g., Eisler, 2000). However little toxicological effects on marine organisms have been observed at exposure levels that mimic concentrations found in natural systems (nM – pM). Hook and Fisher (2001) observed toxicological effects in marine copepods (reduced egg production and viability) at levels that exceeded 400 nM which is rarely observed even in highly urbanized estuaries (Sañudo-Wilhelmy et al., 2004). Other higher marine organisms

require much greater levels of exposure (approaching nM - μ M levels) before toxicological responses are observed (Ward et al., 2006). The toxicology of Ag in freshwater organisms is much better studied (see Ratte, 1999) and the effect-threshold-concentrations are generally lower than those observed for comparable marine organisms.

2.8 International Argentum Conferences

The understanding of silver interaction with the environment improved measurably following a concerted effort, led by the photographic industry, to reduce the amount of silver discharged as industrial waste. Members of the silver industry anticipated tighter restrictions under the Federal Clean Water Act requiring businesses and industries that discharge to publicly-owned waste treatment works and that compliance would occur through industrial pretreatment programs. With industrial backing, the dialogue to better understand the biogeochemical behavior of silver in the environment was enhanced in the mid-1990's by a series of The Argentum International Conferences (1993-1998) in which part of this research was presented (Krahforst and Wallace, 1996). The first five conferences provided the venue for the traditional platform of scientific presentations of recent findings of silver in the environment, covering aspects of sources, concentration levels in natural waters and biota, chemical speciation, particle interactions (adsorption and desorption reactions), toxicology, bioaccumulation, influence of ligands, and transport and environmental fate. As a result, a compendium of research findings was produced (Andren and Bober, 2002) which captured studies funded through the Expanded Silver Research Program as well as research from an expanded community of investigators conducting research on the environmental nature of silver.

CHAPTER 3

THE DISTRIBUTION OF SILVER AND OTHER METALS IN COASTAL WATERS OF THE MASSACHUSETTS BAYS

3.1 Introduction

The coastal marine environment has been and continues to be utilized for disposal site for man-made waste. During the 20th century, problems associated with this practice were exacerbated by the exponential growth of human population and our preference for living near the coast. Ecological thresholds considered necessary for healthy coastal ecosystems were being reached or exceeded and largely attributed to anthropogenic perturbation (*i.e.* Rabalais and Turner, 2001; Bricker et al., 1999; Howarth et al., 2002; Beach, 2003, and others). The large-scale eutrophication of part of the Gulf of Mexico, which has been linked to land-based human activities (Rabalais et al., 2002) within the Mississippi watershed, suggests the extent of the spatial scale that anthropogenic waste can have on coastal ecosystems. In 2003, the Pew Oceans Commission reported on the state of the Worlds' oceans and identified pollution and coastal development in 3 of 10 major threats to the marine environment.

Often times waste materials contain elements that are known to be toxic to marine organisms. Some of these elements are chemicals associated with daily household or industrial uses. These materials are often modified, sometimes becoming more toxic, through waste treatment and disposal processes. Wastewater composition delivered to and derived from U.S.

municipal treatment facilities is regulated under the Clean Water Act (33 U.S.C., Chapter 26). However, little is known about the amount or presence of many non-regulated contaminants or of the cumulative effects contaminants have in general on the quality of ecosystems. Chemical waste associated with the use of personal care products and pharmaceuticals are two contemporary examples of wastewater-borne contaminants that are emerging as concerns for environmental management. (See Daughton, 2004, and references therein, for a good overview.) Understanding the extent of contamination is an important aspect of environmental management and for assessing ecosystem condition. Wells et al. (2001) distinguishes a threshold between contamination and pollution as the point where noticeable deleterious effects to resident organisms are observed. By this standard many urban estuaries are polluted.

Wastewater disposal in many urban areas is often managed through large centralized treatment facilities. In developed countries, like those in the European Union and the United States, contamination from industrial sources and municipal wastewater treatment facilities are regulated by controls on discharge flow and the composition of specific constituents in the waste effluent. Most of the World's urban centers are located in coastal zones (McGranahan and Satterthwaite, 2003). Discharges to coastal waters are subjected to mixing and dispersion by tides and currents and may distribute contaminants across large ecosystems. Knowledge about the fate and dispersion of wastewater in aquatic systems improves environmental management and factors into the design of these facilities (Shea and Kelly, 1992; HydroQual, 2000). Advances in hydrodynamic modeling and aquatic sciences continue to add improvements to wastewater management.

The transport and fate of wastewater in aquatic systems have important human and ecological health implications. Biological contaminants, or pathogens, are of particular

concern to environmental managers because of their known threats to human health (Langmuir, 1997). Most of the human health assessments of surface waters impacted by wastewater rely on determinations of the amount of one or two indicator organisms: *Escherichia coli* or enterococci. These organisms serve as good indicators of recent or continuous wastewater exposure as *E. coli* and enterococci are relatively short lived in the marine aquatic environment and often reflect local sources (Fleisher et al. 1996). Other indicators have been used to understand the fate and transport of wastewater in coastal receiving waters. Silver has been used as a tracer for dispersion and fate of wastewater effluent in coastal waters (Rutherford and Church, 1975; Martin et al., 1988; Sañudo-Wilhelmy and Flegal, 1992). Silver concentrations in municipal wastewater are often elevated by several orders of magnitude over those occurring naturally in seawater (Rutherford and Church, 1975; Sañudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1994; Rivera-Duarte and Flegal, 1997, Beck et al., 2009).

Wastewater discharge in Massachusetts coastal waters continues to be evaluated in light of programs intended to improve the environmental quality of Boston Harbor. Litigation over pollution in Boston Harbor culminated in 1985 when the United States Attorney filed suit on behalf of the U.S. Environmental Protection Agency (EPA) against the Commonwealth of Massachusetts for violations of the Federal Clean Water Act (Dolan, 2004). As a result, the Massachusetts Water Resources Authority (MWRA) was created to oversee multi-billion dollar projects designed to repair and upgrade Metropolitan Boston's sewage treatment facility and relocate wastewater discharge from within the confines of Boston Harbor to a new outfall site located in Massachusetts Bay (Fig. 3.1). These efforts— improved wastewater treatment and the extension of the outfall to a new site in Massachusetts Bay— have provided added

incentive for a better understanding of the sources of contaminants and their relative contributions to the degradation of coastal water quality.

No reliable data to date has been published on the concentration of Ag in Massachusetts and Cape Cod Bay marine waters, and only one data point exists for waters in the Gulf of Maine (GOM) and is limited to surface water particulates (Spencer and Sachs, 1970). This research presents data from field surveys conducted during 1994 – 1996 that were designed to evaluate Ag as a potential tracer of wastewater effluent dispersion and fate in Massachusetts Bay and to provide added information on the geochemical fluxes of silver and other metals in coastal marine waters.

3.2 Study area

The Massachusetts Bays system (MBS) is a semi-enclosed embayment (50 x 100 km) in the southwest portion of the Gulf of Maine (GOM) that consists of two large sub-embayments and a highly urbanized estuary (Fig. 3.1). Massachusetts Bay is the largest component, bounded to the north and east by the relatively pristine waters of the GOM, and to the south by Cape Cod Bay. The Boston Harbor estuary empties into western Massachusetts Bay. The eastern boundary of Massachusetts Bay is delineated by Stellwagen Bank, a large subsurface bank which rises abruptly from depths of 80-100 m to 30-50 m. Stellwagen Bank is an extension of the glacial processes that formed Cape Cod during the Pleistocene (Uchupi, 2004). Stellwagen Basin, defined by 80 – 100 m contours, is the deepest portion of MBS and occupies the northeast third of Massachusetts Bay. Cape Cod Bay is a shallow, relatively circular bay with the deepest portion (>20 m) occurring at its center. Similar to the depositional environment found in Stellwagen Basin, the central region of Cape Cod Bay is of low energy

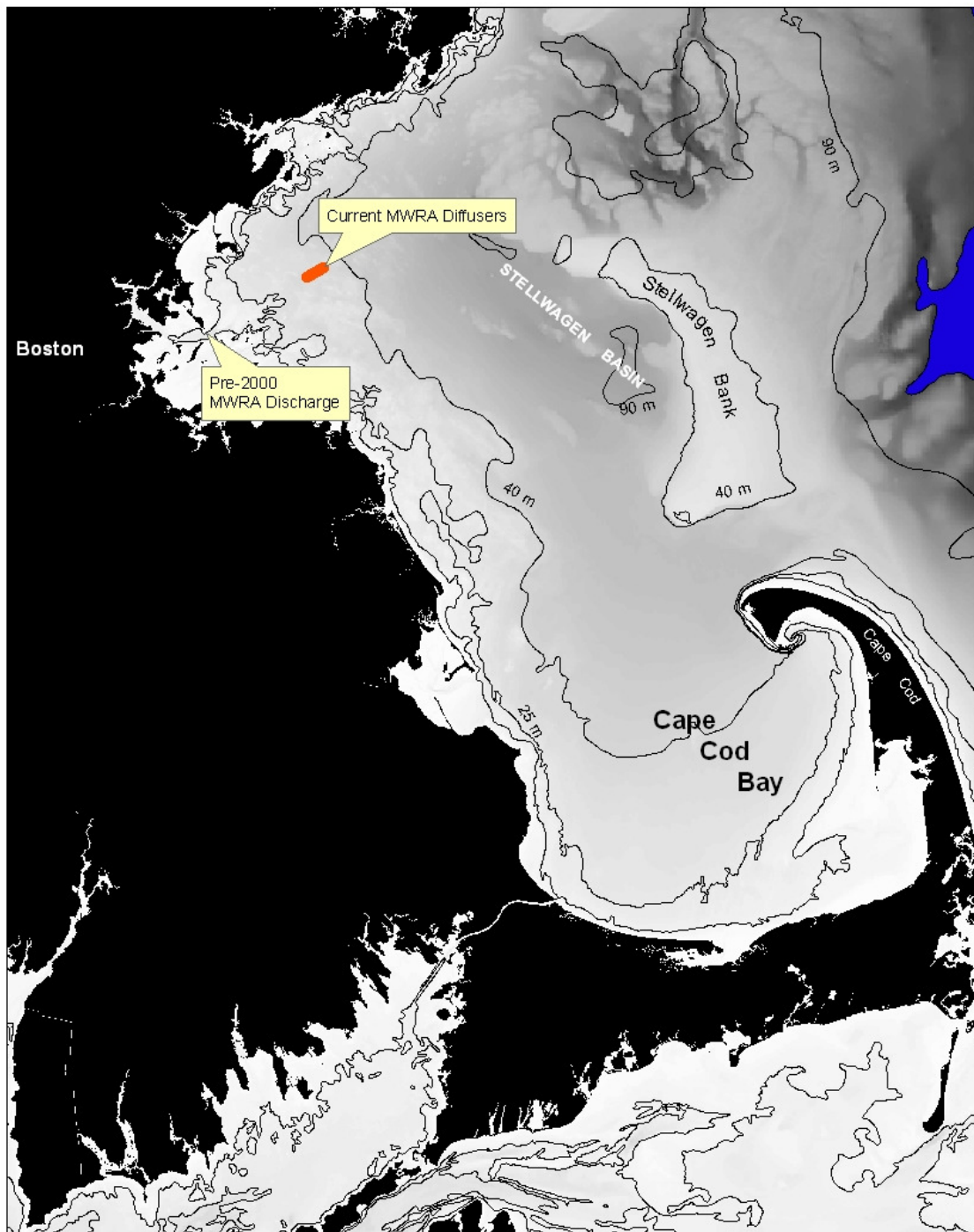


Figure 3.1. Massachusetts Bays Study Area with the locations of the Massachusetts Water Resources Authority (MWRA) outfall sites, before and after relocation into Massachusetts Bay. Bathymetry data layers from MA GIS.

and thus predominantly composed of fine-grained (silt/clay) sediments (Knebel and Circé, 1995; Knebel et al., 1996; Uchupi et al., 2005; Warner et al., 2008). Sedimentary environments in the Bays range from erosional or non-depositional with areas of exposed bedrock, coarse deposits of glacial and coastal plain rocks and sediments that include boulders and sandy gravels; areas of sediment reworking consisting of sediments with broad ranges in grain sizes; and depositional environments with high silt/clay fractions. Over half of Massachusetts Bay is considered non-depositional or erosional (Knebel and Circé, 1995), while the majority of Cape Cod Bay (54%) is considered depositional (Knebel et al., 1996).

The Bays are fairly productive, with reported estimates of primary production rates from satellite images ranging between $174 - 300 \text{ g C m}^{-2} \text{ y}^{-1}$ (Hyde et al., 2008). Taylor,(1999) estimated primary production in Massachusetts Bay over a two year period between $420\text{-}540 \text{ g C m}^{-2} \text{ y}^{-1}$ which are comparable to primary production estimates for nearby systems such as Georges Bank (O'Reilly et al., 1987) and Chesapeake Bay (Cerco and Noel, 2004). Spring and fall phytoplankton blooms are typical for Massachusetts Bay and account for 14 most of the Bay's productivity.

The exchange of water in these bays is controlled mostly by exchange with the GOM proper, generally entering across the northeast boundary of Massachusetts Bay. Because of the large throughput of GOM surface water, transport from the GOM can be significant to the Bays (Menzie-Cura, 1991, Gardner et al., 1986, Sowles, 1998, Bricker et al., 1999). A brief discussion on the circulation patterns in the GOM is therefore necessary to understand mechanisms that affect the distribution and fate of trace metals and other contaminants in the Massachusetts and Cape Cod Bays.

The general circulation of water in the GOM has a marked influence on the circulation and water quality of Massachusetts Bay. The GOM is a semi-enclosed water body adjoining mostly rural watersheds with the open waters of the North Atlantic. The GOM is delineated along the east and south by a series of banks and shoals (Fig. 3.2). Water enters into the GOM as cold, low salinity coastal waters from the Scotian Shelf (Smith, 1983) and through the Northeast Channel as warmer, more saline Slope Water (Ramp et al., 1985). Seasonal runoff from coastal watersheds mixes with these two water masses generally along a cyclonic pattern around the GOM. This pattern may occasionally slow down or reverse, most likely during the winter (Brown and Irish, 1992). Smaller-scale subtidal circulation patterns have been observed over the three major basins in the GOM (Brooks, 1985; Butman and Beardsley, 1991). These gyres are typically cyclonic, though the Wilkinson Gyre—a regional supply of GOM water to Massachusetts Bay—is generally weaker and frequently rotates in an anticyclonic pattern. Smaller scale patterns that result from the variability inherent in seasonal runoff and wind, have marked influence on the circulation along the western boundary of the GOM and are important to the physical oceanography of Massachusetts Bay.

Seasonal runoff contributes significant freshwater to the GOM neritic waters. Nearly one billion m³ of freshwater are added annually to the GOM from the Merrimack, Saco, Androscoggin, Kennebec, and Penobscot rivers (Geyer, 1992; Sowles, 2001). Annual spring runoff from the coastal watersheds of the GOM contributes to a western coastal current (WCC). The WCC is characterized by cold, nutrient-rich, low saline water (Townsend et al., 1987; Bisagni et al., 1995; Lynch et al. 1996; Pettigrew et al., 1998, Anderson et al., 2005; Ji et al., 2007).

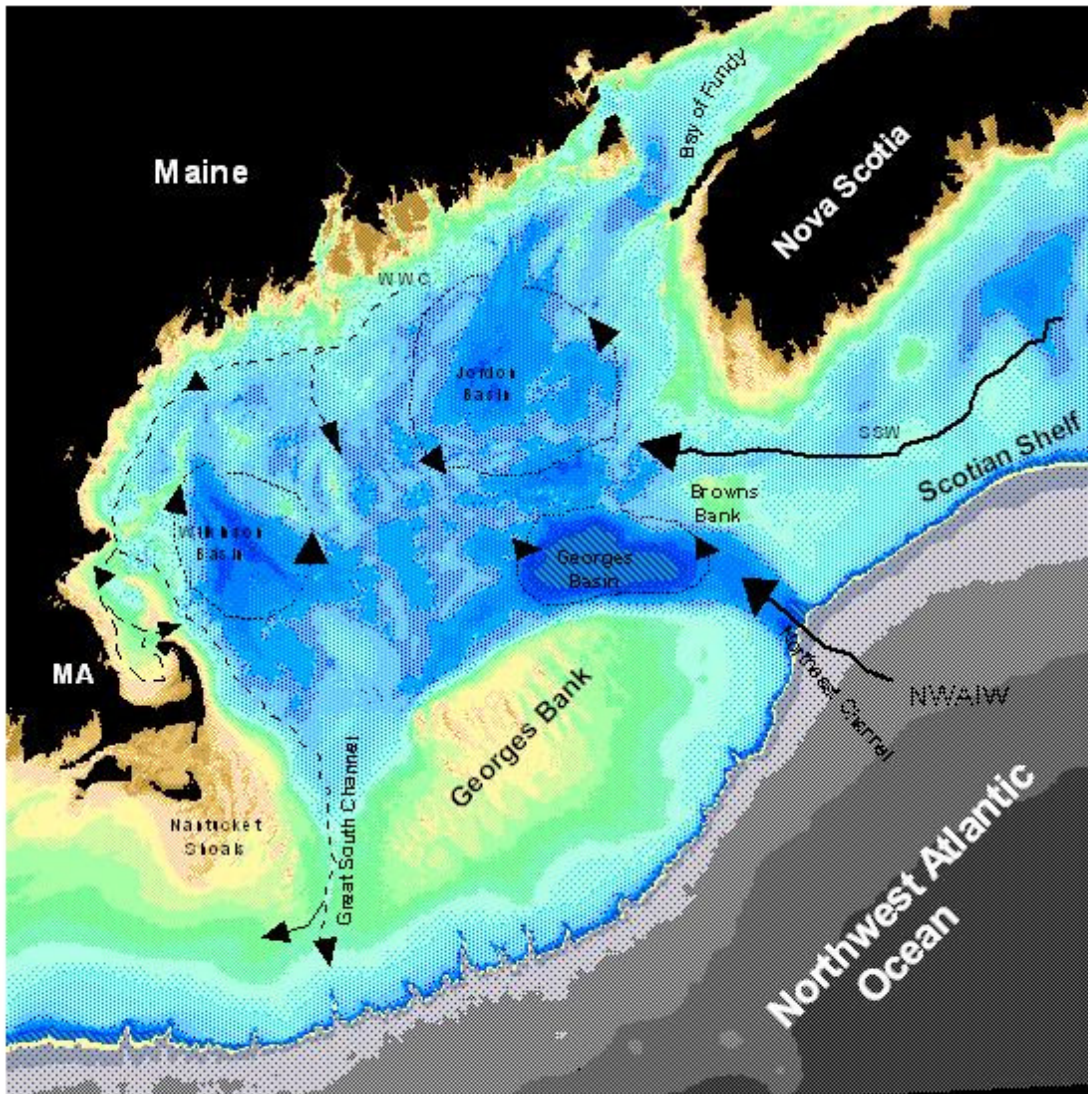


Figure 3.2. This schematic represents the generalized circulation patterns in the Gulf of Maine. During the summer, three gyres may develop over the larger-scale basins (Wilkinson, Jordan, and Georges). Water enters primarily as Scotian Shelf Water (SSW) and Northwestern Atlantic Intermediate water through the Northeast Channel. Most notably during the annual spring runoff, a western coastal current (WCC) is observed along the western fringe of the GOM, generating a predominantly north-south flux of riverine material that on occasion enters into the Massachusetts Bays.

Little is known about the fate and transport of river-borne contaminants or the role of the WCC on contaminant transport in the GOM. Anderson et al. (2005a and b) found that the WCC has a strong influence on the distribution and fate of a toxic dinoflagellate, *Alexandrium fundyense*. The southern most of the major U.S. rivers emptying in the GOM is the Merrimack which drains a large, highly industrialized watershed and feeds into the WCC at the northeastern corner of Massachusetts. Near Cape Ann, Massachusetts, the WCC periodically branches into two legs: one that enters into Massachusetts Bay on occasion and another that continues along the eastern boundary of Stellwagen Bank and out along the eastern edge of Cape Cod.

Massachusetts Bay and coastal GOM water columns undergo marked seasonal variation in stratification; from well-mixed conditions during winter and early spring to strong stratification during the summer (Libby et al., 2009). As a shallow semi-enclosed basin connected to the Gulf of Maine, the Massachusetts Bays system is affected by remote forces, either indirectly from climate effects on boundary conditions, or directly from GOM surface forces, like sea surface salinity and temperature (Jiang et al., 2007). Seasonality in phytoplankton populations can be linked, in part, to the annual changes in the degree of water column stratification and from the influence of GOM surface water into Massachusetts Bay (Jiang et al., 2007). With the exception of Cape Cod Bay, the Massachusetts Bays system is generally light limited under vertically well mixed conditions and thus the onset of the spring bloom is often coupled with the onset of stratification (Hyde et al., 2008). The general circulation in Massachusetts during much of the year moves relatively slowly, predominantly flowing counterclockwise (Geyer et al., 1992, Butman et al., 2002; Jiang and Zhou, 2003) and occasionally isolate the water of Cape Cod Bay (MWRA 2006). Recent numerical modeling

simulations show local currents respond strongly to wind forcing (Jiang et al., 2007; Tian et al., 2009) and include wind-induced upwelling and downwelling and storm events. Summer stratification diminishes the exchange of material between surface and deeper waters. This period is also marked by limited deep water exchange between the GOM and Massachusetts Bay (Jiang and Zhou, 2003).

Residence times for the waters of Massachusetts Bay have been estimated at 20-40 days for surface waters (Geyer et al., 1992). However, water residence times are sensitive to local wind forcing. Winds predominantly from the northwest are considered “normal” years for Massachusetts Bay. Some years the winds are predominantly from the southwest and favor upwelling conditions and reduced bay-wide circulation (Jiang and Zhou, 2008; Tian et al., 2009). The deep water residence time in Massachusetts Bay may be comparable to surface waters during periods when the water column is well-mixed (winter) and lengthen during the summer to several months. Freshwater input into Massachusetts Bay is relatively limited, with most originating from the rivers to the north. The major direct discharge of freshwater into the Massachusetts Bay system enters through Boston Harbor from the Charles River and from waste water discharges from Boston’s Massachusetts Water Authority (MWRA). Overall, the contribution of freshwater from Boston Harbor is small compared to the discharge of the rivers emptying into the GOM to the north (Geyer et al. 1992). However, discharges from the Charles and Neponset Rivers and the MWRA effluent have significant influence on water quality of western Massachusetts Bay (Wallace et al., 1987; Menzie-Cura, 1995). Transport process in the nearshore waters of western Massachusetts Bay, where exchange with Boston Harbor occurs, are sensitive to the influence of tidal mixing; wind strength, duration, and direction; and changes in the amount of fresh water inflow. Therefore, residence times of water in the western

portions of Massachusetts Bay are expected to be much shorter than the 20 to 45 days estimated for surface water of the entire Bay.

Massachusetts Bay is unique in the GOM region in that a severely anthropogenically impacted urban estuary empties into its western portion. Because of urban wastewater disposal in Boston Harbor during this period of study (1994-1996), water exchange between Massachusetts Bay and Boston Harbor provided the potential to evaluate wastewater dispersion in coastal systems, because the largest wastewater discharge in the Massachusetts Bays system was located at that time at the mouth of Boston Harbor. Hydrographic surveys in Massachusetts and Cape Cod Bays, as well as a near coastal survey in the southern GOM were conducted to evaluate levels of silver and other trace metals in Massachusetts coastal waters, trace wastewater dispersion, and provide additional information on the biogeochemical behavior silver and other metals in the coastal waters of the Massachusetts Bays system.

3.3 Methods and materials

3.3.1 Water sampling

Discrete water samples and hydrographic data were collected during six cruises from August 1994 through September 1996 to investigate the transport, distribution, and fate of silver and other selected metals in the Massachusetts Bays system. One of the six cruises detailed below (February, 1995) was aboard a “cruise of opportunity” during one of a series of physical oceanographic cruises to Cape Cod Bay aboard the 24 m *RV Argo Maine*. Dr. Bernie Gardner of the Environmental, Earth, and Ocean Sciences Program of the University of Massachusetts, Boston, kindly provided the physical data for part of this analysis. The remaining cruises were conducted aboard small boats, the University of Massachusetts at Boston’s *RV Neritic* (25’

Parker) and a 28 ft, fiberglass hull personal craft (The Healey). The locations and dates for each cruise are given in Table 3.1.

Table 3.1. Cruise Schedule.

Date	Cruise	Vessel
9 August 1994	Boston Harbor – Stellwagen Bank Transect	Neritic
23 February 1995	Cape Cod Bay Surface Water	Argo Maine
31 July 1995	Massachusetts and Cape Cod Bays, Surface Water	Neritic
7 September 1995	Merrimack Estuary, MA	Neritic
18 July 1996	Gulf of Maine Portland, ME Coastal Transect	Healey
11 September 1996	Massachusetts Bay Nearshore Survey, Surface Water	Neritic

Discrete water samples collected for the determinations of filterable ($<0.4\ \mu\text{m}$, polycarbonate filters, Poretics Corp.) and particulate concentrations of selected trace metals (Ag, Pb, Cu, Zn, Cd, and Fe) were obtained by peristaltic pump (American Sigma Streamline Autosampler, Series 700) through silicon tubing that had been acid-cleaned and rinsed with deionized water. A Teflon intake was attached to the Kevlar® conducting cable used to deploy a Sea-Bird Electronics, Inc. *911plus* CTD or *19Plus* SEACAT profiling system in a manner to ensure upstream sampling of the ship's drift while lowered to desired depths. Water samples were stored in trace metal-clean, sample-rinsed 2L polycarbonate bottles (Nalgene). Sub-samples (500 - 1000 ml) were vacuum-filtered ($<10\ \text{psi}$) through pre-cleaned $0.4\ \mu\text{m}$ polycarbonate filters in a laboratory clean room equipped with a filtered air supply and class-100 clean benches. Filtered samples were acidified with pre-screened ultra-pure HNO_3 (Optima, Seastar Chemicals, Inc.) to pH 2 and stored in 500 mL polyethylene bottles for later

analysis. Filters used in the filtration process were carefully folded and placed in pre-cleaned plastic vials, capped, and stored frozen for further processing. It is important to note that the designation of filterable metals data presented in the results below is operationally defined and estimates the amount of metals that passed through a 0.4 μm filter. Therefore, the “filtered” fraction includes both naturally occurring colloidal as well as “truly dissolved” metal species.

Sub-samples from the 2L discrete water samples were also processed for chlorophyll *a*, particulate organic carbon and nitrogen (POC, PON) and total suspended matter (TSM). Particulates containing chlorophyll were collected on glass fiber filters (Whatman® GF/F, 0.7 μm nominal pore size) via vacuum filtration (<10 psi) following a modified procedure in Parsons (1984). Chlorophyll filter samples were carefully folded in half, wrapped in aluminum foil and frozen for later analyses. Similarly, POC and PON samples were obtained by filtration but using pre-combusted (24 hr @ 450°C) GF/F filters and stored in polystyrene Petri dishes (BD Falcon™) for later analyses. Total suspended matter concentrations (TSM) were determined by filtering sub-samples through tared 0.4 μm polycarbonate filters (Poretics Corp.) and briefly rinsed with 0.2 μm -filtered deionized water to remove any salts that may have been trapped within the filter following filtration.

3.3.2 Physical data

Depth, temperature, salinity, and chlorophyll *a* fluorescence water column profiles were determined using the aforementioned CTD systems. Near-continuous profiles of these parameters were derived from a 24 Hz (4 Hz for the SEACAT) sampling frequency of the CTD and uploaded to a laptop computer. When CTD fluorescence data are presented, the data was obtained from a Seapoint chlorophyll fluorometer mounted to the 911*plus* CTD. The CTD-

mounted fluorometer measures *in situ* the excitation and emission wavelengths at 470 nm and 685 nm (30 nm FWHM), respectively. The reported minimum detectable level for the *in situ* fluorometer is 0.02 µg/l. In limited instances of the ensuing analyses the *in situ* fluorometric values are meant to highlight relative rather than quantitative differences, as calibration with corresponding water column samples was not performed.

Physical data (temperature, salinity, density, and fluorescence) were processed using SEASOFT© software (SBEDDataProcessing-Win32) available from Sea Bird Electronics, Inc (<ftp://ftp.halcyon.com/pub/seabird/OUT/SeasoftWaves-Win32/>). The CTD station data were processed into 1 m bins and then used to generate surface and vertical cross-section contour plots using Surfer® (Golden Software, CO). Contour maps were generated from grids constructed for the study area from station observations during each cruise. Data points from the CTD and water column data were used to interpolate grid node values using the point kriging function, a linear least squares estimation in Surfer®. Open boundary blanking for contour maps were constructed freehand and delineated from the furthest offshore station by approximately ½ the largest distance between neighboring stations from each survey. A comparison of surface salinity contour plots using CTD data and data derived from discrete surface water samples gave similar results (see Appendix A.1).

3.3.3 Trace metal sample processing and analytical techniques

Filterable metal concentrations were derived using a liquid/liquid extraction technique similar to those described by Kinrade and Van Loon, (1974); Danielson et al., (1978); Bruland et al. (1979); and Wallace et al., (1983) in which dithiocarbamates of heavy metals are formed in natural water samples and extracted into Freon or chloroform. The ammonium 1-pyrrolidine dithiocarbamate/diethylammonium diethyldithiocarbamate extraction technique has been

modified such that quantitative extraction of silver is included with the extraction of Zn, Cu, Cd, Fe, and Pb (Chapter 5). Particulate trace metal samples were prepared for spectrometric analysis by oxygen plasma digestion of the polycarbonate filters using the low temperature ashing (LTA) techniques described by Wallace et al. (1983). Filtered and particulate silver, zinc, cadmium, copper, iron and lead were analyzed using a Perkin-Elmer Zeeman/5000 spectrometer equipped with a HGA 400 graphite atomizer. All metals were analyzed using pyrocoated graphite tubes fitted with L'vov platforms and using appropriate matrix modifiers. Absorbance observations were measured in the peak area mode with Zeeman background correction. Metal concentration results from field surveys are reported as moles per kilogram of seawater (Mol kg^{-1}). When precision for field observations is reported, the relative standard deviation is used, unless noted. The relative standard deviation (RSD) is the standard deviation of the mean (SD) divided by the sample mean (\bar{x}) and its percentage is represented as:

$$\%RSD = 100 \frac{SD}{\bar{x}} \quad (1)$$

For filterable and particulate trace metal analysis, Chl *a*, TSM, POC and PON, the method detection limits (MDLs) in most cases were determined as 3 x the SD of procedural blanks for each of the six cruises. Trace metal MDLs and exceptions to the method used in their estimation for each sampling event are listed and noted, respectively, in Table 3.2. Actual blank values for each parameter are reported in the Appendix C. Potential matrix effects were investigated by the method of standard additions to natural samples and analyzed for significant differences from standards prepared in 10% HNO_3 . For the metals reported, no significant difference was observed in standard factors obtained from standard additions or by standard

comparative methods. The extractions of Ag, Pb, Cd, Zn, Cu and Fe from spiked seawater samples show recoveries close to 100% (Table 3.3).

Table 3.2. Method limit of detection for trace metal analysis.

A. Filterable ($>0.4\ \mu\text{m}$) Metals (ng)

Cruise	Ag	Pb	Cu	Zn	Cd	Fe
94 Aug.	0.08	0.6	1.6	1.6	0.27	17
95 Feb.	0.15	0.7	1.6	4.9	0.15	190
95 Jul.	0.04	1.0	3.2	1.6 [†]	0.11	14 [†]
95 Sept.	0.06	0.7	1.6	3.3	0.28	11
96 Jul.	0.01	0.4	9.5	1.6	0.10	7.0 [‡]
96 Sept.	0.02	1.1	7.9	4.9	0.30	18

[†]Determined from replicate analysis (n=4) of previously extracted seawater that was spiked with 5 ng Zn and 150 ng Fe.

[‡]Determined from replicate analysis (n=4) of reagent blanks.

B. Particulate ($\geq 0.4\ \mu\text{m}$) Metals (ng)

Cruise	Ag	Pb	Cu	Zn	Cd	Fe	Al
94 Aug.	0.03	0.14 [†]	0.79 [†]	3.3	NA	NA	67
95 Feb. [†]	0.04	0.80	NA	1.6	NA	1061	155
95 Jul.	0.04	0.26	1.7	9.8	0.25	56	54
95 Sept.	0.03	0.13	1.4	1.6	0.28	140	6.7 [†]
96 Jul.	0.02	0.17	0.64	NA	0.08	14	27
96 Sept.	0.01	0.13	0.48	1.6	0.17	56	13

[†]estimated from 3X range observed between two field blanks. NA- not assessed. Blanks not determined during analytical run.

Table 3.3. Percent recovery of added metals from seawater samples collected from Boston Harbor, Massachusetts, USA.

Sample	Ag	Pb	Cd	Zn	Cu	Fe
BH7	102.6	99.2	99.9	103.5	92.3	96.6
BH15	102.4	102.7	100.0	102.8	96.2	112.7
BH22	100.1	97.8	99.3	98.6	96.5	96.7
Mean:	101.7	99.9	99.7	101.6	95.0	102.0
SD:	1.4	2.5	0.4	2.7	2.3	9.3

Samples collected 11 June 1996. BH7, BH15 and BH22 from 42° 21'N 71° 1'W, 42° 18'N 71° 2'W and 42° 17'N 70° 56'W, respectively. Salinities ranged from 27.9 to 29.9 psu. SD: = standard error of mean.

Analysis of certified reference materials (CRM) for metals in seawater and estuarine water (NASS3 and CASS3, respectively; from the National Research Council of Canada) were conducted as a measure of accuracy of filterable trace metal concentrations determined during these coastal surveys. No certified reference material exists for metals bound to suspended material (particulates). Concentrations in 86% of seawater CRMs analyzed for Cd, Zn, Cu, and Fe fell within 2 SD of the certified values (Table 3.4). Except for one occasion (one of two CRM extractions accompanying the analysis of the Sept. 1996 samples), the analyses for Pb in CRM seawater was generally low and just outside the lower confidence intervals for both NASS4 and CASS3. Both seawater CRMs have relatively large uncertainties for certified Pb concentrations (~20% RSD) and thus Pb-“recoveries” at the lower confidence intervals are consistently near 90%. There has been some suggestion that organic ligands present in these seawater CRMs can effectively compete with metal chelating complexation during solvent-liquid extraction (Ndung'u et al., 2003). Recoveries in metal extraction techniques that use solvent-extraction preconcentration methods may be improved when water samples are pre-treated with ultraviolet (UV) irradiation and potentially competing organic matter is broken

down. Ndung'u et al. (2006) report that UV radiation may be necessary for adequate extraction and preconcentration of Ag from natural waters using chelating resin column partition (CRCP)-ICP-MS.

No certified reference material exists for Ag in natural waters. However, the analyses of Ag in the National Research Council of Canada CRMs conducted with the analyses of Massachusetts coastal waters are in good agreement with those values reported in the peer-reviewed literature (Table 3.5).

Table 3.4. Observed concentration of metals in certified reference material: Reference Seawater and Estuarine Water (NASS4, CASS3) from the National Resource Council of Canada

NASS4	Ag (pM)	Pb (pM)	Cu (nM)	Zn (nM)	Cd (pM)	Fe (nM)
Jul-96 Survey	6.1 5.3	38 33	3.69 3.39	2.48 2.54	162 154	0.03 1.93
Certified Value: (+/- 2 SD)	NA	63 (24)	3.59 (0.17)	1.76 (0.28)	142 (27)	1.88 (0.3)
Mean Recovery %	NA	56.3	98.6	143	111	103
CASS3						
Feb-95 Survey	58.3 61.4	31 36	8.1 8.2	18.9 19.5	186 197	129.3 21.1
Sep-96 Survey	63.7 58.2	52 27	7.1 10.4	22.2 77.9	271 260	20 40.7
Certified Value: (+/- 2 SD)	NA	58 (19)	8.1 (1.0)	19.0 (3.8)	267 (44)	22.6 (3.0)
Mean Recovery %	NA	62.9	96.3	106	85.6	90.9

Bold numbers indicate suspected contamination/incomplete extraction; treated as outliers based on 3 x the standard error of the remaining subset.

Table 3.5. Silver in Certified Reference Material from the National Research Council of Canada.

CASS2		Ag	SD	Anal. Method
	Barriada et al. (2007)	62.2	2.4	APDC/ICPMS
CASS3		Ag		
	This Work	60.4	2.7	APDC/GFAAS
CASS4				
	Ndung'u et al. (2001)	56.6	8.3	APDC/ICPMS
	Yang and Sturgeon (2002)	50.2	0.7	AER/ICPMS
	Ranville and Flegal (2005)	101	2.6	UV-digest/AER/ICPMS
	Ndung'u et al. (2006)	78.6	18.2	UV-digest/AER/ICPMS
	Flegal (2008, pers.com.)	60.6	8.4	APDC/GFAAS
	Flegal (2008, pers.com.)	64.6	7.6	UV-digest/AER/ICPMS
NASS2		Ag	AgSD	
	River-Duarte e al. (1999)	6.3	1.5	APDC/GFAAS
NASS4		Ag	AgSD	
	River-Duarte e al. (1999)	12	1.5	APDC/GFAAS
	This Work	7.3	1.8	APDC/GFAAS

APDC Dithiocarbamate solvent extraction,
ICPMS Inductively Coupled Plasma Mass Spectrometry
AER Anion Exchange Resin
UV-digest UV digestion prior to pre-concentration and analysis

3.3.4 Ancillary analysis

Chlorophyll *a* and phaeophytin concentrations were measured following standard analytical procedures for seawater analysis as detailed by Parsons et al. (1984). Salinity was measured with an inductive salinometer (Seabird CTD) calibrated with a standard reference solution of KCl and reported in practical salinity units (psu). Total suspended matter concentrations were determined using an ultrabalance (Perkin-Elmer AD-2Z). Potential minor artifacts due to changes in humidity from when filters were tared and processed were controlled for by randomly selecting unused tared filters, reweighing them during analysis, and treating these as blanks for TSM analyses. Particulate organic carbon (POC) and nitrogen (PON) were

analyzed using a Perkin-Elmer 2400 elemental analyzer with modifications to the procedures detailed in Hedges and Stern (1984). Table 3.6 gives the limits of detection (3 x standard deviation of procedural blanks) for POC, PON, TSM, and chlorophyll.

Table 3.6. Limits of detection for particulate organic carbon and nitrogen ($\geq 0.7 \mu\text{m}$), total suspended matter ($\geq 0.4 \mu\text{m}$), and chlorophyll based on 3 x standard deviation of field blank determinations.

Cruise	POC (ug C)	PON (ug N)	TSM (mg)	Chl <i>a</i> (ug)
9 Aug. 1994 Boston Transect	3.1	3.6	0.06	NS
23 Feb. 1995 MB	2.6	0.8	0.01 [†]	NS
31 Jul. 1995 MB	5.3	1.1	0.05 [†]	0.03 [‡]
7 Sept. 1995 Merrimack Est.	4.1	1.7	0.03	NS
18 Jul. 1996 GOM Transect	9.1	0.6	0.01	0.03 [‡]
11 Sept. 1996 Nearshore MB	2.2	0.8	0.05	0.04

[†]n=2, LOD determined as 3* the absolute difference between two measurements. NS – not samples collected.

[‡]Estimated detection limit reported as 3 x the instrument fluorescence of field blanks that had been extracted according to the method of Strickland and Parsons (1972).

MB – Massachusetts Bay

GOM – Gulf of Maine

3.4 Results

3.4.1. Boston Harbor to Stellwagen Bank transect, August 1994

A preliminary survey was conducted on 9 August 1994 along a west-to-east transect from Boston Harbor to beyond the northern tip of Stellwagen Bank (Fig. 3.3). CTD data reveal typical summer stratification of Massachusetts Bay with a well-stratified, two layer system comprised of a warm surface layer of about 10 m (Fig. 3.4, a-d) overlaying a cold, well-mixed deep layer. The freshest water was observed in Boston Harbor (Stations SI, PU, and DI). Fig. 3.4b shows lower saline surface water further offshore near Stations BO5 and GM1A. Doming of the pycnocline appears near the boundary between Boston Harbor and Massachusetts Bay (Fig. 3.4c) and may reflect localized upwelling (Jiang and Zhou, 2003).

Relative fluorescence values for chlorophyll *a* (Chl *a*) distributions, obtained from the CTD-mounted fluorometer, are shown in Fig. 3.4d. (No discrete samples were collected for chlorophyll analyses and thus Chl *a* is reported as “relative fluorescence units” RFU for this cruise). The highest Chl *a* fluorescence observed (>5 RFU) was confined to an area within Boston Harbor near the MWRA outfall plume. A subsurface fluorescence maximum was observed just below the pycnocline at all stations beyond BO1 (10 km offshore). The amount of suspended matter decreased markedly with increasing salinity from around 5 - 8 mg L⁻¹ in Boston Harbor to near 2 mg L⁻¹ in the surface waters of Massachusetts Bay (Fig. 3.5).

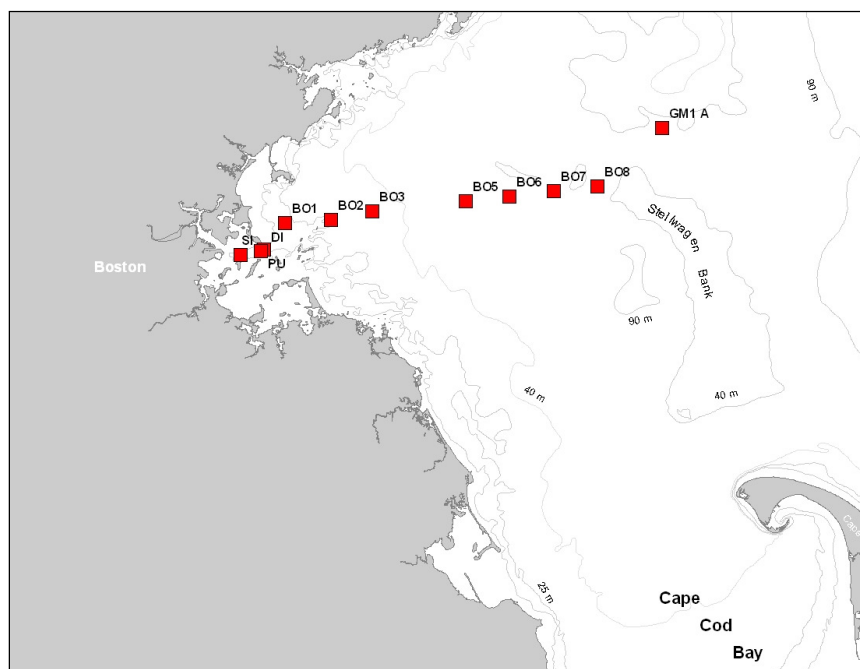


Figure 3.3. Station locations during the Boston to Stellwagen Bank transect, 09 August 1994.

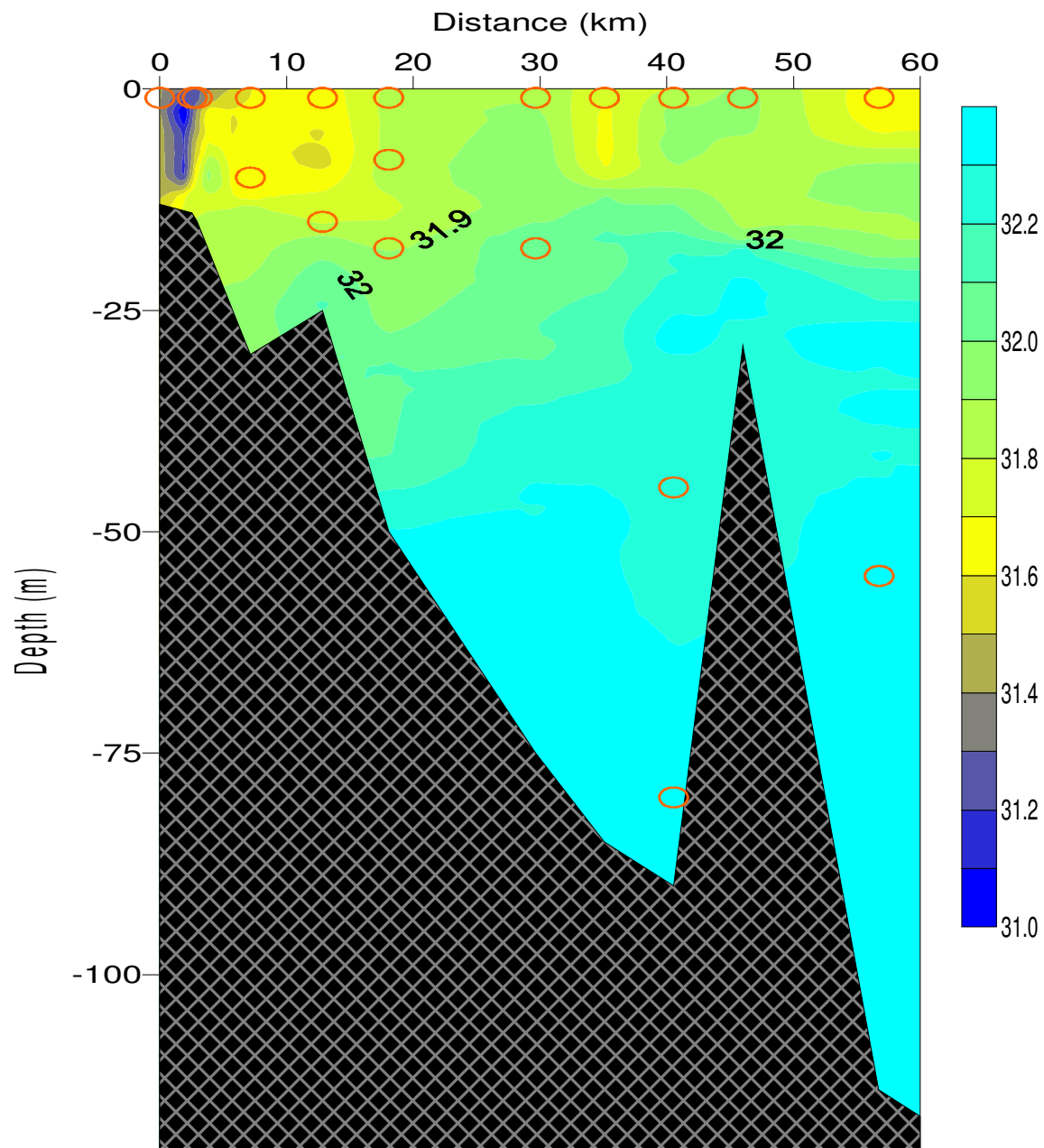


Figure 3.4a. Salinity (PSU) contour plot constructed from CTD data collected during August 1994 Boston Transect. Circles indicate location and depth where discrete water samples were obtained.

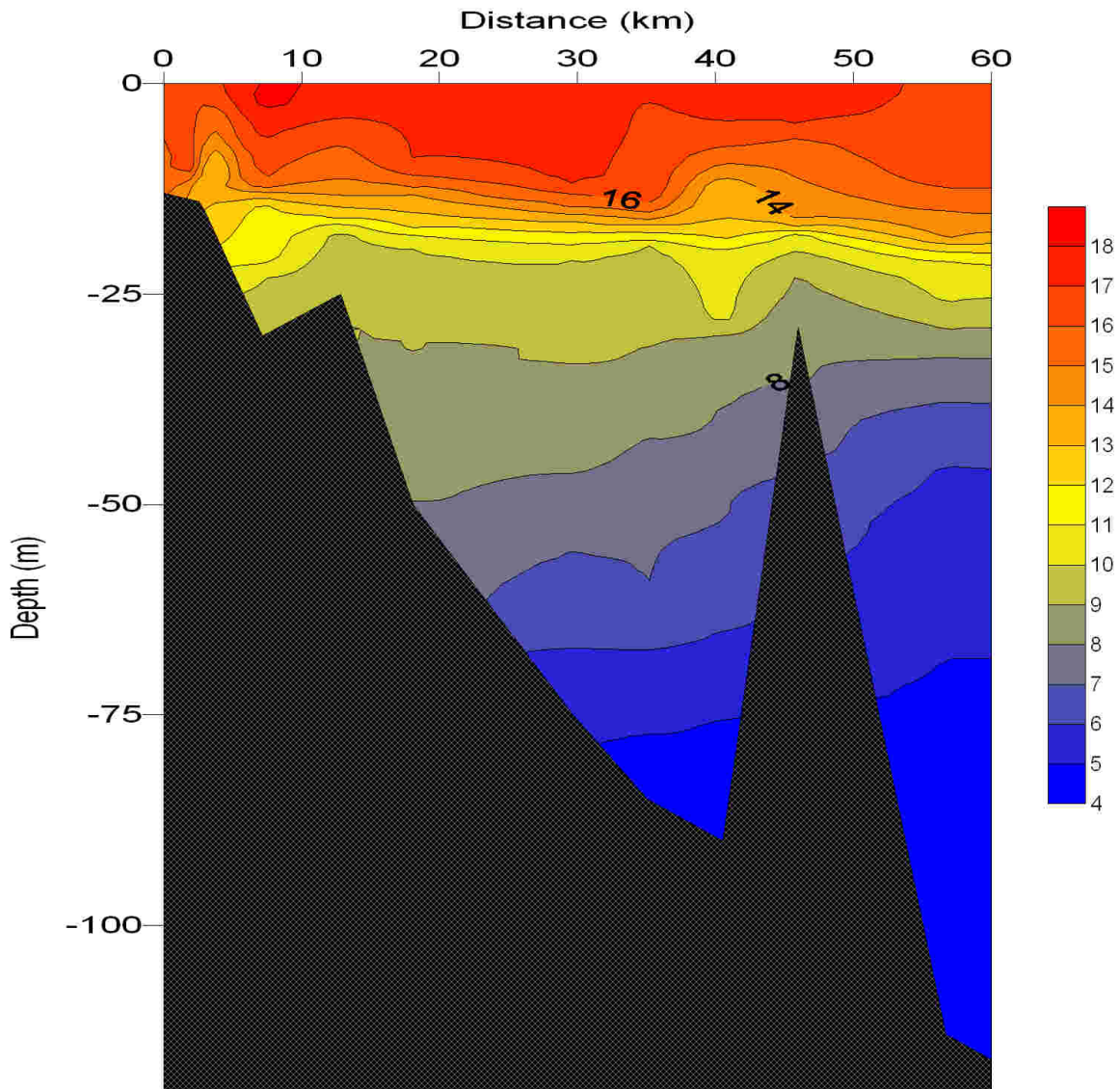


Figure 3.4b. Temperature ($^{\circ}\text{C}$) contour plot constructed from CTD data collected during August 1994 Boston Transect.

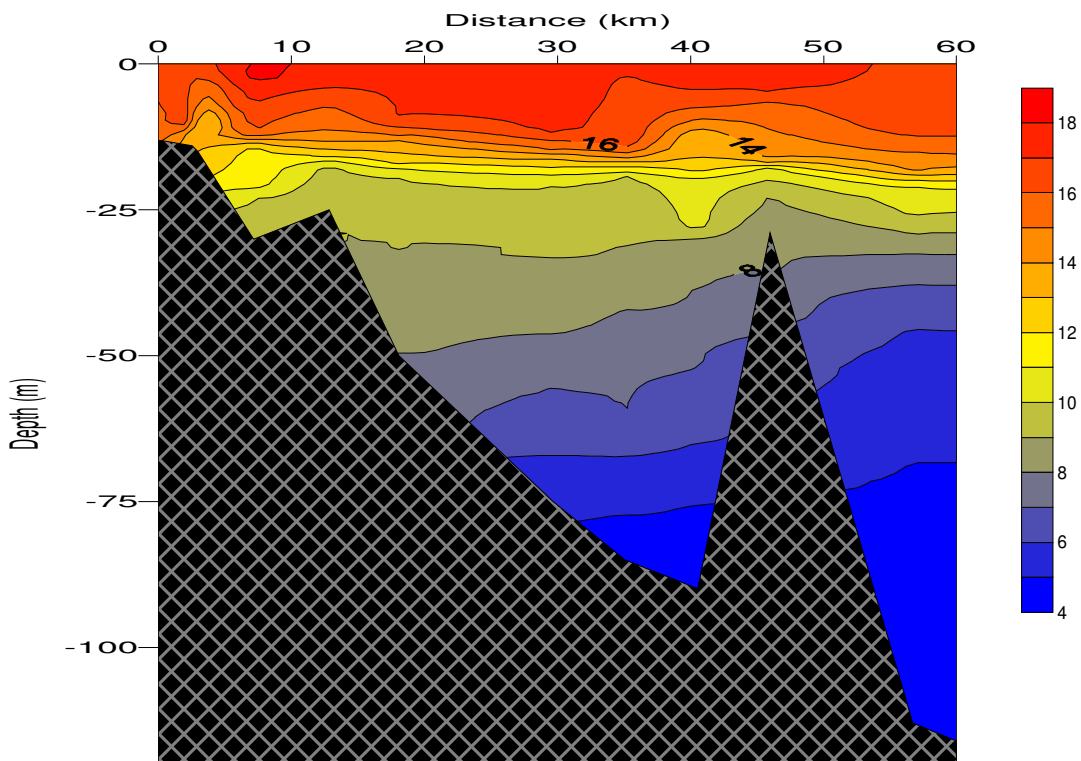


Figure 3.4c. Contour plot of water column density (σ_θ) from CTD data collected during August 1994 Boston Transect.

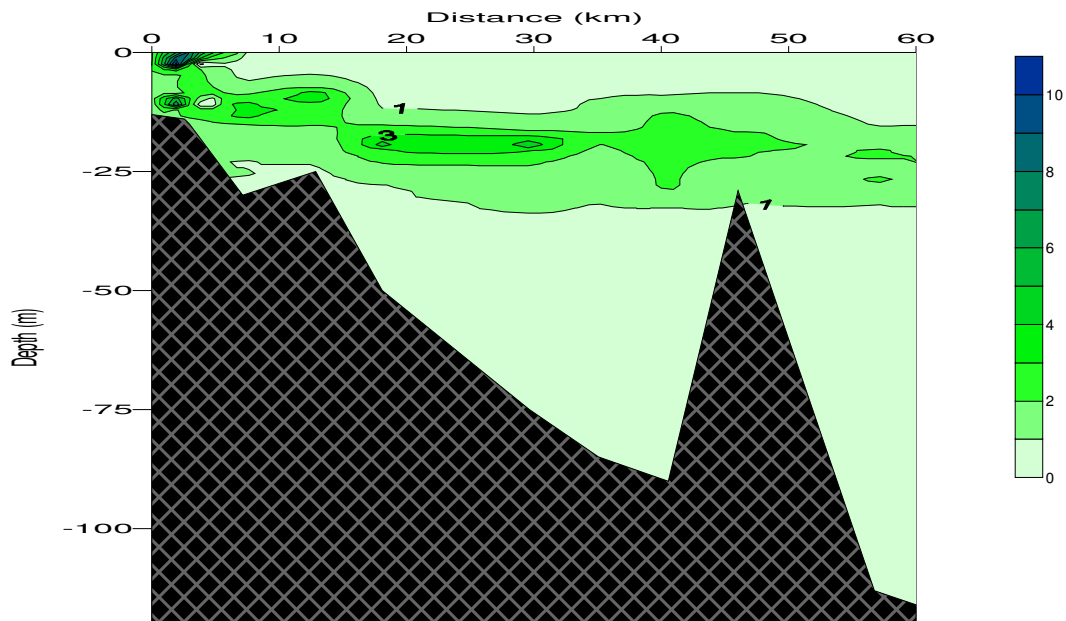


Figure 3.4d. Distribution of chlorophyll *a* fluorescence (as relative fluorescence) from CTD data collected during August 1994 Boston Transect. Scale is in relative fluorescence units (RFU).

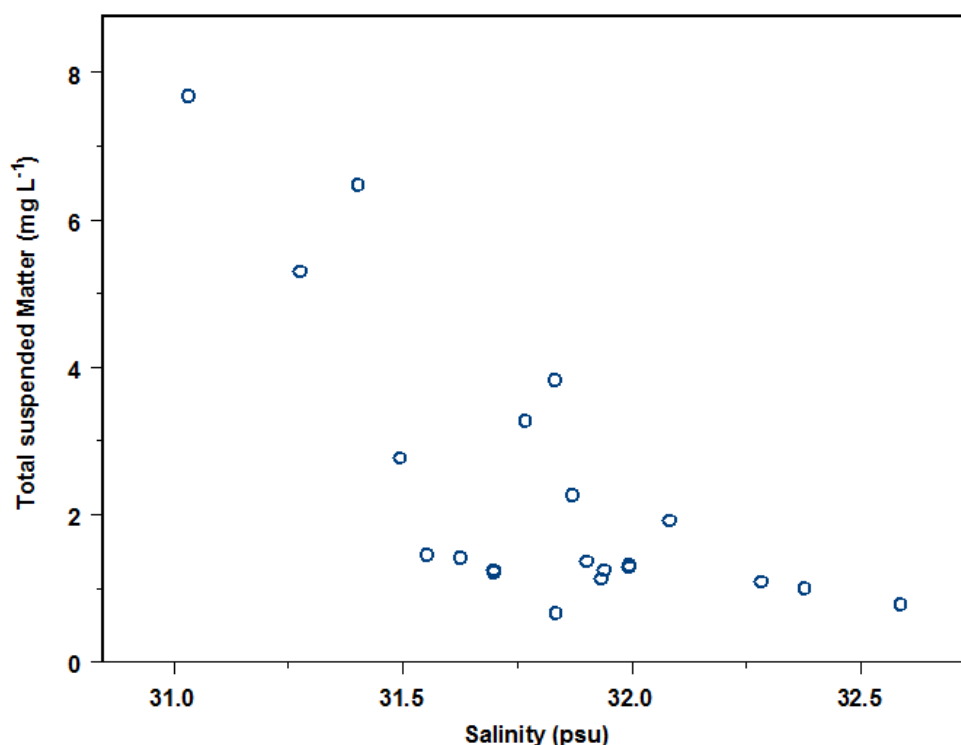


Figure 3.5. The distribution of total suspended matter (TSM) along the salinity gradient observed in Massachusetts Bay during 09 August 1994. Suspended matter is operationally defined by 0.4 μm -filtration.

The water concentrations of Ag, Pb, Cu, Zn, Cd, Fe, particulate Al, and ancillary station data are reported in Table 3.7, a-c. The distributions of filterable and particulate Ag concentrations (Ag_F and Ag_P , respectively) along the observed salinity gradient are illustrated in Fig. 3.6. Concentrations of Ag_F and Ag_P ranged from a maximum of 210 and 484 pmol kg^{-1} , respectively, in Boston Harbor, to a minimum of 12.7 and 2.4 pmol kg^{-1} , respectively, in the surface waters in the eastern portions of Massachusetts Bay. Both Ag_F and Ag_P decrease linearly by two orders of magnitude with respect to salinity in the surface waters within the first 10 km offshore. In lower salinity waters, both silver fractions appear to mix conservatively; changes in Ag concentrations appear to be linearly related to the conservative properties (e.g.,

Table 3.7a. Boston Harbor and Massachusetts Bay filtered (<0.4 μm) trace metal concentrations, August 1994.

Station	Depth (m)	Ag (pmol kg^{-1})	Pb (pmol kg^{-1})	Cu (nmol kg^{-1})	Zn (pmol kg^{-1})	Cd (pmol kg^{-1})	Fe (nmol kg^{-1})
GM1 A	1	18.0	43	3.7	1.8	276	4.3
	55	33.5	23	1.8	1.5	189	< 1.2
BO8	1	16.4	33	3.1	1.0	241	2.7
BO7	1	12.7	46	5.0	2.5	242	4.7
	45	4.0	92	1.9	1.2	187	3.8
	80	3.4	19	2.6	2.3	225	3.7
BO6	1	14.2	44	4.6	1.9	269	12.5
BO5	1	8.0	57	5.1	2.9	304	8.59
	18	< 3.1	< 11	1.8	0.9	137	4.3
BO3	1	28.3	72	6.2	4.3	305	23.8
	8	10.8	32	3.3	3.2	119	2.8
	18	10.6	24	3.8	2.9	183	5.6
BO2	1	28.1	35	6.1	3.9	269	8.8
	15	9.7	14	2.6	3.3	109	2.1
BO1	1	88.3	130	10.8	13.9	761	21.6
	10	19.2	28	4.1	4.3	178	8.2
DI	1	147	146	16.8	18.4	413	47.7
PU	1	211	224	21.7	35.3	404	114.6
SI	1	75.2	80	7.6	13.3	201	29.6

Table 3.7b. Boston Harbor and Massachusetts Bay particulate ($\geq 0.4 \mu\text{m}$) trace metal concentrations, August 1994.

Station	Depth (m)	Ag (pmol kg^{-1})	Pb (pmol kg^{-1})	Cu (nmol kg^{-1})	Zn (pmol kg^{-1})	Fe (pmol kg^{-1})	Al (nmol kg^{-1})
GM1 A	1	2.9	14	0.13	0.6	15	46
	55	5.4	42	0.13	0.6	146	613
BO8	1	2.9	16	0.14	0.4	12	35
BO7	1	4.1	17	0.23	0.4	31	72
	45	4.9	68	0.28	0.8	245	818
	80	4.6	112	1.22	1.5	262	993
BO6	1	4.9	32	0.31	0.7	44	41
BO5	1	2.4	12	0.31	0.4	14	22
	18	5.8	12	0.14	0.6	2	51
BO3	1	7.1	42	0.60	0.7	40	79
	8	18.0	77	0.56	1.3	89	145
	18	14.3	94	0.61	1.4	96	201
BO2	1	11.0	51	0.22	0.9	41	78
Rep.	1	11.1	52	0.32	1.5	71	131
	15	17.5	85	0.72	1.7	84	185
BO1	1	46.4	150	1.01	6.1	599	1670
	10	25.7	66	0.71	3.4	375	947
DI	1	252	53	5.62	14.1	1879	4892
PU	1	484	292	11.5	28.2	2586	6426
SI	1	117	113	2.24	5.6	660	1539

Table 3.7c. Boston Harbor and Massachusetts Bay ancillary measurements, August 1994.

Station	Lat. N	Lon. W	Depth (m)	Sal (PSU)	TSM (mg/L)	POC (μ M)	PON (μ M)
GM1 A	42° 28.30170°	20.9051	1	31.940	1.25	10.4	1.2
			1			17.5	7.3
			55	32.585	0.79	20.2	5.9
BO8	42° 24.48070°	26.8201	1	31.933	1.13	15.4	4.5
BO7	42° 24.20170°	30.7781	1	31.833	0.67	14.9	6.5
			45	32.282	1.09	5.5	4.3
			80	32.376	1.00	9.1	6.0
BO6	42° 23.88070°	34.7401	1	31.698	1.22	11.9	3.8
Rep.			1		1.25	11.6	2.4
BO5	42° 23.56770°	38.6811	1	31.901	1.37	6.6	3.0
			18	32.081	1.92	13.3	5.3
BO3	42° 22.95270°	47.0981	1	31.831	3.83	11.8	3.8
			8	31.624	1.42	15.0	3.1
			18	31.551	1.45	12.9	3.7
BO2	42° 22.43870°	50.8541	1	31.992	1.29	12.7	5.0
Rep			1		1.32		
BO1	42° 22.22570°	54.9961	15	31.870	2.27	13.0	4.0
			1	31.493	2.77	23.2	5.3
			10	31.766	3.27	17.9	7.0
DI	42° 20.46570°	56.8991	1	31.275	5.30	42.3	9.0
PU	42° 20.38970°	57.1661	1	31.031	7.69	14.9	3.7
SI	42° 20.09170°	58.9901	1	31.401	6.48	21.1	7.2

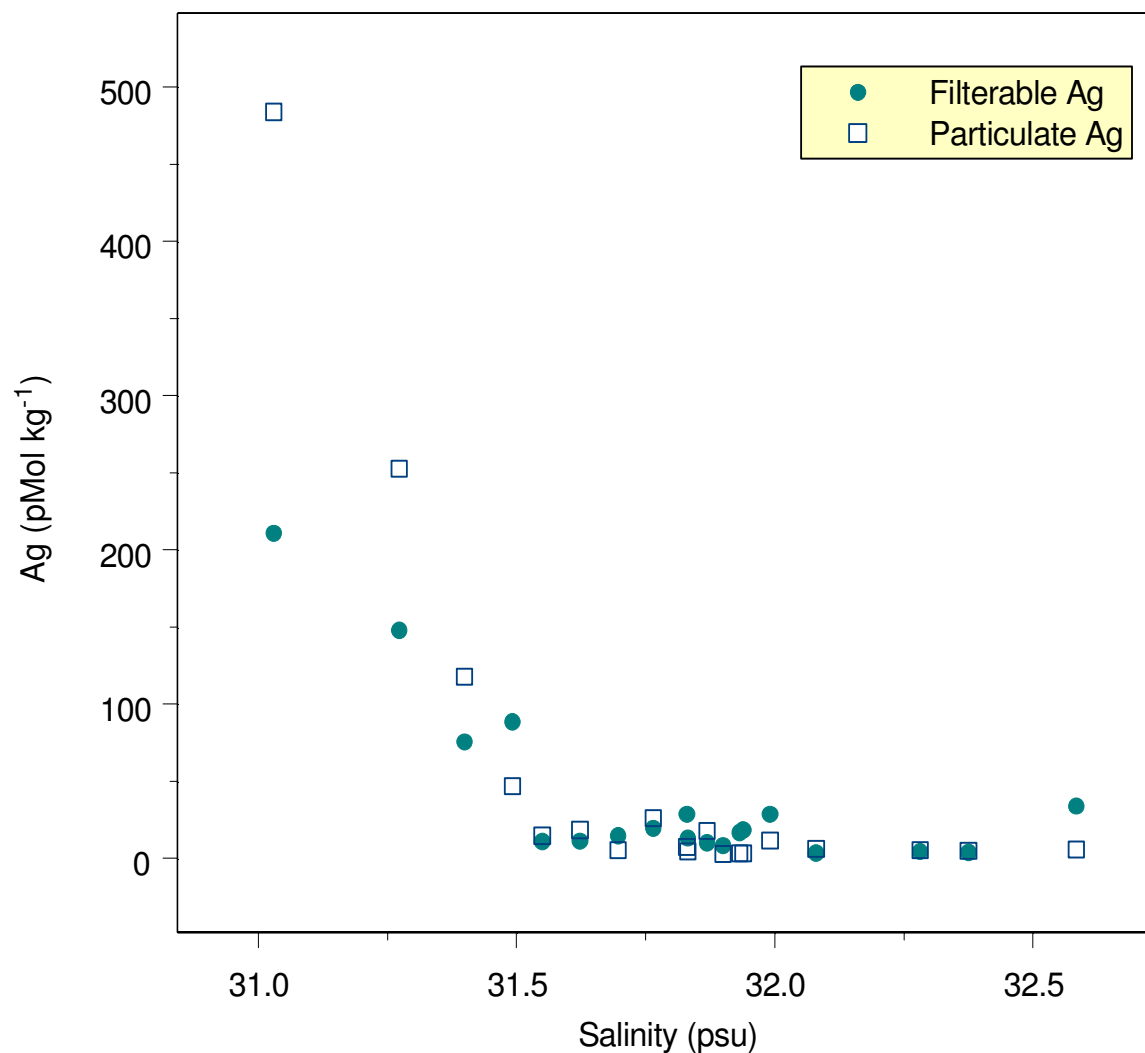


Figure 3.6. The distribution of Ag along the salinity gradient observed in Massachusetts Bay during 09 August 1994. Particulate and filterable fractions are operationally defined by 0.4 μm -filtration.

salinity) of the water sample. Thus, mixing in salinity waters below 31.6 psu may reflect simple mixing of silver-labeled Boston Harbor water with Massachusetts Bay. Ag_P shows a steeper mixing curve with salinity compared to Ag_F .

Most of the Ag_F and Ag_P concentrations were substantially higher than concentrations reported for coastal waters of similar salinities (Sañudo-Wilhelmy et al., 1996). A significant portion of Ag in the surface waters samples of Massachusetts Bay samples existed in the filtered fractions ($76 \pm 6\%$, $n=8$). In contrast, only $35 \pm 5\%$ of the total silver in surface water samples collected in Boston Harbor ($n=3$) was in the dissolved or colloidal fraction. The transition to predominately Ag_F in Massachusetts Bay surface waters is most likely a non-linear processes and include contributions from particle loss through settling and transport, quasi-equilibrium and stabilization of silver by natural ligands, and increasing relative end-member strengths for Ag_F and Ag_P of higher salinity surface water from the GOM. The Ag -salinity data suggest that there may be, at a minimum two groups of relationships among the data as indicated by the sharp change in the observations of silver with salinity. Regression tree models (SPlus 7, see Appendix A.2) were used to explore where the demarcation exists with respect to salinity. The partition of the data into two parts is accomplished such that the sum of the squared deviations from the mean is minimized the in the separate parts. For the August 1994 Boston Transect cruise, the regression tree analyses identify that salinity to be 31.59 psu. This value will be used to later evaluate distinctions between Boston Harbor water as it mixes with Massachusetts Bay.

3.4.2 Boston Harbor exchange and Cape Cod Bay, February 1995

Winter sampling of Massachusetts Bay waters near the mouth of Boston Harbor, as well as a NW transect in Cape Cod Bay (CCB), was conducted in conjunction with a physical oceanographic survey on 23 February, 1995 (Fig. 3.7). The surface salinity distribution derived from hydrographic stations reveals the lowest salinity water in the Bays occurred near

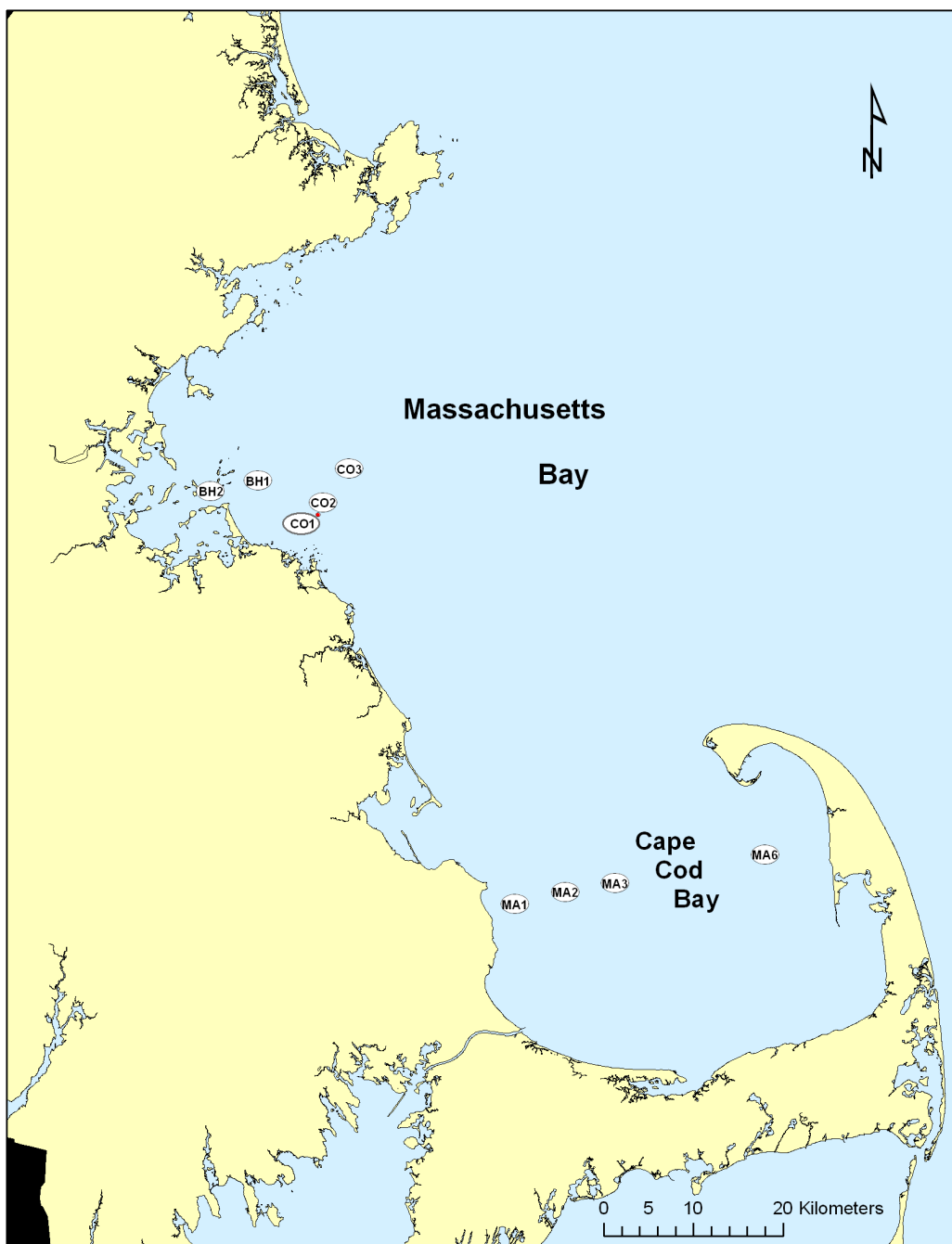


Figure 3.7. Sampling stations during winter, February 1995.

Boston Harbor and was confined along a narrow portion of the west and south perimeter of CCB (Fig. 3.8). Strong vertical salinity fronts were apparent in the salinity and temperature data obtained from Cape Cod Bay indicating typical strong vertical mixing during winter (Fig. 3.9). Salinity and temperature were fairly uniform among stations, varying by < 1 psu and $^{\circ}\text{C}$, respectively.

Discrete surface water samples for trace metal analysis were collected from a subset of the hydrographic stations (Fig. 3.7). The data for filtered and particulate concentrations of Ag, Pb, Cu, Zn, Cd, Fe, particulate Al, and ancillary measurements are given in Table 3.8.

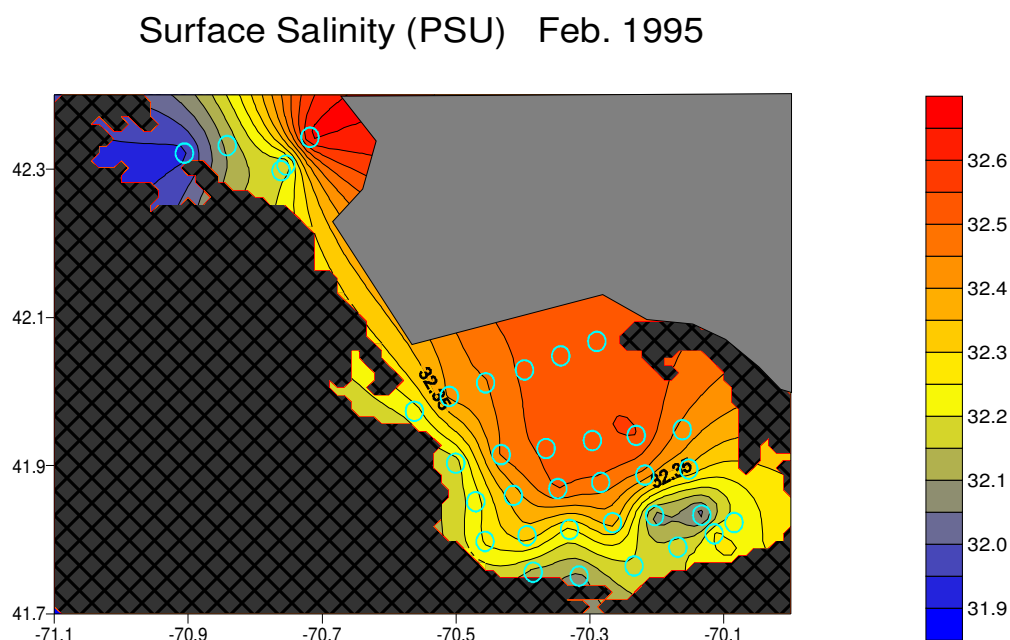


Figure 3.8. Salinity distribution in the surface waters near Boston Harbor and Cape Cod Bay. Circles indicate locations where water samples were collected.

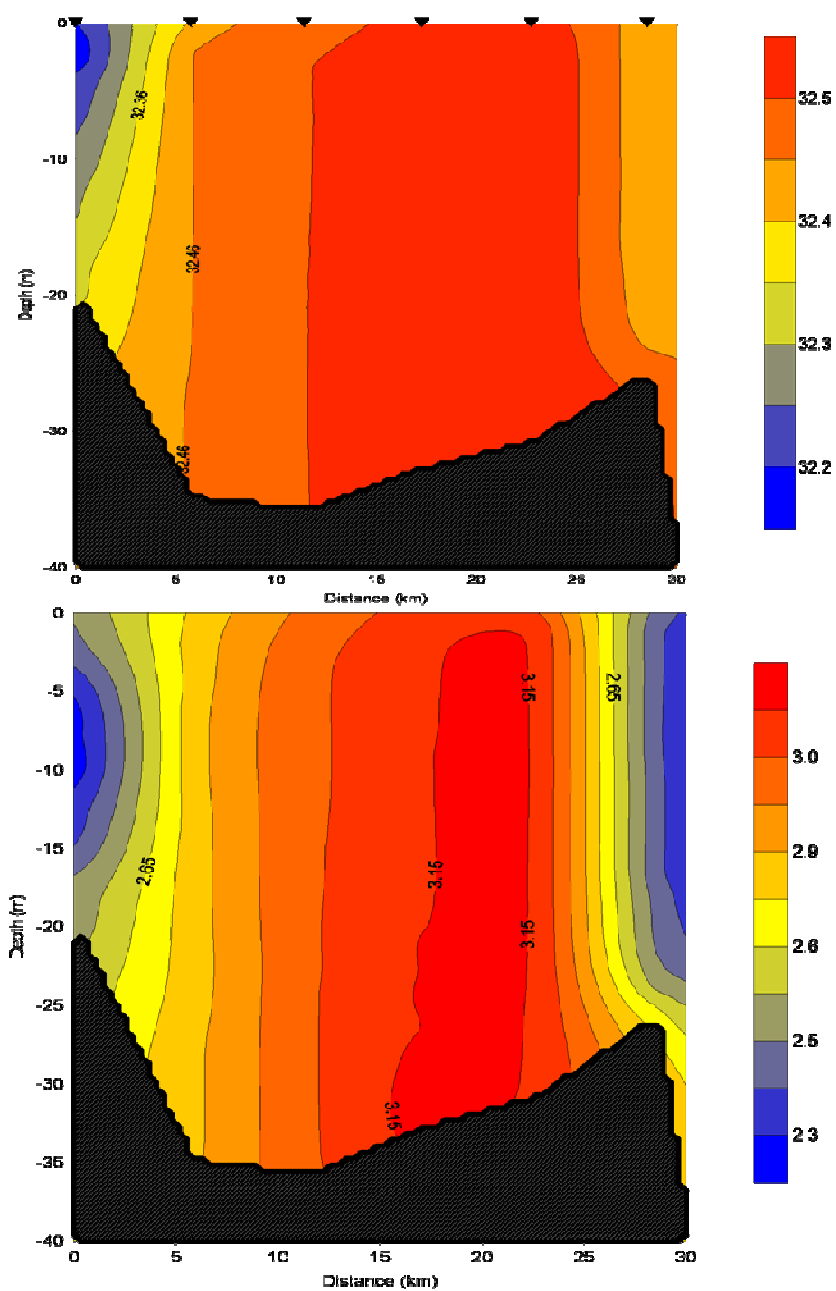


Figure 3.9. Salinity (psu, upper panel) and temperature (°C, lower panel) along the Cape Cod Bay “Manomet” transect, February 1995. Data provided by Dr. Bernie Gardner, UMB.

Table 3.8a. Filtered (<0.4 μm) trace metal concentrations of samples collected from Massachusetts Bay and Cape Cod Bay, February 1995.

Station #	Depth (m)	Ag pmol kg^{-1}	Pb pmol kg^{-1}	Cu nmol kg^{-1}	Zn nmol kg^{-1}	Cd pmol kg^{-1}	Fe nmol kg^{-1}
BH1	1	53.8	174	6.7	15.2	226	32
	18	56.0	170	6.2	10.9	262	40
BH2	1	115	381	8.5	81.7	297	31
CO1	1	80.1	376	7.5	14.5	269	93
CO2	1	93.5	374	8.9	55.5	290	224
CO3	1	6.4	80	3.1	3.1	187	21
MA1	1	38.7	110	5.8	8.4	222	32
MA2	1	40.8	101	3.6	7.5	189	23
MA3	1	27.7	58	4.0	6.3	251	96
MA6	1	13.8	95	3.6	6.9	146	62

Table 3.8b. Particulate ($\geq 0.4 \mu\text{m}$) trace metal concentrations of samples collected from Massachusetts and Cape Cod Bay, February 1995.

Station	Depth (m)	Ag pmol kg^{-1}	Pb pmol kg^{-1}	Cu nmol kg^{-1}	Zn nmol kg^{-1}	Cd pmol kg^{-1}	Fe nmol kg^{-1}	Al nmol kg^{-1}
BH1	1	20.4	274	1.79	5.10	23	1320	1730
	18	35.9	693	2.93	7.71	19	1294	1889
BH2	1	41.5	1762	5.47	7.53	114	71	3635
CO1	1	4.5	122	1.30	10.13	17	1013	1815
CO2	1	13.8	234	1.52	3.20	31	970	716
CO3	1	<1.5	87	1.12	1.60	23	475	696
MA1	1	19.7	749	1.14	4.37	26	947	1428
MA2	1	<1.5	20	0.29	1.04	16	294	225
MA3	1	17.2	29	0.69	3.39	105	186	98
MA6	1	4.3	46	0.39	1.22	19	128	109

Table 3.8c. Ancillary measurements on samples collected from Massachusetts and Cape Cod Bay, February 1995.

Station:	Depth (m)	Lat. N	Lon. W	Salinity PSU	TSM (mg L^{-1})	POC μM	PON μM
BH1	1	42° 19.90	70° 50.51	32.151	2.58	17.9	3.0
	18	42° 19.90	70° 50.51	NA	4.51	15.7	3.0
BH2	1	42° 19.29	70° 54.34	31.933	3.30	22.1	3.0
CO1	1	42° 17.87	70° 45.68	32.136	2.34	15.2	2.5
CO2	1	42° 18.33	70° 45.24	32.191	2.55	19.1	2.7
CO3	1	42° 20.57	70° 43.09	32.664	1.19	4.7	0.9
MA1	1	41° 54.21	70° 30.03	32.153	3.88	39.3	7.1
MA2	1	41° 54.90	70° 25.96	32.457	1.59	8.8	1.7
MA3	1	41° 55.40	70° 21.93	32.508	2.33	10.4	1.8
MA6	1	41° 56.98	70° 09.79	32.432	1.77	41.5	7.8

Ag_F concentrations ranged from 115 pmol kg⁻¹ in Boston Harbor to a low of 6.4 pmol kg⁻¹ in Massachusetts Bay (CO3). Cape Cod Bay Ag_F concentrations (±SD) were relatively uniform: 35 ± 11 pmol kg⁻¹ (n=7). Overall, most of the Ag was in the filterable fraction (80%, RSD = 18%), with highest concentrations of Ag_P observed in the furthest inshore stations. In general, Ag concentration decreased from north (Boston Harbor) to south (Cape Cod Bay) along the western edge of the Bays.

3.4.3 Massachusetts Bay survey, July 1995.

A bay-wide survey was conducted on 31 July 1995 to investigate metal distribution in surface waters when the water column of the Bays was highly stratified. Five transects for trace metal chemistry were conducted, extending from just north of Boston Harbor to the western portion of Stellwagen Bank to the northern boundary of Cape Cod Bay (Fig. 3.10). Prior meteorological conditions were most likely important to setting the physical conditions of the Bays, and this cruise followed an abnormally long period of little to no precipitation. The meteorological record from Logan Airport, Boston, MA shows seven continuous months (Feb. – Aug.) where monthly mean precipitation was well below the long-term mean (Fig. 3.11). The July 1995 survey took place towards the end of a long extended drought for the region. The northeastern U.S. region extending from West Virginia through the coastal states north to Maine experienced the second driest 7-month period in 101 years of record (Northeast Climate Impact Reports, Cornell Regional Climate Center, Cornell University). This period was also recorded as the eighth hottest on record for the entire Northeast. Flow discharge records for the Penobscot, Merrimack, and Charles rivers also show a lower than normal contribution from the annual spring runoff (Fig. 3.12).

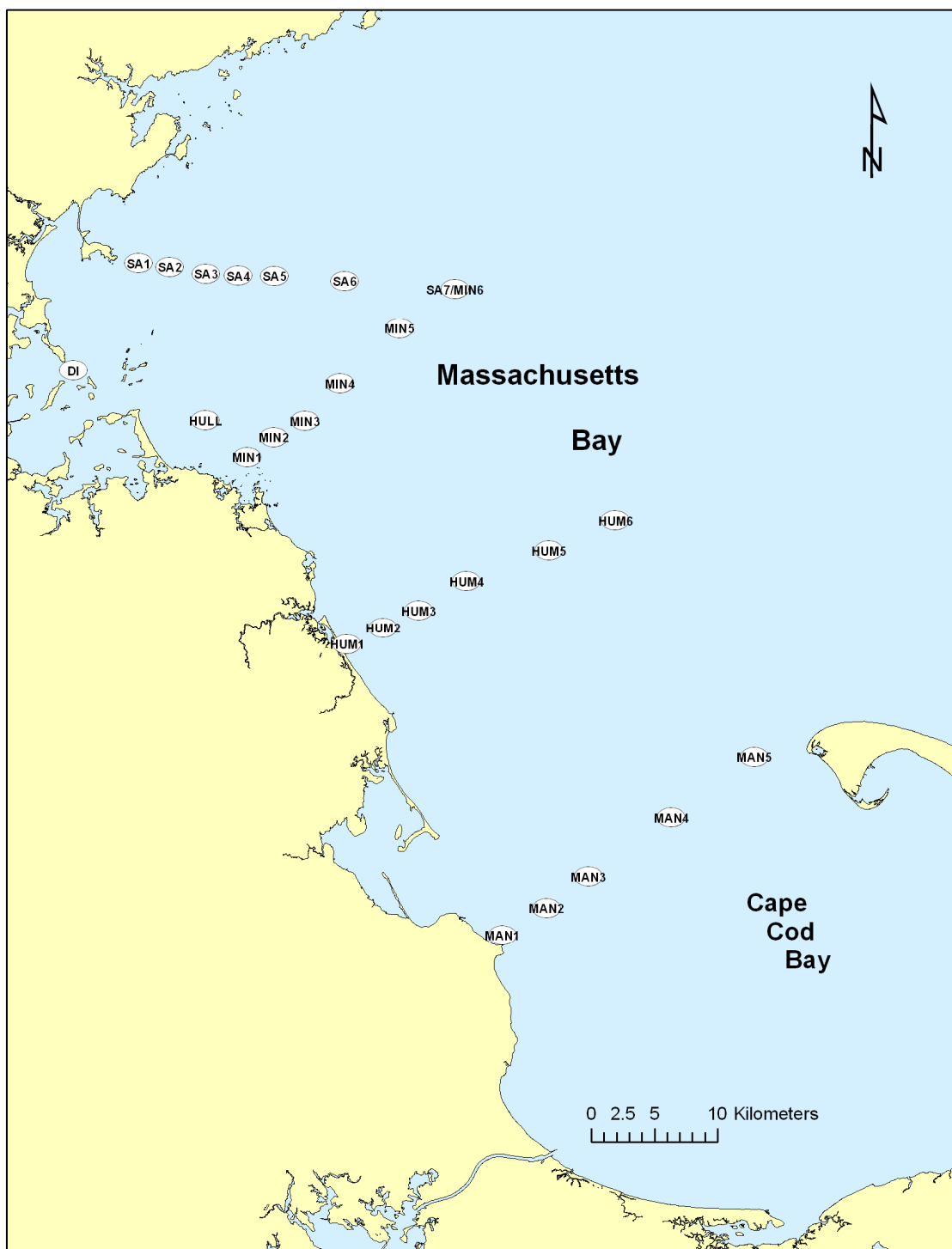


Figure 3.10. Sampling stations, *RV Neritic* Cruise, 31 July 1995.

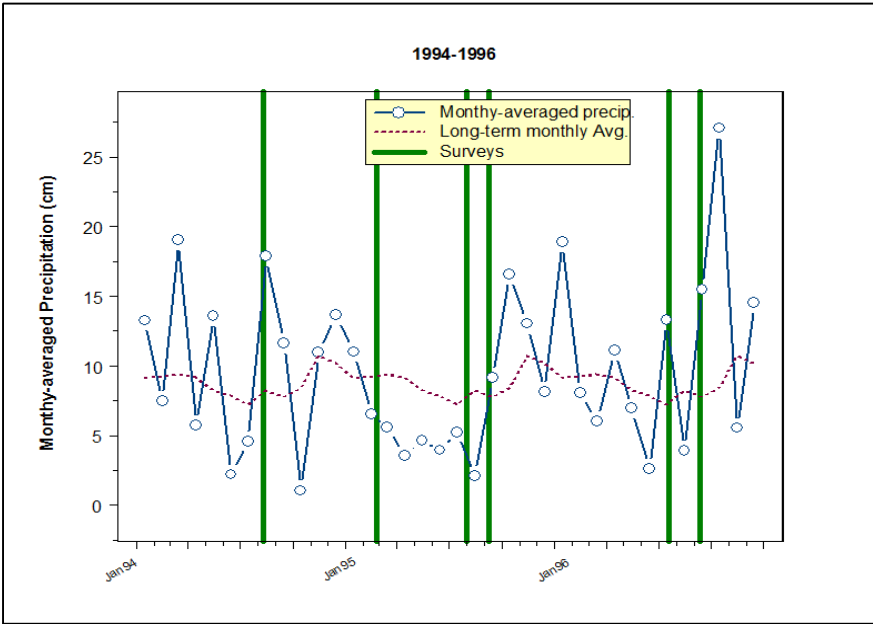


Figure 3.11. Monthly precipitation (cm) recorded at Logan International Airport, Boston, MA for the years 1994 through 1996. Dashed line shows the mean historical monthly precipitation observed at Logan and solid vertical lines indicate when surveys for this work were conducted.

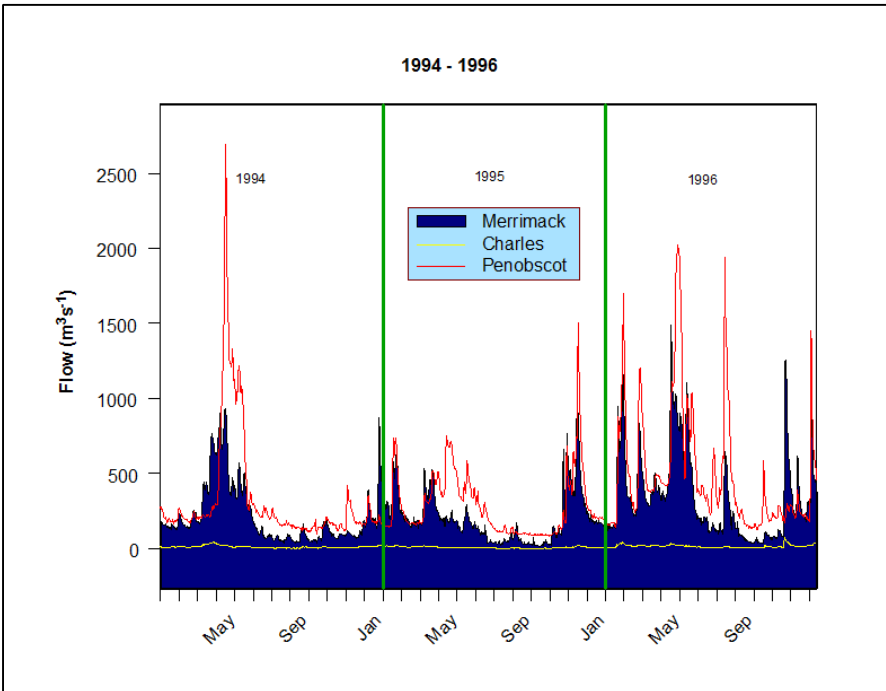


Figure 3.12. Discharges ($\text{m}^3 \text{s}^{-1}$) for the Penobscot, Merrimack and Charles Rivers, 1994 - 1996.

Salinity determinations from the discrete surface samples are plotted in Figure 3.13. Lowest salinities observed during this cruise were in the northeastern portion of Massachusetts Bay, most likely from intrusion of freshwater from the GOM. Recent observations have shown the presence of a freshwater plume interior to the WCC in near coastal waters of the GOM (Anderson et al., 2007). Wind forcing can be important in the positioning of the legs of the WCC (Gyer et al., 1996; Pettigrew et al., 2005; Churchill et al., 2005; Hetland and Signell, 2005). Deflection of the coastal freshwater sources from the GOM into Massachusetts Bay would be most favorable under winds with a strong northerly component (Jiang et al., 2007). However, winds were generally weak and out of the east for many days prior to sampling (Fig. 3.14) and probably not important to the transport of surface water from the GOM into

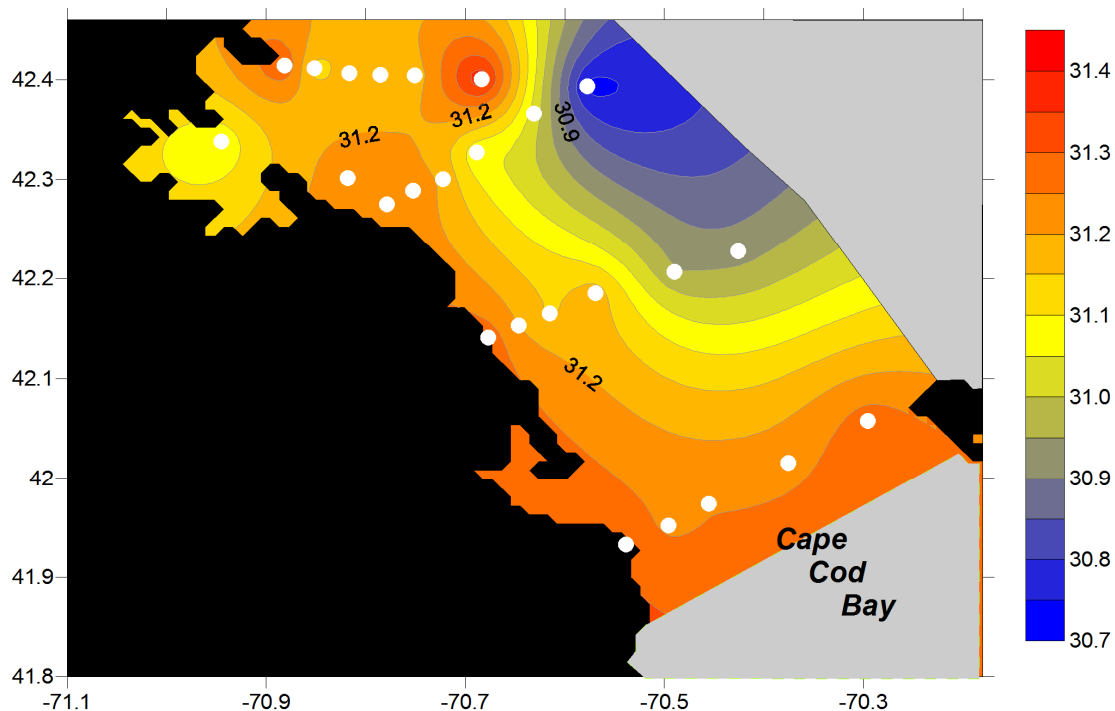


Figure 3.13. Surface salinity contour plot (July 1995) constructed from CTD data. Hydrographic stations indicated by white circles.

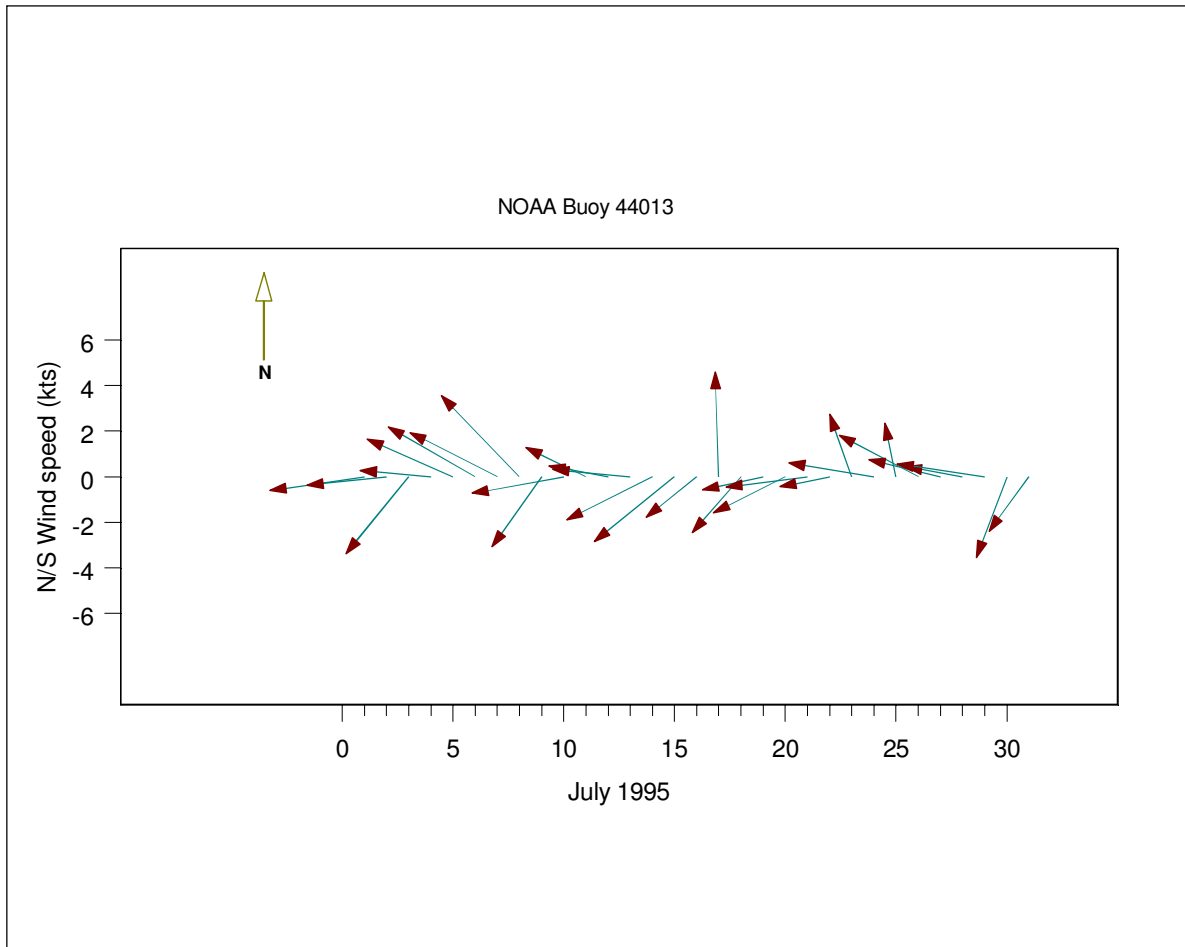


Figure 3.14. Wind speed (kts) and direction during July 1995 from the national marine buoy NOAA 44013 (http://www.ndbc.noaa.gov/station_page.php?station=44013).

Massachusetts Bay. Cross sectional salinity contour plots for each transect show an offshore freshwater lens largely confined to the upper 5 m of the water column along the eastern boundary of the survey region (Fig. 3.15). A well-defined pool of higher density (Fig. 3.16), more saline water (>32 PSU) occupied the shallow northwestern portion of Massachusetts Bay. These features in the salinity and density distributions were not evident south of the Minot (MIN) transect. Further, some wind-driven downwelling of higher salinity water appeared to have occurred along the MBS western boundary during the survey.

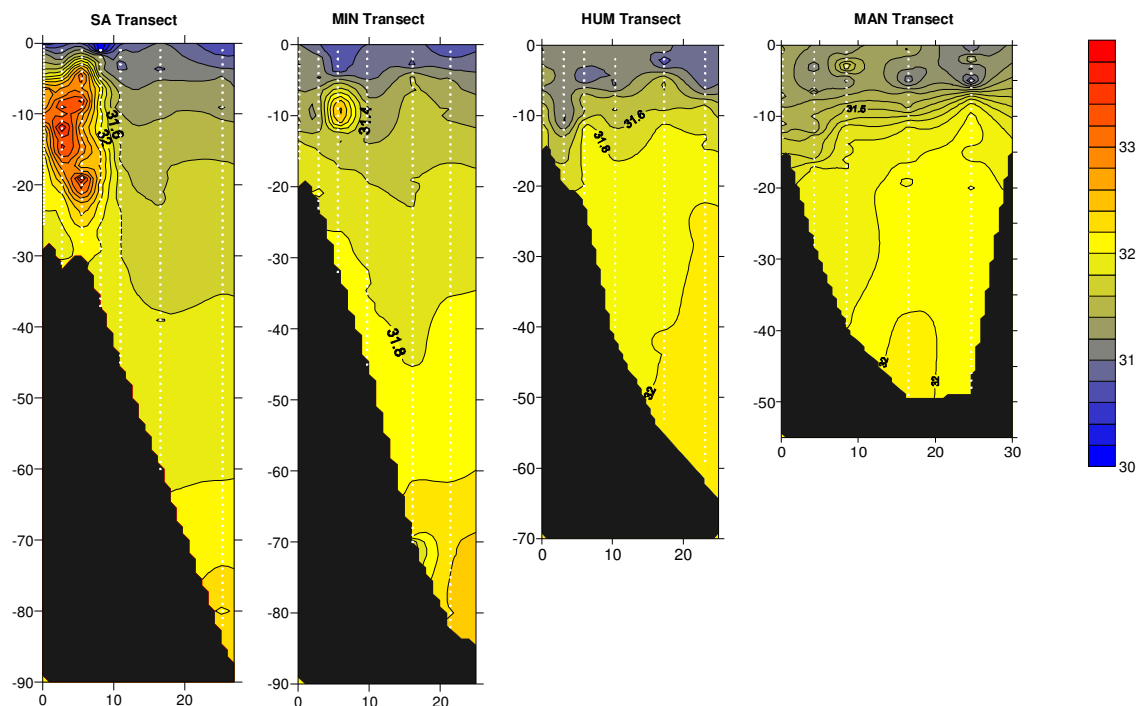


Figure 3.15. Massachusetts Bay, Salem (SA) Minot (MIN) Hummarock (HUM), and Manomet (MAN) transects, salinity (psu) – depth (m) contour plot, July 1995. White dots indicate bin-averaged CTD data used to derive contour field.

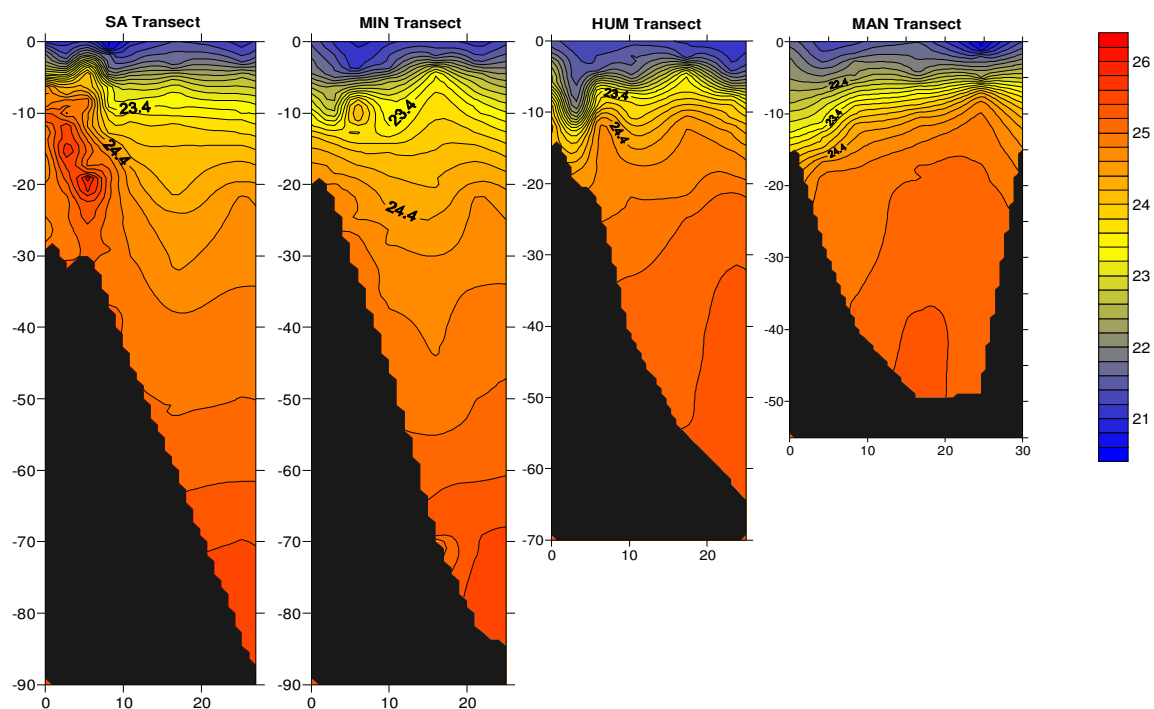


Figure 3.16. Massachusetts Bay, Salem (SA) Minot (MIN) Hummarock (HUM), and Manomet (MAN) transects, density (σ_θ) – depth (m) contour plot, July 1995.

Surface TSM and Chl *a* concentrations in the Bays were generally low, typically less than 2 mg L⁻¹ and 4 µg L⁻¹, respectively (Fig. 3.17). The highest TSM and Chl *a* values observed were in samples taken in Boston Harbor. Chlorophyll *a* concentrations in Cape Cod Bay and lower Massachusetts Bay were less than 0.5 µg L⁻¹. Trace metal concentrations and ancillary station data and information from the July 1995 survey are presented in Table 3.9, a-c.

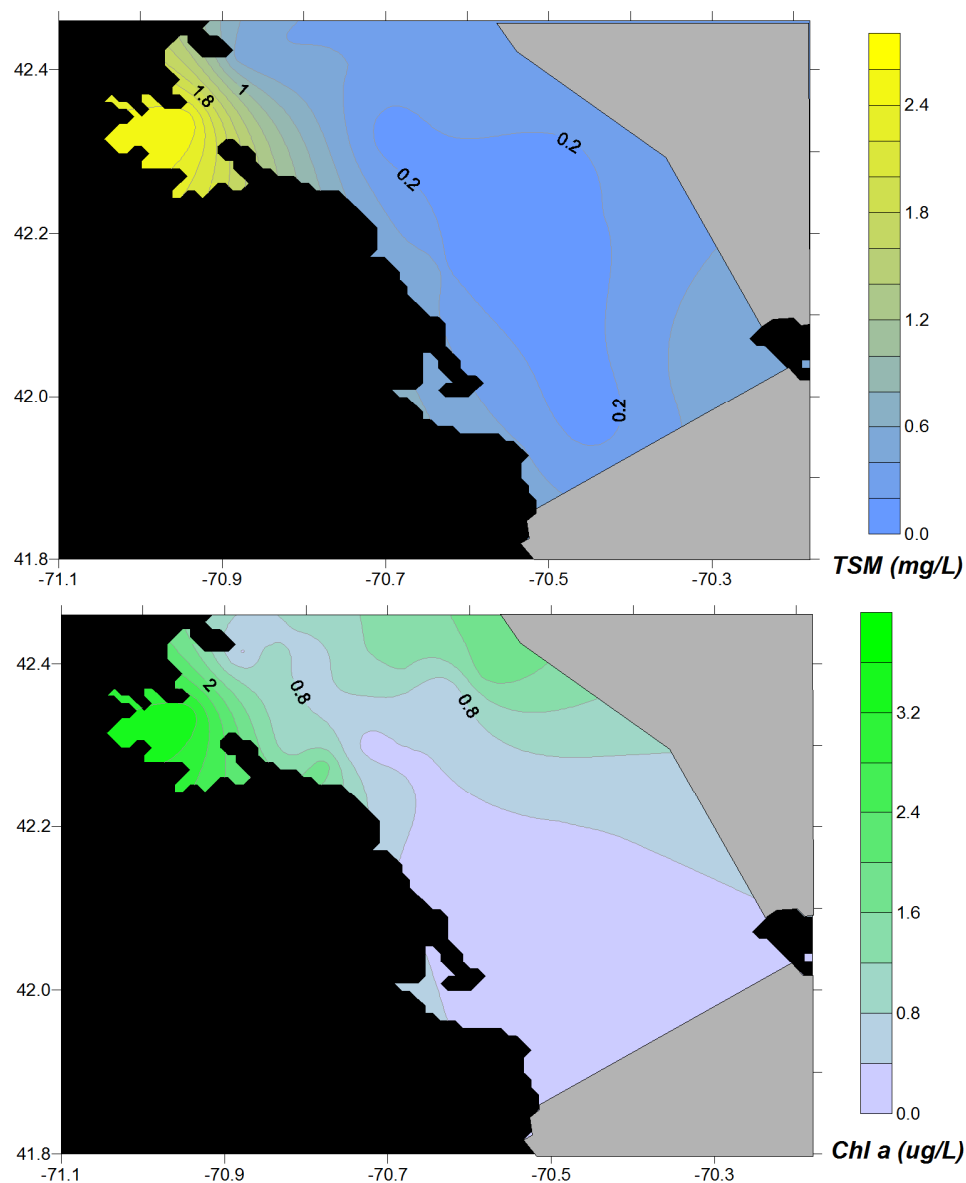


Figure 3.17. Massachusetts Bay surface water total suspended matter (mg L⁻¹, upper panel) and chlorophyll *a* (ug L⁻¹, lower panel), July 1995.

Table 3.9a. Massachusetts Bay July 1995cruise: Filterable (<0.4 μm) trace metal concentrations.

Station	Ag (pmol kg^{-1})	Pb (pmol kg^{-1})	Cu (nmol kg^{-1})	Zn (pmol kg^{-1})	Cd (pmol kg^{-1})	Fe (nmol kg^{-1})
SA1	51.5	1001	5.44	10.5	312	10.3
SA2	40.6	72	5.29	4.4	221	5.5
SA3	51.5	78	5.31	4.9	598	6.7
SA4	43.2	67	5.08	4.1	201	6.0
SA5	27.9	58	4.06	3.1	194	8.3
SA6	41.8	74	4.85	4.6	290	4.5
SA7/MIN6	9.9	30	2.76	1.9	177	7.5
MIN5	24.4	56	3.29	6.3	231	16.8
MIN4	15.8	26	2.75	2.5	147	5.8
MIN3	25.0	53	3.14	4.6	193	6.7
MIN2	51.9	107	5.63	7.9	395	6.0
MIN1	44.2	77	4.96	5.3	162	7.5
HUM1	19.6	22	2.51	1.7	140	4.2
HUM2	27.4	32	3.37	2.0	253	1.7
HUM3	28.1	30	3.38	2.0	260	1.4
HUM4	23.3	52	3.61	2.4	272	2.2
Rep.	22.6	59	3.63	1.7	256	3.1
HUM5	16.6	42	3.56	2.5	216	7.6
HUM6	12.5	23	2.47	1.1	146	2.5
MAN1	20.4	47	3.25	4.2	217	6.1
Rep.	20.3	32	3.17	2.7	183	6.8
MAN2	57.4	39	3.35	3.1	201	6.3
MAN3	14.6	31	2.66	1.8	228	3.5
MAN4	16.1	35	2.66	1.4	166	1.1
MAN5	23.5	< 19	3.77	2.5	200	8.5
Hull	64.0	75	5.18	5.5	279	5.6
DI	87.7	183	9.64	11.0	396	30.7

Table 3.9b. Massachusetts Bay July 1995 cruise: Particulate ($\geq 0.4 \mu\text{m}$) trace metal concentrations.

Station	Ag pmol kg ⁻¹	Pb pmol kg ⁻¹	Cu nmol kg ⁻¹	Zn nmol kg ⁻¹	Cd pmol kg ⁻¹	Fe nmol kg ⁻¹	Al nmol kg ⁻¹
SA1	37.2	337	0.72	2.69	53	135	210
SA2	16.5	114	0.38	1.44	37	54	88
SA3	25.2	124	0.41	15.00	65	77	103
SA4	16.7	118	0.32	1.32	24	54	92
SA5	15.1	115	0.34	0.99	20	48	69
SA6	12.4	64	0.26	0.75	31	35	21
SA7/MIN6	5.9	47	0.16	0.76	39	43	62
MIN5	10.3	72	0.20	0.83	38	44	41
MIN4	6.9	59	0.23	0.64	21	31	27
MIN3	5.3	51	0.18	0.42	16	24	34
MIN2	16.0	114	0.18	1.38	23	58	80
MIN1	45.5	349	0.57	2.22	45	116	188
HUM1	6.6	53	0.16	0.56	21	62	125
HUM2	3.4	37	0.13	0.34	16	22	27
HUM3	2.2	36	0.15	0.36	16	19	41
HUM4	3.4	48	0.19	0.55	23	27	50
Rep.	3.2	51	0.20	0.48	24	25	59
HUM5	6.9	34	0.18	0.65	30	30	49
HUM6	5.2	37	0.09	0.93	53	31	64
MAN1	8.0	61	0.28	0.44	19	44	101
Rep.	5.6	55	0.23	0.37	11	47	133
MAN2	5.7	29	0.21	0.44	33	22	55
MAN3	2.8	23	0.14	0.68	13	22	47
MAN4	6.6	27	0.16	0.39	34	12	29
MAN5	6.3	138	0.29	1.10	23	142	205
Hull	14.9	93	0.30	1.32	14	46	121
DI	80.7	784	2.74	5.86	47	663	1268

Table 3.9c. Massachusetts Bay July 1995 cruise: Ancillary measurements.

Station	Lat. N	Lon. W	Salinity PSU	TSM (mg L ⁻¹)	POC uM	PON uM	Chl a (ug L ⁻¹)	Phaeo (ug L ⁻¹)
SA1	42° 24.837	70° 52.880	31.299	0.54	14.4	2.5	0.3	1.4
SA2	42° 24.674	70° 51.077	31.126	0.46	10.3	1.5	0.9	1.5
SA3	42° 24.368	70° 48.999	31.176	0.45	10.1	2.0	0.8	0.8
SA4	42° 24.278	70° 47.121	31.162	0.44	11.4	1.9	0.6	0.6
SA5	42° 24.253	70° 45.039	31.169	0.41	10.8	1.5	1.1	0.6
SA6	42° 24.004	70° 40.992	31.392	0.35	9.0	1.4	1.3	0.7
SA7/MIN6	42° 23.603	70° 34.630	30.733	0.33	7.1	1.1	1.9	1.8
MIN5	42° 21.949	70° 37.849	31.030	0.37	9.3	1.4	0.4	0.4
MIN4	42° 19.609	70° 41.302	31.058	<0.11	7.4	1.1	0.6	0.7
MIN3	42° 18.021	70° 43.348	31.191	0.27	7.1	1.2	0.2	0.3
MIN2	42° 17.312	70° 45.148	31.227	0.52	11.2	3.3	0.8	0.7
MIN1	42° 16.505	70° 46.704	31.230	0.74	20.8	4.6	1.8	2.6
HUM1	42° 08.466	70° 40.604	31.279	0.41	11.9	2.8	0.3	0.5
HUM2	42° 09.167	70° 38.777	31.198	0.61	13.4	3.9	0.2	0.4
HUM3	42° 09.884	70° 36.903	31.144	0.04	7.5	1.1	0.3	0.4
HUM4	42° 11.121	70° 34.133	31.176	<0.11	8.0	1.1	0.3	0.3
Rep.			31.126	<0.11	8.0	1.0	0.3	0.4
HUM5	42° 12.389	70° 29.384	30.953	<0.11	11.3	1.6	0.4	1.1
HUM6	42° 13.642	70° 25.529	30.927	0.22	8.1	1.2	0.5	0.5
MAN1	41° 55.979	70° 32.308	31.296	0.43	10.3	3.1	0.2	0.3
Rep.			31.330	0.60	10.2	2.9	0.2	0.7
MAN2	41° 57.117	70° 29.744	31.238	0.27	8.3	2.6	<0.15	0.2
MAN3	41° 58.447	70° 27.315	31.246	<0.11	7.5	1.9	0.2	0.6
MAN4	42° 00.921	70° 22.522	31.230	0.34	8.7	1.2	0.2	0.6
MAN5	42° 03.450	70° 17.719	31.277	0.57	13.7	2.2	0.3	1.4
HULL	42° 18.086	70° 49.082	31.236	0.99	14.2	3.2	0.9	0.8
DI	42° 20.260	70° 56.686	31.062	2.61	29.3	8.2	3.5	2.2

Overall, Ag values were comparable in magnitude to those observed along the Boston Transect of August 1994. Total Ag concentrations in the surface water of the Bay ranged from a high of 169 pmol kg⁻¹ at the mouth of Boston Harbor to a low of 16 pmol kg⁻¹ in the freshwater lens observed offshore at Station SA7. Surface concentration contour plots for Ag are shown in Figure 3.18. Decreasing concentration gradients from west to east across the Bay

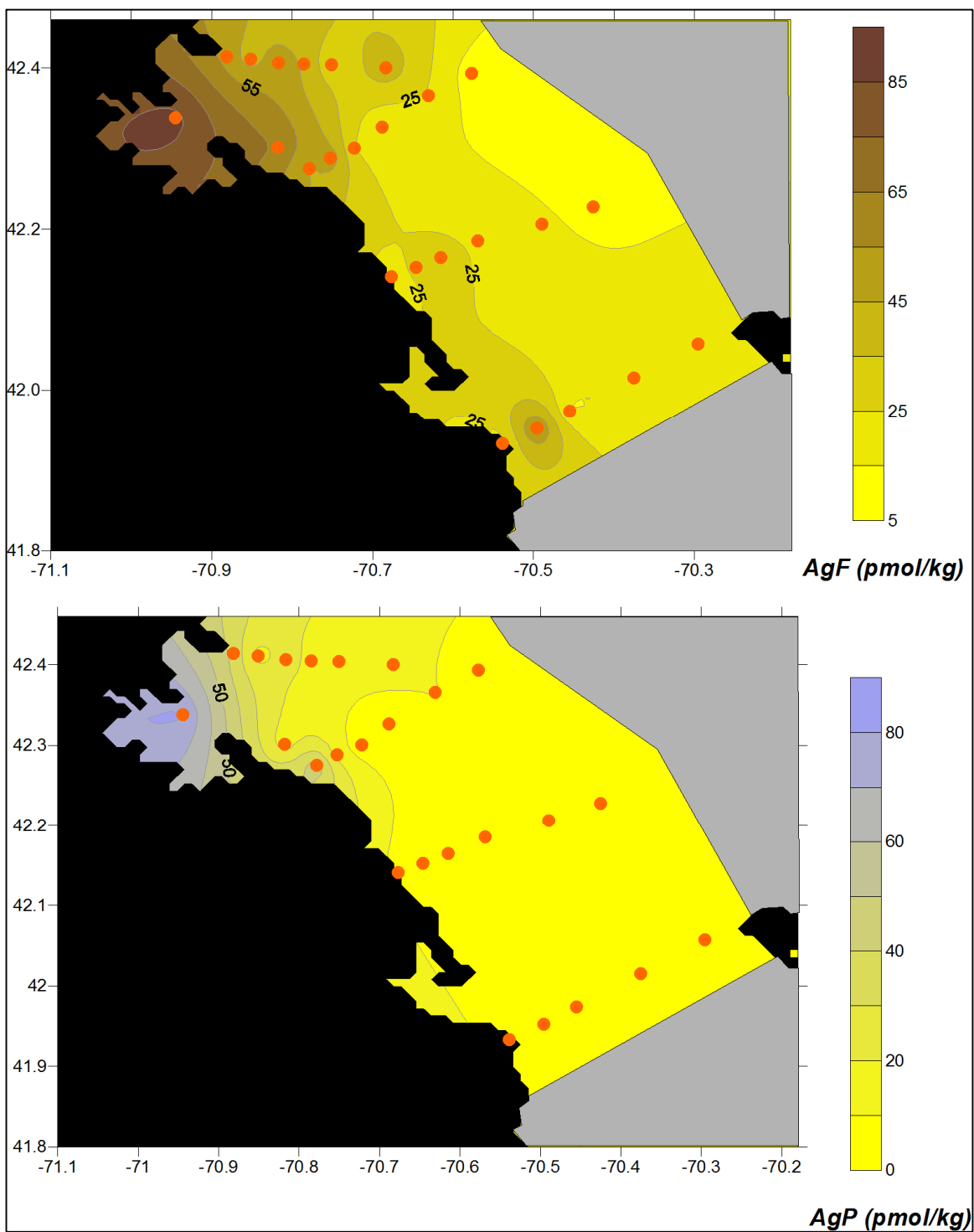


Figure 3.18. Filterable (upper panel) and particulate (lower panel) Ag ($pmol\ kg^{-1}$) in the surface waters of Massachusetts Bay, July 1995.

and to the south from Boston Harbor were observed in both Ag_F and Ag_P concentrations for this period. Lower Bay concentration averages (HUM and MAN transects) were markedly uniform for both filterable and particulate Ag: (20 ± 5) and (5 ± 2) $pmol\ kg^{-1}$, ($n=10$), respectively. Relative uniform metal distribution in the lower Bay was also observed for the filterable fraction of Pb (35 ± 12 $pmol\ kg^{-1}$), Cu (3.2 ± 0.5 $nmol\ kg^{-1}$), and Cd (211 ± 43 $pmol\ kg^{-1}$).

3.4.4 Nearshore survey, September 1996.

A nearshore coastal survey was conducted on 11 September 1996 to examine the exchange of metals from Boston Harbor into Massachusetts and Cape Cod Bays. Modeled tidal exchange between Boston Harbor and Massachusetts Bay (Signell, 1992) was reviewed to guide the sampling in the region of exchange between Boston Harbor and Massachusetts Bay. Water column sampling targeted western Massachusetts Bay, from Boston Harbor and extended approximately 30 km to the south (Fig. 3.19).

Surface salinity concentrations for this sampling period indicate much of the fresh water was confined to Boston Harbor and within a few km offshore along the southwestern boundary of Massachusetts Bay (Fig. 3.20a). There was also a north – south gradient in surface water temperature with cooler waters observed at the southern-most stations along the Duxbury transect (Fig. 3.20b). Cross-sectional contour plots of density (Fig. 3.21), salinity (Fig. 3.22) and temperature (Fig. 3.23) reveal the presence of a warm freshet that appears to be pinned beneath the warmer Massachusetts Bay surface water at the Cohasset Transect and expressed in the surface waters about 3 km offshore from Duxbury, MA. Cross sectional chlorophyll *a* concentration gradients derived from both CTD fluorescence and discrete samples for each

transect are illustrated in Figure 3.24 (a and b). Wind directions two weeks prior to sampling were variable between north and south and typically less than 5 kts (Fig.3.25).

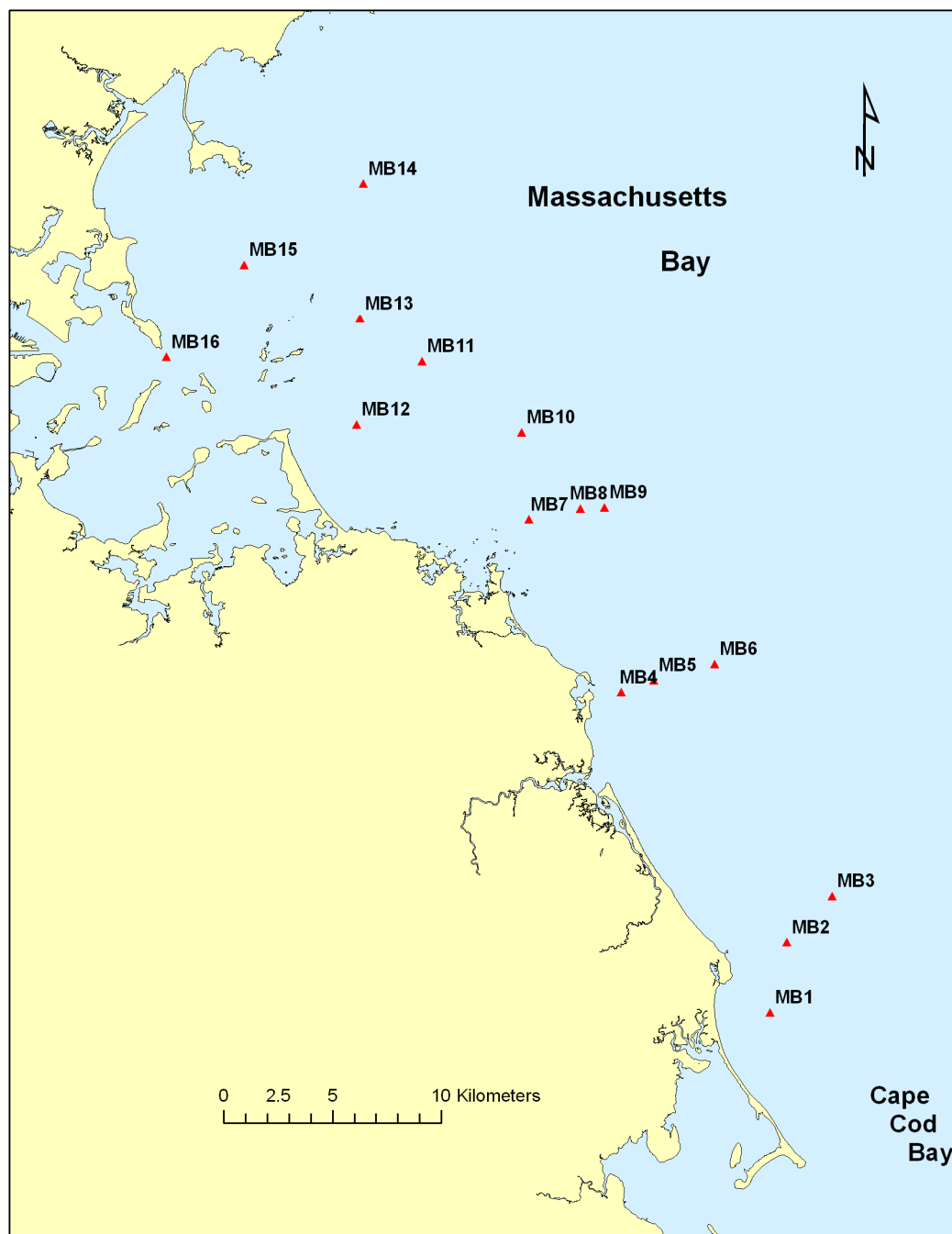


Figure 3.19. Station locations, Massachusetts Bay nearshore survey, September 1996.

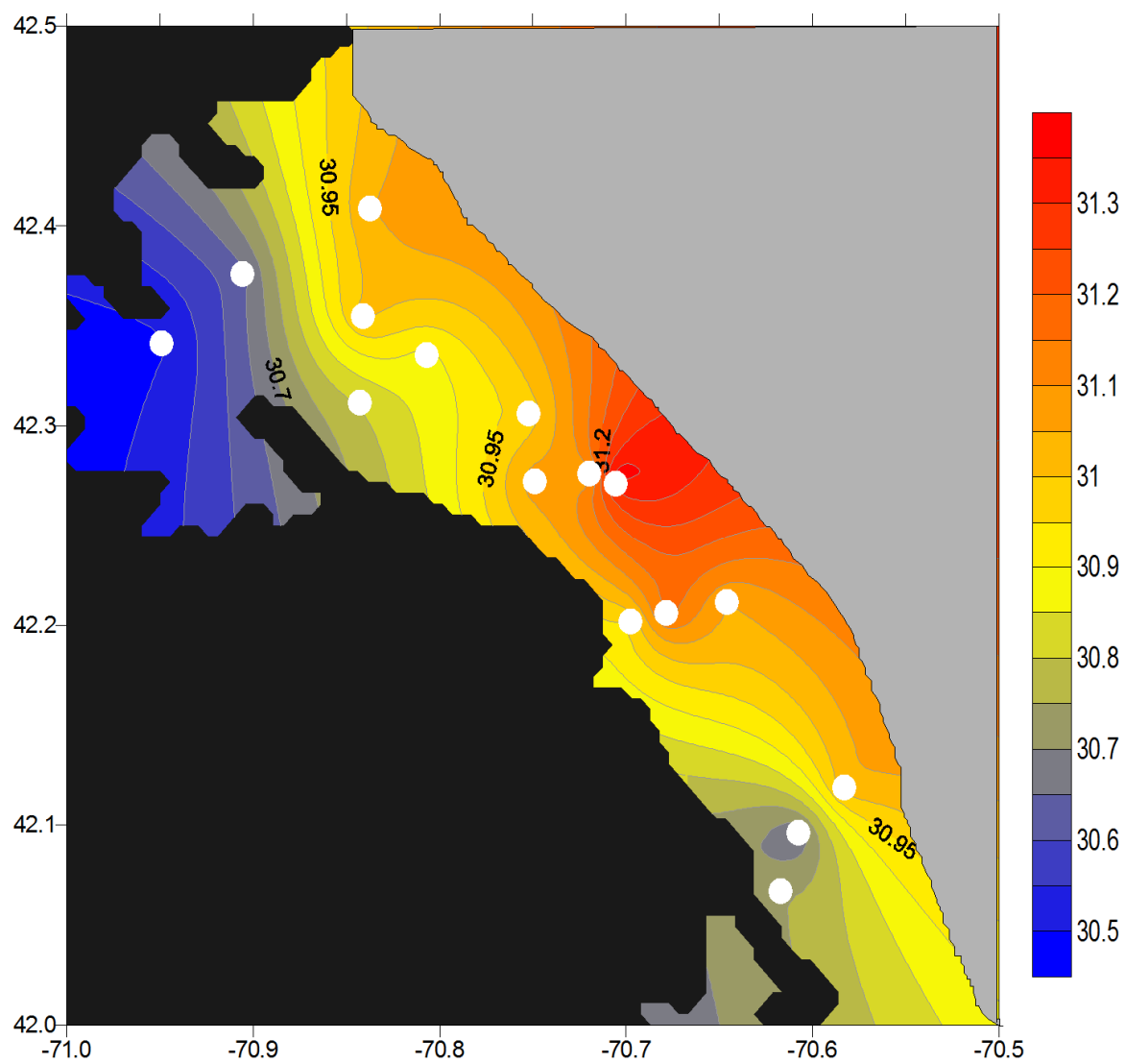


Figure 3.20a. Surface salinity (psu), Massachusetts Bay nearshore survey, September 1996. White dots indicate station locations used for generating surface gradients.

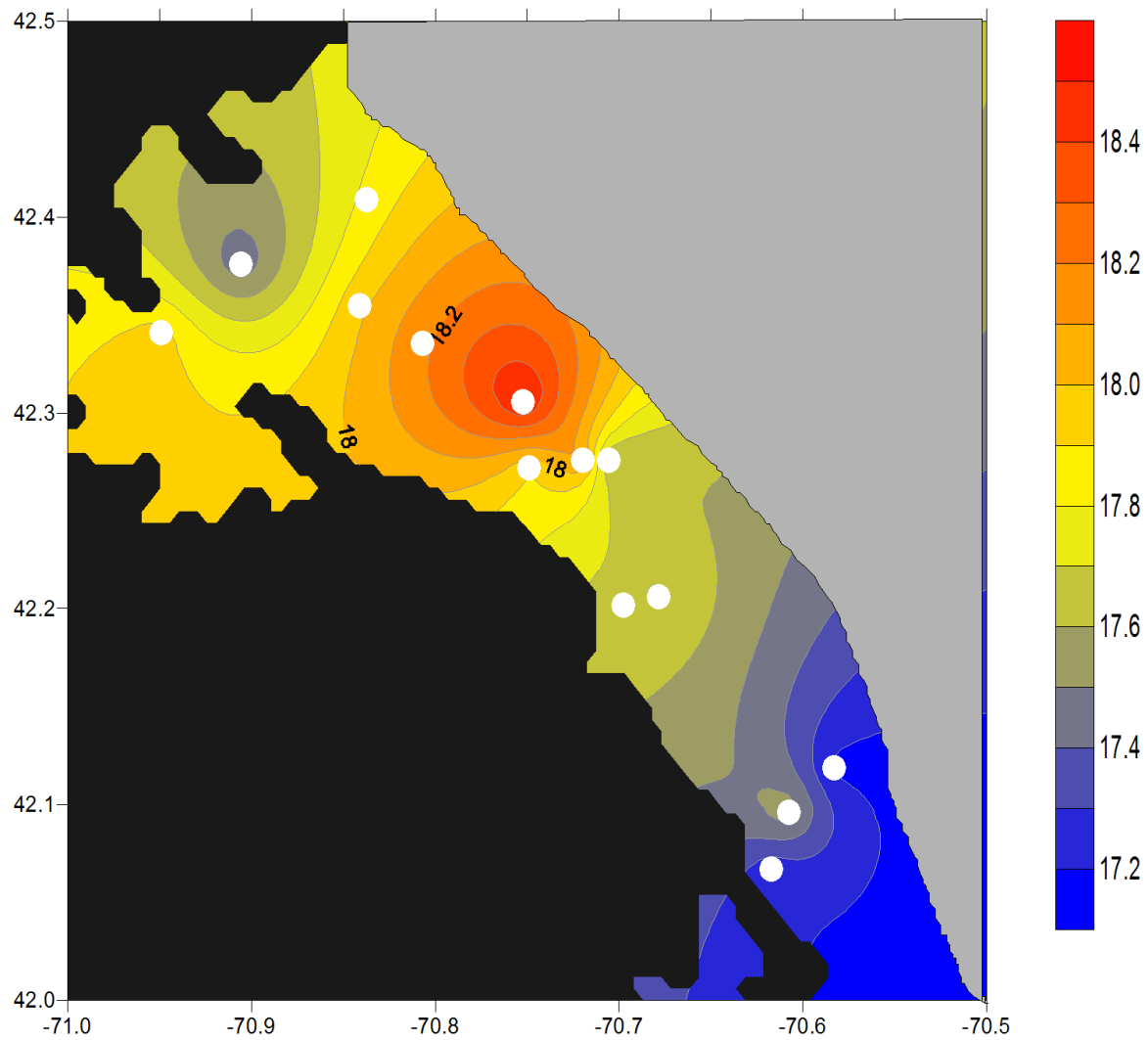


Figure 3.20b. Surface temperature ($^{\circ}\text{C}$), Massachusetts Bay nearshore survey, September 1996. White dots indicate station locations used for generating surface gradients.

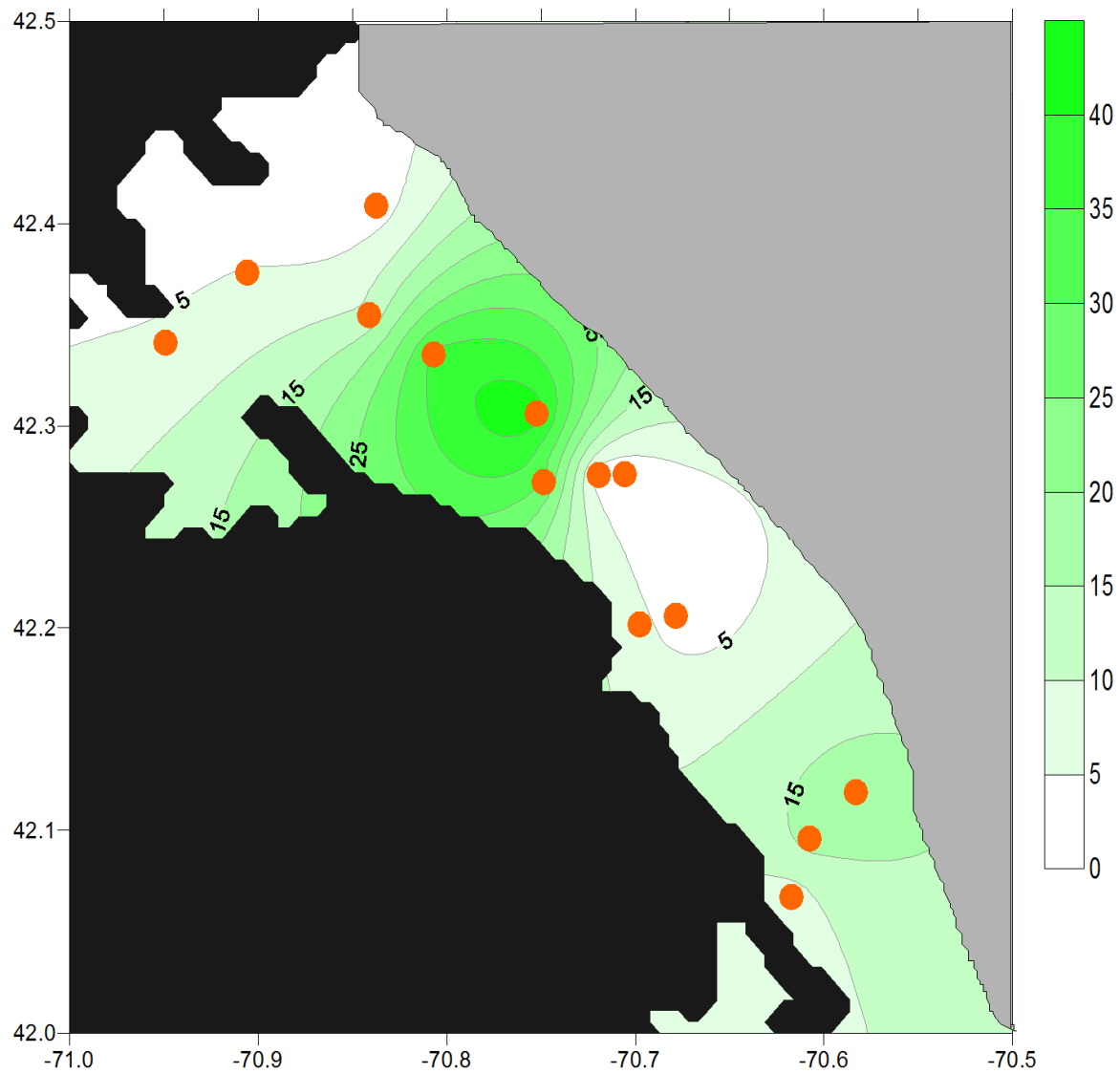


Figure 3.20c. Surface chlorophyll *a* ($\mu\text{g L}^{-1}$) from discrete samples, Massachusetts Bay nearshore survey, September 1996. Orange dots indicate station locations used for generating surface gradients.

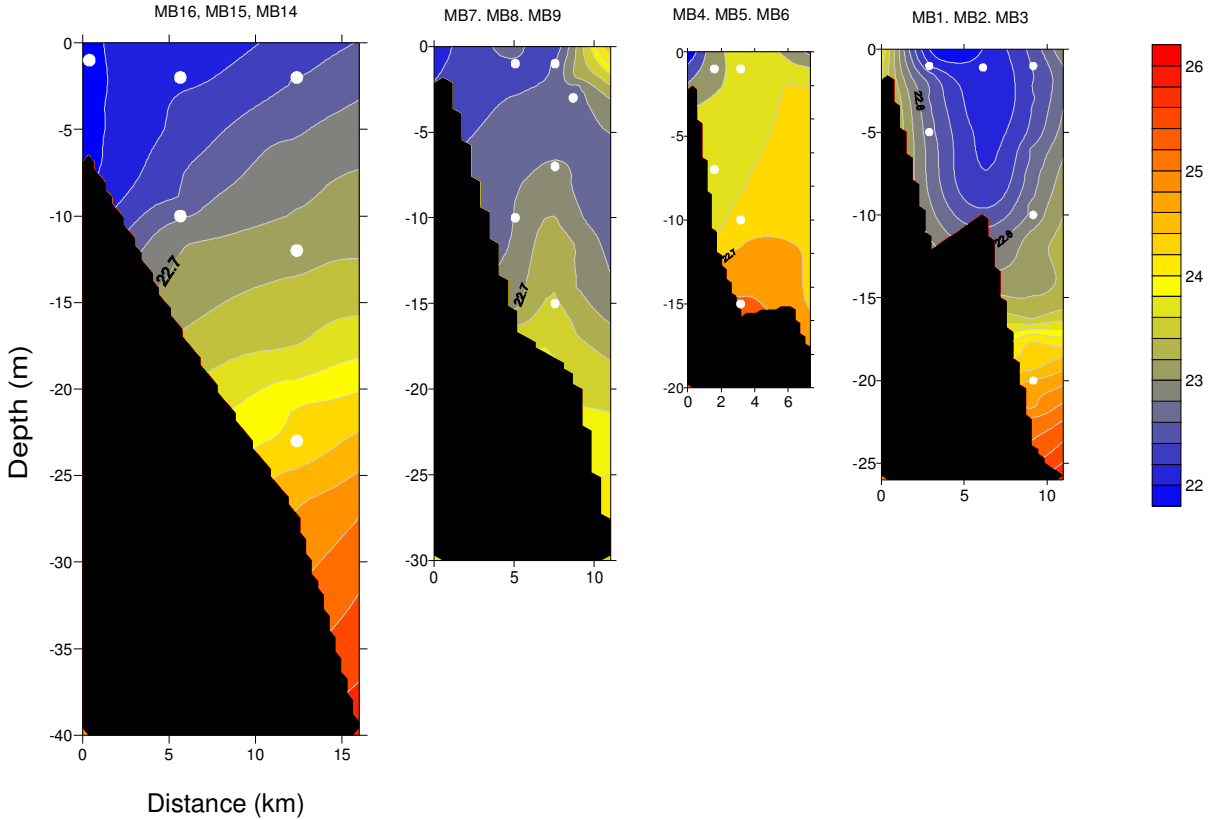


Figure 3.21. Density (Sigma-T) distribution off Boston Harbor (Stations MB14-MB16), Cohasset (MB7-MB9), Scituate (Stations MB4-MB6), and Duxbury (Stations MB1-MB3), September 1996. Data derived from station CTD hydrocasts. Locations where discrete water samples were collected are indicated by white circles.

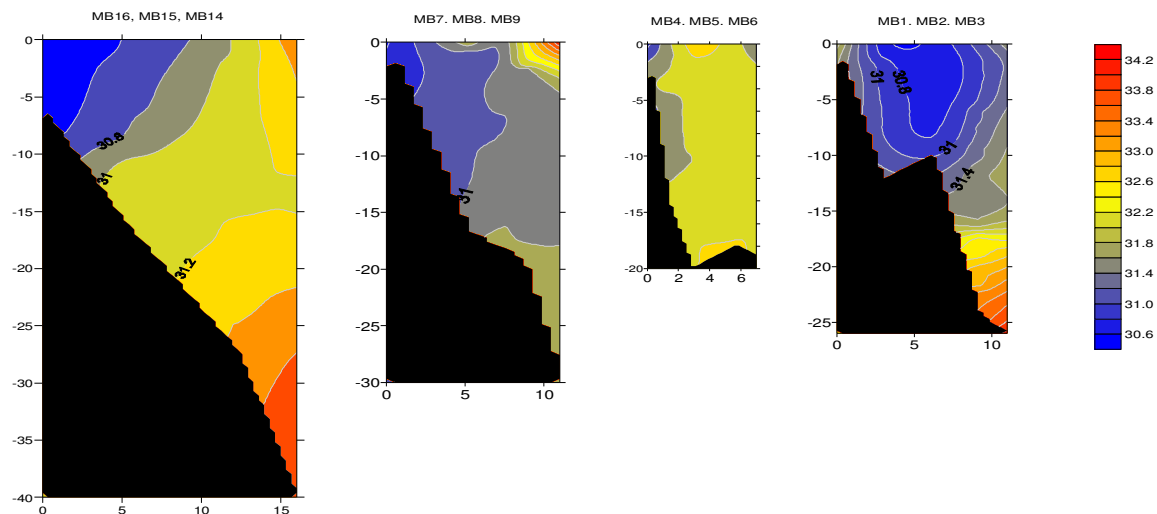


Figure 3.22. Salinity (psu) distribution off Boston Harbor (Stations MB14-MB16), Cohasset (MB7-MB9), Scituate (Stations MB4-MB6), and Duxbury (Stations MB1-MB3), September 1996. Data derived from station CTD hydrocasts.

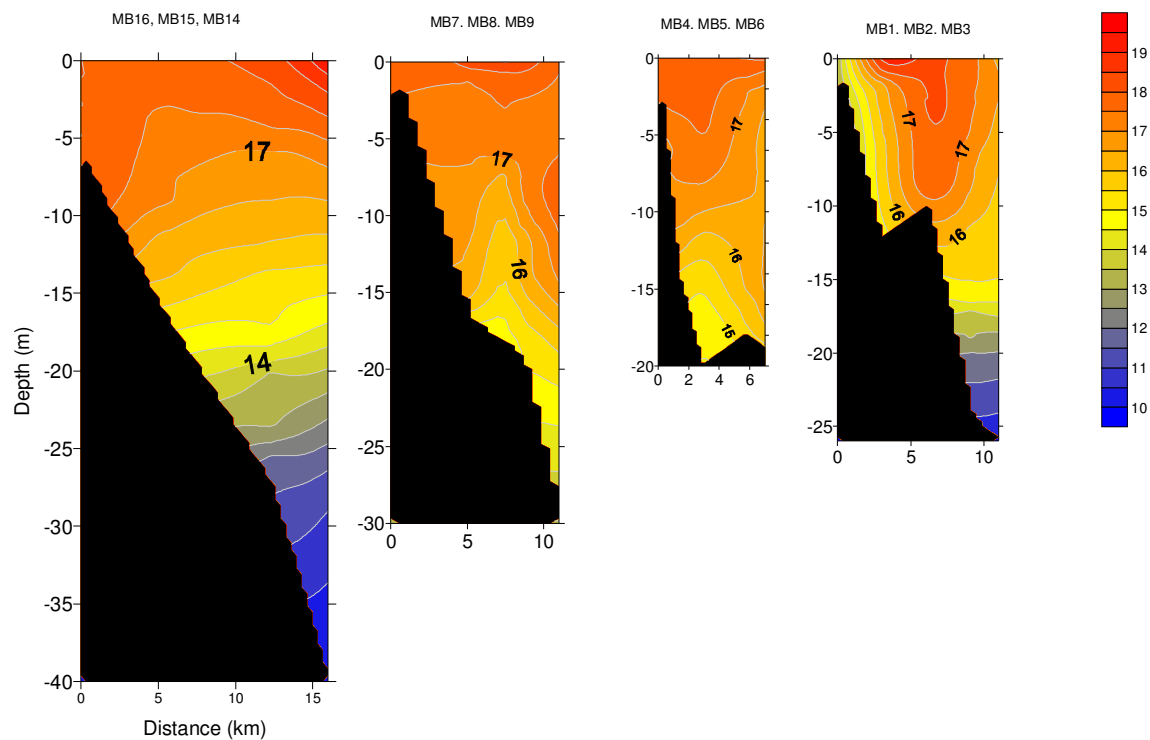


Figure 3.23. Water temperature (°C) distribution off Boston Harbor (Stations MB14-MB16), Cohasset (MB7-MB9), Scituate (Stations MB4-MB6), and Duxbury (Stations MB1-MB3), September 1996. Data derived from station CTD hydrocasts.

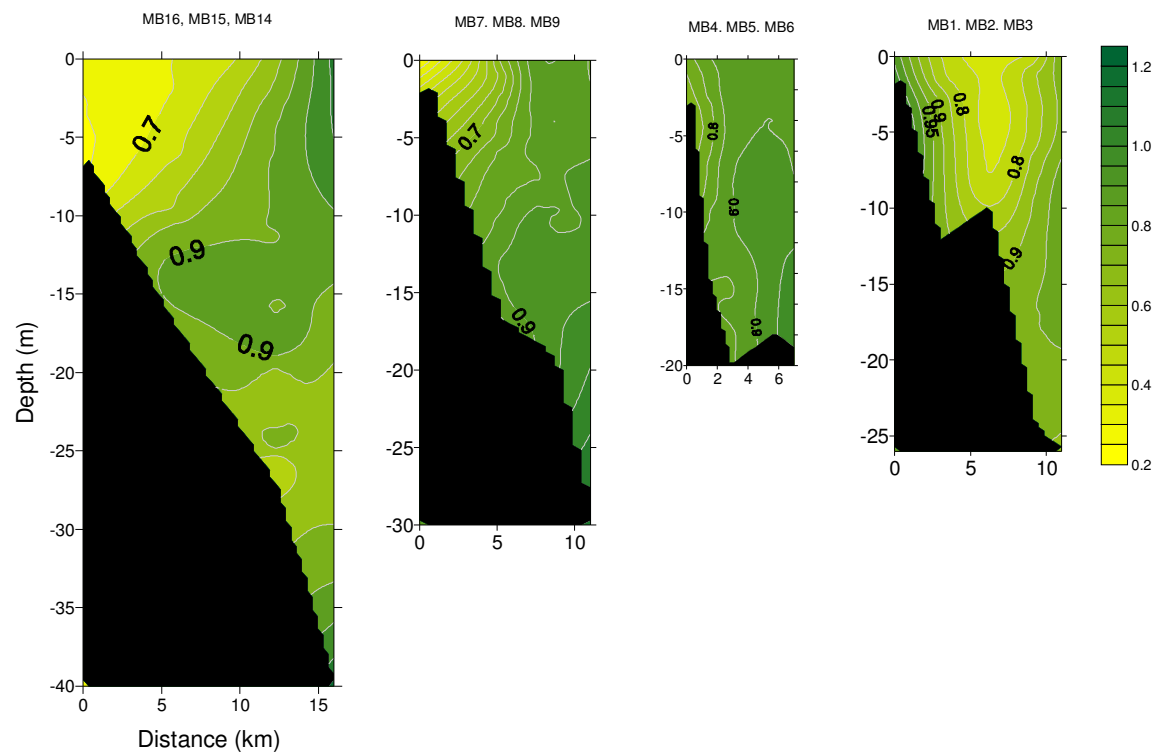


Figure 3.24a. Chl *a* (relative fluorescence) distribution derived from station CTD hydrocasts for Boston Harbor (MB14-MB16), Cohasset (MB7-MB9), Scituate (MB4-MB6), and Duxbury (MB1-MB3) transects, September 1996.

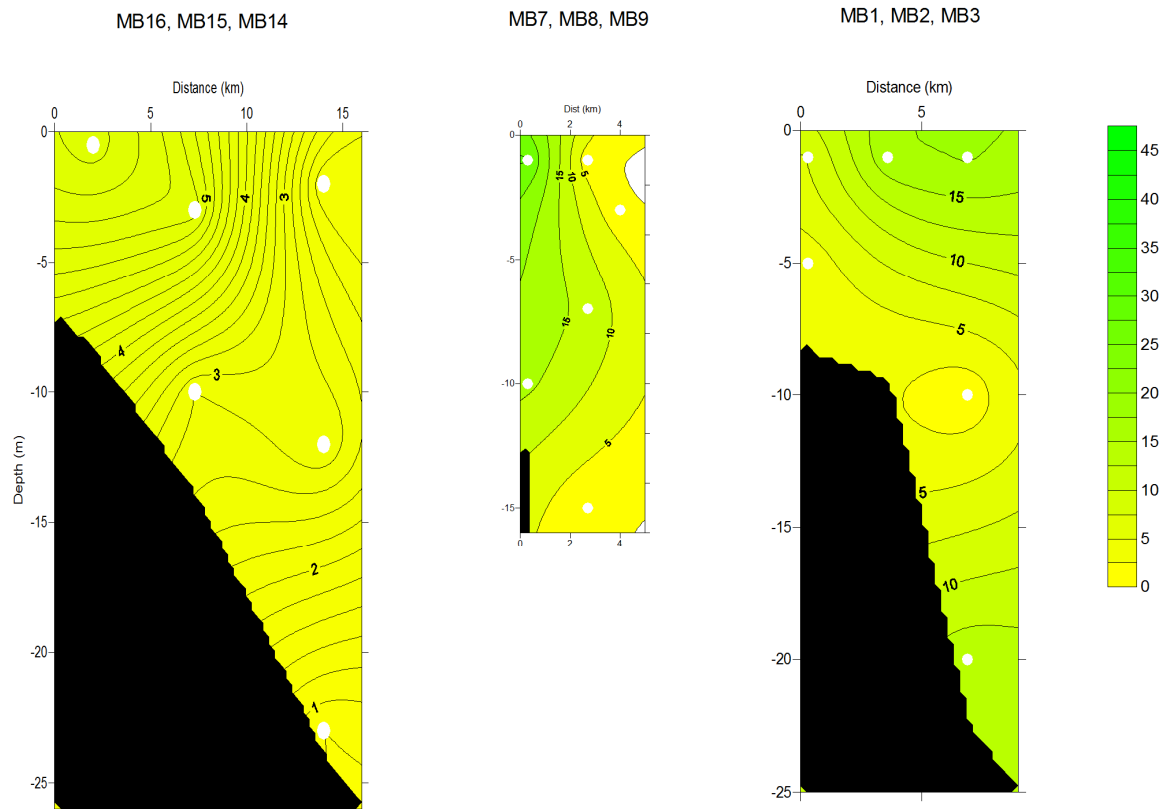


Figure 3.24b. For comparison, Chl a ($\mu\text{g L}^{-1}$) distribution derived from discrete water samples (white dots) for Boston Harbor (MB14-MB16), Cohasset (MB7-MB9), and Duxbury (MB1-MB3) transects, September 1996. Not enough data exists to display Scituate transect (Stations MB4-MB6).

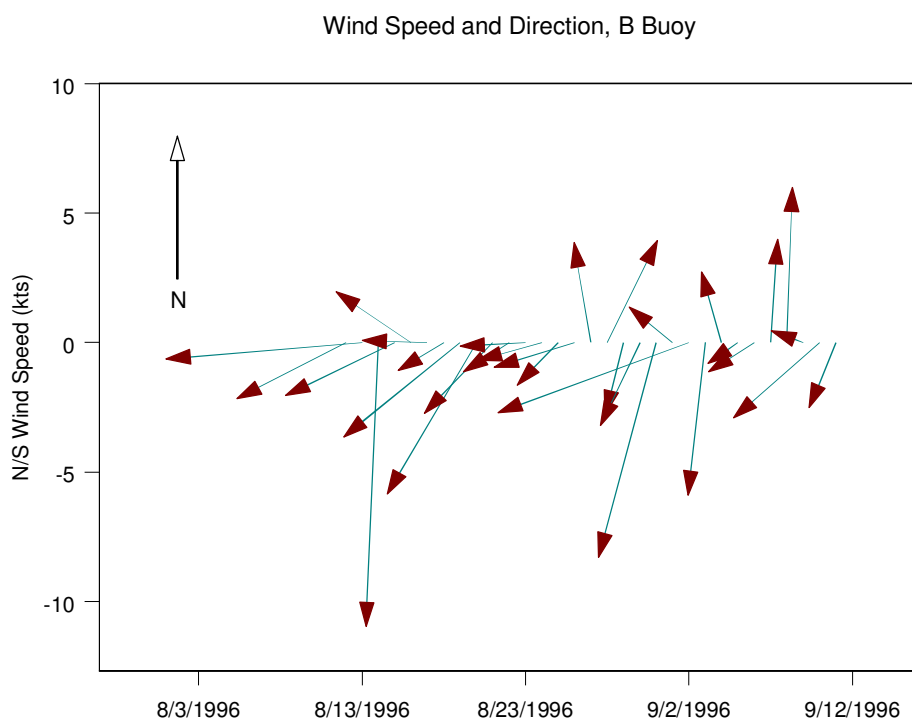


Figure 3.25. Historical wind speed (kts) and direction recorded at the Massachusetts Bay NOAA marine buoy #44013 two weeks prior to the nearshore survey.

Trace metal and ancillary data as well as station information from September 1996 are presented in Table 3.10, a-c. Total suspended matter (TSM) was typically less than 1.5 mg L^{-1} in the nearshore waters and reached 2.8 mg L^{-1} at station MB16 in Boston Harbor. Overall, Ag values were comparable in magnitude to those observed in the previous surveys. Total Ag concentrations in the surface water of the Bay ranged from a high near 270 pmol kg^{-1} at the mouth of Boston Harbor to a low of 15 pmol kg^{-1} at the furthest offshore station near Cohasset (MB9). Except for samples collected in Boston Harbor and near its mouth, Ag existed primarily in either dissolved or colloidal form ($82 \pm 7\%$). Ag filterable and particulate fraction concentrations were similar in the Boston Harbor sample (MB16),

Table 3.10a. Massachusetts Bay near shore survey, filterable (<0.4 µm) trace metal concentrations, September 1996.

Station	Depth (m)	Ag (pmol kg ⁻¹)	Pb (pmol kg ⁻¹)	Cu (nmol kg ⁻¹)	Zn (nmol kg ⁻¹)	Cd (pmol kg ⁻¹)	Fe (nmol kg ⁻¹)
MB1	1	37.3	121	5.18	8.5	223	14.4
	5	35.2	95	4.46	5.3	230	14.8
MB2	1	27.3	88	5.36	5.8	220	19.3
MB3	1	29.6	115	4.43	5.3	217	7.5
	10	39.1	252	5.78	6.1	269	15.2
	20	43.9	50	3.49	4.4	267	6.8
MB4	1	34.7	104	4.99	7.5	250	<1.3
	7	36.1	82	5.70	6.5	215	13.1
Rep.	7	39.6	81	5.47	6.9	241	12.1
MB5	1	15.4	40	2.52	2.4	209	16.1
	10	32.5	84	4.33	5.0	232	9.4
Rep.	10	29.4	61	4.38	5.6	212	9.6
	15	43.2	100	5.09	7.5	295	11.9
MB7	1	115.7	137	5.54	8.9	233	13.3
	1	121.9	139	5.80	11.1	242	14.0
	10	47.9	102	5.13	6.2	232	9.0
MB8	1	18.0	<21	2.39	1.5	209	6.5
	7	21.2	74	3.30	4.2	162	4.4
Rep.	7	31.4	83	4.57	4.5	205	5.0
	15	13.2	45	2.09	1.8	143	3.8
MB9	3	13.6	<21	2.04	2.1	193	4.4
	3	12.5	<21	2.04	1.7	187	4.1
MB10	1	52.3	107	6.46	10.5	231	8.3
	5	73.4	119	6.21	9.6	233	13.3
	15	44.1	96	4.84	6.4	224	12.7
MB11	3	53.8	91	6.34	8.6	227	8.4
	15	33.2	110	3.42	3.6	225	11.7
MB12	4	66.5	118	7.70	11.8	244	18.3
MB13	1	25.5	60	4.13	6.6	198	5.8
	15	23.4	97	2.47	4.1	221	8.4
MB14	2	18.0	42	2.43	6.8	201	30.0
	12	14.8	77	2.47	2.3	244	4.1
	23	23.6	63	3.06	6.1	300	5.1
Rep.	23	25.3	72	3.01	7.9	322	6.6
MB15	2	85.3	174	9.28	24.9	261	23.7
	10	46.3	117	5.37	11.9	225	10.3
Rep.	10	46.5	56	5.75	19.0	231	12.8
MB16	1	125.9	52	12.08	32.1	264	25.9
Rep.	1	142.1	97	11.70	30.4	268	38.9

Table 3.10b. Massachusetts Bay near shore survey, particulate ($\geq 0.4 \mu\text{m}$) trace metal concentrations, September 1996.

Station	Depth (m)	Ag (pmol kg^{-1})	Pb (pmol kg^{-1})	Cu (nmol kg^{-1})	Zn (nmol kg^{-1})	Cd (pmol kg^{-1})	Fe (nmol kg^{-1})	Al (nmol kg^{-1})
MB1	1	5.5	102	0.15	0.92	22.1	87	203
	5	6.5	110	0.22	0.96	15.2	122	403
MB2	1	15.7	96	0.36	1.71	16.6	150	353
MB3	1	9.6	54	0.23	1.51	18.8	98	245
	10	6.3	37	0.29	1.18	29.0	77	105
	20	2.3	55	0.15	0.79	7.0	108	211
MB4	1	8.4	42	0.22	1.11	21.2	53	104
	7	12.7	59	0.35	1.63	20.4	118	237
MB5	1	2.5	17	0.14	0.52	28.5	24	58
	10	4.8	48	0.19	0.90	16.1	135	289
	15	10.3	170	0.41	1.64	15.9	378	761
MB7	1	12.0	31	0.26	1.74	11.4	29	66
	10	7.7	44	0.27	1.25	12.9	108	197
MB8	1	4.2	18	0.11	0.53	16.8	20	44
	7	5.8	47	0.24	1.20	21.1	70	148
Rep.	7	6.1	45	0.31	1.61	17.0	83	125
	15	4.0	46	0.26	0.76	61.2	112	330
MB9	3	2.4	12	0.09	0.49	20.6	17	37
MB10	1	12.1	94	0.54	3.37	16.0	82	103
	5	8.0	99	0.39	2.51	14.3	101	246
	15	5.5	100	0.25	1.12	35.3	151	276
MB11	3	15.1	9	0.55	3.13	22.0	120	303
	15	12.9	167	0.39	1.48	16.4	305	635
MB12	4	29.1	21	0.63	2.79	34.9	253	554
MB13	1	6.6	33	0.21	1.39	20.3	48	79
	15	6.2	118	0.27	1.26	24.5	221	432
MB14	2	2.0	7	0.07	0.79	15.3	39	23
	12	3.4	15	0.07	0.33	9.1	22	44
	23	6.9	134	0.40	1.68	76.8	315	651
MB15	2	86.7	491	2.66	0.48	21.4	88	1967
	10	39.6	271	1.05	2.53	45.5	449	739
Rep.	10	42.5	272	1.31	2.58	17.2	393	847
MB16	1	153.2	615	4.11	9.18	76.7	1339	2889
Rep.	1	122.7	582	3.57	7.06	48.2	1270	2681

Table 3.10c. Massachusetts Bay near shore survey, station information and ancillary measurements, September 1996.

Station:	Lat. N	Lon. W	Depth (m)	Salinity PSU	TSM (mg L ⁻¹)	POC (μM)	PON (μM)	Chl a (ug L ⁻¹)	Phaeo (ug L ⁻¹)
MB1	42° 04.023	70° 37.028	1	30.881	0.93	20.0	4.40	7.6	1.7
			5	31.011	0.90	11.8	2.78	3.4	1.1
MB2	42° 05.763	70° 36.455	1	30.687	1.35	10.8	2.51	16.9	2.0
MB3	42° 07.125	70° 34.979	1	30.903	1.19	34.0	5.57	17.8	1.1
			10	30.977	0.67	32.9	5.88	0.9	0.5
			20	31.250	0.47	17.9	4.01	14.2	<0.2
MB4	42° 12.104	70° 41.868	1	30.968	0.91	7.4	1.86	7.0	0.4
			7	30.900	1.43	22.9	3.48	24.9	<0.2
MB5	42° 12.358	70° 40.718	1	31.088	0.52	34.5	5.93	1.7	0.3
			10	31.051	0.76	10.2	3.23	7.0	0.8
Rep			10	31.124		12.4	3.28		
MB7	42° 16.334	70° 44.926	15	30.956	1.12	11.9	4.71	1.3	0.9
			1	31.002	1.26	10.2	2.51	30.2	5.2
MB8	42° 16.563	70° 43.176	10	31.021	0.63	37.6	6.70	16.0	1.7
			1	31.104	0.36	19.0	4.21	1.8	0.6
			7	31.192	0.87	11.6	2.43	13.4	4.1
MB9	42° 16.578	70° 42.344	15	31.115	0.42	19.1	4.31	1.2	0.8
			3	30.924	0.47	6.9	2.16	1.6	1.7
MB10	42° 18.362	70° 45.141	1	30.930	1.76	10.7	2.13	42.7	2.1
			5	31.070	1.24	43.7	10.25	26.7	7.5
			15	30.952	0.43	25.1	6.60	3.8	1.3
MB11	42° 20.131	70° 48.411	3	31.221	1.42	8.3	2.60	36.4	6.0
			15	30.839	0.62	40.3	8.44	1.2	0.8
MB12	42° 18.704	70° 50.577	4	31.056	1.14	6.5	1.33	12.4	2.9
MB13	42° 21.294	70° 50.475	1	31.390	0.92	26.4	5.44	11.3	2.2
Rep			1	31.133		20.9	4.88		
Rep			15	31.241	0.46	25.0	7.89	1.2	0.5
			15	31.373		7.5	2.23		
MB14	42° 24.531	70° 50.240	2	30.689	1.18	16.0	4.21	2.0	<0.2
			12	30.978	0.44	8.5	1.70	3.0	1.1
			23	30.527	0.97	9.0	2.03	0.8	0.5
MB15	42° 22.556	70° 54.353	2	30.881	2.54	9.4	1.74	5.3	2.5
Rep			2	31.011				5.1	2.0
MB16	42° 20.466	70° 56.949	10	30.687	1.18	19.2	3.13	2.8	1.8
			1	30.903	2.68	14.0	2.67	5.9	3.5
Rep			1	30.977	2.97	30.5	7.33		

Surface concentration contour plots for Ag_F and Ag_P are shown in Figure 3.26, (a and b, respectively). Decreasing concentration gradients from west to east out from the Harbor and to the south into Massachusetts Bay were observed in both the Ag_F and Ag_P concentrations for this period, similar to Ag concentrations observed during the summer of 1995. It should be noted that sampling began at the Duxbury Transect and commenced in Boston Harbor, covering ~ 40 km and spanning approximately 10 hours. Significant influence of wind patterns on coastal transport processes in Massachusetts and Cape Cod Bays have been shown (Jiang et al., 2007). Interpretation of the Sept. 1996 results must be sensitive to the potential for significant tidal excursion effects. However, winds immediately prior to and during the survey were weak and southwesterly (Fig. 3.25) which generally act to reduce coastal transport (Jiang et al., 2007). Individual transect gradients of Ag concentrations are presented in Figures 3.27 and 3.28. Near vertical gradients in both the filterable and particulate Ag concentrations along the Boston Harbor Transect are similar in pattern to those observed for salinity (Fig. 3.22, first panel). Figure 3.29 shows the distribution of Ag with salinity for all samples collected during the survey. A conservative mixing plot is constructed by plotting a known chemically conservative property (e.g., salinity) against the constituents of interest. Both Ag_F and Ag_P fall below the conservative mixing line (drawn by connecting observations with the lowest and highest salinity), suggesting either important removal processes (e.g., biological uptake, particle scavenging, and particle settling) and/or that mixing is more complex than simple two end-member mixing (Loder and Reichard, 1981) between Massachusetts Bay and Boston Harbor. However, the highest Ag concentrations observed correspond to the lowest salinities found in Boston Harbor.

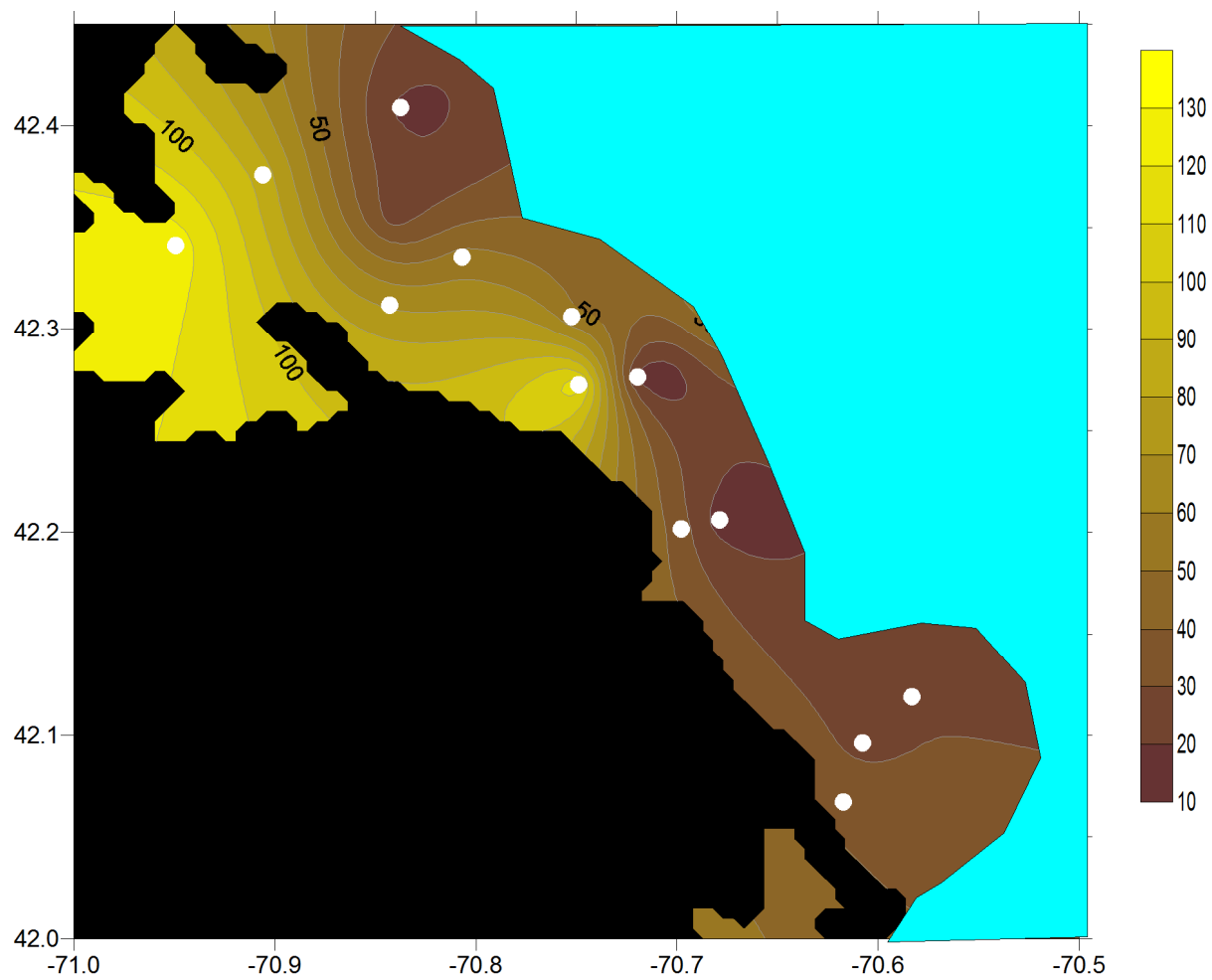


Figure 3.26a. Distribution of filterable Ag in the near shore surface waters of Massachusetts Bay, September 1996. Station locations are indicated by the white dots.

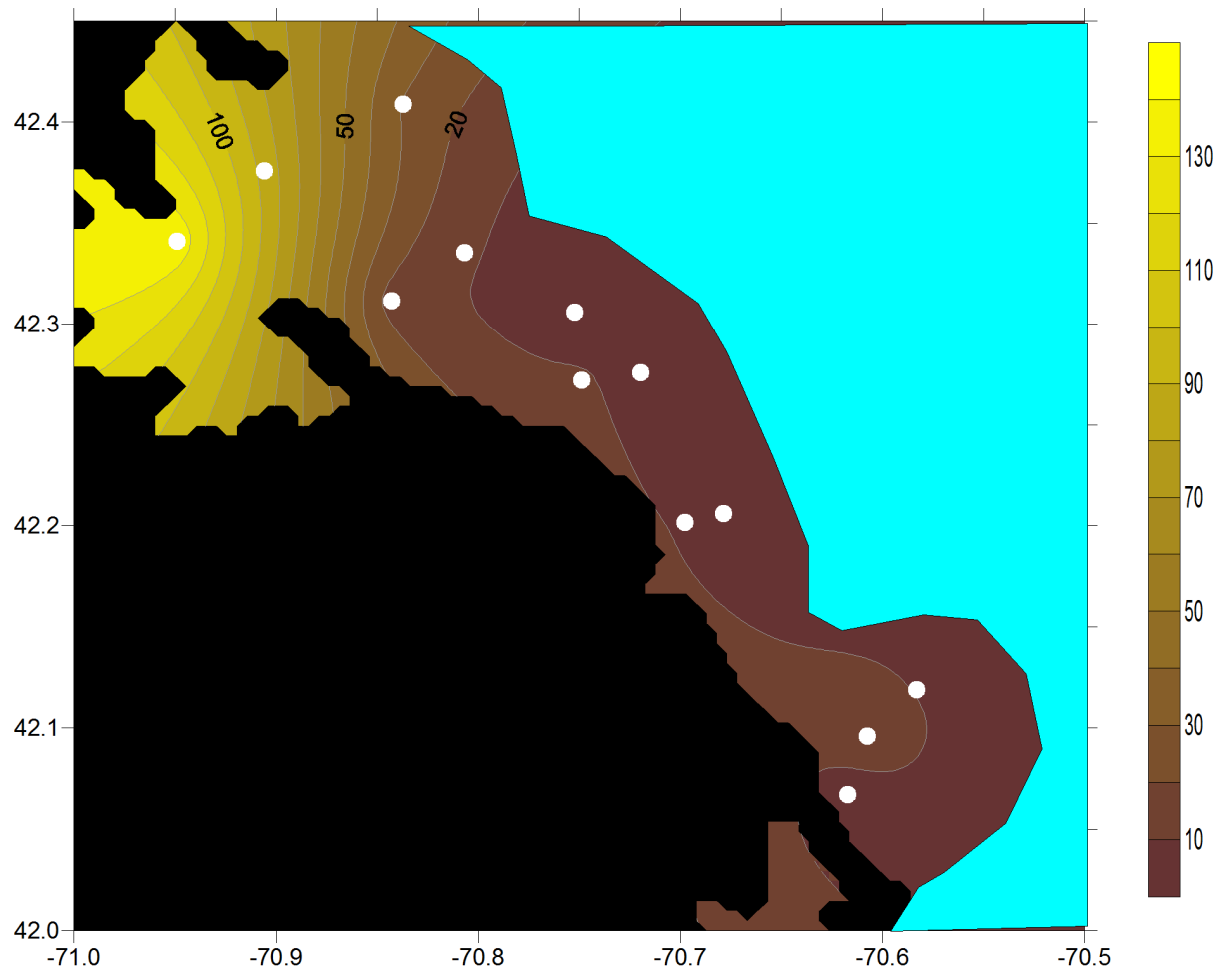


Figure 3.26b. Distribution of particulate Ag in the near shore surface waters of Massachusetts Bay, September 1996. Station locations are indicated by the white dots.

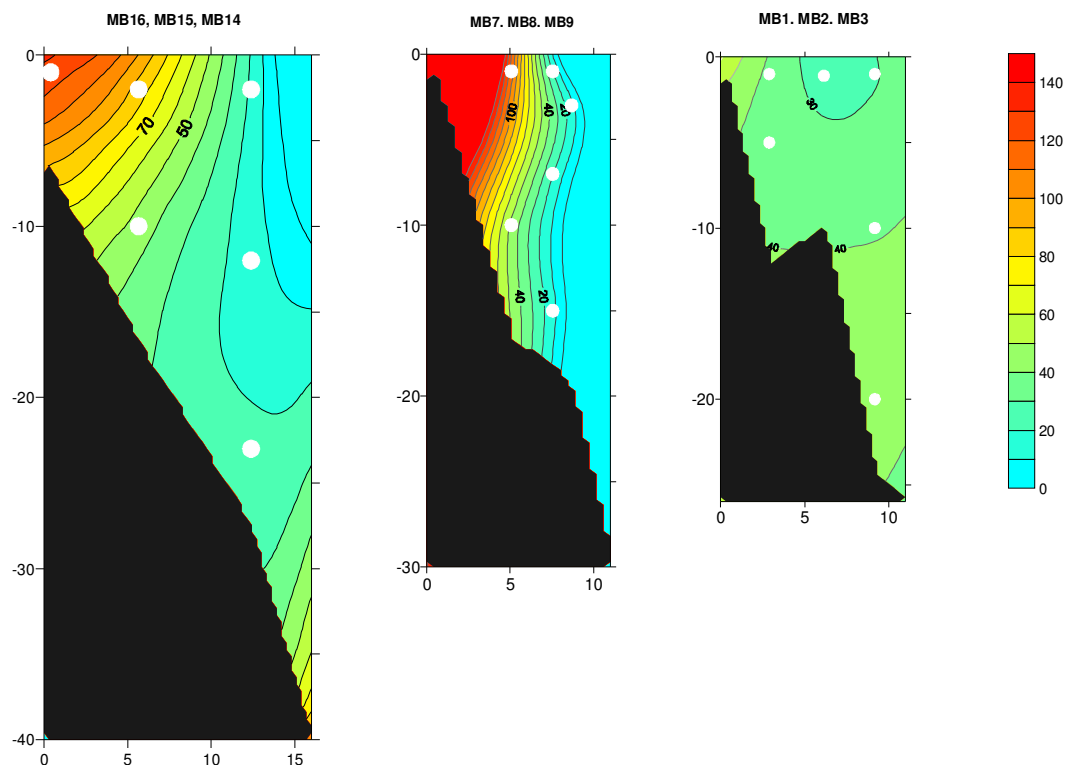


Figure 3.27. Filterable Ag (pmol kg^{-1}) distribution along the Boston (MB16, MB15, MB14), Cohasset (MB7-MB9), and Duxbury (MB1-MB3) transects, September 1996. White dots indicate locations of discrete water samples. *Note: The apparent increase in Ag in the bottom waters is an artifact of the interpolation and has no supporting data.*

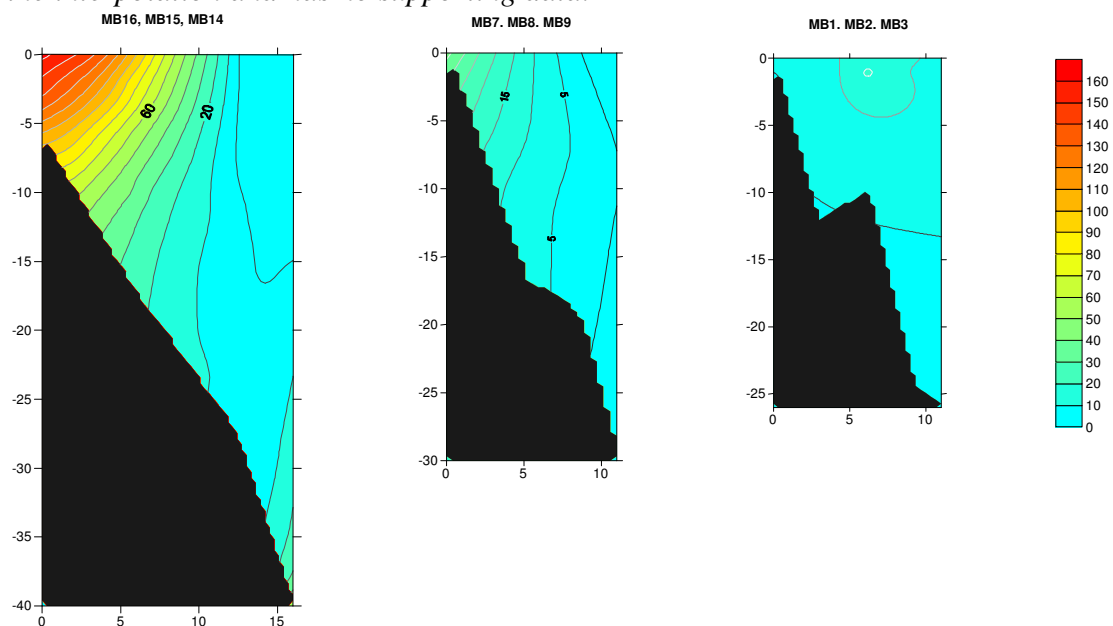


Figure 3.28. Particulate Ag (pmol kg^{-1}) distribution along the Boston (MB16, MB15, MB14), Cohasset (MB7-MB9), and Duxbury (MB1-MB3) transects, September 1996.

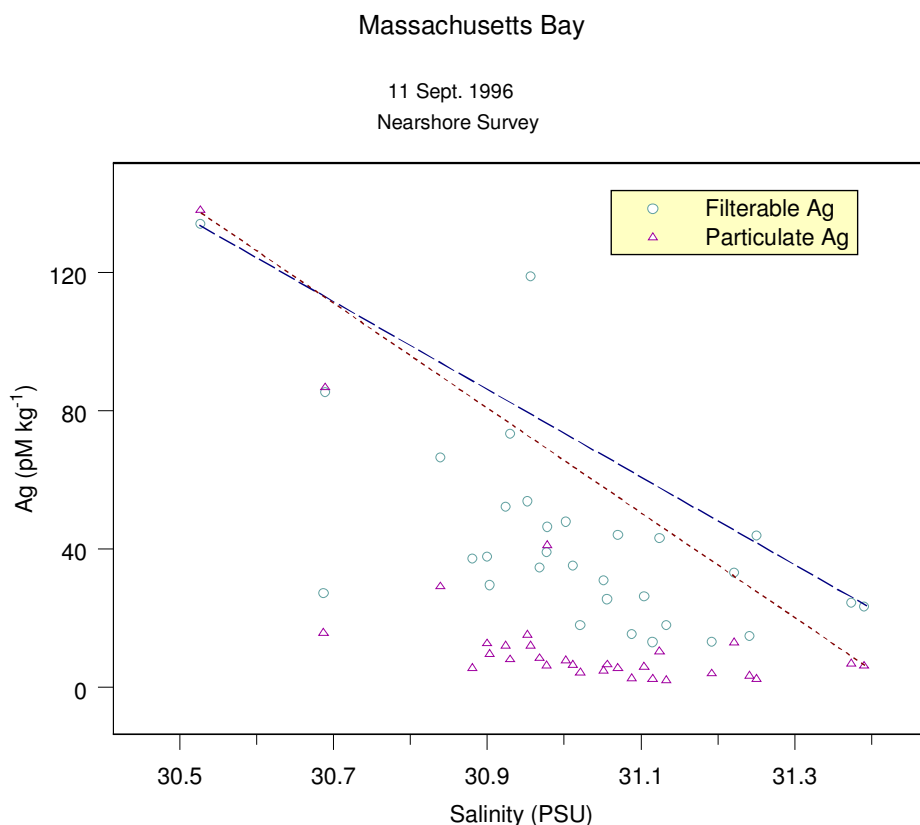


Figure 3.29. Distribution of Ag along the salinity gradient observed in all samples collected on 11 September 1996. Conservative mixing lines (constructed by connecting the observations at extremes in salinity) are also illustrated.

3.4.5 Western Gulf of Maine survey, 18 July 1996

Five stations were occupied in the southern coastal GOM above the northern boundary of Massachusetts Bay and the Merrimack River in order to (1) provide an estimate of the northern boundary conditions with respect to metal concentrations and (2) assess the contribution of metal loading to Massachusetts Bay outside the potential influence of the Merrimack River. A transect was conducted off of Portland, ME out to approximately 60 km offshore (Fig. 3.30). As discussed earlier, the waters of Massachusetts Bay are largely controlled by conditions established by the larger GOM system. However, exchange across the Massachusetts Bay/GOM boundary is difficult to generalize. Hydrodynamic models of the

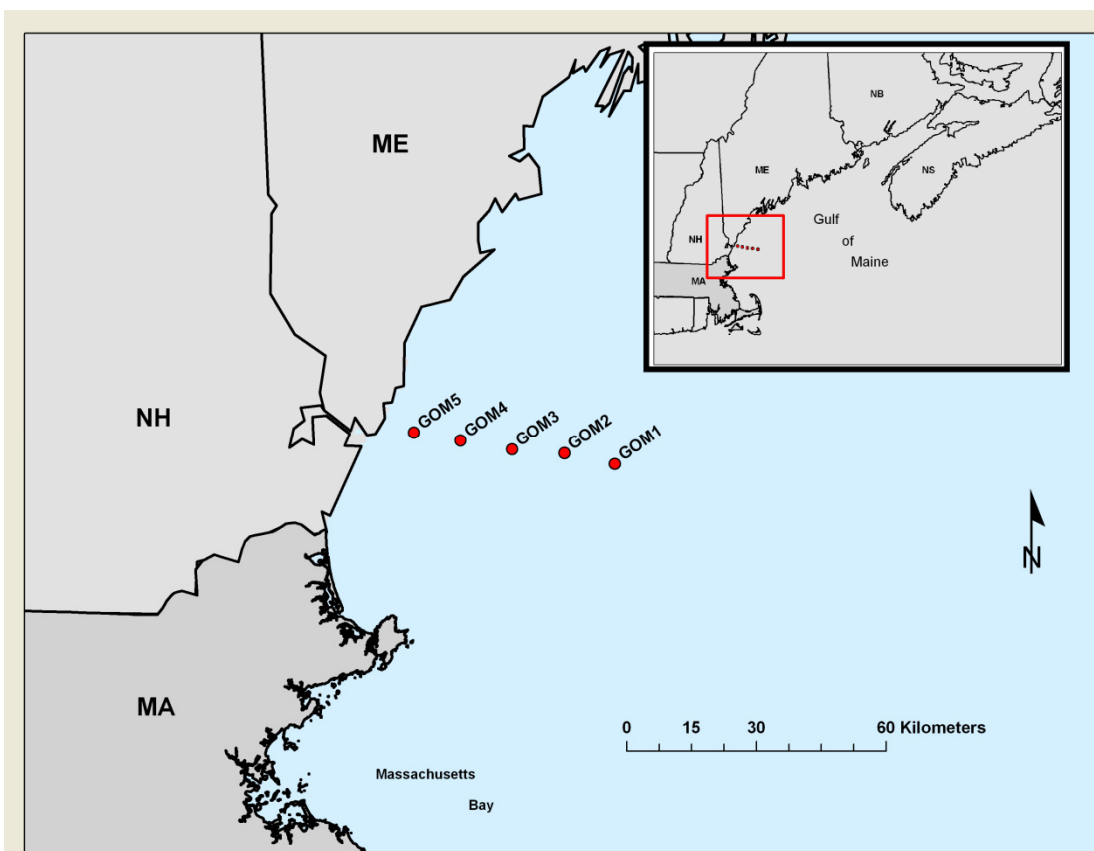


Figure 3.30. Station locations occupied during the near shore GOM transect off of Portland, ME.

Massachusetts Bays system indicate local wind patterns as important to circulation and retention of water masses within Massachusetts Bay (Jiang et al., 2003, 2007, 2008) and to transport across the boundaries.

The upper 50 meters of the water column was characterized by 20 samples collected on 18 July 1996. CTD hydrocasts were conducted, but the data were corrupted. Salinities presented here were determined on pumped discrete water samples. The complete suite of data and station information from the GOM cruise are presented in Table 3.11.

The GOM surface water was stratified with respect to salinity showing a halocline extending down to approximately 20 m by the second offshore station (Fig. 3.31). Apparent down sloping of the isoclines occurs at the margins of the transect, possibly representing shallow upwelling of

deeper 32 psu GOM surface water. Shallow coastal upwelling in the GOM is more favorable under wind conditions that have a significant southerly component. However, winds were generally light and variable, more typically between 5 and 10 knots out of the east during July 1996 (Fig. 3.32). Interpretations of observations from this survey are limited by the scales of length and depth of sampling when water column characteristics are influenced by larger scale GOM processes. Chl *a* concentrations were less than 2 $\mu\text{g L}^{-1}$ overall. Subsurface Chl *a* and TSM maxima were observed near the base of the surface mixed layer at each of the stations (Fig. 3.33) except at the 2nd inner-most station (GOM4), perhaps due to upwelling and consistent with transect isoclines. However, no significant correlations exist when POC and particulate Al are compared with TSM concentration (Fig. 3.34; Kendall's $\tau = 0.1$ and 0.3 , respectively). Thus, TSM distribution may be related as much to the continentally derived material as to biogenic particles produced *in situ*.

Table 3.11b. Gulf of Maine, Portland near shore transect, particulate ($\geq 0.4 \mu\text{m}$) trace metal concentrations, July 1996.

Station	Depth (m)	Ag pmol kg^{-1}	Pb pmol kg^{-1}	Cu nmol kg^{-1}	Zn nmol kg^{-1}	Cd pmol kg^{-1}	Fe nmol kg^{-1}	Al nmol kg^{-1}
GOM1	5	1.38	16.8	0.081	0.39	31.8	24.0	62.0
	30	1.99	22.1	0.082	0.48	30.5	64.8	139
	60	1.31	43.7	0.136	0.76	24.9	203	288
GOM2	5	1.87	13.9	0.112	0.31	25.4	21.1	38.6
	10	1.72	10.4	0.086	0.37	41.8	16.9	29.0
	20	5.73	10.0	0.089	0.48	51.4	23.9	52.0
	30	2.12	20.6	0.096	0.49	31.8	50.8	113
	60	1.14	43.7	0.143	0.71	36.7	263	735
GOM3	5	1.56	12.0	0.079	0.31	40.9	16.1	36.0
	10	1.50	10.9	0.095	0.35	33.7	15.5	30.4
	20	1.14	5.0	0.096	0.39	34.5	9.0	23.0
	35	1.30	11.0	0.068	0.27	31.7	21.1	63.4
	60	7.38	50.6	0.142	1.02	84.5	245	715
GOM4	5	1.51	15.7	0.083	0.24	39.8	26.6	53.8
	10	1.20	7.8	0.094	1.91	16.1	28.7	32.5
	20	1.16	27.8	0.120	0.46	24.1	85.4	240
	35	1.11	40.3	0.126	0.45	23.6	190	449
	50	1.52	31.5	0.126	0.83	52.1	179	405
GOM5	5	2.11	49.8	0.150	0.78	NA	106	234
	20	2.14	29.8	0.160	1.19	60.4	71.2	180

NA – not analyzed

Table 3.11c. Gulf of Maine, Portland near shore transect, station information and ancillary measurements, July 1996.

Station:	Lat.	Lon.	Depth (m)	Salinity	TSM	POC	PON	Chl a	Phaeo
	N	W		PSU	(mg L ⁻¹)	(μ M)	(μ M)	(ug L ⁻¹)	(ug L ⁻¹)
GOM1	43° 00.08	69° 59.70	5	30.800	0.34	6.3	0.9	0.31	0.09
			30	31.684	0.39	< 3.8	0.9	0.08	0.06
			60	32.022	0.40	< 3.8	0.50	0.04	0.08
GOM2	43° 01.55	70° 08.27	5	30.869	0.57	9.9	1.1	0.42	0.10
			10	31.157	0.53	7.3	1.2	0.85	0.46
			20	31.679	0.39	5.9	1.4	1.30	1.08
			30	31.919	0.41	5.6	1.5	0.31	0.32
			60	32.067	0.58	3.8	0.4	0.05	0.16
GOM3	43° 02.09	70° 17.17	5	30.882	0.38	7.1	0.9	0.28	0.09
			10	31.052	0.61	8.8	1.2	0.43	0.36
			20	31.678	0.53	9.1	1.4	1.21	0.55
			35	32.044	0.35	< 3.8	0.2	0.22	0.18
			60	32.136	0.49	< 3.8	<0.2	0.03	0.12
GOM4	43° 03.31	70° 25.90	5	30.889	0.47	7.0	0.8	0.51	0.41
			10	31.425	0.57	7.0	0.9	0.53	0.48
			20	31.737	0.55	4.9	0.5	0.26	0.22
			35	31.834	0.62	< 3.8	0.4	0.05	0.18
			50	31.886	0.42	< 3.8	0.3	0.06	0.18
GOM5	43° 04.40	70° 33.81	5	30.496	0.51	9.0	1.1	0.47	0.32
			20	31.055	0.62	21.1	3.2	1.21	0.55

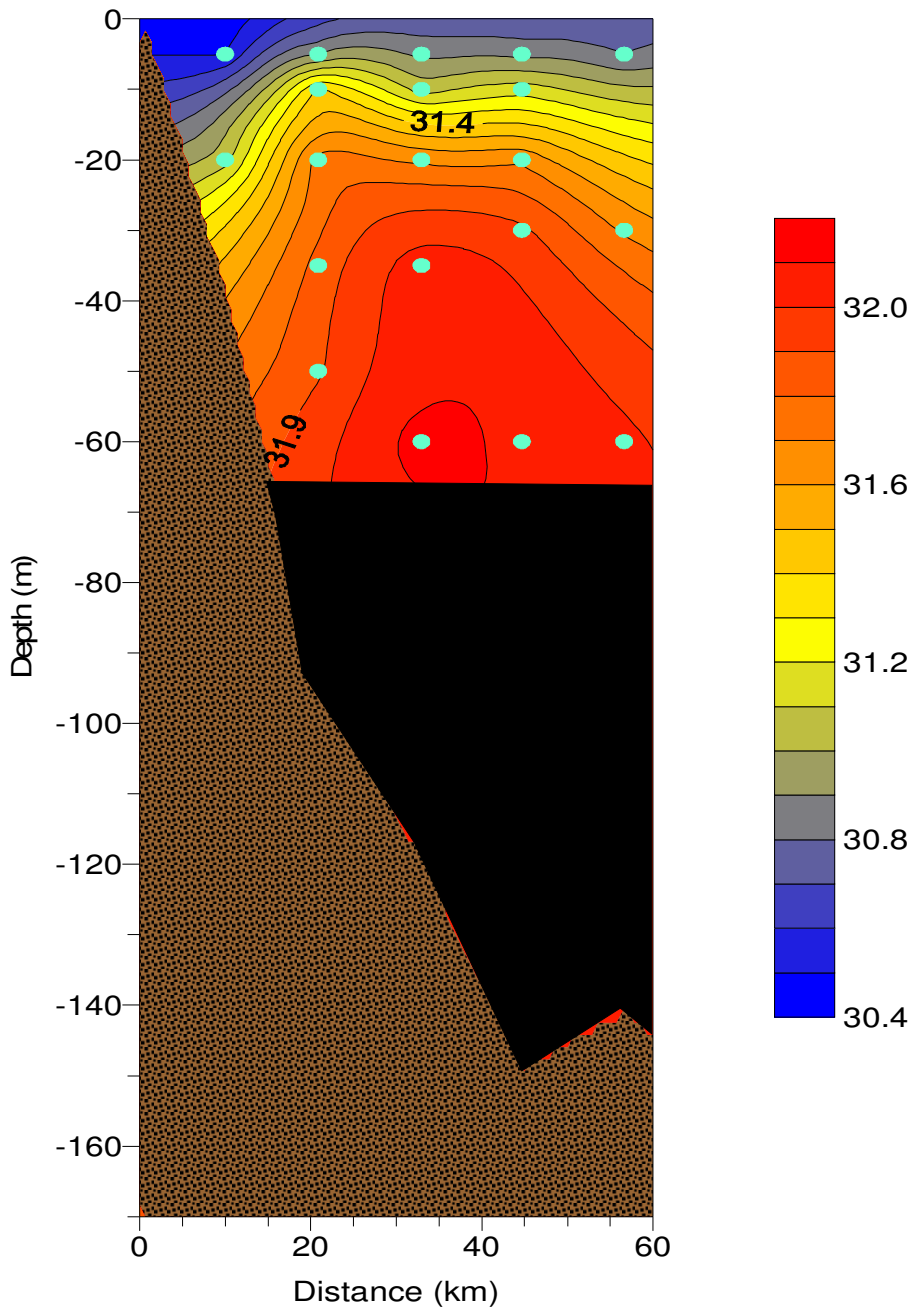


Figure 3.31. Salinity (psu) contours (derived from salinity determined on discrete water samples) in the upper water column, Portland transect, near shore Gulf of Maine, July 1996. Circles indicate depth and location where discrete water samples were collected.

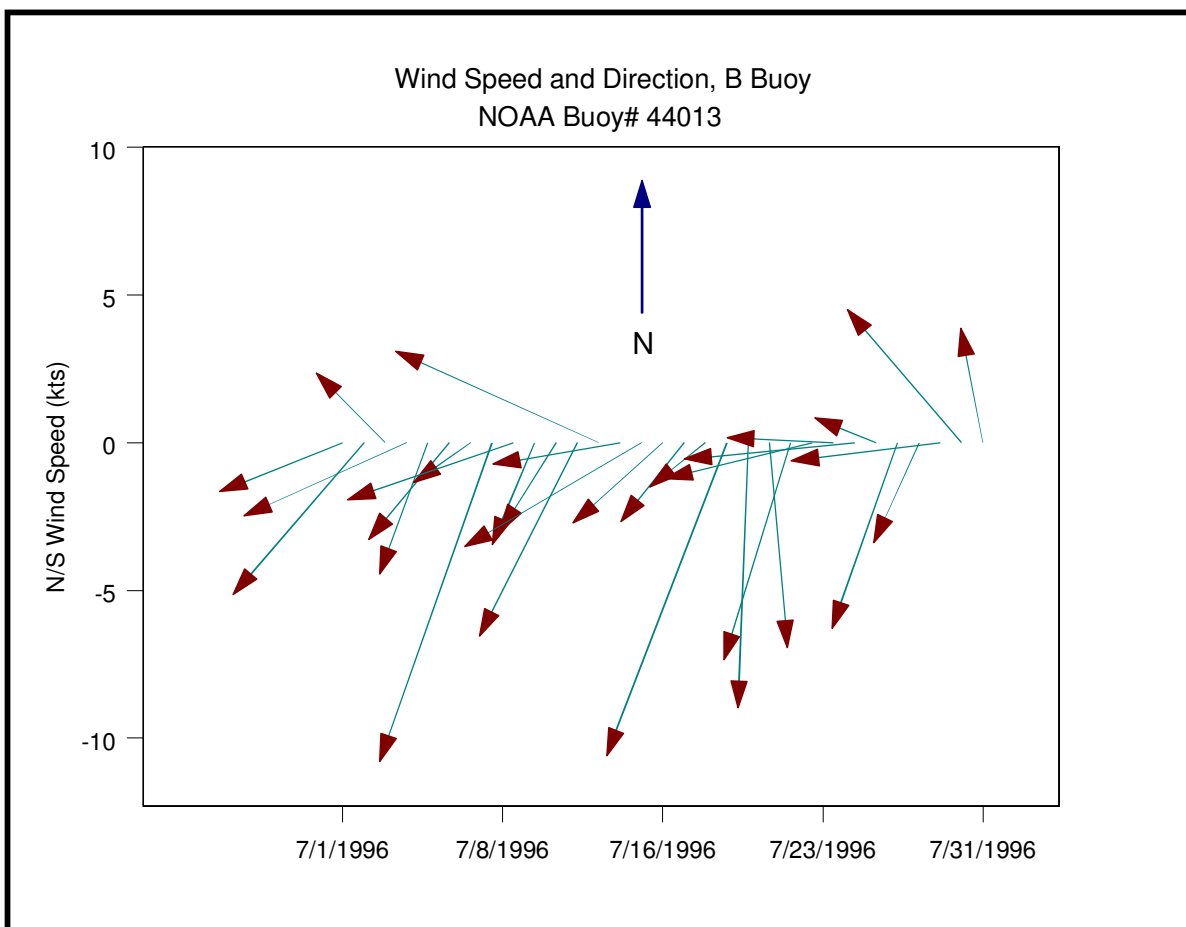


Figure 3.32. July 1996 historical wind speed and direction recorded at the NOAA marine buoy #44013 in Massachusetts Bay.

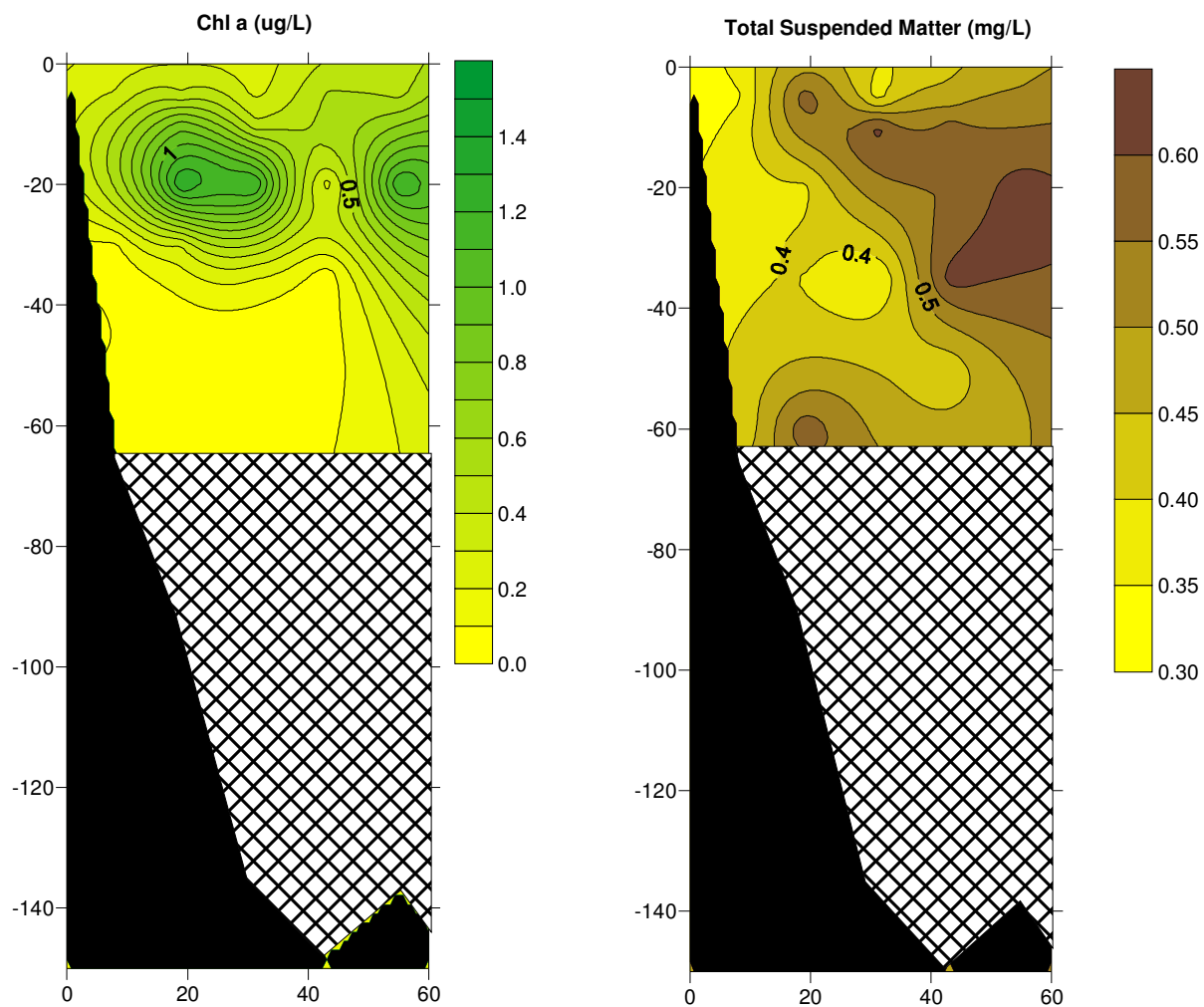


Figure 3.33. Distribution of chlorophyll a ($\mu\text{g L}^{-1}$) and total suspended matter (mg L^{-1}) in the upper water column, Portland transect, near shore Gulf of Maine, July 1996.

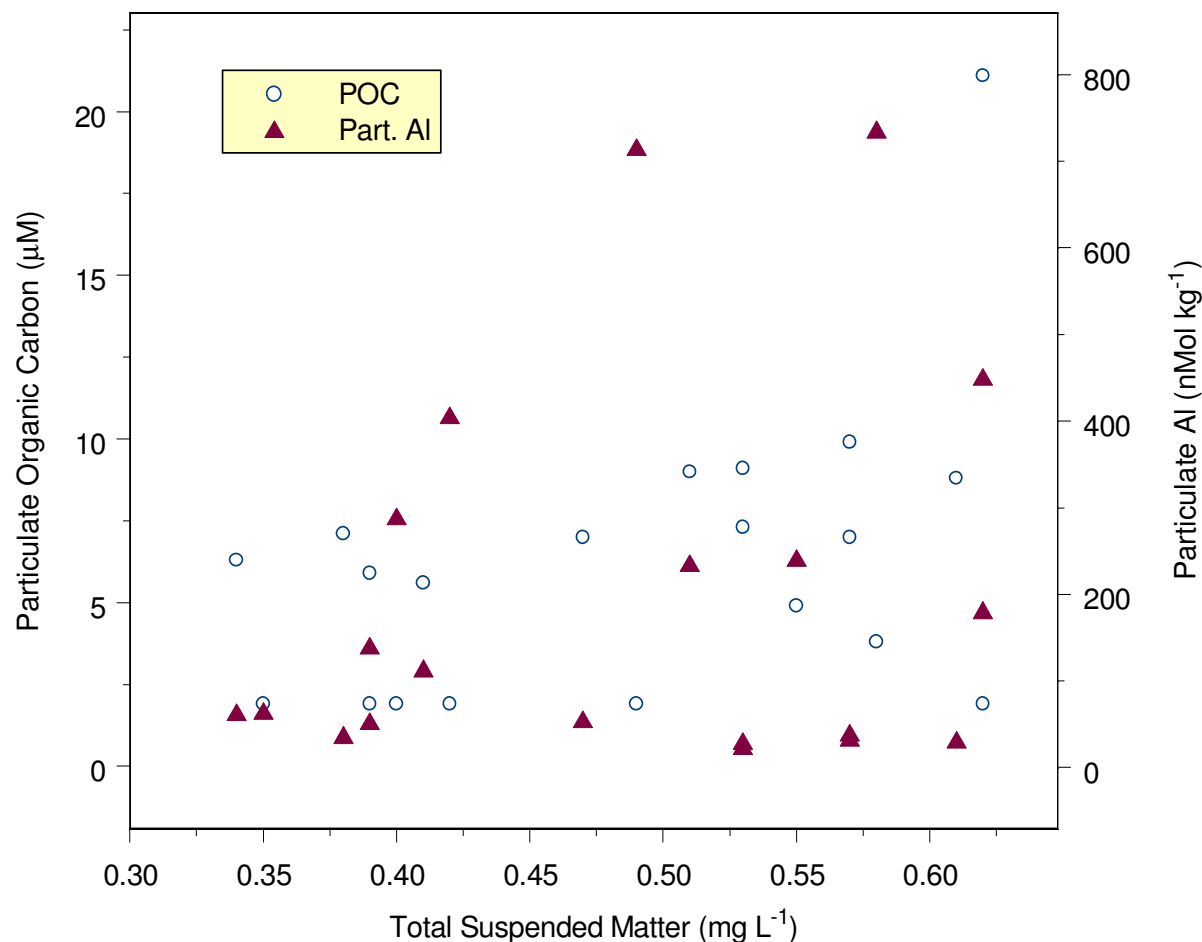


Figure 3.34. Selected relationships of particulate characteristics from parameters monitored during the Gulf of Maine Transect, July 1996.

The concentration for filterable Ag, Cu, and Pb in the surface mixed layer appears to be bimodal with a minimum near 30 m (Fig. 3.35; a,b). Particulate Fe and Al concentrations were higher below the mixed layer (Fig. 3.36). Total Ag concentrations ranged about 5 pmol kg⁻¹ (GOM3, 10 m) to about 24 pmol kg⁻¹ offshore at GOM2 (10 m depth). In all samples, most of the Ag was present in the filterable fraction ($82 \pm 8 \%$, $n=24$). Mean concentrations values for Ag, Pb, Cu, Zn, Cd, Fe, and particulate Al in the GOM waters are presented in Table 3.12.

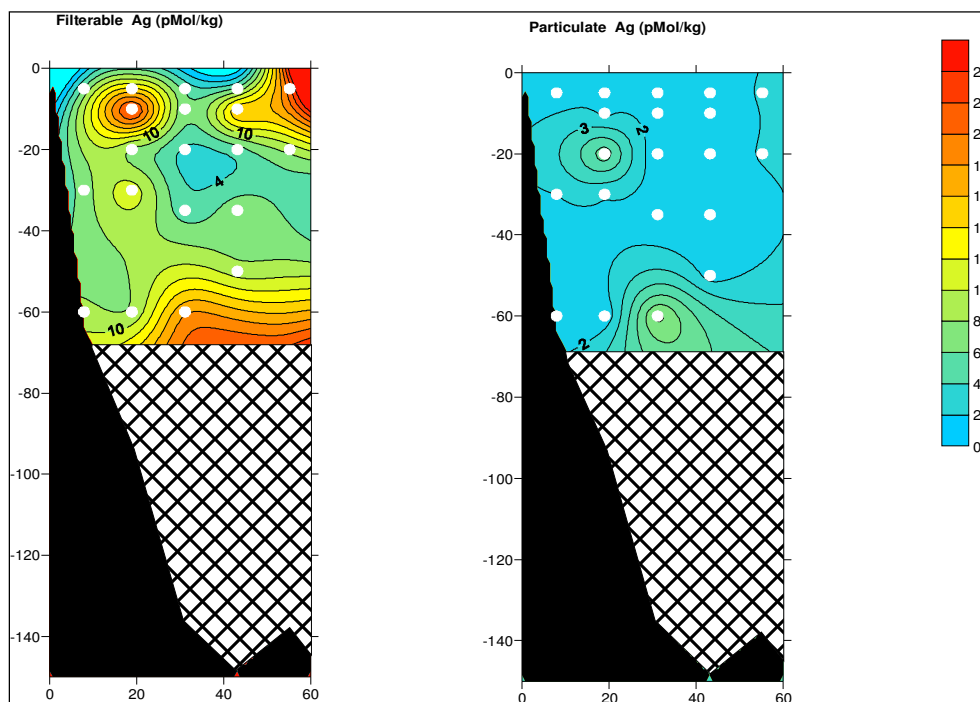


Figure 3.35a. Distribution of filterable and particulate Ag (pMol kg^{-1}) in the upper water column, Portland transect, near shore Gulf of Maine, July 1996. Circles indicate the location of discrete water samples.

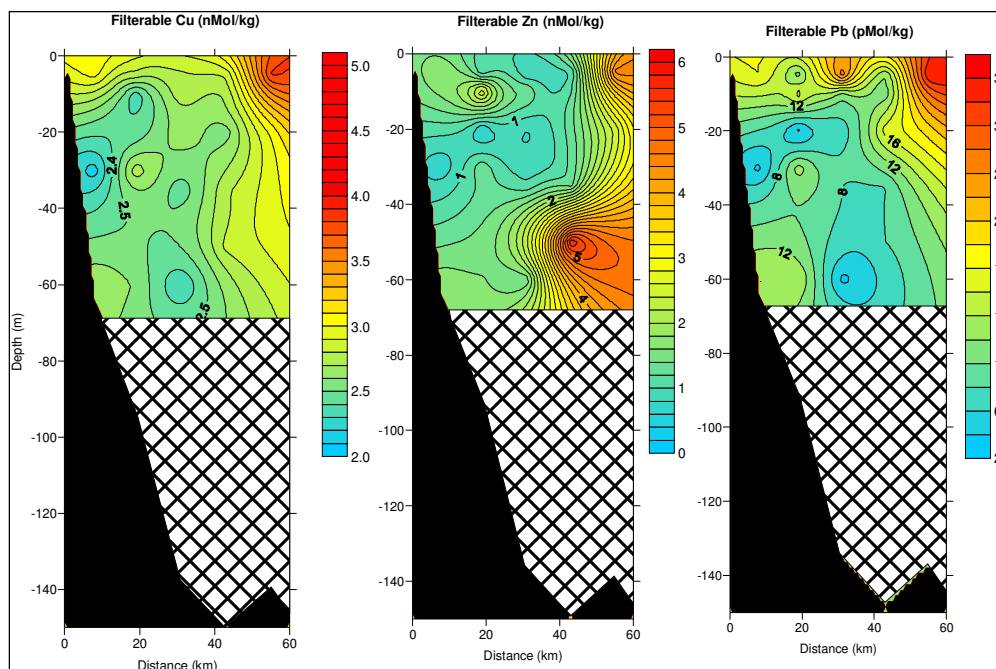


Figure 3.35b. Distribution of filterable Cu (nMol kg^{-1}), Zn (nMol kg^{-1}), and Pb (pMol kg^{-1}) in the upper water column, Portland transect, near shore Gulf of Maine, July 1996.

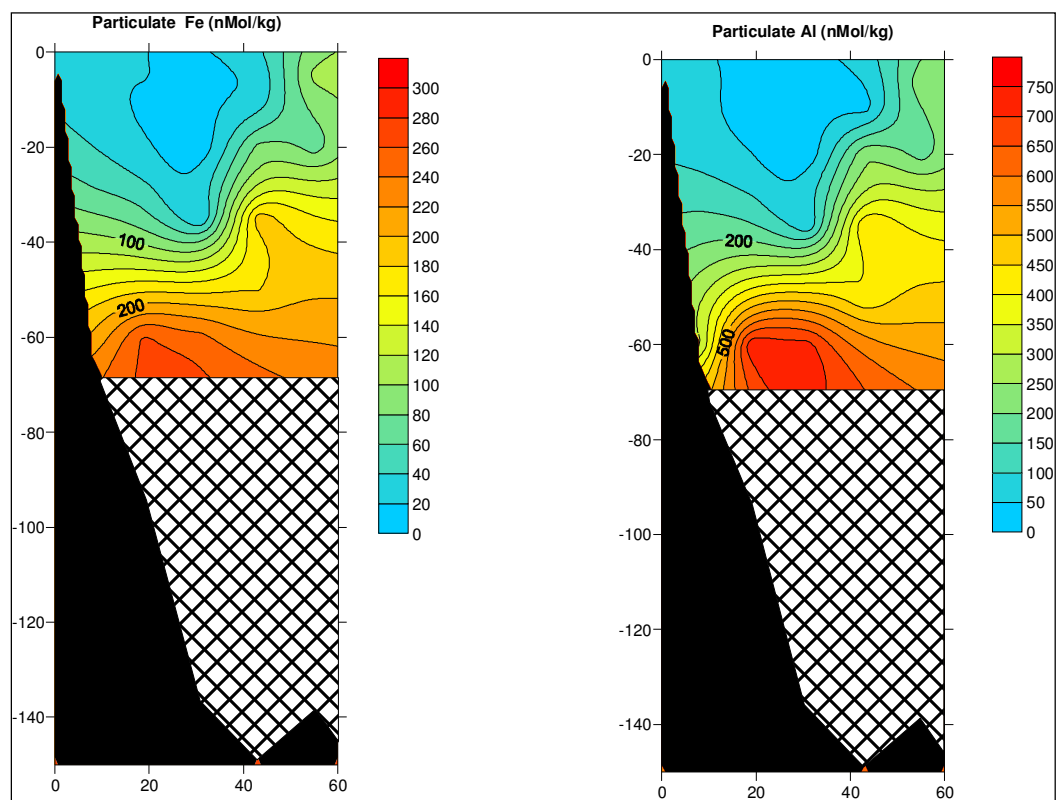


Figure 3.36. Distribution of particulate Fe and Al (nmol kg^{-1}) in the upper water column, Portland transect, near shore Gulf of Maine, July 1996.

Table 3.12. Mean values of trace element concentrations metals observed along the Portland, ME Transect in the GOM, 18 July 1996

Metal:	Ag	Pb	Zn	Cu	Cd	Fe	Mn	Al
	pmol kg^{-1}	pmol kg^{-1}	nmol kg^{-1}	nmol kg^{-1}	pmol kg^{-1}	nmol kg^{-1}	nmol kg^{-1}	nmol kg^{-1}
Filterable (STDs)	10 (6)	13 (7)	1.7 (1.2)	2.7 (0.4)	204 (26)	3 (5)	NA	NA
Particulate (STD)	2 (2)	24 (15)	0.6 (0.4)	0.11 (0.03)	39 (16)	83 (84)	8 (3)	196 (221)

3.4.6 Merrimack River and Estuary, 7 Sept. 1995

The Merrimack River's importance to salinity distributions, circulation dynamics and contaminants in the Massachusetts Bays is well documented (Butman et al., 1978 and 2002; Lynch et al., 1996; Jiang et al., 2007). The Merrimack River estuary is located to the north of Massachusetts Bay and is the largest and southern most of the primary U.S. rivers contributing to the WWC. The Merrimack River drains a historically highly-industrialized watershed and was sampled to estimate its role on the marine chemistry of Ag in the Massachusetts Bays system.

Water samples were collected in September 1995 along the salinity gradient in the Merrimack River estuary, beginning below the dam in Haverhill, MA out to the mouth of the Merrimack River in Newburyport, MA (Fig. 3.37). The distribution of Ag as a function of salinity through the Merrimack Estuary is shown in Figure 3.38. Relatively large variations in filterable Ag concentrations were observed from samples collected from the upper estuary where salinities were < 5 psu making the apparent freshwater endmember concentration for Ag_F difficult to assess. This assessment is further complicated by the approximately 4.5×10^6 m³ of wastewater daily discharged at various points throughout the estuary (Table 3.13). If the values for Ag_F and Ag_P observed in the sample with the lowest salinity (0.09 psu in ME2) is representative of the zero salinity end-member for the Merrimack River, then significant Ag input occurs within the estuary, and may be due to wastewater discharges throughout the estuary. Observed total Ag concentrations ranged from 57–192 pmol kg⁻¹ in the upper estuary and most likely reflect heterogeneity of mixing in the upper estuary. The potential of significant non-riverine input of silver to the estuary remains unclear. Conservative mixing of Ag_F in the estuary appears to occur in salinities >5 psu. Particulate Ag behaved remarkably conservative

in the Merrimack Estuary (other than at Station ME2, which had the lowest salinity), and was inversely correlated with salinity ($r^2 = 0.88$, $n = 16$).

The upper estuary was relatively more turbid with TSM levels approaching 15 mg L^{-1} (Fig. 3.39). POC concentrations co-varied with TSM ($r^2 = 0.70$, $n = 16$) and the particles were typically 11% (+/- 4, $n = 16$) organic carbon. Most of the other selected particulate metals, with possible exceptions for Zn and Cd, show removal in the estuary, (Fig. 3.40) and all of the filterable metals show some addition to the water column in the estuary (Fig. 3.41).

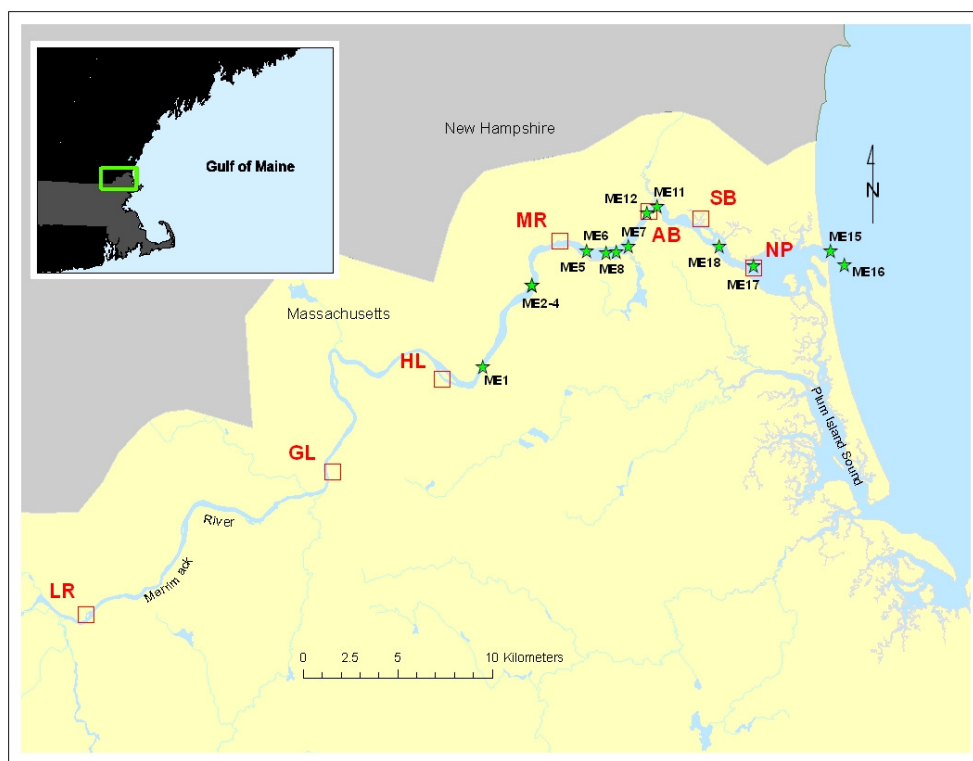


Figure 3.37. Location of samples (ME#) collected along the salinity gradient in the estuarine portion of the Merrimack River on 7 Sept. 1995. Also shown are the location of wastewater outfalls from Lowell Regional (LR), Greater Lawrence (GL), Haverhill (HL), Merrimack (MR), Amesbury (AB), Salisbury (SB) and Newburyport (NB) wastewater treatment facilities.

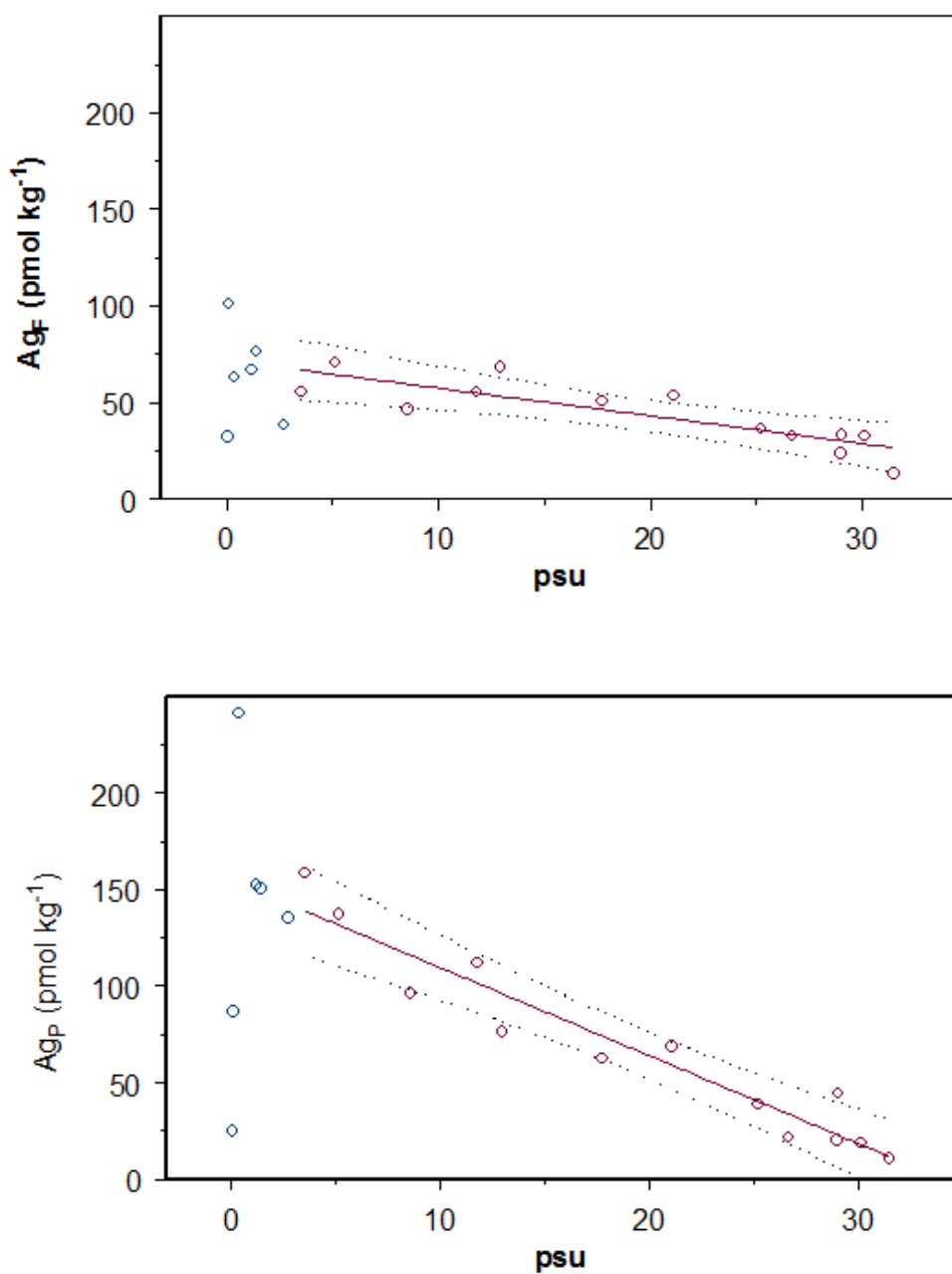


Figure 3.38. Distribution of filterable and particulate Ag with salinity along the Merrimack River Estuary, 7 September, 1995. Linear regression analyses for observations at salinities (psu > 5) were significant ($p < 0.001$) for both Ag_F and Ag_P . (99% confidence intervals are shown by dashed lines.)

Table 3.13. Wastewater discharges within the Merrimack River Estuary, from MRPC

Municipality	Discharge m ³ d ⁻¹
Haverhill	23848
Amesbury	7003
Salisbury	2082
Merrimack	1401
Newburyport	10675
Total	45008
Merrimack River [†]	18.9 x 10 ⁶

[†] 75 year Avg from USGS Gauging Station
01100000: 42° 38' 45"N, 071° 17' 56"W.

Table 3.14a. Ancillary data and station information from station occupied in the Merrimack River estuary, 7 September 1995

Station	PSU	POC	PON	TSM
	psu	(μM)	(μM)	mg/L
ME1	0.10	121.5	18.5	7.56
ME2	0.09	85.9	12.2	10.26
ME3	1.19	98.6	12.5	13.79
ME4	1.42	96.6	12.8	15.00
ME5	0.38	99.6	12.6	15.01
ME6	2.72	108.5	14.5	13.06
ME7	5.15	95.2	12.3	9.19
ME8	3.53	92.2	11.9	10.67
ME9	8.56	NA	NA	6.47
ME10	11.79	129.9	16.6	5.72
ME11	21.09	67.9	9.2	3.38
ME12	17.74	38.3	4.9	5.50
ME13	12.95	47.3	6.5	4.93
ME14	25.22	NA	NA	3.40
ME15	31.50	NA	NA	0.89
ME16	26.69	37.3	4.9	1.76
ME17	30.13	37.9	6.0	4.99
ME18	29.01	36.6	5.8	1.55
ME19	29.00	24.3	4.0	2.12

NA-not analyzed, sample lost.

Table 3.14b. Selected filterable (<0.4 µm) trace metals observed in the Merrimack River estuary, 7 September 1995.

Station	Ag	Pb	Cu	Zn	Cd	Fe
	pmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	pmol kg ⁻¹	nmol kg ⁻¹
ME1	100.8	1.35	33.1	104.7	303	330
ME2	31.9	0.69	21.1	48.0	168	141
ME3	66.8	0.72	30.5	60.3	243	132
ME4	75.9	0.79	32.2	65.5	279	119
ME5	63.2	0.75	28.0	59.7	220	124
ME6	38.3	0.46	18.2	41.0	162	56
ME7	70.3	0.57	30.2	59.5	289	83
ME8	55.1	0.58	27.4	62.2	278	75
ME9	46.3	0.49	26.6	56.2	309	65
ME10	55.6	0.47	28.7	53.2	355	97
ME11	53.4	0.55	20.1	43.2	327	197
ME12	50.5	0.47	21.4	49.1	340	113
ME13	68.0	0.52	25.3	55.0	345	102
ME14	36.4	0.49	23.9	47.4	553	143
ME15	13.0	0.07	4.3	7.0	226	38
ME16	32.6	0.21	10.5	20.2	284	59
ME17	32.3	0.12	8.0	10.7	300	65
ME18	33.0	0.13	8.5	13.8	290	89
ME19	23.3	0.18	9.4	17.2	326	96

Table 3.14c. Selected particulate trace metals ($\geq 0.4 \mu\text{m}$) observed in the Merrimack River estuary, 7 September 1995.

Station	Ag	Pb	Cu	Zn	Cd	Fe	Al
	pmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	pmol kg ⁻¹	umol kg ⁻¹	umol kg ⁻¹
ME1a	86.7	3.40	4.1	167.7	1748	3.01	3.60
ME1b	96.1	3.45	4.1	164.6	632	3.04	3.65
ME1c	91.3	3.40	4.4	155.1	311	3.15	3.76
ME2a	24.7	0.49	5.9	30.2	414	2.84	4.84
ME3a	152.3	7.93	9.5	45.7	377	6.10	10.64
ME4a	150.3	9.45	11.8	64.6	320	8.12	16.06
ME5a	241.1	9.54	11.3	54.5	362	8.52	15.96
ME6a	135.1	7.59	10.0	53.9	352	6.19	12.54
ME6b	179.4	7.91	9.2	56.3	311	5.26	13.58
ME7a	137.0	8.18	7.3	43.8	281	3.57	9.50
ME8a	158.2	6.82	7.1	48.2	240	4.18	9.93
ME9a	96.2	3.93	5.3	27.8	282	2.48	5.55
ME9b	111.3	3.99	6.1	32.0	207	2.77	6.94
ME10a	112.1	4.28	5.0	26.8	196	2.56	5.55
ME11a	68.6	3.06	3.7	13.3	119	2.17	5.66
ME12b	62.4	2.26	3.2	13.9	262	1.86	4.59
ME13	75.9	2.81	4.5	1.9	111	2.10	4.31
ME14	38.8	1.88	2.4	8.0	65	1.55	3.99
ME15	10.7	0.57	0.6	2.6	46	0.73	2.30
ME16	21.7	0.96	1.3	4.3	73	0.81	1.69
ME17	18.6	0.89	1.3	3.8	78	0.77	2.19
ME18	44.5	0.93	1.2	3.6	42	0.76	2.03
ME19	20.0	1.01	1.4	4.3	144	0.86	2.34

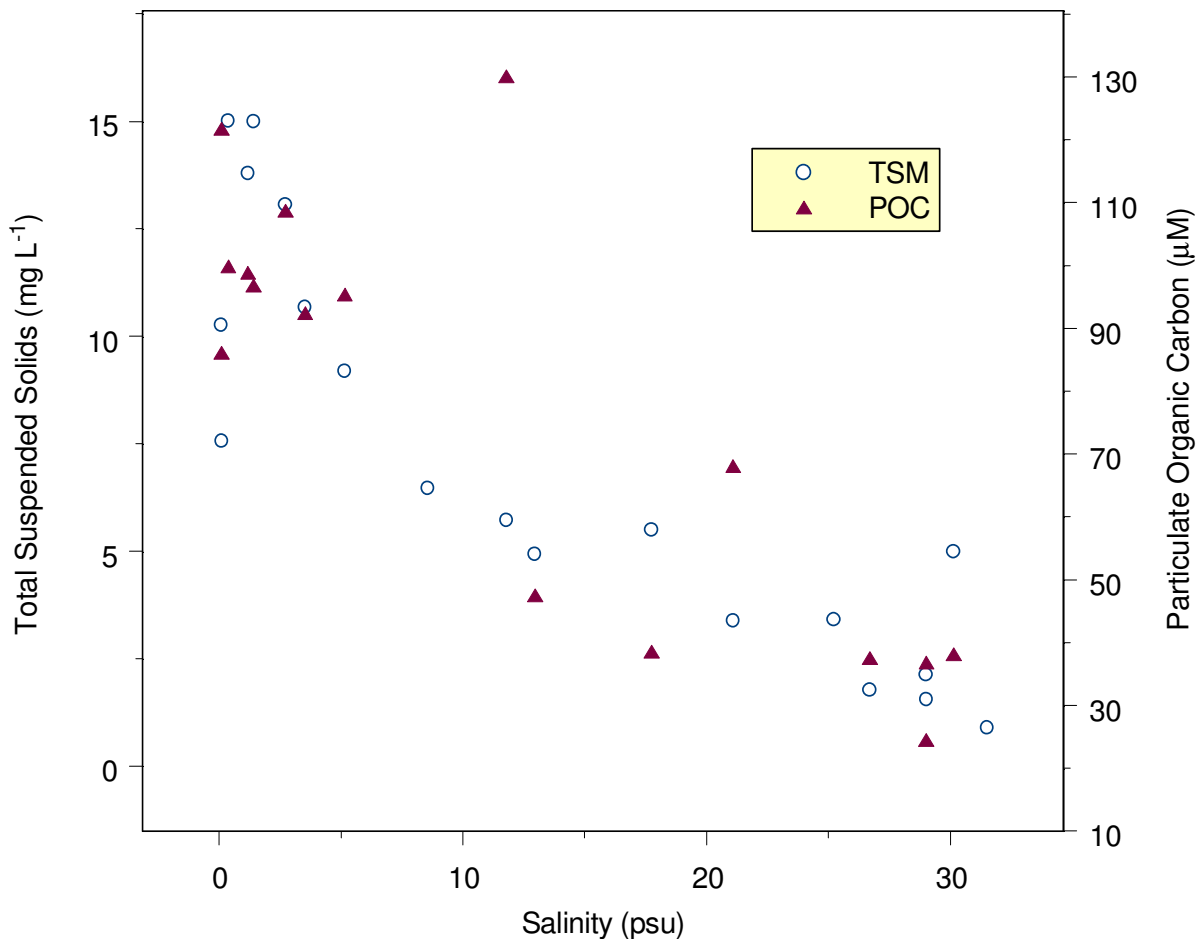


Figure 3.39. Distribution of total suspended matter (TSM) and particulate organic carbon (POC) along the Merrimack River Estuary, 7 September, 1995.

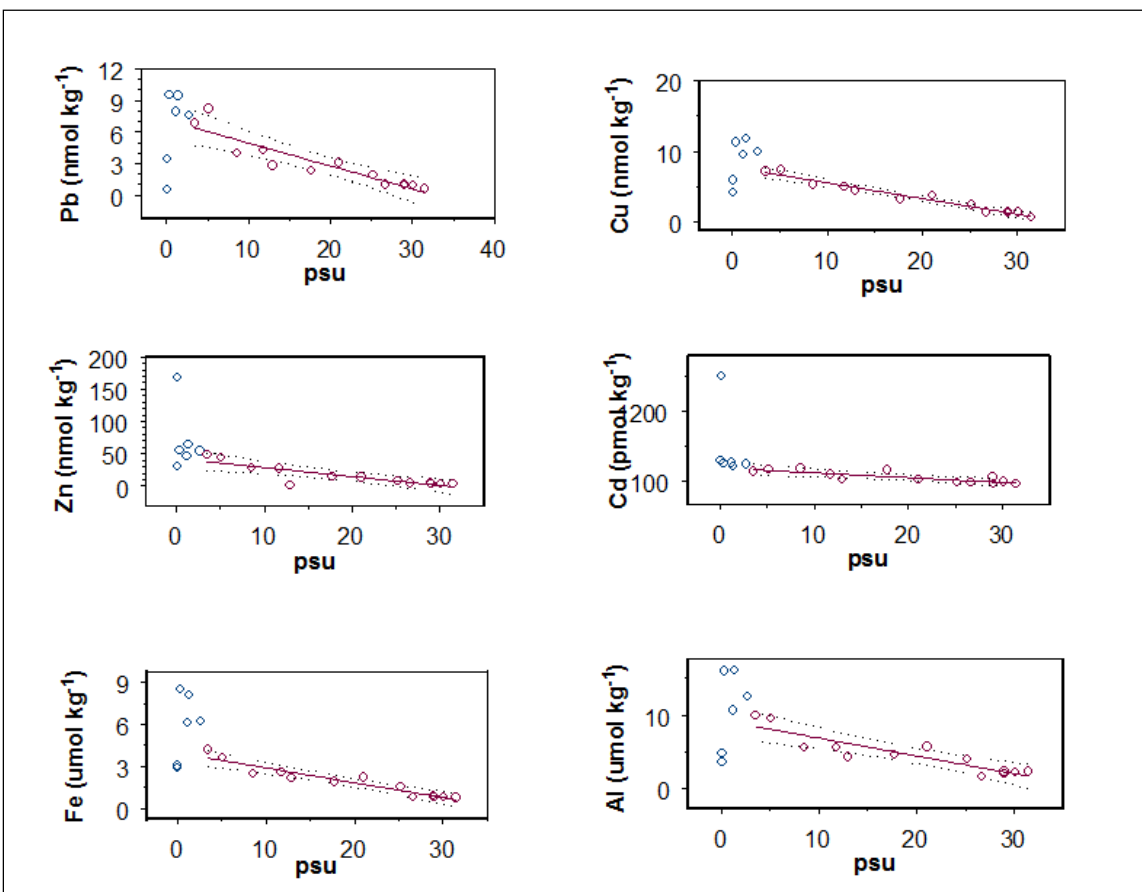


Figure 3.40. Distribution of selected particulate metals with salinity along the Merrimack River Estuary, 7 September, 1995. Linear regression analyses for observations at salinities (psu > 5) were significant ($p < 0.001$) for all particulate metals evaluated. (99% confidence intervals are shown by dashed lines.)

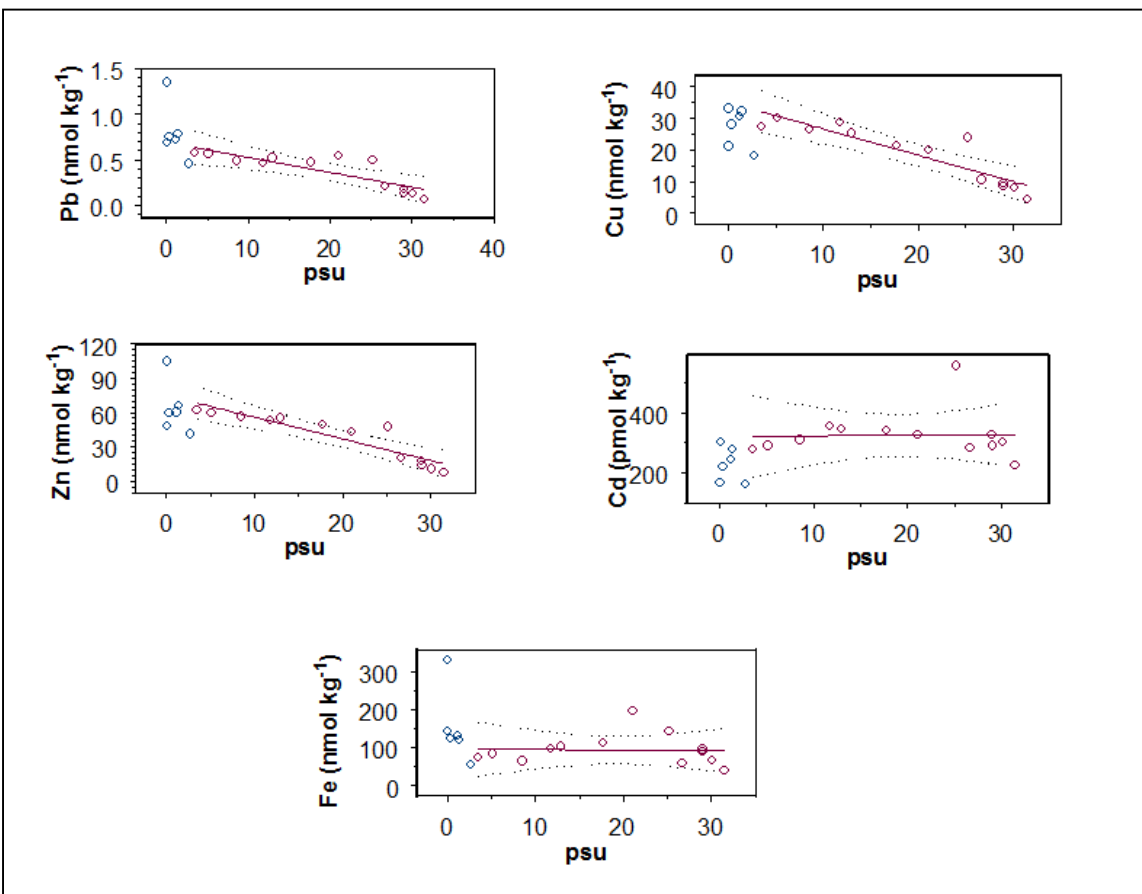


Figure 3.41. Distribution of selected filterable metals with salinity along the Merrimack River Estuary, 7 September, 1995. Linear regression analyses for observations at salinities (psu > 5) were significant ($p < 0.001$) for Pb_F, Cu_F, and Zn_F. (99% confidence intervals are shown by dashed lines.)

3.5 Discussion

3.5.1 Silver as a tracer for wastewater fate and dispersion in the Massachusetts Bays

Metal-salinity relationships may be useful for providing insight into source strengths of water borne contaminants to coastal waters. The greatest source of wastewater to the Massachusetts Bay at the time of this study originated from the municipal discharge near the mouth of Boston Harbor (See Figure 3.1). Previous physical surveys (Bumpus, 1973) and models (e.g., Signell, 1992) suggest that much of the material introduced into Massachusetts

Bay from Boston Harbor are constrained within a transition zone near the mouth of Boston Harbor and transported predominantly south into Massachusetts and Cape Cod Bays. Mixing in the western portion of the Bay and Boston Harbor is dominated by tidal forces, wind stress and river inflow (Geyer et al., 1992, Butman, 1976, Jiang and Zhou, 2003). Surface water residence times in the bay waters adjacent to Boston Harbor are therefore expected to be much less than the mean residence time of 20-45 days reported by Geyer et al. (1992) for Massachusetts Bay.

From the August 1994 survey results, high correlations of silver and other trace metal concentrations with salinities were observed among the samples collected in the nearshore waters (≤ 31.6 psu) adjacent to Boston Harbor (Fig. 3.42, Table 3.15). The 31.59 psu demarcation among the Ag-salinity data emerged from regression tree models (see Appendix A.2). Simple linear regression of silver and salinity yielded significant correlations ($r^2 = 0.91$ and 0.995 , $n=5$, for Ag_F and Ag_P , respectively), suggesting relatively simple two end-member mixing occurred between Boston Harbor and Massachusetts Bay in a region extending out to approximately 20 km at the time of sampling. Because of silver concentrations observed in the lower salinity water at depth (8 and 18 m), the BO3 station appears to have been within this mixing zone. With the exception of Pb, the high percentage of common variance (r^2) observed for the particulate metal-salinity relationships in this region suggest that settling of particles is minimal. Typical settling velocities for fine particles are on the order of $0.5 - 1 \text{ m d}^{-1}$ (La Roux, 2004). Water column settling is typically 1st order for particles. Therefore, in order to display the apparent linear relationship with salinity, mixing processes must overwhelm settling losses of fine particulate material in the water column. From the range in water column depth for this

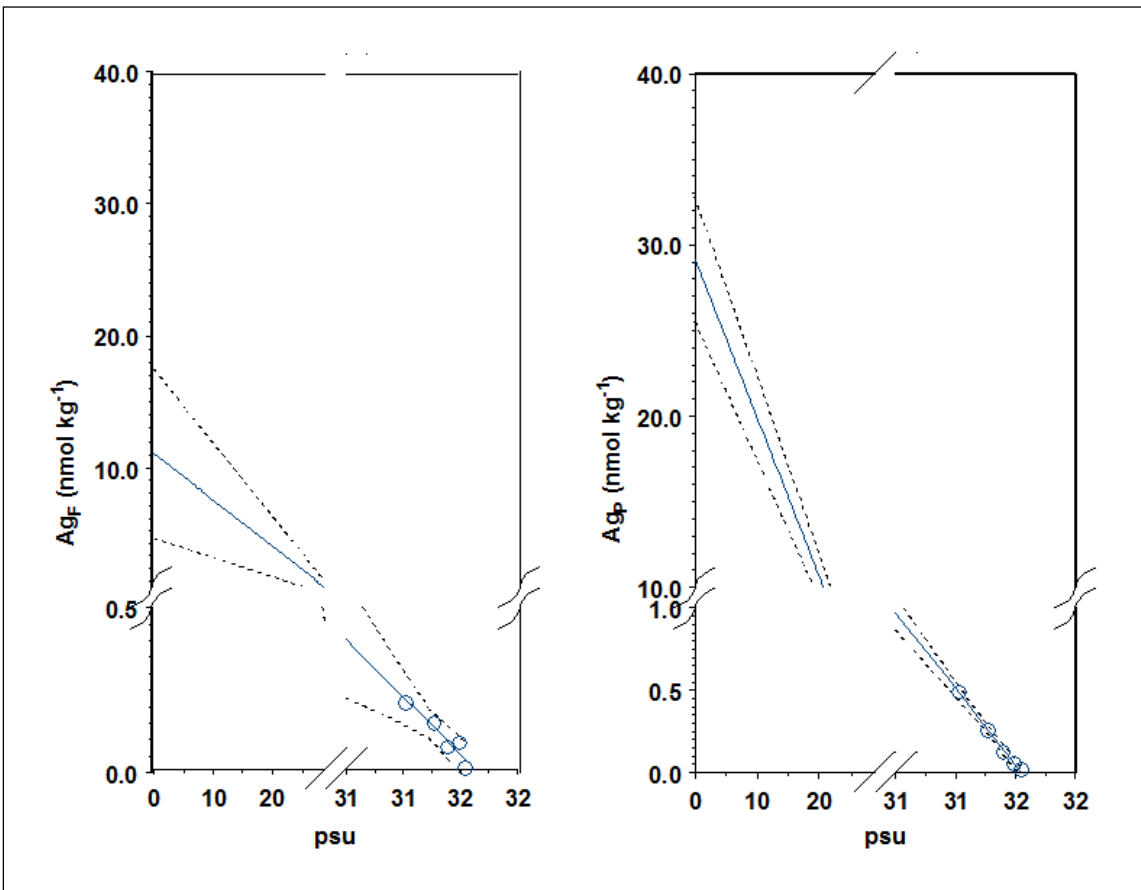


Figure 3.42. Fresh water end member silver concentrations (filterable and particulate) derived from linear regressions of metal-salinity relationships (from samples with salinities < 31.6 psu) during the Boston Harbor – Stellwagen survey, Aug. 1994. The dashed lines represent 95% confidence intervals. (Note: actual axis breaks).

Table 3.15. Squared correlation coefficients (r^2) from linear regressions of selected metals-salinity relationships for all Boston Transect samples (Aug. 1994) with salinities ≤ 31.6 psu. (n=5).

	Ag	Pb	Cu	Zn	Cd	Fe	Al
Filterable	0.908	0.792	0.861	0.928	0.000	0.968	NA
Particulate	0.995	0.454	0.981	0.967	NA	0.946	0.920

NA – not analyzed,

region (10-40 m), the particulate metals concentration data support estimates of mixing for Boston Harbor water with Massachusetts Bay to be on the order of several days.

Extrapolation of regression lines and respective 95% confidence intervals from the linear regression analyses of metal concentrations with salinity in Boston Harbor samples (< 31.6 psu) to 0 psu are used to estimate the apparent fresh water end member Ag concentrations. The zero psu endmember represents a composite of the freshwater sources draining into Boston Harbor (e.g. Fig. 3.42, Table 3.16). The apparent zero end member concentrations are within the order of magnitude of metal effluent concentrations reported by MWRA for the study period data (Excel files from Maury Hall, MWRA, 2004) though zero end member extrapolations tended to be higher than those reported for the MWRA effluent. This difference may be due, in part, to differing methods used to determine total metal concentrations (particulate, colloidal, and dissolved fractions). For instance, the particulate metal concentrations reported here are derived from the LTA technique described earlier which may be more effective at extracting of metals from water column particle samples than techniques used for reported total effluent metal concentrations. Superior recoveries of the LTA method could translate into moderately greater loading estimates and probably better reflect a truer estimate of wastewater load. It is unlikely that other water-borne sources of Ag to Boston Harbor during the study period were important, since the MWRA effluent is estimated to be nearly 40% of the total freshwater to Boston Harbor (Stolzenbach and Adams, 1998). The other freshwater sources (e.g., Charles and Neponset Rivers) are unlikely as “other” sources since these would then need to have metal concentrations in excess of the

MWRA effluent concentrations in order to account for the difference between values reported by MWRA and the higher concentration values derived from linear interpolations of metal-salinity observations reported here (bottom of Table 3.16).

Table 3.16. Boston municipal wastewater total metal concentrations from (a) both flow and load data reported by the Massachusetts Water Resources Authority for the months surrounding field surveys of this report and (b) from extrapolation by linear regression to 0 psu from observed metal-salinity relationships in lower salinity samples (psu < 31.6) from nearshore waters of Massachusetts Bay, August 1994. Included are apparent freshwater end member concentrations. Standard error is provided in parentheses. NS: regression not significant at $p = 0.01$.

	Silver (nmol/Kg)	Lead (nmol/Kg)	Copper (umol/Kg)	Zinc (umol/Kg)
(a) MWRA loading data				
Jul 94	27	72	1.3	1.6
Aug 94	24	63	1.1	1.4
Feb 95	24	37	0.9	1.1
Jun 95	30	45	1.1	1.3
Jul 95	33	49	1.2	1.4
Aug 96	34	52	1.1	1.2
Sep 96	28	43	1.0	1.0
Mean:	29 (4)	51 (12)	1.1 (0.1)	1.3 (0.2)
(b) Apparent zero salinity end member extrapolation				
Filterable	11 (2)	10 (3)	1.0 (0.2)	1.7 (0.3)
Particulate	29 (1)		0.7 (0.1)	1.6 (0.2)
Total:	40 (3)		1.7 (0.3)	3.3 (0.5)

[†]NS=Regression not significant

Relationships of metal concentrations with salinity were also examined from the Feb 1995 winter surface water samples from Massachusetts Bay (see Table 3.8c) to assess mixing and transport between Boston Harbor and Cape Cod Bay. Of the metals analyzed, the Feb. 1995 metal-salinity relationships revealed linear relationships ($p < 0.01$, $n=9$) for the filterable fraction of Ag (slope = -135 ± 31) and Cu (slope = -8.6 ± 1.7), as well as particulate Al (slope = 4067 ± 1039). Extrapolation of these regressions to 0 psu gave results for $Ag_F = 4.4$

(± 1.0) nmol kg⁻¹ and Cu_F = 0.28 (± 0.05) μ mol kg⁻¹. Assuming a sole source of silver (in this case Ag_F) from MWRA effluent to Boston Harbor and conservative mixing, a dilution factor for wastewater in the sampled Massachusetts Bay region (i.e., Boston Harbor south into Cape Cod Bay, see Fig.3.7) is on the order of 70 – 80%. However, if significant sources for Ag to this region exist elsewhere (e.g., Merrimack River, atmosphere, etc.), this estimate would need to be revised upward. The assumption that Ag_F is conservative is also important since filterable Ag can be rapidly stabilized by ligands present in the filterable fraction of seawater and serve as a good tracer for mixing across salinity gradients. Of the elements determined on the suspended particles, only Al shows significant conservative (or moderate first order) removal. This observation also supports the reasoning that a greater portion of the Al particulates were derived from non-effluent sources. A significant terrigenous component (e.g., riverine or atmospheric sources) in the suspended matter samples from the Feb. 1995 survey can account for the lower enrichment of metals when compared to metal enrichments calculated from apparent wastewater end member concentrations. Particle enrichment ratios (ER_P) are calculated as follows:

$$ER_P = \frac{[Me]_P / [Al]_P}{[Me]_C / [Al]_C}$$

where [Me]_P / [Al]_P and [Me]_C / [Al]_C are the metal – Al ratios observed for particulate samples and reported for crustal abundances (Wedepohl, 1995).

Under typical winter conditions, Massachusetts and Cape Cod Bays are well-mixed and dispersion of coastal material to surface waters is most likely more efficient. Winter

freshwater input from Boston Harbor to the Bays may be proportionally greater when compared to that in the spring, summer and fall conditions when riverine input is minimal and MWRA effluent discharge is maximum (Wu et al., 2008).

Metal – salinity plots of MBS surface water from the 1995 summer cruise exhibited high scatter and, as noted above, may reflect the presence of other significant sources of freshwater and associated contaminants to the Bays. Reduced circulation during this period was also likely, since weak winds and moderate freshwater runoff were associated with the extended dry period that characterized the region's summer. The intrusion of high salinity (>32 psu) water along the western boundary of Massachusetts Bay was also apparent (See Fig. 3.13). Unfortunately, no samples from this water mass were collected for characterizing metal content. When sampling was targeted to the nearfield region (Sept. 1996), significant salinity relationships with filterable Ag and Cu concentrations were again observed (Fig. 3.43).

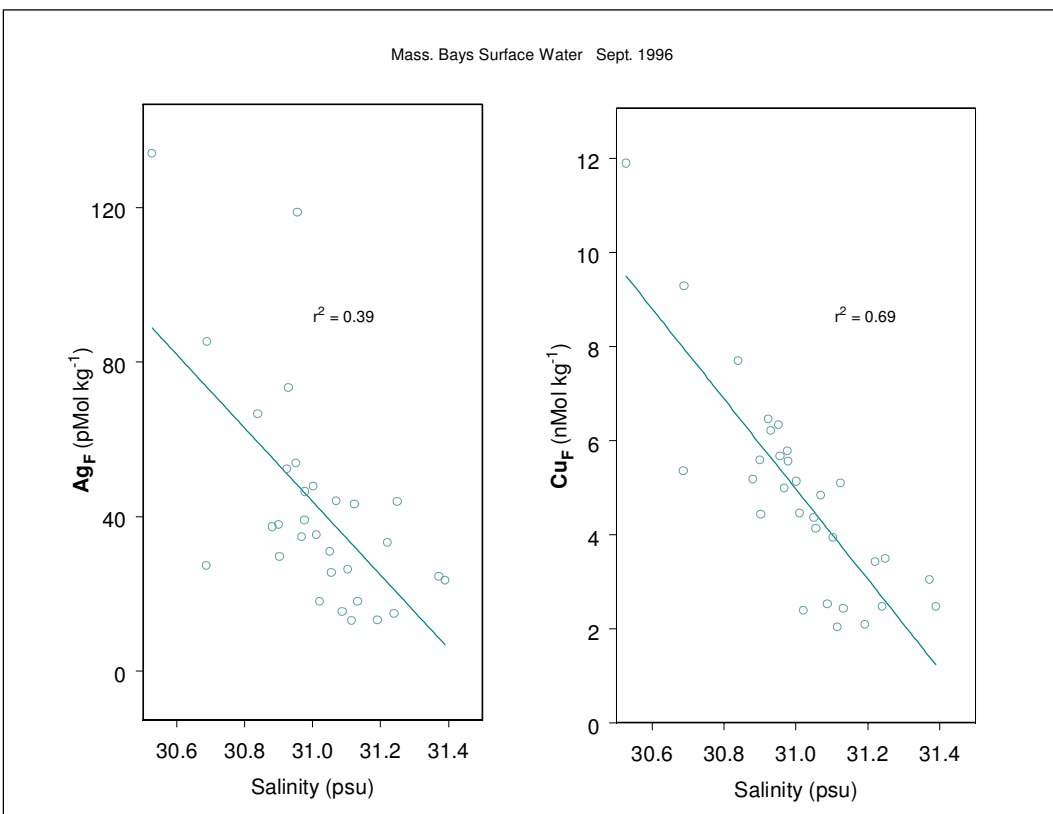


Figure 3.43. Linear regression of filterable silver (Ag_F) and copper (Cu_F) in the nearshore waters of Massachusetts and Cape Cod Bays, September 1996.

3.5.2 Sources and cycling of silver in the Massachusetts Bays

Based on the silver distributions observed above, much of the cycling of Ag through the Massachusetts Bays system (MBS) is thought to be influenced by inputs predominantly associated with fresh water entering into the Bay. In order to further evaluate this assumption, a detailed inventory of freshwater fluxes to the MBS is attempted in order to aid the development of a budget for silver in the Massachusetts Bays system. Fresh water in the MBS is attributable to inputs across the open ocean boundary from the GOM, which include contributions from the Merrimack River and other northern coastal rivers; fresh water in Boston Harbor (from municipal wastewater, rivers, and surface water runoff to Boston Harbor); direct precipitation;

and from ground-water discharges. The importance of riverine freshwater is often cited in circulation and contaminant studies of the Massachusetts Bays (Gardner et al., 1986; Menzie-Cura, 1991; Studer, 1995) and its contribution to the overall freshwater in Massachusetts Bay (Butman, 1976; Jiang et al., 2007). Based on the results presented above, much of the silver present in western Massachusetts Bay is thought to be the result of wastewater discharges, either from exchange with Boston Harbor or from river sources contaminated by wastewater discharges. A simple conceptual diagram of the MBS, shown as a box model in Fig. 3.44, is used first to evaluate the importance of freshwater inputs and then to develop loading estimates of Ag into and through the MBS. Based in part on physical oceanographic and sediment characteristic surveys conducted in the 1990's and the efforts reported here, the MBS is divided into four areal regions: Boston Harbor (BH), western Massachusetts Bay (WMB), Stellwagen Basin (SB), and Cape Cod Bay (CCB). The marine sedimentary environment of this system has been described in detail (Knebel and Circé, 1995; Crusius et al., 2004; Warner et al., 2008) and is used to characterize each component of the MBS with respect to the degree of deposition, reworking, or erosion.

3.5.2a Estimates of freshwater and associated Ag flux to northeastern Massachusetts Bay

The western portion of Massachusetts Bay is distinct in the MBS with respect to freshwater sources, mean depth (shallower), the importance of tidal and wind mixing-processes, and, by proximity, the importance of exchanges with Boston Harbor water. Circulation to the north and east in Massachusetts Bay appears to be dominated more by density-driven flow rather than currents and winds, at least during the winter-summer transition period where both seasonal warming and episodic freshwater inflow contributed to water column stratification (Geyer et al., 1996; HydroQual., 2001; Geyer et al., 2002; Jiang

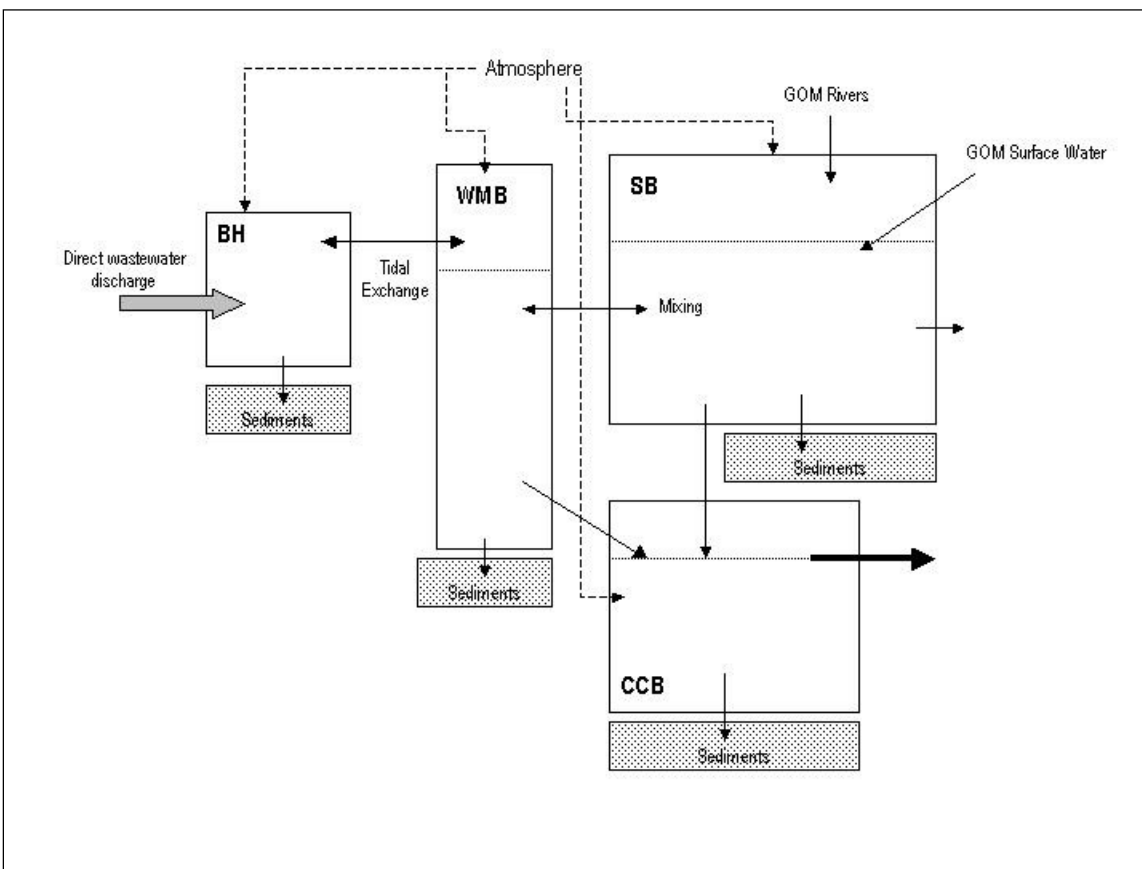


Figure 3.44. Conceptual diagram of major water fluxes among components of the Massachusetts Bays system. BH = Boston Harbor; WMB = transition zone, western Massachusetts Bay; SB = Stellwagen Basin; CCB = Cape Cod Bay. Dashed line represents seasonal (summer) stratification of the Bays.

et al. 2008). This region is predominantly comprised of the relatively deep Stellwagen Basin (SB) with water depths of about 80 meters and is considered an area of long-term sediment accumulation.

Most of the GOM river water entering Massachusetts Bay is thought to come from the Merrimack River (Menzie and Cura, 1991, Butman, 1976, Jiang and Zhou, 2008)) with additional input from the rivers draining into the GOM. The volumes of freshwater added by the major rivers thought to be important to this the region are given in Table 3.17.

Table 3.17. Annual Major River flows to the Gulf of Maine.

River	Annual total ($\times 10^{10} \text{ m}^3 \text{ y}^{-1}$)	(RSD) %	% GOM Contribution	Period of Record
Boston Harbor Rivers [‡]	0.07	NA	1	
Gulf of Maine Rivers				
Merrimack	0.68	29	9	1924-2002
Penobscot	1.23	23	15	1980-1995
Kennebec	0.88	22	11	1994-1999
Androscoggin	0.55	21	7	1929-2002
Saco	0.24	22	3	1917-2002
Bay of Fundy Rivers (St John, St. Croix) [†]	3.44	NA	43	
Total to Gulf of Maine [†]			8.12	

[†] In Townsend (1998).

[‡] Alber and Chan (1994)

Ultimately, in the model presented here, only a small portion of the freshwater entering into Massachusetts Bay is derived from coastal riverine sources.

The salinity conditions of Stellwagen Basin portion (SB) of the MBS are characterized by MWRA monitoring data from monthly far field surveys that include two sites (F27 and F28) in Stellwagen Basin (Fig. 3.45). The box model (Fig. 3.44) presented here uses a simple mixing model that estimates net exchange among the components of the model in the directions indicated by the arrows which are supported by MBS model particle trajectories (Jiang et al. 2007). Further, freshwater input from the GOM water is restricted to the Stellwagen Basin in this model.

As a first order analysis, the MWRA water quality data from the two stations are extrapolated to the entire SB box (a potentially large error, because two points are used to represent $1 \times 10^{11} \text{ m}^3$ of water!). However, the MWRA data show annual patterns of changes

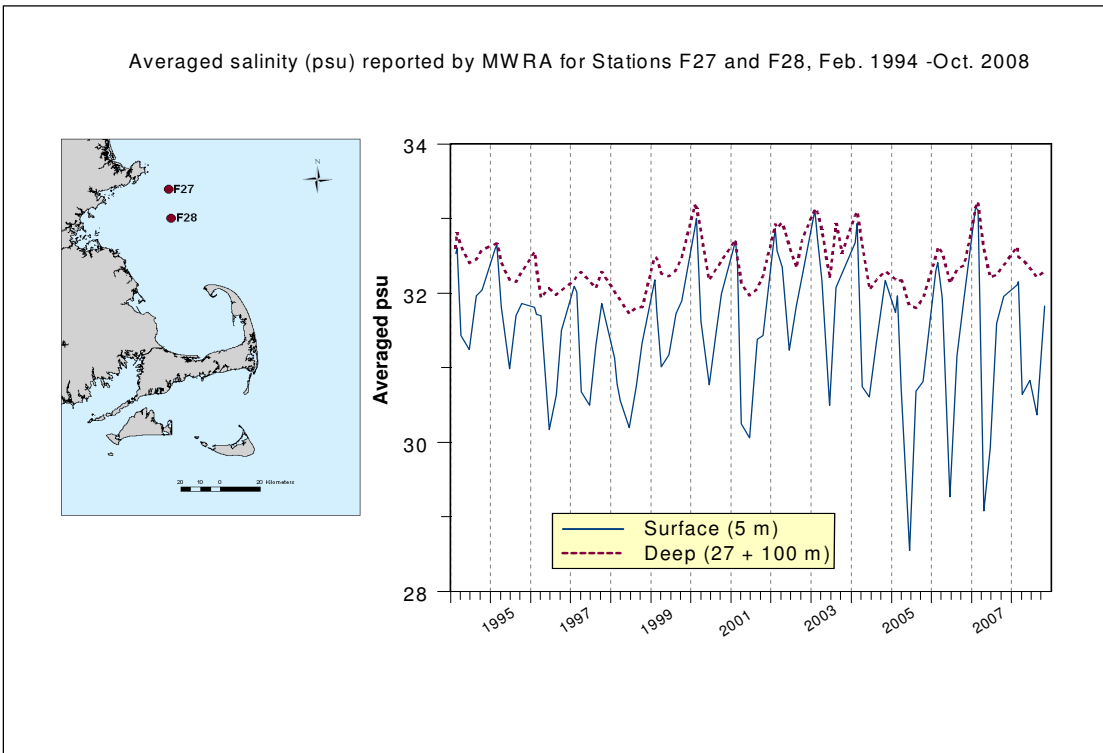


Figure 3.45. Averaged surface (5m) and bottom (27 m and 100 m at Stations F28 and F27, respectively) salinities combined from data obtained from far-field MWRA monitoring surveys in northern Massachusetts Bay, 1992-2008. (Data provided by and used with permission from MWRA.)

in salinity that coincide with changes in seasons (e.g., pronounced freshening during spring runoff) and suggest to some degree the appropriate application to time scales on the order of weeks to months; which are within the range of water residence times estimated for this portion of the MBS.

Corresponding decreases in surface (5 m) and deep water (101 m for F27 and 27 m for F28) at the MWRA stations indicate basin-wide processes controlling salinity and further support extrapolation of the MWRA data to box model scales. In addition, surface and deep water salinity were remarkably similar at both locations for the period of record (1994-2008) and are highly correlated (Fig. 3.46). The importance of GOM water exchange with the MBS is well documented (Jiang et al., 2007), especially along the MBS northeastern

boundary. Further, dissolved oxygen levels in Stellwagen Basin bottom water were highly correlated with conditions observed at the Massachusetts Bay/GOM boundary (HydroQual., 2001.; Geyer et al., 2002; Jiang et al., 2007) and also support the approximation of homogeneity of water for SB.

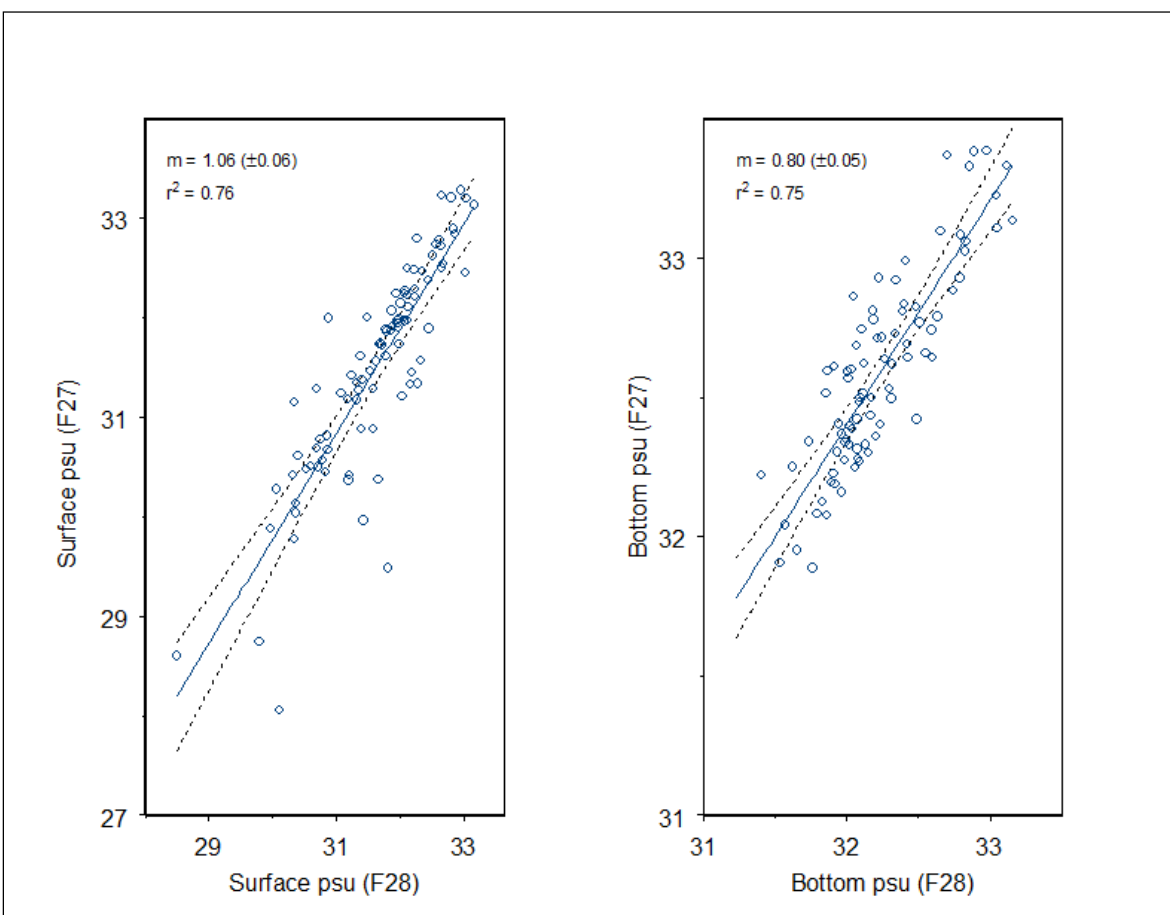


Figure 3.46. Least squares regressions (and 99% confidence intervals) of surface and bottom water salinity (psu) observations by MWRA at two stations (F27 and F28) located in Stellwagen Basin from Feb. 1994 – Oct. 2008. Regression slopes m (and standard error) are listed.

MWRA salinity data were averaged for surface and deep waters at F27 and F28 during the period from 1994 – 1997 and used to estimate freshwater inputs to the northeastern portion of MBS and evaluate the importance of riverine water to the annual freshening of the MBS. The seasonal variability of freshwater in the SB portion of Massachusetts Bay is evident in Fig. 3.47 showing significant changes in salinity in surface-averaged (5m) and deep waters (100 m and 27 m, F27 and F28, respectively). Salinity changes were pronounced during spring periods when rapid changes were observed coincident with annual spring runoff and coincident with middle to late spring (April - June) annual minima. During

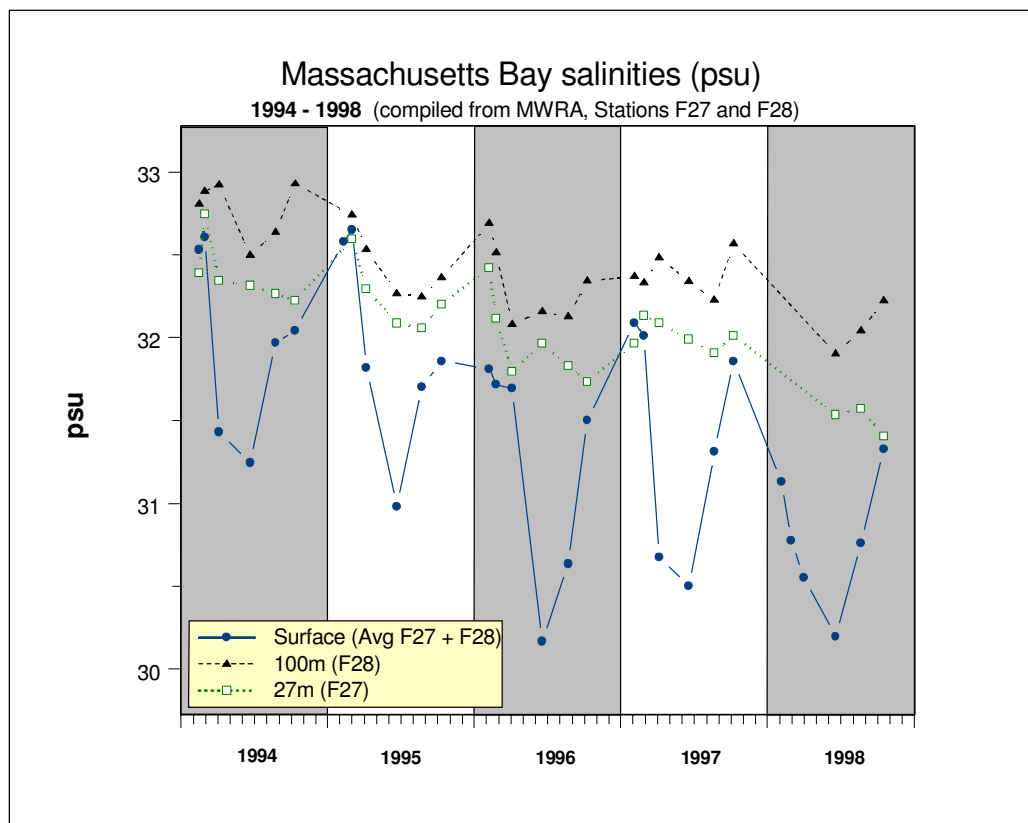


Figure 3.47. Averaged surface (●) and individual bottom water (Station F28□ and Station F27▲) salinities in Stellwagen Basin from hydrographic surveys conducted by MWRA during 1994 – 1998.

summer periods when river runoff is minimal, largely-wind driven, localized, short term upwelling and downwelling become more important mechanisms for transport, especially in the immediate nearshore coastal waters (Jiang et al., 2007).

For the years shown in Fig. 3.47, the reduction of freshwater supplied to the Bay after the spring runoff is evident as salinity increases through the summer. The onset of stratification between the surface and deep mixed layers is noticeable where the salinity traces between water-column top and bottom salinities converge. For instance, during 1994 the onset of stratification in Stellwagen Basin occurred during the month of March and lasted through October. Further, Stellwagen Basin remained mostly stratified from March 1995 through until the end of 1996.

Freshwater volumes (V_{fw}) in Stellwagen Basin from MWRA hydrographic surveys conducted during 1994 through 1996 were calculated using a reference salinity of 32.6 psu (which represented the 75th percentile of the bottom averaged data from Stations 27F and 28F during 1994-1996). Stellwagen Basin V_{fw} at the time of MWRA sampling is estimated using the following equation modified from by Ketchum (1950):

$$V_{fw} = (1 - S_t/S_R)V_{SB}$$

Where:

S_t = salinity observed at time (t),

S_R = reference salinity, and

V_{SB} = volume of Stellwagen Basin

The box model considers MBS well-mixed when surface water and deep water averaged salinity values differed by less than 0.2 psu. This assumption is consistent with the

observations shown in Fig. 3.46, when deep water and surface water salinity traces fell within or near the range observed in the bottom water at MWRA stations 27F and 28F. The Massachusetts and Cape Cod Bays box model also assumes quasi-steady state by simplifying Massachusetts Bay as alternating between a one- and two- layer system, representing well-mixed and stratified systems during annual winter and summer periods, respectively. The total volume of water in Massachusetts Bay is approximately $1.24 \times 10^{11} \text{ m}^3$ (derived from Knebel and Circé, 1995). Assuming an average surface mixed layer of 10 m (this study; Geyer et al., 1996) yields an approximate summer mixed-layer volume of $3.6 \times 10^{10} \text{ m}^3$.

Changes in V_{fw} observed from MWRA sampling events were then used to estimate the amount of freshwater exchange in Stellwagen Basin (Fig. 3.48). Net freshwater exchange during 1994 was nearly balanced (slightly more freshwater lost $\sim 8 \times 10^6 \text{ m}^3$), while freshwater accumulated ($2\text{-}3 \times 10^8 \text{ m}^3$) during 1995 and 1996. Freshwater volumes and estimated fresh water exchange for Massachusetts Bay (F_{MB}) and major rivers for time periods defined by the MWRA sampling schedule are listed in Table 3.18 and Fig. 3.49 respectively.

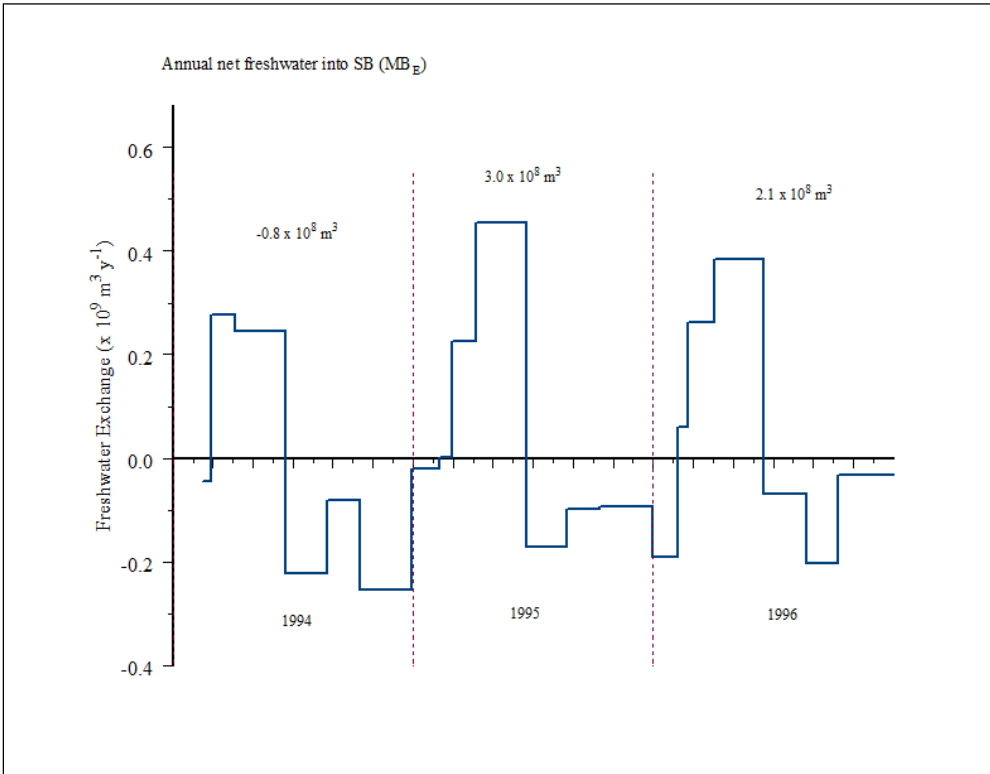


Figure 3.48. Net annual freshwater exchange in Stellwagen Basin. Negative values indicate freshwater loss from the Stellwagen portion of Massachusetts Bay with a reference salinity equal to 32.6.

Table 3.18. Estimates of freshwater volume (V_{fw}) and exchange (MB_E) in the northeastern portion of Massachusetts Bay (Stellwagen Basin), 1994-1996, from averaged salinity data from MWRA hydrographic surveys at Stations 27F (42.550°N, 70.447°W) and 28F (42.41°N, 70.433°W). Box model initial conditions set at 15Feb1994 ($t=0$) and reference salinity (S_R) equal to 32.6.

Year	Date	Surface (2m) psu	Deep (64m) psu	Time Period (days)	Mixed layer V_{fw} ($m^3 \times 10^9$)	Deep layer V_{fw} ($m^3 \times 10^9$)	MB_E $m^3 \times 10^9$ y^{-1}
1994	2/15/1994	32.5305	32.5990	41	0*	0.01	
	3/1/1994	32.6050	32.8145	14	0	-1.15	-0.044
	4/6/1994	31.4300	32.6325	36	1.79	-0.12	0.278
	6/22/1994	31.2445	32.4050	77	2.08	0.75	0.244
	8/24/1994	31.9675	32.4505	63	0.97	0.57	-0.222
	10/12/1994	32.0420	32.5765	49	0.86	9.01	-0.080
	12/31/1994	32.3979	32.6418	79	0	-0.22	-0.255
Total:							-0.08
1995	2/10/1995	32.5779	32.6748	41	0	-0.40	-0.020
	3/2/1995	32.6505	32.6673	20	0	-0.36	0.002
	4/7/1995	31.8179	32.4128	36	1.20	0.72	0.225
	6/22/1995	30.9815	32.1770	76	2.48	1.62	0.455
	8/23/1995	31.7029	32.1523	62	1.38	1.72	-0.172
	10/11/1995	31.8576	32.2802	49	1.14	1.23	-0.098
	12/31/1995	31.6730	32.4650	81	1.42	0.52	-0.094
Total:							0.30
1996	2/7/1996	31.8103	32.5552	0	0	0.24	-0.191
	2/24/1996	31.7175	32.3136	41	0	1.54	0.060
	4/4/1996	31.6949	31.9382	17	1.39	2.54	0.262
	6/18/1996	30.1680	32.0613	40	3.73	2.07	0.384
	8/22/1996	30.6353	31.9766	75	3.01	2.39	-0.070
	10/8/1996	31.5004	32.0381	65	1.69	2.15	-0.202
	12/31/1996	31.5919	32.0381	47	1.55	2.15	-0.032
Total:							0.21

* Stellwagen Basin considered well-mixed (no surface mixed-layer); defined when $S_{DEEP} - S_{SURF} < 0.2$ psu

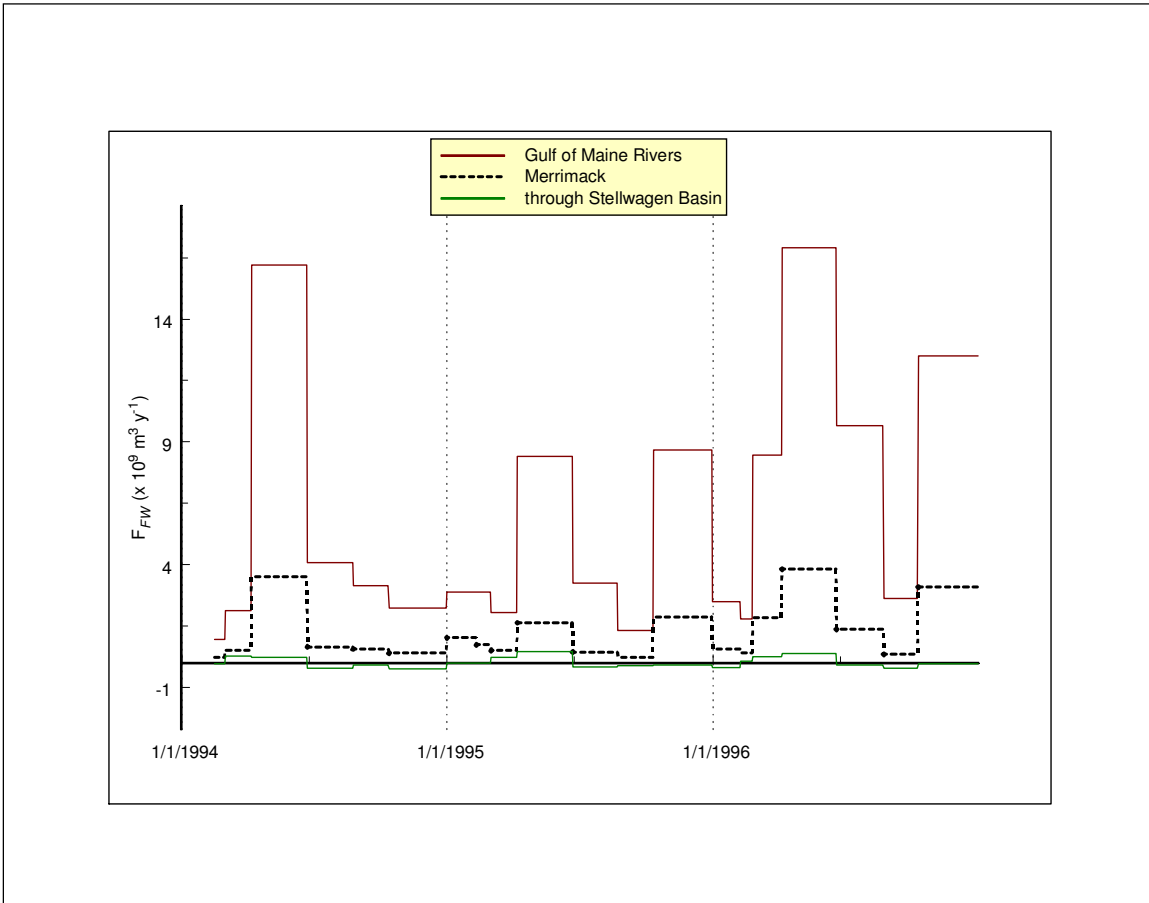


Figure 3.49. Freshwater exchange in the Stellwagen Basin portion of Massachusetts Bay compared with comparable (30 day lagged) time-averaged estimates of flow from the Merrimack and total Gulf of Maine Rivers.

For the study period, freshwater flow from the GOM Rivers (Merrimack, Penobscot, Kennebec, Androscoggin, and Saco = GOM_{RIV}) are compared to freshwater flows of the Merrimack River and freshwater exchanges within the Stellwagen Basin region of Massachusetts Bay (MB_E). Freshwater flux estimates were made from average daily flows derived from the farthest downstream USGS gauging stations and integrated for the time periods between corresponding MWRA water column surveys. Each river flux estimate was offset by 30 days to better reflect the lag in mean transport of the WCC to northern Massachusetts Bay (Geyer et al., 1996; Smith et al., 2001). While the river flow derived

from USGS gauging stations does not account for freshwater added to the river from the portion of watershed below the gauges, this error is considered negligible, probably offset by losses due to evaporation (Dai and Trenberth, 2002), and would underestimate fluxes by no more than 5% (Ashjian et al., 2001). Massachusetts Bay freshwater exchange was generally an order of magnitude or two less than the riverine flow from the Merrimack River and the collective GOM rivers, respectively (Fig. 3.49).

To estimate the flux of Ag associated with GOM exchange, the freshwater flux considered was thought to consist of two components, one originating from river sources and the other from GOM surface water exchanges. The later is characterized separately from the WCC and captures GOM freshening that results from relatively cold, low salinity Scotian Shelf Water entering into GOM surface water which then mixes with more saline warmer bottom shelf water as its progress southerly through the GOM (Weibe et al., 2002). Ji et al. (2007) and Belkin (2004) have shown significant negative sea surface salinity anomalies during the 1990s for the GOM and North Atlantic. Thus, the estimate for the GOM Ag flux into SB considers the percentage of the variability of the freshwater exchange in SB explained by changes in the freshwater input from the GOM rivers, the percentage of Merrimack contribution to the WCC, the Ag concentrations of the Merrimack river end member (0 psu) and the average Ag concentrations observed in the GOM in 1996.

For the WCC, the Ag flux estimate assumes Merrimack River Ag concentrations observed in Sept. 1995 as typical (113 pmol kg^{-1} particulate and 68 pmol kg^{-1} filterable, psu = 0). Thus, the Merrimack River Ag contributes approximately 115 - 225 kg Ag annually to the GOM (Table 3.19). The Merrimack River discharge is typically 20% of the flow of the major rivers emptying into the GOM (Fig. 3.50). However, the Merrimack may be a more

significant component of the freshwater flux to Massachusetts Bay because it discharges near the boundary of MBS and the GOM. To accommodate this possibility, the contribution of the Merrimack to the WCC is estimated to range from 20% – 50%. Silver fluxes from the Penobscot, Kennebec, Androscoggin, and Saco Rivers, though not measured, are assumed to be negligible because these rivers drain watersheds that are relatively undeveloped and essentially non-industrialized.

The Ag flux from GOM surface water intrusions not associated with the WCC is estimated assuming mean total Ag concentrations ($\sim 12 \pm 6$ pM) observed from samples

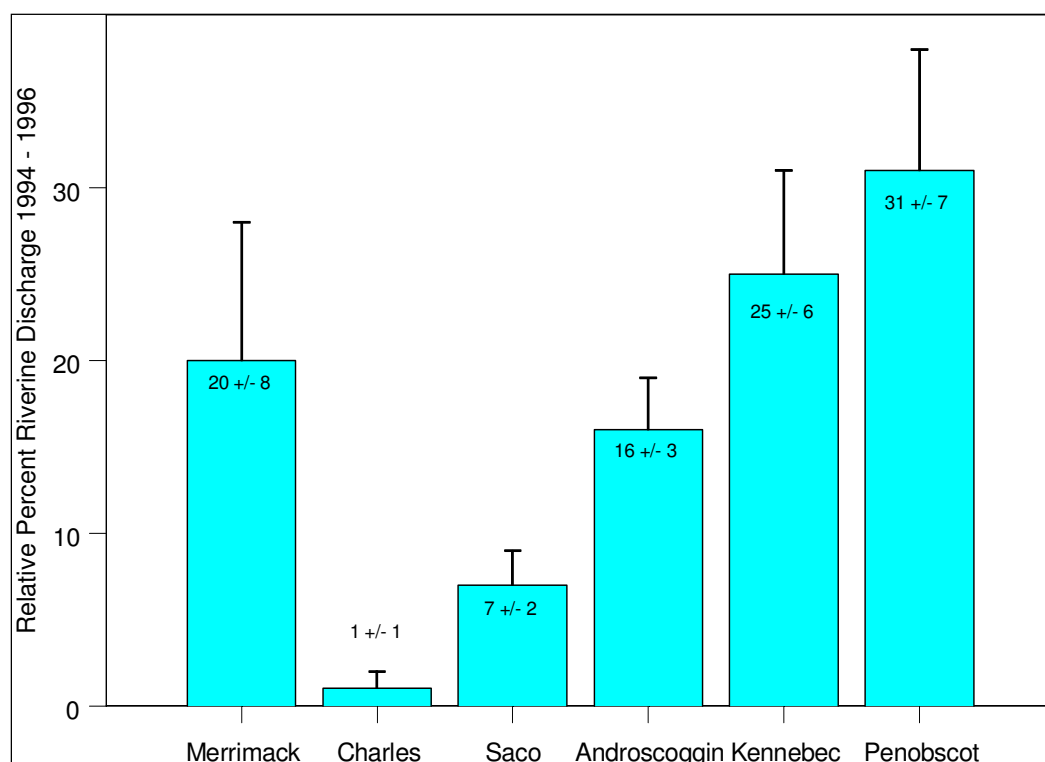


Figure 3.50. Percentage of discharges from the Merrimack and Charles Rivers and the major rivers draining into the Gulf of Maine. Error bars represent 1 SD of the mean. Data compiled from USGS at <http://waterdata.usgs.gov/ma/nwis/rt>

collected during the 1996 Portland, ME Transect to be representative of Ag in the GOM surface waters. Silver concentrations and the estimates of Ag fluxes associated with freshening by the GOM surface water (including contributions from WCC) yield Ag flux estimates from the GOM ranging from 0.1 – 0.5 kg Ag y⁻¹ (Table 3.19).

Table 3.19. Flux estimates of Ag (kg y⁻¹) associated with fresh water from the Gulf of Maine to the Stellwagen Basin (SB) portion of the Massachusetts Bay system. Estimates of the Ag flux from the Merrimack River to the coastal waters of the Gulf of Maine are provided for comparison. The western coastal current (WCC) is estimated to contribute between 20 -50 % of freshwater flux in SB. A similar percentage (20-50%) of this freshwater flux is derived from the Merrimack.

Year	WCC to SB		Ag GOM _{Surf} to SB	Ag _{MR} to Coastal GOM
	20%WCC	50%WCC		
1994	0	0.01	-0.10	115
1995	0.05	0.13	0.37	127
1996	0.02	0.04	0.27	225

3.5.2b Estimate of advective Ag flux from the Gulf of Maine to northeastern Massachusetts Bay

Geyer et al. (1992) estimated an advective transport across the northern boundary of the MBS from a mooring located in the passage north of Stellwagen Bank (University of New Hampshire; 42.533°N, 70.483°W) to be $\sim 1 \times 10^{12} \text{ m}^3 \text{ y}^{-1}$. Assuming background silver concentrations between 1-4 pM observed for surface North Atlantic water (Rivera-Duarte et al., 1999) to be representative of GOM water entering into the MBS, the advective silver flux from the GOM is estimated to be $\sim 130 - 520 \text{ kg y}^{-1}$. This range does not consider the

assumption of spatial uniformity applied to length scales of several kilometers (14 – 20 km) and depth (down to 40 m) nor of the seasonal variability of advective transport in this region (Geyer et al., 2004) that are inherent with the steady state assumption necessary for these estimates. Further, it is well known for natural systems that solute concentrations can be inversely correlated with flow (e.g. Verry, 1975) and flux estimates derived from multiplying the averages of concentration and flow would be overestimated. Where contaminants concentration correlates positively with discharge (e.g. TSM – Surbeck et al., 2006) fluxes would be underestimated. Because time series data are not available we assume the variance in Ag concentration is independent of flow. Thus, these estimates only serve to highlight that while the waters of the GOM may be relatively low with respect to Ag concentrations, the potential for significant Ag flux exists, given the relatively large contribution that the GOM contributes to the waters of the MBS (Jiang et al., 2007).

3.5.2.c Estimates of freshwater and Ag flux to western Massachusetts Bay

Based on the results of this study, most of the Ag in Boston Harbor is associated with municipal discharges of waste water. Municipal wastewater discharges to Boston Harbor over the period of sampling accounted for about 50% of the annual mean freshwater input to the harbor (Alber and Chan, 1994). Reported total Ag fluxes to Boston Harbor from the metropolitan Boston discharges ranged from $2.2 - 2.8 \times 10^3 \text{ kg y}^{-1}$ (Fig. 3.51, data provided by M. Hall, MWRA) during 1994 -1996. Some of the material associated with wastewater discharge in Boston Harbor is captured in the sediments of depositional areas and is reflected in the elevated Ag concentrations ($1 - 12 \mu\text{g g}^{-1}$) reported for Boston Harbor sediments

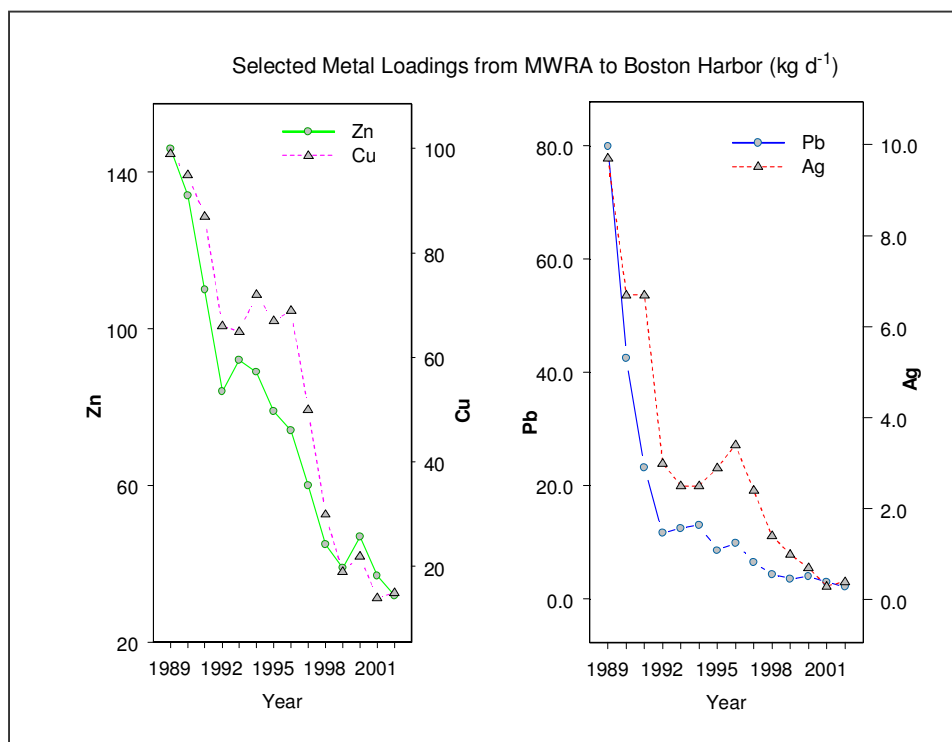


Figure 3.51. Loadings (kg d^{-1}) of selected metals to Boston Harbor from metropolitan Boston's municipal wastewater treatment facility.

(Bothner et al., 1993; Long et al., 1993; Buchholtz ten Brink et al., 2002; Kalnejais, 2005) and observed in recent data from EPA's National Coastal Assessment ("Northeast Region Data Pages").

During the study period, approximately 60% ($n=7$) of Ag in Boston Harbor during the study period water existed as particulates. Stolzenbach and Adams (1998) estimated 30% of effluent particles discharged into Boston Harbor are retained within the harbor sediment. Using the reported discharge rates for Ag during 1994-1996 given above, assuming 60% is on particles, and a 30% retention of those particles in Harbor sediments, the Ag flux to the sediment becomes 236 kg y^{-1} . This flux would support general surface sediment concentration ranging from $3 - 6 \text{ ug Ag g}^{-1}$ (assuming sediment accumulation rates between $0.1 - 0.2 \text{ cm y}^{-1}$) which is in good agreement with the range reported for surface sediments in

Boston Harbor. However, conservative transport of Ag was apparent in Massachusetts Bay waters adjacent to Boston Harbor during the July 1994 survey (see Figs. 3.6 and 3.42) and apparent zero psu end-member Ag concentration from these data support alternative mechanisms for Ag retention in Boston Harbor sediments. Thus, equilibrium between sediment and the overlying water column, the quality of the sediment (e.g., organic carbon content) or sediment redox conditions (presence of sulfides) may be of importance in considering the fate of metals in coastal marine systems (Zago et al., 2001; Caccia et al., 2003, Kalnejais, 2005; Morford et al., 2008). . Using the estimate that approximately half of Boston Harbor is considered as depositional (Knebel and Circé, 1995) and varying the inventory of silver in Harbor surface sediments (top 2 cm) derived from sediment contaminant data, the Ag flux to Boston Harbor sediment during the study period is further refined as being within the range of 200 - 400 kg y⁻¹ (Table 3.20). Based on the estimates of

Table 3.20. Estimates of Ag concentrations in Boston Harbor (BH) sediments based on variable Sediment Accumulation Rates (SAR) and fluxes to the sediment.

Ag Flux (kg y ⁻¹)	SAR (m y ⁻¹)	[Ag _{Sed}] (ug g ⁻¹ dw)*
100	0.001	1.02
	0.002	0.51
	0.005	0.2
200	0.001	2.03
	0.002	1.02
	0.005	0.41
400	0.001	4.04
	0.002	2.03
	0.005	0.81

* assumes a depositional area of 49.2 km (Stolzenbach and Adams, 1998) and a porosity of 0.5 for fine grained sediments (Warner et al., 2008).

Ag retention in recent Harbor sediments, the flux of Ag from Boston Harbor to western Massachusetts Bay would be on the order of $2.0 - 2.6 \times 10^3 \text{ kg y}^{-1}$.

3.5.2d Estimates of the advective Ag flux in Cape Cod Bay

Geyer et al. (1996) computed water transport values at three locations in Massachusetts Bay from oceanographic cruises conducted between April 1990 and June 1991. The southerly, down-bay transport from central Massachusetts Bay and outflow around the northern tip of Cape Cod Bay into the southern GOM were on the order of $1.8 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ and $1.6 \times 10^4 \text{ m}^3 \text{ s}^{-1}$, respectively. Their model extrapolates these values to length scales of 30 km and 10 km, respectively. Two monitoring stations operated and maintained by the USGS located in the southwestern portion of the MBS provide high temporal resolution of current speed and direction (Fig. 3.52). Data from USGS long term monitoring sites in western Massachusetts Bay clearly indicate the highly variable nature of water column current speed and direction and yield variable annual means in both speed and direction (Table 3.21). Clearly, annual transport among the components defined in the MBS is variable and challenge approximations based on application of such generalized models as is attempted here. Thus, the annual approximation of this box model and the extrapolation of single point measurements to scales of several km can only provide order of magnitude estimates of metal transport and fate in the MBS. The annual averages reported for USGS LTB monitoring station (from 1997-2003) for current speed at 10 m water depth ranged from $1.2 - 3.1 \text{ cm s}^{-1}$ with remarkably consistent vector angles but in nearly 180° apart with respect to vector direction. Because of the shallow nature of this portion of the MBS, the orientations of currents are strongly affected by topography. The annual mass transport

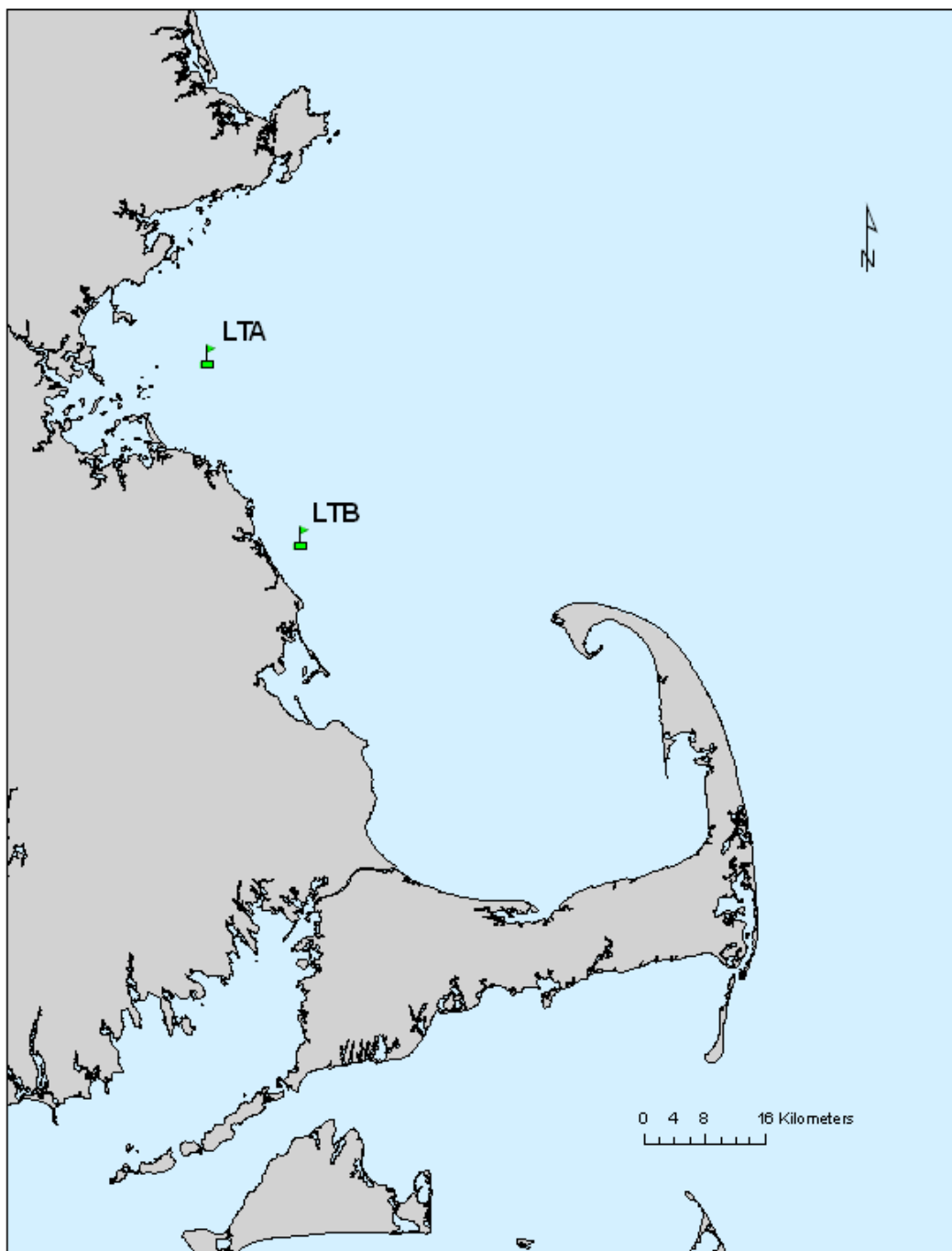


Figure 3.52. Location of the USGS Long Term Monitoring Moorings: LTA ($42^{\circ} 22.6' \text{ N}$, $70^{\circ} 47.0' \text{ W}$) and LTB ($42^{\circ} 9.8' \text{ N}$, $70^{\circ} 38.4' \text{ W}$).

Table 3.21. Acoustic Doppler Current Profile observations in western Massachusetts Bay. USGS moorings, mid-depth at LTA (42° 22.6' N, 70° 47.0' W) and LTB (42° 9.8' N, 70° 38.4' W). Data available from <http://pubs.usgs.gov/ds/74/>

Year	LTA 22m Vector Speed (cm/s)	Vector Direction (degrees)	LTB 10 m Vector Speed (cm/s)	Vector Direction (degrees)
1990	0.17	74		
1991	0.39	160		
1992	0.19	114		
1993	0.38	74		
1994	0.90	-12		
1995	0.43	38		
1996	0.31	66		
1997	0.60	123	3.07	157
1998	0.57	20	2.84	161
1999	0.60	-38	2.04	157
2000	0.25	-46	2.33	-175
2001	0.95	56	1.75	170
2002			1.17	-168
2003			2.37	171
All Years	0.22	31	2.09	170

values in the western near coastal MB are on the order of $10 - 20 \times 10^6 \text{ m}^3 \text{ s}^{-1}$ but either towards the SSE or NNE for the last four years of USGS record (2000-2003).

However, for the observation period, an estimated Ag flux to Cape Cod Bay from western and northeastern Massachusetts Bay is derived using a long-term transport value into CCB generated from the LTB station data ($\sim 4 \times 10^6 \text{ m}^3 \text{ s}^{-1}$) for the years 1997-1999 and the difference between mean total concentrations in lower Massachusetts Bay observed during July, 1995 (25 pM), and the values observed in the mixing zone near the Boston Harbor

entrance (see Figs 3.18 and 3.25). The presence of a south-east gradient of silver concentration observed during the near coastal survey conducted in September 1996 supports the concept of a predominantly southerly transport to Cape Cod Bay. The resultant average annual Ag flux to CCB is $2.5 \times 10^3 \text{ kg Ag y}^{-1}$ and of similar magnitude to that reported above for fluxes from the MWRA effluent ($2 - 3 \times 10^3 \text{ kg Ag y}^{-1}$) and from Boston Harbor to WMB ($1.8 \times 10^3 \text{ kg Ag y}^{-1}$) with little or no long-term removal to in sediments in western Massachusetts Bay. Ag flux out of CCB into the North Atlantic was estimated using the mass transport value reported in Geyer et al. (1996) of $\sim 1.6 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ for water exiting CCB around the south passage near Race Point at the tip of Cape Cod. The Ag flux derived from using this value and a “typical” total Ag concentration of $\sim 19 \text{ pM}$ (central CCB, July 1995) results in an export of $\sim 1 \times 10^3 \text{ kg Ag y}^{-1}$. Clearly, the Ag flux derived for the MBS is highly sensitive to the length scales assigned (here the relevant Ag transport was confined to the near coastal region, out to 5 km) and to the interpretation of a depth-integrated mass transport value (derived from the acoustic Doppler current data at the LTB station; see Table 3.21). A comparison of these estimates suggests, over the long term, that most of the Ag originating near or within Boston Harbor during the study period was transported to CCB. Based on the difference between the southerly mid-bay transport and the Cape Cod Bay outflow reported by Geyer et al., (1996) about 11% of the transport ($\sim 2 \times 10^3 \text{ m}^3 \text{ s}^{-1}$) was unaccounted for and can be explained as transport to the eastern portion of Massachusetts Bay across the open boundary into the GOM. This transport value is a relatively small, and beyond the resolution that can be discerned by the MBS box model.

Table 3.22. Scales and mean velocities used to estimated transport from WMB into CCB. Velocities derived from data from USGS mooring: LTB (42° 9.8' N, 70° 38.4' W) for the years 1997-1999.

Depth (m)	LTB current (1997- 1999) (cm s ⁻¹)	Width (km)	Transport (m ³ s ⁻¹)
0 - 5	3.0	5	750
5 - 10	2.6	4	520
10 – 17	0.1	3	21

3.5.2.e Losses of Ag to the sediments of the Massachusetts and Cape Cod Bays

As noted for Boston Harbor, sediments can play an important role in sequestering a portion of trace metal flux from the water column and ultimately removing them by burial in areas of long term deposition. Some of the silver lost from the Bays occurs through accumulation and burial in long-term depositional areas. The seafloor sedimentary environments of Boston Harbor and Massachusetts Bay have been well characterized by USGS from a compilation of sidescan sonographs and sediment texture samples from surveys conducted in the region over the previous three decades (Knebel and Circé, 1995; Knebel et al., 1996; Poppe et al., 2003). A summary of the seafloor sedimentary environment for the MBS is given in Poppe et al. (2003) and Warner et al., (2008).

For Cape Cod Bay, Knebel et al. (1996) estimate that approximately 54% of the seafloor sedimentary environment is depositional and essentially confined to the central basin of the Bay. This is consistent with estimates obtained here using the EPA's National Coastal Assessment (NCA) grain size data from samples collected in Cape Cod Bay during 2000 - 2005 (Fig. 3.53). The areal distribution of grain size and Ag concentration was estimated using the kriging function in Surfer® 8 (Golden Software, Inc). Sediment silver concentrations in the NCA data ranged from near zero to 0.7 ug g⁻¹ dry wt. (median value =

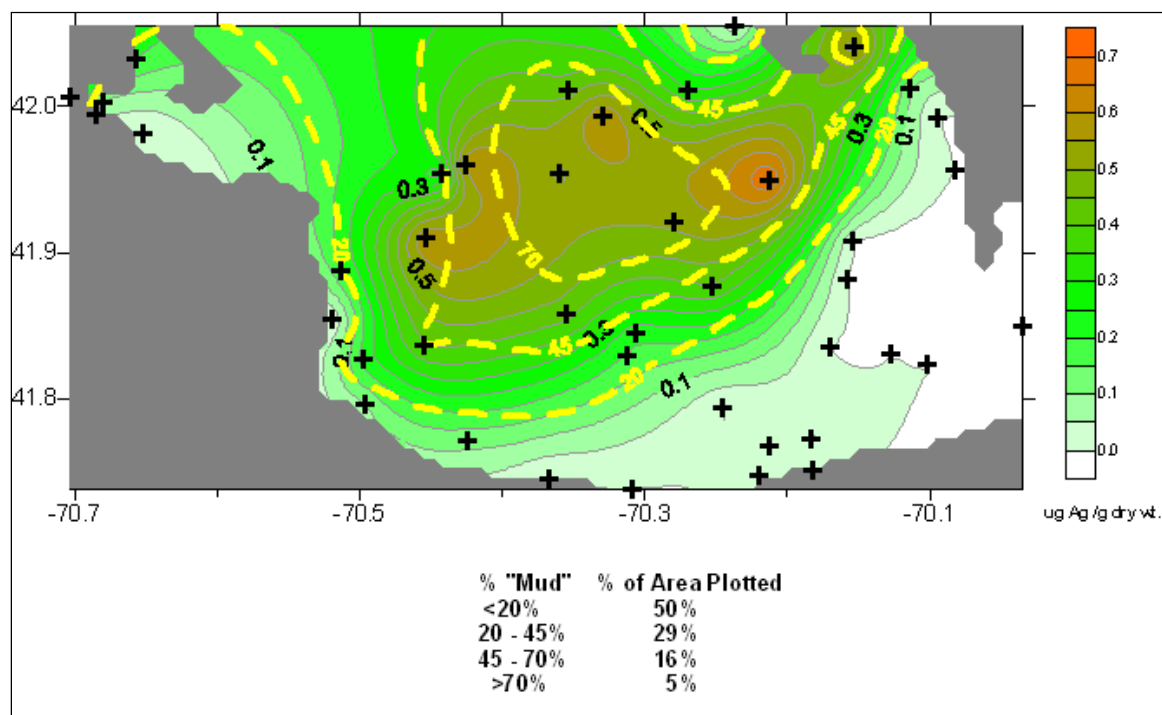


Figure 3.53. Distribution of silver ($\mu\text{g g}^{-1}$ dw) in surface sediments (top 2 cm) of Cape Cod Bay. An overlay of the areal distribution of silt/clay fraction ("mud") is shown by the yellow heavy-dashed contours. Sediment sample locations indicated by + symbols. Data from EPA's National Coastal Assessment, 2000 – 2005: <<http://www.epa.gov/emap/nca/html/regions/northeast.html>>.

0.1 $\mu\text{g g}^{-1}$ dry wt.) and consistent with previously reported values for CCB surface sediment (Ravizza and Bothner, 1996; Bothner, 1998; Bothner et al., 2002). The inventory of Ag in recent CCB sediments (top 2 cm) estimated from the distribution of silver concentration and sediment grain size (for approximating sediment density) in NCA samples was approximately 5.7×10^3 kg (see Appendix A.5 for computation).

Sediment accumulation rates in Massachusetts and Cape Cod Bays have been reported to range from 0.05 – 0.5 cm y^{-1} (Ravizza and Bothner, 1996; Crusius et al., 2004; Butman et al., 2006). These estimates typically rely on interpretations based on naturally-occurring radionuclide activities (i.e., ^{210}Pb , $^{239} + ^{240}\text{Pu}$) and are often complicated by processes that can

alter their distribution in sediments and limit their capacity as tracers for sediment accumulation. For instance, bioturbation can transport these nuclides to depths of several centimeters. Because of these biologically-mediated processes, Crusius et al. (2004) report the upper limit of radionuclide-base sedimentation accumulation of $\sim 0.3 \text{ cm y}^{-1}$ for sediments in Massachusetts Bay. Using the inventory of Ag in CCB surface sediments and using a range of sediment accumulation rates between $0.05 - 0.3 \text{ cm y}^{-1}$, the flux of Ag to CCB sediment is estimated to be between $142 - 850 \text{ kg y}^{-1}$ (Table 3.23).

Three distinct seafloor sedimentary regions have been identified in the Boston Harbor and Massachusetts Bay system: estuary (Boston Harbor), inner shelf (gentle sloping region extending approximately 20-25 km offshore) and Stellwagen Basin. Both Boston Harbor and Stellwagen Basin contain long-term deposition areas: 46-51% and 70%, respectively (Knebel and Circé, 1996), while the shallow region of western MB was considered predominantly an area of erosion or non-deposition. Only 3% of western Massachusetts Bay was considered to contain areas of long-term deposition (Knebel and Circé, 1996) and thus was considered insignificant to the overall flux of Ag to the sediment of the MBS estimated here.

Table 3.23. Estimates of Ag flux to Cape Cod Bay (CCB) sediments based on variable sediment accumulation rates (SAR).

CCB Ag Inventory: 5666 kg in upper 2 cm (2833 kg cm ⁻¹)	
SAR: (cm y ⁻¹)	kg Ag y ⁻¹
0.05	142
0.1	283
0.3	850

Using similar sediment accumulation rates employed for estimating CCB sediment Ag flux, bulk sediment density of 1.1 g cm^{-3} (an average derived from NCA data and the CCB analysis), and surface sediment Ag concentrations reported by Bothner et al. (1993) and Bothner (1998) to be representative of the depositional area of Stellwagen Basin, the annual Ag flux to the sediments of Stellwagen Basin is estimated to be approximately $0.5 - 1.0 \times 10^3 \text{ kg y}^{-1}$.

3.5.2.f Atmospheric deposition of Ag to the Massachusetts Bays system

Pike and Moran (2001) estimated an annual Ag deposition of $1 \times 10^3 \text{ kg}$ for the entire Gulf of Maine. Based on surface area ratios (MBS:GOM) this translates to approximately 54 kg y^{-1} to the MBS. As an alternative approximation for estimating the atmospheric Ag flux, the value of lowest total Ag concentration (approximately 7 pM) observed in the surface mixed layer at Station 1 of the July 1996 GOM transect (see Table 3.11) is considered. This is about twice the background observed for the upper North Atlantic (Rivera-Duarte et al., 1999). Using a simple steady state approach that assumes $\sim 3.5 \text{ pM}$ Ag in the MB surface waters to be solely the result of direct atmospheric deposition, a Massachusetts Bay mixed-layer depth = 10 m , and a mixed layer residence time of 30 days (Geyer et al., 1991), the atmospheric Ag flux to the Massachusetts Bay system is estimated to be near 20 kg y^{-1} . This is of the same order of magnitude as the estimated atmospheric deposition of Pike and Moran (2001) and is more significant than sources from the major GOM rivers and less than the magnitude of advective flux from GOM exchange with Massachusetts Bay.

It is important to note that changing deposition rates and sources of atmospheric Ag remain poorly known. The estimate for the GOM atmospheric flux based on results reported

by Pike and Moran (2001) is over an order of magnitude lower than the global Ag atmospheric flux reported previously (see Chapter 2). Van de Velde et al. (2000) report on accumulation of silver from atmospheric sources in Mont Blanc (French-Italian Alps) ice and were able to reconstruct historic atmospheric deposition with sub-annual resolution extending back 200 years. Of the metals investigated (Ag, Au, Pt, Pd, and Rh), Ag exhibited the greatest seasonal and annual variability and related to seasonal troposphere changes and the relative importance of local and regional sources. The implication of important local sources (e.g., waste incineration concentrated in the north coastal region of MA) and the potential for seasonality in atmospheric loading must be considered in applying the estimates arrived above.

A summary of Ag fluxes for the box model representing the Massachusetts Bays system during 1994-1996 is presented in Fig. 3.54. A table of the parameters used to construct the Massachusetts Bays box model and estimate Ag fluxes is presented in Appendix A.6.

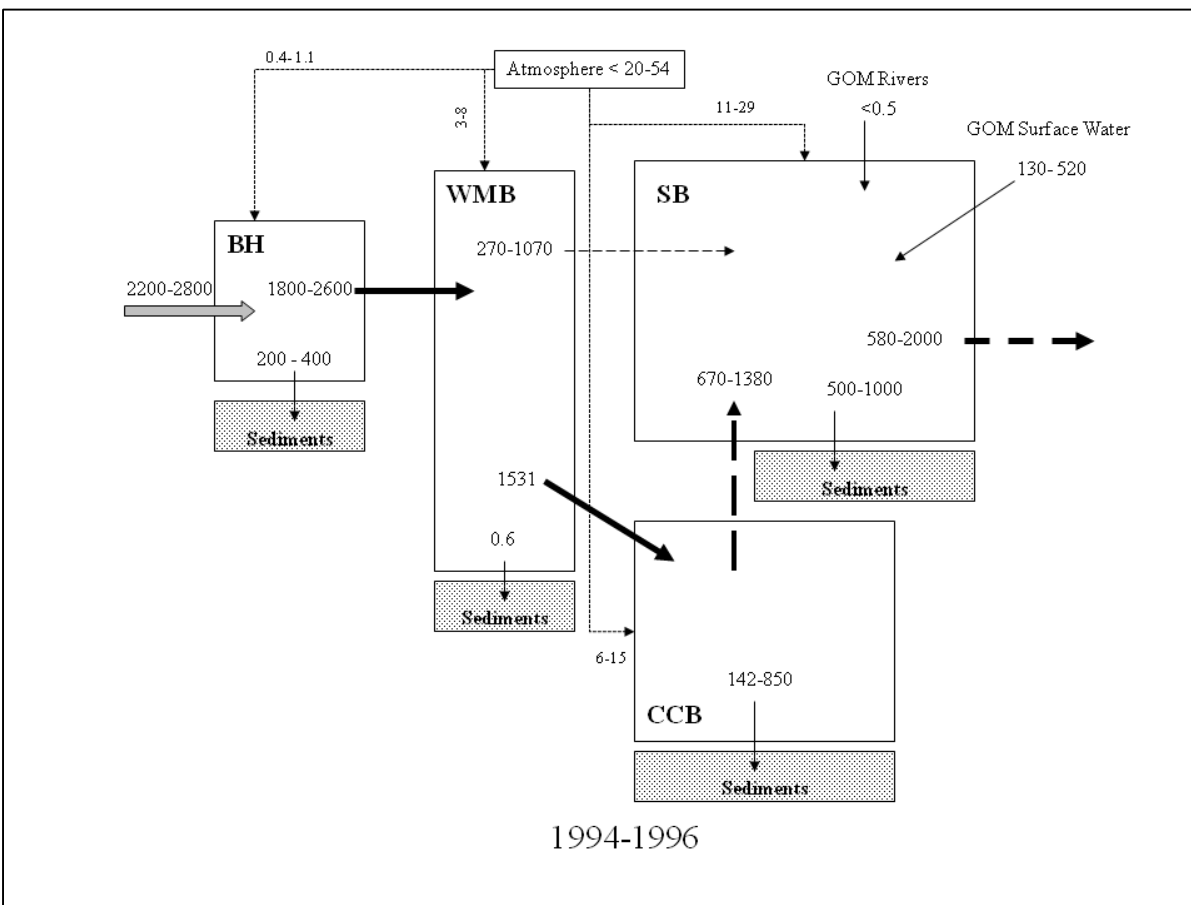


Figure 3.54. Massachusetts Bays System (MBS) box model of silver fluxes (kg y^{-1}) to and between Boston Harbor (BH), western Massachusetts Bay (WMB), Stellwagen Basin (SB), and Cape Cod Bay (CCB), 1994-1996. The grey arrow into Boston Harbor is the flux estimated from the Massachusetts Water Resources Authority's wastewater discharge data. Dashed arrows indicate estimates based on input-output balance to the SB compartment of the MBS.

3.6 Conclusions

Data generated from the surveys conducted in the Massachusetts Bays system and adjacent coastal waters provide the first reported values of Ag concentrations in these waters. Overall, mean water column Ag concentrations decreased from Boston Harbor ($Ag_F = 103 \pm 48$, $n=12$; $Ag_P = 117 \pm 127$, $n=13$ pmol kg^{-1}), to western Massachusetts Bay ($Ag_F = 34 \pm 23$, $n=70$; $Ag_P = 10 \pm 8$, $n=66$ pmol kg^{-1}), to Stellwagen Basin and Cape Cod Bay ($Ag_F = 11 \pm 7$, $n=10$; $Ag_P = 7 \pm 5$, $n=10$, pmol kg^{-1}). Total Ag concentrations in southern GOM surface water averaged near 12 pM ($Ag_F = 9.6 \pm 5.2$, $n=24$; $Ag_P = 2.0 \pm 1.6$, $n=20$, pmol kg^{-1}). Both summer and winter surveys revealed significant correlations with salinity and demonstrate the utility of silver as a tracer of dispersion and fate of wastewater in the coastal waters of the Massachusetts Bays system.

Beyond the near-field region of the Boston wastewater outfall, most of the silver ($78 \pm 12\%$, $n = 85$) existed in the “filterable” ($<0.4 \mu\text{m}$) size range. This observation is of significance because fine-grained sediment transport in the MBS has often been invoked to explain transport and fate of silver in the MBS (see references in Warner et al., 2008). Strong correlations have been observed for metal sediment concentrations with sediment organic carbon content (Hilbig et al, 1996; Zago et al., 2001; Wallace et al. 2006) or associated with the deposition and burial of biogenic material (Sanders and Abbe, 1987; McKay and Pedersen, 2008). In fact, silver (and other metals) in recent Cape Cod Bay sediment (collected for the EPA’s National Coastal Assessment, 2000-2006) were found to be strongly correlated with the amount of organic carbon (Fig. 3.55). Organic carbon is an important metal partitioning phase in soils and surface water particulate matter (Gustafsson et al., 2003; Turner and Millward, 2002; Turner and Mawji, 2005; Li et al., in press). Though strong correlations were also

observed with the clay/silt fractions in these samples (Table 3.24) the predominance of dissolved/colloidal (filterable) Ag in the water column of the MBS during 1994-1996 and its advective transport would be plausible for supporting the recent inventory of silver estimated for Cape Cod Bay sediments if chemical equilibrium between sediments and the overlying water column, as suggested by Wallace in Hilbig et al. (1996), and/or the potential for mediation by biogenic particulate flux are considered.

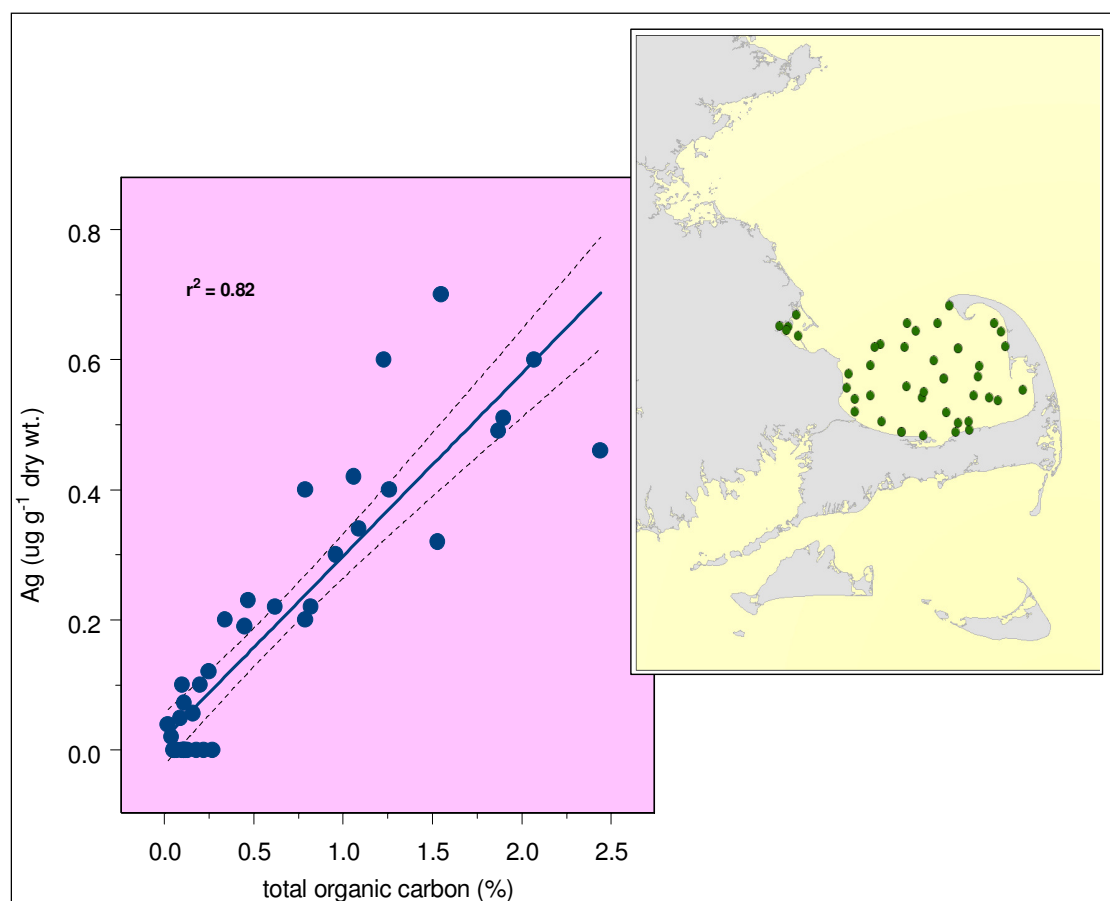


Figure 3.55. Least squares regression of silver with organic carbon content in Cape Cod Bay Sediments (n=45). Data from EPA's National Coastal Assessment surveys, 2000 - 2005. 95 % confidence intervals are also shown (dashed lines).

Table 3.24. Regression coefficients of selected metals with % organic carbon and silt/clay fractions in samples collected in Cape Cod Bay (2000-2005). Data from the National Coastal Assessment surveys.

	Ag	As	Cr	Cu	Hg	Ni	Pb	Zn
Organic Carbon	0.82	0.93	0.91	0.90	0.80	0.91	0.84	0.91
Silt/Clay Fraction	0.79	0.88	0.88	0.87	0.90	0.88	0.88	0.90

The budget for Ag in the Massachusetts Bays system is reasonably well-represented by a quasi steady-state model in which Ag inputs from Boston Harbor, most of which came from the Boston municipal wastewater effluent, are ultimately removed by exchange of Cape Cod Bay water with the southern portion of the GOM or trapped in the MBS sediments. The three major inputs to Massachusetts Bay occur from the GOM surface waters across the northern and eastern boundaries of Massachusetts Bay and from exchanges of water with Boston Harbor. By far, the majority of Ag loading (84-94%) is associated with ocean disposal of municipal wastewater from Boston. The advective transport of Ag from the GOM is estimated to be on the order of 100-500 kg y⁻¹, with the Merrimack River contributing less than 1% of this total. However the GOM flux is poorly understood and these estimates are constrained by the uncertainty associated with the estimates of GOM surface water transport into Massachusetts Bay. Jaing and Zhou (2008) used a hydrodynamic model to estimate circulation forces and found their model underestimates salinity in the MBS and thus overestimates the contribution of the western Maine coastal current to water exchanges in Massachusetts Bay. By the authors reasoning, the role of the western Maine coastal current, which includes discharges from the Merrimack River, remains difficult to assess. The relative importance of wind-induced upwelling and downwelling features on circulation and transport are related to wind patterns and these can shift the dynamics of circulation and contaminant accumulation (Jiang et al.,

2007; Jiang and Zhou, 2008; Tian et al., 2009). For periods of southwesterly winds, (more typical in late summer and early fall) localized near-shore upwelling is established and transport can be more northerly and opposite from more typical northwesterly prevailing wind conditions. While the GOM Ag flux is a distant second to the flux associated with wastewater disposal, the potential for contaminant loadings associated with the GOM surface water remains important because of the magnitude of water transport across the open boundary into Massachusetts Bay. Further, between 40-64% of the Ag entering the Massachusetts Bay system during 1994-1995 is estimated to be retained in areas of long-term deposition while the remaining Ag (~40-60%) is transported to southern GOM waters.

Even though the location of Boston's wastewater discharge has changed and the loading of Ag has markedly decreased in recent years (see Fig. 3.51), Ag input from ocean wastewater disposal remains the major source to the Massachusetts Bays system, (Table 3.25) but now similar to fluxes estimated from exchange with the GOM. However, the current role of sediments in the biogeochemical cycling of Ag may have changed (Wallace et al., 2006; Li et al., *in press*). These sediments may become a more important source of silver and other contaminants to the overlying water column (Smith and Flegal, 1994). Li et al., (*in press*) have shown that despite significant advancements in wastewater treatment and the removal of wastewater discharges from Boston Harbor altogether, trace metal water column concentrations remain elevated and comparable to prior periods.

Based on the relative size of the Stellwagen Basin depositional area, most of the sediment-bound silver (44%) in the MBS is estimated to reside in Stellwagen Basin. In addition, the Charles River contributes a comparable amount of freshwater to Boston Harbor as did the MWRA wastewater effluent. Given the relocation of Boston's wastewater discharge to western

Massachusetts Bay, the role of the Charles River in metal loading to Boston Harbor may be important but probably secondary to fluxes from contaminated harbor sediments.

Table 3.25. Massachusetts Bays System Silver Budget Summary

1994-1996: kg y ⁻¹			2000-2002 kg y ⁻¹ kg y ⁻¹		
Inputs:			Inputs:		
MWRA	2200-2800	84-94%	MWRA	300-700	53-58%
GOM	130-520	6-16%	GOM	130-520	25-40%
Rivers	0.1-0.5	0%	BH	70 ¹	5-13
Atmosphere:	20	1%	Rivers	0.1-0.5	0%
			Atmosphere:	20	2-4%
Input Totals	2350-3341		Input Totals	520-1310	
Outputs:			Outputs:		
Sediments	842-2250	40-43%	Sediments	850-2250	41-43%
	BH	200-400 18-24%	Exchange Flux	1250	24-60%
		500-			
	SB	1000 44-59%	Output Totals	2100-3500	
	CCB	142-850 17-38%			
		842-			
	Total	2250			
Exchange					
Flux	1250	1250 24-60%			
Output Totals	2092	5184			

¹Steady-state net sediment (and Charles R) flux needed to support ~100 pM Ag in Boston Harbor water.

CHAPTER 4

THE COMPARATIVE BIOGEOCHEMISTRY OF SILVER WITH OTHER SELECTED TRACE METALS IN COASTAL WATERS NEAR MASSACHUSETTS, USA.

4.1 Introduction

The distribution of trace metals in the water column provides important clues to the factors controlling contaminant fate and transport in aquatic systems. Beyond the influence of source loading, the biogeochemical cycling of trace metals is controlled by competing interactions among particles (Collier and Edmond, 1984; Honeyman and Santchi, 1989), colloids, dissolved ligands (van den Berg et al., 1987, 1991; Kozelka and Bruland, 1998; Millward and Turner, 1995; Muller, 1998; Shine and Wallace, 1995; Tang et al., 2001), and sediments (Froelich et al., 1979; Murray and Leinen, 1993; Nameroff et al., 2002). The speciation of metals in natural waters, therefore, is complex and consists of many different chemical and physical forms. Evaluating whether biogeochemical similarities exist among the metals in coastal marine waters would strengthen these interpretations (Murray et al., 1983; Landing and Bruland, 1987).

To improve our understanding of the behavior of silver in coastal marine waters, we investigate the distributions of particulate ($\geq 0.4 \mu\text{m}$) and filtered trace metal concentrations and selected water quality parameters (see Table 4.1) of coastal waters near Massachusetts, USA. For this exercise, we focus on three data sets generated from the Massachusetts Bays July

1995 and Sept. 1996 surveys and the southwestern Gulf of Maine (GOM) July 1996 survey. These data sets were selected for their consistent suite of analytical parameters used to characterize discrete coastal water samples (Table 4.1). Station location and sampling details were presented earlier (Chapter 3). It is important to note that the sample size (n) of individual sampling events were between 20-33 for each survey and samples were evaluated for 17 parameters and thus may limit the ability to resolve latent factors influencing each data set. A value of ½ the method detection limit was substituted for non-detectable levels. Non-detectable data among the combined data sets were < 1.5%.

Table 4.1. Data sets from Massachusetts Bays and the Gulf of Maine, 1995-1996 and parameters measured.

Data set	Sample Design	# Stations	# Samples (n)	Physical setting
July 1995	Surface water survey, Mass. Cape Cod Bays	25	25	Summer, well-stratified, period of extended drought
July 1996	Southern coastal Gulf of Maine Mixed layer depth profiles	5	20	Summer conditions
Sept 1996	Near coastal survey, plume mapping, Massachusetts Bay	16	33	Reduced exchange between Boston Harbor and Mass.Bays, summer conditions
Parameters:	Filtered metals: pmol kg ⁻¹ (Ag _F , Pb _F , Cd _F), nmol kg ⁻¹ (Cu _F , Zn _F , Fe _F)			
	Particulate metals: pmol kg ⁻¹ (Ag _P , Pb _P , Cd _P), nmol kg ⁻¹ (Cu _P , Zn _P , Fe _P , Al _P),			
	Particulate organic carbon, uM (POC)			
	Total suspended matter, mg L ⁻¹ (TSM)			
	Chlorophyll <i>a</i> , ug L ⁻¹ (Chl <i>a</i>)			
	Salinity, psu (S)			

The data sets have distinct differences among their field sampling designs as well as the physical setting from which samples were collected. With these distinctions in mind, this

analysis begins with a review of the physical settings encountered during the surveys and the temporal and spatial distributions of selected water/particle parameters.

The distribution of particulate organic carbon (POC) and total suspended matter (TSM) along the salinity gradient were markedly different among each sampling event (Fig. 4.1). Higher concentrations of TSM and POC were observed in water samples collected during the nearshore survey conducted in Sept. 1996, most probably the result of the targeted sampling of Boston Harbor water mixing into the southwestern portion Massachusetts Bay. The GOM survey was conducted in waters with higher salinity (above 32 psu) and was typically low in both TSM and POC. Except for a 2 or 3 samples, the summer 1995 Massachusetts Bay survey show POC and TSM concentrations characteristic of the 1996 GOM survey due, in part, to abnormally low freshwater input (Chapter 3). The combined data illustrate adequate sampling of mixing between inshore, lower salinity, higher TSM with more oceanic water along a minimum of two possible salinity gradients within the pooled data (n=76).

To test if pooling these data is feasible for the comparative geochemical analyses, the clustering around medoids within the salinity and TSM data of the combined sets were examined and the results plotted in two-dimensional principle components (salinity and TSM) space. The medoid represents the point in the cluster whose average dissimilarity to all the other points in the cluster is minimal. Outliers (determined as $> 1.5 \times$ interquartile range of observations) exist in the data (Fig. 4.2) and clustering around medoids is considered to be more robust (i.e., less sensitive to outliers) than the more traditional k means clustering when outliers are suspected. Euclidean distances for the dissimilarity matrix were calculated using the

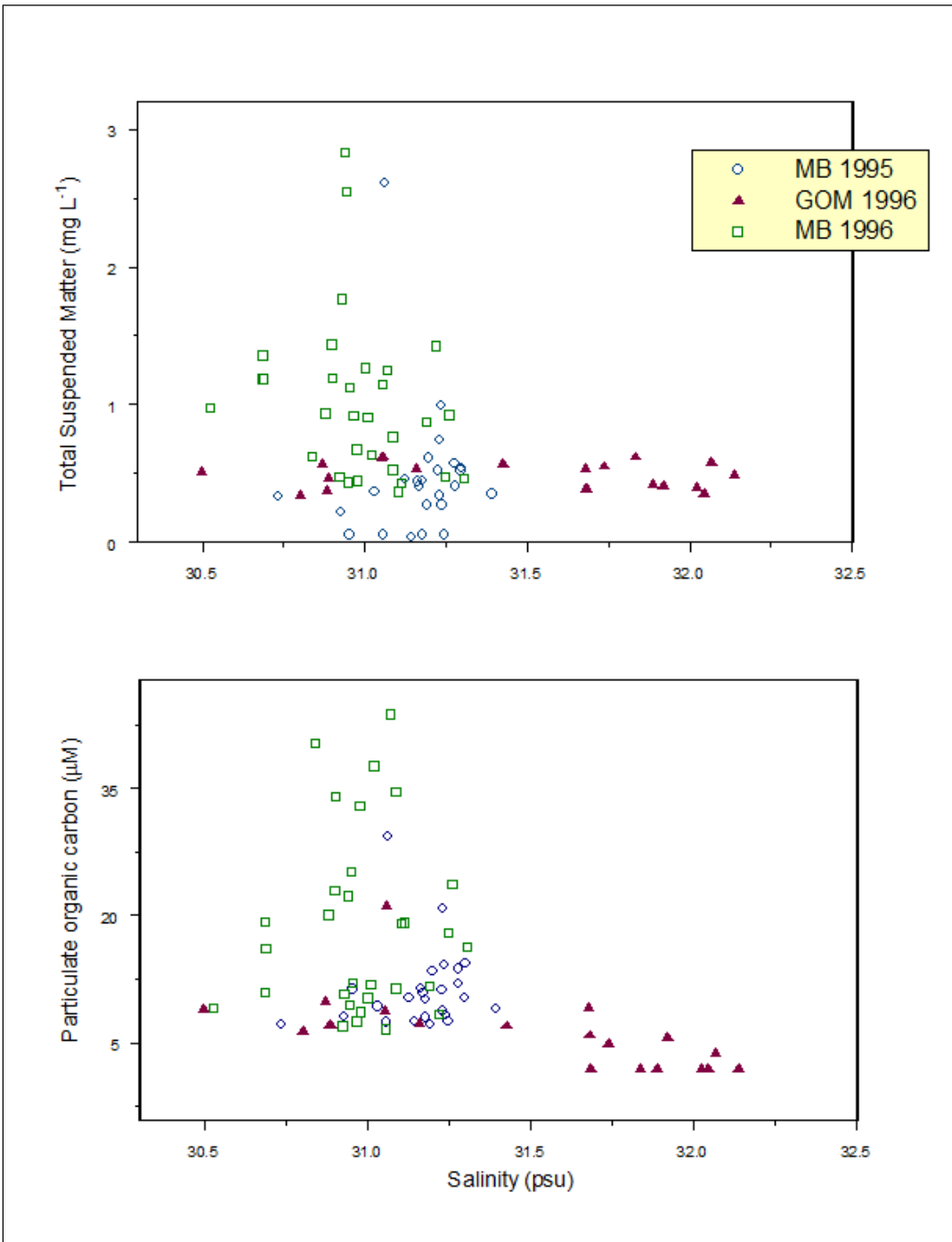


Figure 4.1. Distribution of TSM and POC along salinity gradients; July 1995, July 1996, and Sept. 1996.

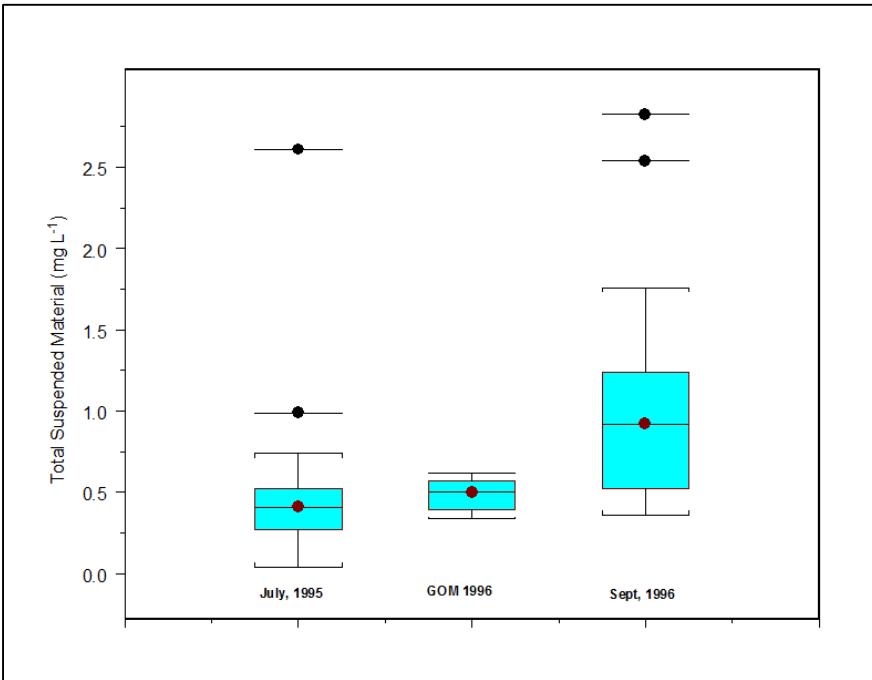


Figure 4.2. Box and whisker plots of total suspended material (mg L^{-1}) from the July 1995 Massachusetts Bay survey, July 1996 Gulf of Maine survey, and Sept 1996 Massachusetts Bay survey. Outliers $> 1.5 \times$ the interquartile range. $\text{IQR} = (\text{Q3} - \text{Q1})$.

statistics package S-Plus 7 (Insightful Corp., 2005). The samples that populate the outer portions of the two clusters are listed with the distribution in Figure 4.3. The data sets from 1995-1996 are assumed to be representative of a steady-state system and the clustering of the data represents, at a minimum, two unique sources of freshwater supplied to Massachusetts Bay: from the Gulf of Maine (which includes influences from the Merrimack River) and the mixing of freshwater from Boston Harbor.

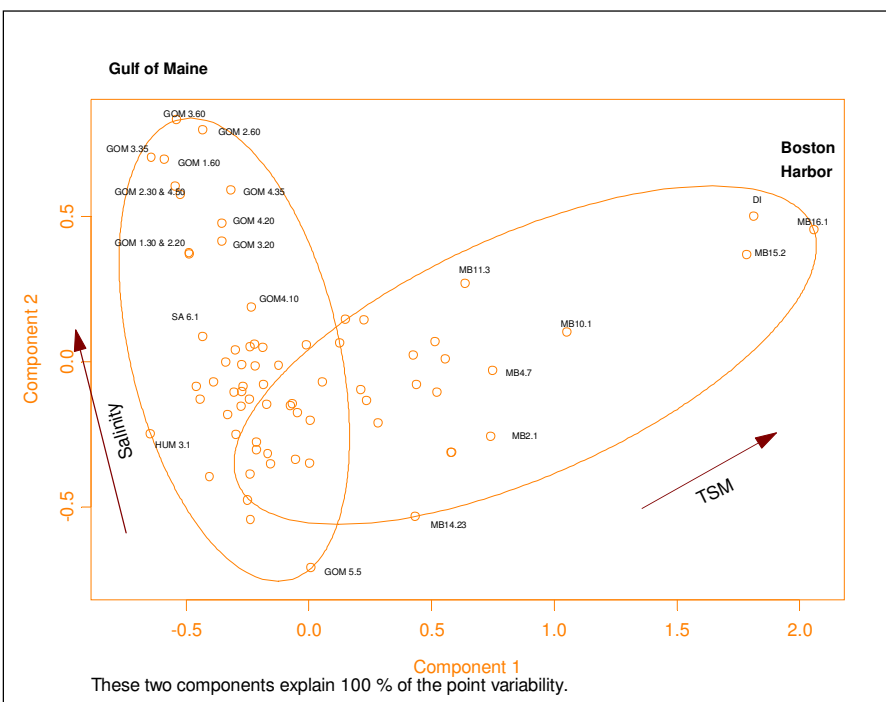


Figure 4.3. Cluster analysis of TSM and salinity data from July 1995 – Sept. 1996.

4.2 Distribution coefficients

Distribution coefficients (K_D s) for metals have been used as a measure for generalizing differences in the geochemical behavior of metals observed across space and time (Tang et al., 2002). In a broad sense, K_D represents a reversible equilibrium process describing the distribution of metal in aquatic systems as the ratio of metal sorbed onto solid phases (e.g., soil, sediment, particles) to metal concentrations present in the liquid phase near a solid/liquid interface. Early geochemical models used K_D to describe the distribution of elements among crustal abundance and reported oceanic concentrations in order to highlight patterns of metal residence times and binding strength to mineral surfaces (Whitfield, 1981). For our purposes, the distribution (or partitioning) coefficient is empirically derived from measured analyte

(metal) mass associated with particle mass relative to the amount dissolved per unit volume of water:

$$K_D = [Me_P]/[Me_F] \quad (1)$$

where $[Me_P]$ is the mass of filter-retained metals/mass solids,

and $[Me_F]$ = mass of filter-passing metal/volume of water (cf., Benoit et al., 1994).

For comparative purposes, particulate metal concentrations are typically normalized to 1 kg of solid matter and “dissolved” concentrations to 1 kg of seawater. For the purposes here, $[Me_P]$ has units of mol kg⁻¹ of particulate matter, and $[Me_F]$ has units of mol kg⁻¹ of seawater and reflects the amount of metal that passes through a 0.4 μm filter (see Chapter 3). Further, we assume that the observed K_D reflects local equilibrium and that the reactions that result in metal binding to solids occur rapidly relative to the advective-dispersive transport time scales (hours – weeks) of the Massachusetts Bays system.

To help evaluate the anthropogenic factors of metal loading to Massachusetts Bays, the potential contribution from crustal weathering to the concentration of metals observed in the water column was evaluated by attributing the observed particulate aluminum concentration of the sample solely to crustal weathering processes. Thus, the K_D 's were evaluated for the need to correct for potential inputs from crustal weathering using the ratios of crustal abundances relative to the aluminum concentration for an average crustal material. We determine excess particulate metal concentrations using the elemental crustal ratios (CR) reported in Wedepohl (1995) and given in Eq. 2.

$$[Me_P]_{\text{excess}} = ([Me_{P,\text{Sample}}] - CR[Al_{P,\text{Sample}}]) \quad (2)$$

where $(CR) = ([Me_{\text{Crust}}] / [Al_{\text{Crust}}])^{-1}_{\text{Wedepohl1995}}$

Least-squares linear regression of the apparent K_D with those adjusted for crustal abundances ($K_{D,-Crust}$) revealed the correction for crustal abundances to be minor (Table 4.2) and supported by earlier observations and the order of crustal influence on the K_D to be $Ag < Cd < Cu < Pb < Zn < Fe$. When $\text{Log } K_{D,-Crust}$ (or $\text{Log } K_D$) values for each of the three surveys are plotted along the salinity gradient (Fig. 4.4), a few noticeable trends emerge. For each metal studied, the $K_{D,-Crust}$ (and K_D) data show a range of scatter that extends 3-4 log units. Further, the lowest K_D values observed for all metal analytes (Ag, Pb, Cu, Zn, Cd, and Fe) were from a portion of the September 1996 nearshore survey where sampling was targeted in the Boston Harbor – Massachusetts Bay mixing zone (cf. Chapter 3).

Table 4.2. The results from least-squares linear regression comparing the apparent K_D s with corrections made using crustal abundances values of Wedepohl (1995) and listed in increasing order of crustal influence.

$\text{Log } K_D : \text{Log } K_{D,-Crust}$	Slope (m)	y-intercept (b)
Ag	1.001	-0.0009
Cd	0.9999	0.0005
Cu	0.9995	0.0034
Pb	0.9989	0.0089
Zn	0.9981	0.0119
Fe	0.9965	0.0326

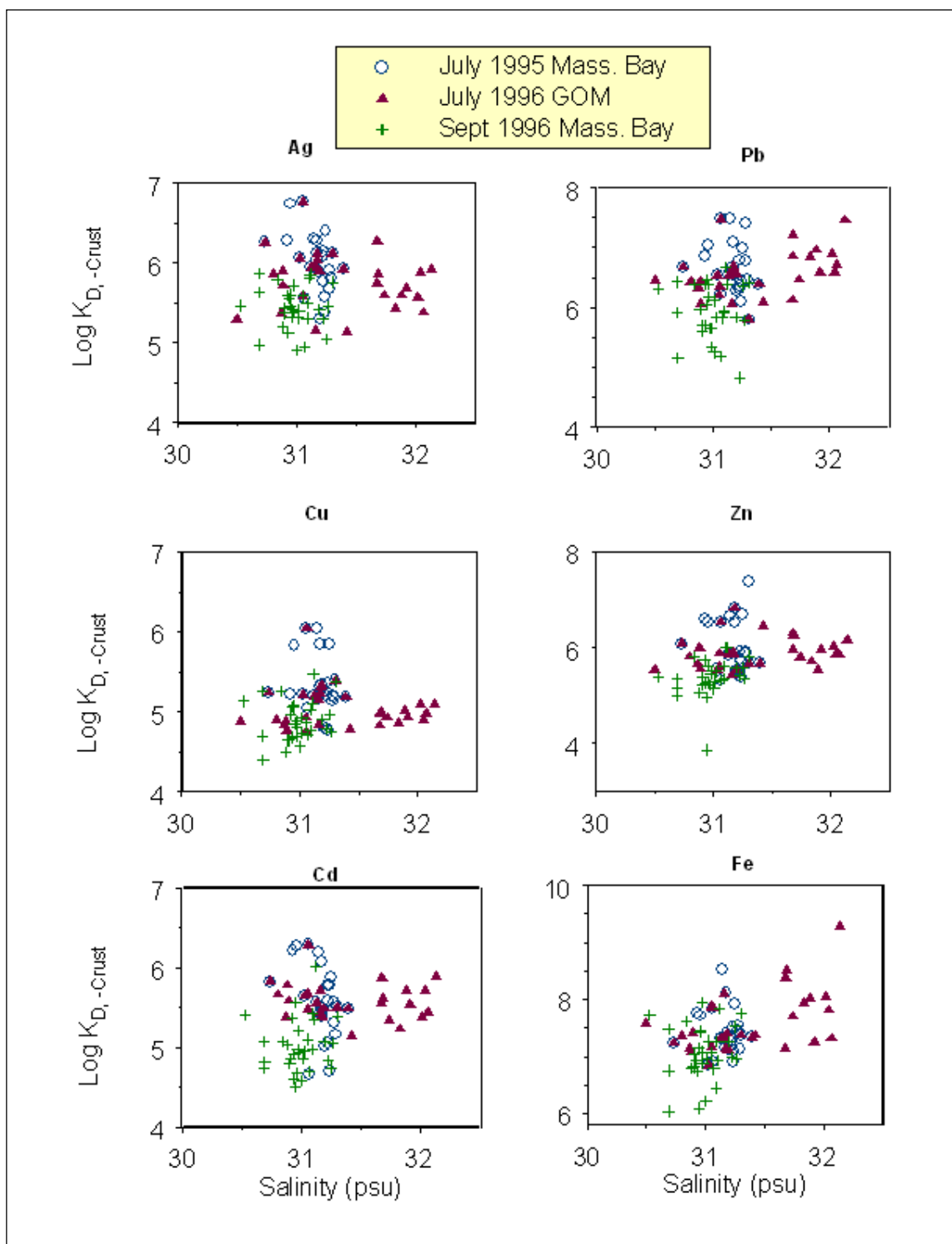


Figure 4.4. The apparent distribution coefficient ($K_{D, -crust}$) for selected metals, corrected for crustal abundances (Wedepohl, 1995), along salinity gradients observed in coastal waters near Massachusetts, USA 1995-1996.

The distribution of $K_{D,-Crust}$ data for each metal among all three are shown in the box and whisker plots in Figure 4.5. Higher K_D values imply greater affinity for sorption onto particles or complexation with compounds involved in particle genesis. With the exception of a few outliers, all the observed Log $K_{D,-Crust}$ (and K_D) values ranged over several orders of magnitude. To test for differences among all three surveys for each of the trace elements investigated, a conservative analysis of variance (ANOVA) was conducted, using Bonferroni method, to estimate the familywise error rate (i.e., the probability of having one or more false findings

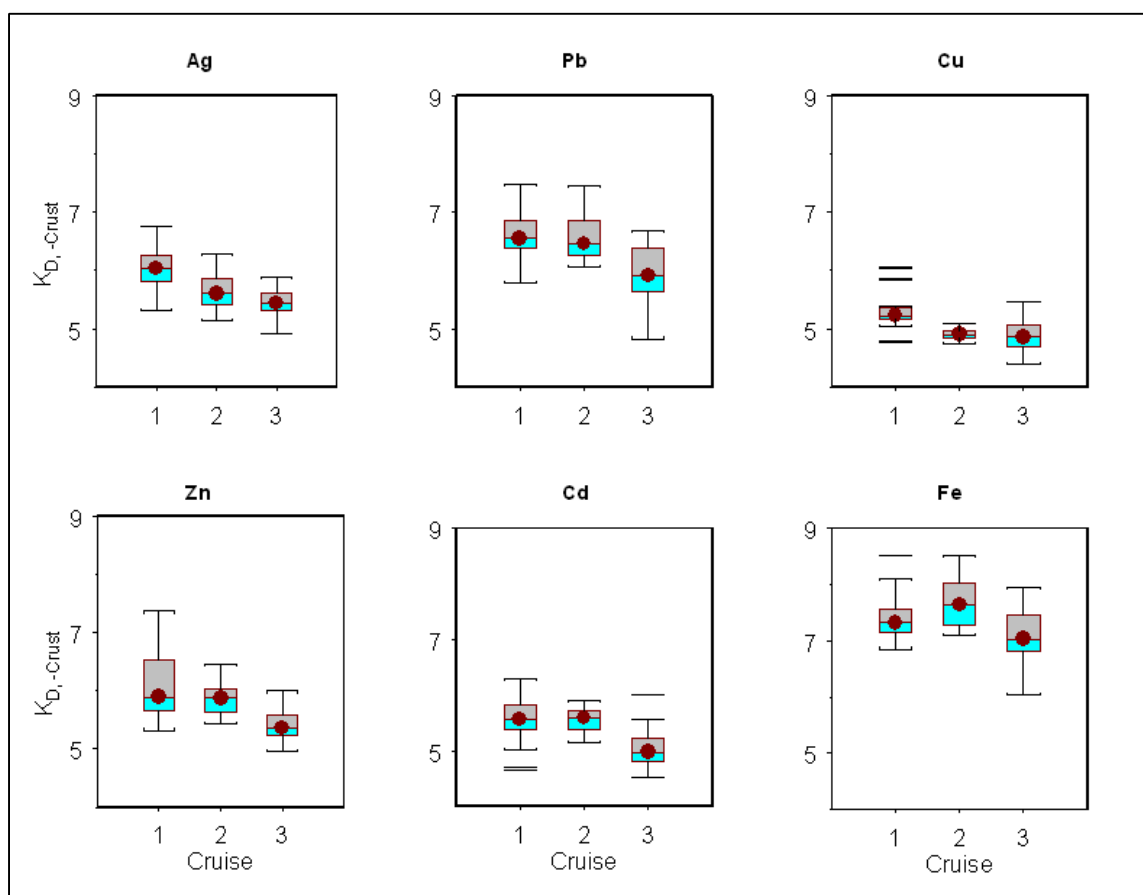


Figure 4.5. Box and whisker plots illustrating the median, upper and lower quartiles, and range of conditional $K_{D,-Crust}$ (kg⁻¹), observed for Mass. Bay water, July 1995 (1); coastal southern Gulf of Maine, July 1996 (2); and southwestern Massachusetts Bay water, Sept. 1996 (3). Outliers are indicated by isolated horizontal lines. Significance at the 95 confidence intervals are indicated as follows: (a) between July 1995 and July 1996; (b) between July 1996 and Sept. 1996.

among all the hypotheses when performing multiple pairwise tests). The ANOVA test revealed distinct intervals existed (at the 95% confidence level) for all the metals investigated, with the exception of Fe (Fig. 4.6). Specifically, conditional K_{DS} for Ag and Cu during the July 1995 Massachusetts Bay survey were greater than the values observed from samples that targeted the Boston Harbor-Massachusetts Bay mixing zone (Sept. 1996) and those collected from Gulf of Maine surface waters (July, 1996). In contrast, lower conditional K_{DS} values for Cd, Pb, and Zn were observed during the Sept 1996 survey. These metals also showed greater similarity of conditional K_{DS} from samples collected during the GOM and July 1995 Massachusetts Bay surveys when compared to those observed for Ag and Cu.

The observed differences may reflect changes in the quantities and binding qualities among the particulate, colloidal and dissolved ligands and resultant changes in the ambient free ion activities of ambient metals. Though no significant differences in the % organic carbon content of suspended solids were observed among the three surveys (Appendix B.2), changes in the ligand quality and quantity of the particles and soluble (filterable) fraction may be important to observed differences in K_{DS} . Soluble ligands include anions, molecules, and colloids ranging in molecular weight sizes from ~100 Da to greater than 10,000 Da (Smith et al., 2002). The contribution of colloids and their associated metals in the soluble fraction of natural waters have been studied and observed as highly variable in natural waters (Adams and Kramer, 1999; Shafer et al., 2004; Tang et al., 2000, Wells and Goldberg, 1994). Smith et al. (2002) provide an excellent summary of metal-ligand (ML) equilibria with natural organic matter (NOM) and use the biotic ligand model (BLM) as a means of modeling important NOM functional groups.

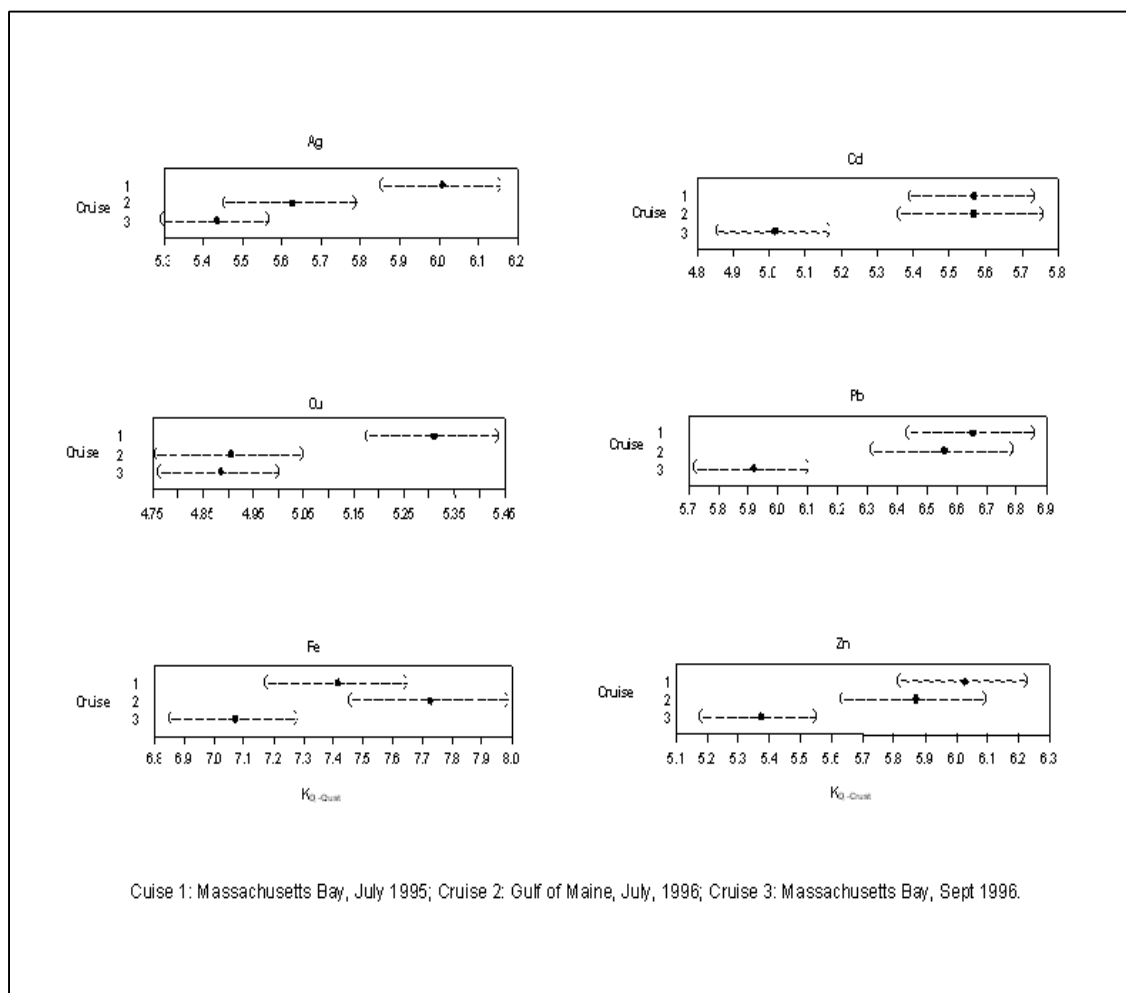


Figure 4.6. Analyses of variances of $K_{D,-Crust}$ among the two Massachusetts Bays (July, 1995, and Sept, 1996) and the Gulf of Maine (July, 1996) surveys. Dashed lines indicate 95% confidence intervals (based on the Bonferroni method) are shown.

The biotic model predicts binding constants (K^*) and ligand quantities (L_T) based on metal formation constants for known compounds representing each functional group. Important metal binding functional groups in NOM include carboxyl (-OOC), alcohol (-OH), amino (-NH), phenolic (-OAr), metal sulfide (-RM') and thiols (-SR). Transition metals (e.g., Zn and Fe) and the soft "B-type" metals (readily deformable, polarizable, and interaction mainly covalent) favor similarly "soft" ligands, like sulfides. Table 4.3 present the log K^* s summarized by Smith et al.

(2002) for functional groups simplified to include the metals studied here and demonstrate the potential significance of reduced sulfur ligands to transition and B-type metal biogeochemistry.

Though a minor component of NOM (Thurman, 1985), reduced sulfur ligands like biogenic thiols, or thiol-like compounds, have been implicated as important ligands for trace metal complexation in marine waters (Tang et al., 2000; Rozan et al., 2003) and have been identified as key ligands for soft B-type metals like Ag^+ , Cd^{2+} , and Pb^{2+} and the intermediates Zn^{2+} and Fe^{2+} (Wooland and Linder, 1999; Kogut et al., 2001; Smith et al., 2002).

Table 4.3. Formation constants ($\log K^*$) summarized for three functional groups of NOM. (From Smith et al., 2002)

	carboxyl (-OOC)	amino (-NH)	sulfide (-SR)
Fe(II)	2.16	3.42	6.3
Cu(II)	2.00	7.34	7.6
Ag(I)	2.07	3.40	12.1
Pb(II)	2.55	4.53	10.2
Cd(II)	2.24	3.84	8.5
Zn(II)	2.19	1.40	6.8

The role of wastewater-borne colloidal and soluble ligands in Massachusetts coastal waters is unknown. It is probable that the distribution of metal-complexing ligands in wastewater and their degradation products are important to metal speciation during wastewater dispersion in Massachusetts Bay. With the exception of Cu, the remaining metals displayed lower K_D (and $K_{D,-\text{Crust}}$) in the mixing zone between Boston Harbor and Massachusetts Bay where the potential for wastewater artifacts in the apparent K_D 's are more likely to occur. Smith et al. (2002) report the ligand $-\text{SCu}$ as potentially important in waters containing effluent from wastewater treatment facilities.

Highlighting the differences of apparent K_D s among the data sets serves two purposes: (1) to illustrate the potential for real differences among the data sets that limit interpretations of the statistical results of the combined data, and (2) support a comparative biogeochemical analysis of trace metals in Massachusetts coastal waters. In terms of a generalized solid-liquid partition model (eq. 1), the relative apparent K_D s were $\text{Cu} < \text{Cd} < \text{Ag}$, $\text{Zn} < \text{Pb} < \text{Fe}$ (Fig. 4.5; left panel), which is similar to the order reported by Guo et al. (2000).

Complexation of Cu by dissolved organic matter has been observed in natural waters for decades (van den Berg et al., 1987; Coale and Bruland, 1988, Shine and Wallace, 1996; Wells et al., 1998; Kozelka and Bruland, 1998; Shafer et al., 2004) and is reflected by the overall lower K_D values. Further, Cu exhibited departure from behavior observed for other metals in the Harbor-Bay mixing zone.

Advancements in the sampling of colloids in natural waters have allowed assessment of metal partitioning to colloids in estuarine and coastal waters (Muller, 1996; Gordon et al., 1996; Kozelka and Bruland, 1998; Wells et al., 1998, Shafer, 2004). The $K_{D,\text{Colloid}}$ is more often found to be significantly greater than has been traditionally reported for particle-based partition coefficients (Guo et al., 2000; Shafer et al., 2004). Colloids and meta-stable sulfide complexes have been identified as important elements of speciation for Zn and Pb (Benoit et al., 1994, Shafer et al., 2004, Rozan e t al., 2003). These species may be important with respect to water column residence times and thus to the transport and fate of metals in natural waters. Because Ag exhibits intermediate partitioning among filter-passing and filter-retained material, complexation reactions with colloids or dissolved organic matter are likely important in the transport and fate of silver in the marine environment, especially if they involve reduced sulfide ligands (Smith et al., 2002).

When metal conditional partition coefficients are compared the following sequence emerges: $\text{Cu} < \text{Cd} < \text{Ag}$, $\text{Zn} < \text{Pb} < \text{Fe}$ (Fig. 4.7). This order is a departure from the Irving/Williams order of increasing stability of metal complexes and is generally thought to be independent of ligand type (Irving and Williams, 1953; Stumm and Morgan, 1996). Guo et al. (2000) attribute departure in the $K_{D,\text{Colloid}}$ for metals from predicted Irving-Williams order to differences in the chemical composition of colloids and suspended matter. Gorelsky et al. (2005) observed that stability constants for metal-thiolate complexes did not follow the Irving-Williams series and demonstrate the importance of the changing roles of covalent and ionic contributions, and by extension, ligand quality to metal-ligand bonding strength.

A further review of recent soluble metal speciation findings indicates the importance of ambient ligands on chemical speciation in natural waters (Muller, 1996; Gordon et al., 1996; Kozelka and Bruland, 1998; Wells et al., 1998). Metal complexing ligands (L_T) in natural waters include anions, molecules, colloids (clusters, polymers) and small particles and their contribution to metal complexation varies among the metal types (e.g., A, B, or transitional). For instance, the strong Pb-binding ligand class (Pb- L_1) in Narragansett Bay waters was colloidal (1 kDa – 0.2 μm) while the L_1 (the strongest ligand class) for Cu was dissolved (< 1 kDa). Both Muller (1996) and Gordon et al. (1996) report predominantly dissolved Cu- L_1 complexes for English coastal and Chesapeake Bay waters, respectively. Organic complexes of Cd were predominantly colloidal in coastal waters of England (Muller, 1996). However, Wells et al. (1998) observed predominantly dissolved Cd organic complexes in Narragansett Bay. Wells et al. (1998) point out that colloidal separation techniques used by various investigators could contribute to significant differences in the interpretation of metal speciation among the different size classes in filtered natural waters.

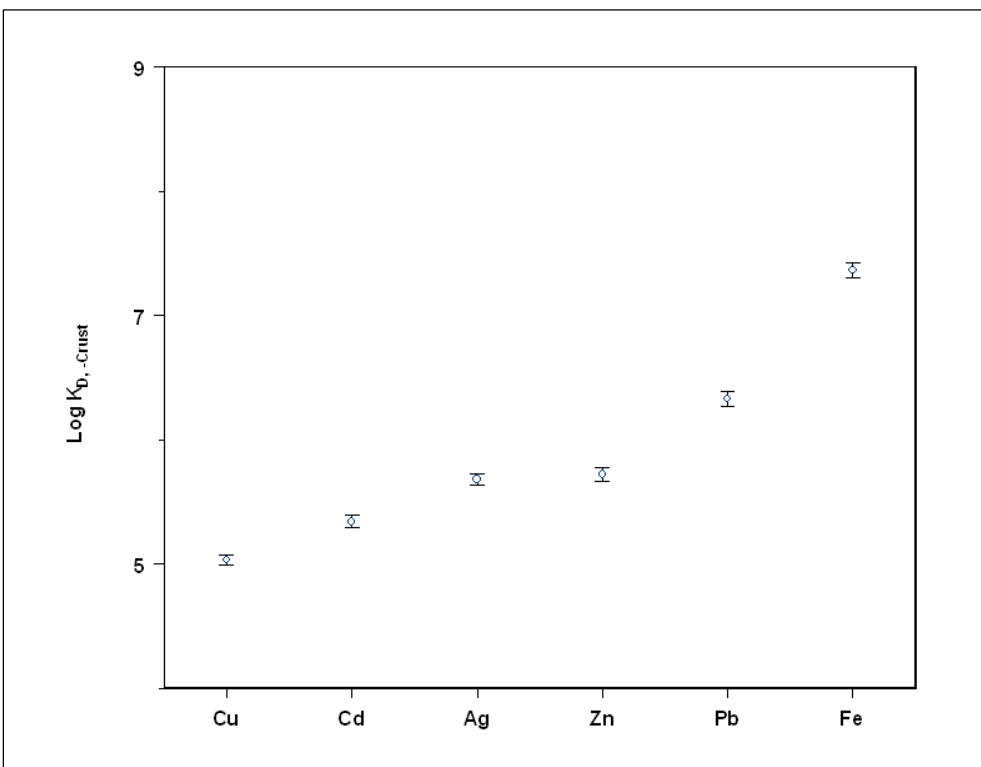


Figure 4.7. Mean (\pm SE) conditional metal partitioning coefficients (K_D and $K_{D, -Crust}$) between particulate and 0.4 μ m-filtered metals observed in coastal waters near Massachusetts, 1995-1996. $K_{D, -Crust}$ represents metal partitioning between the *non*-crustal component of suspended matter and filtered coastal water.

Our conditional partition coefficients (both K_D and $K_{D, -Crust}$) are operationally defined by our filtration technique and include potential colloidal complexes in the filtered fraction (cf., Eq. 1). Thus, the importance and potentially variable contribution of the colloidal component in our filtrate, the nature of other soluble ligands, and variable contribution from biogenic particulate matter (e.g., plankton, terrestrial detritus, etc.) could explain, in part, the differences observed among the conditional partition coefficients; such as the higher K_D values observed for Ag and Cu from the July 1995 Massachusetts Bay samples, the lower values observed for Cd, Pb, and Zn from the Sept 1996 Boston Harbor - Massachusetts Bay mixing survey (see Fig. 4.6), and the similarities in K_{DS} for Pb, Cd, and Zn between the 1995 Massachusetts Bay and 1996 GOM

surveys. Our ability to understand important processes controlling the biogeochemistry of trace metals in the Massachusetts Bay is limited by the empirical separation between filtered seawater and particles and the poor understanding of the nature of NOM. We use multiple factor analyses to explore hidden multivariate structures in the data sets and the concepts presented above with the goal to elucidate source strengths and potential biogeochemical controls affecting the observed trace metal concentrations and distributions in coastal waters of Massachusetts.

4.3 Exploratory factor analyses

Factor analysis (FA) is a statistical technique that is being more frequently used to explain the covariance structure in multivariate data by reducing the data set to a few unobserved latent features (or factors). Typically factor analysis includes principal components analysis (PCA) as a starting point for indentifying the number of factors to be tested. Both factor analysis and PCA use linear combinations of variables to identify these latent factors, but FA is only concerned with the portion of variance that covaries. PCA attempts to explain all of the variance with decreasing importance of sequential principal components.

In PCA, the actual variables are considered while true FA relies on identified factors to reduce the dimensionality of data. While PCA generally leads to a unique solution, FA develops models that explain the covariance or correlations by means of a few common factors and can lead to a number of possible factor solutions. The results from an exploratory approach can then be used in developing conceptual models and hypotheses for further testing in more confirmatory settings.

Briefly; for q number of variables (x), FA can be formally represented as:

$$x = \Lambda f + u \quad (3)$$

where (x) is explained by a linear combination of factors derived from a matrix of (Λ) regression coefficients (λ) for k factors (f) plus a specific residual term (u). A starting value for f is selected, often from preliminary PCA analyses based on the relative importance of the principle components are evaluated. For multivariate data, then:

$$x_1 = \lambda_{11} f_1 + \lambda_{12} f_2 + \lambda_{13} f_3 + \cdots + \lambda_{1k} f_k + \mu_1 \quad (4)$$

$$x_2 = \lambda_{21} f_1 + \lambda_{22} f_2 + \lambda_{23} f_3 + \cdots + \lambda_{2k} f_k + \mu_2$$

$$x_3 = \lambda_{31} f_1 + \lambda_{32} f_2 + \lambda_{33} f_3 + \cdots + \lambda_{3k} f_k + \mu_3$$

↓

$$x_q = \lambda_{q1} f_1 + \lambda_{q2} f_2 + \lambda_{q3} f_3 + \cdots + \lambda_{qk} f_k + \mu_q$$

Fundamental to FA, as implied in equation (4), is that the variance of each observed value can be divided into two fractions; common and unique (Venables and Ripley, 1994). Therefore, common factor solutions arrived by FA seldom explain the total variance of the data. Exploratory and confirmatory approaches define two important subdivisions of FA. Exploratory factor analysis (EFA) is used to explore the data structure and postulate theories based on factor solutions, rather than developing theory-testing models using the more common confirmatory FA approach (Sainfort, 2002). In the following analyses, these distinctions are muddled, at least to the degree at which we have assigned potential roles to our variables prior to exploratory FA.

Exploratory R- factor analyses (where similarities among the parameters are investigated) of the concentrations of parameters determined on each of the survey data sets

listed in Table 4.1 were conducted using S-Plus 7.0 (Insightful, Inc., 2006). Linearity among the variables is critical for both PCA and FA and we have seen (Chapter 3) that strong covariance exists among some of the variables (e.g., $Fe_P : Al_P$, Fig. 4.8). Multivariate normal distribution is also critical to FA and PCA. Thus, the results can be affected by non-normally distributed data. As evidenced by the histograms shown along the diagonal in Fig. 4.8 and typical of most geochemical data, our data often show skewed and/or multi-modal patterns (see Appendix B.2) and contain potential outliers (e.g., $K_{D, -Crust}$, Fig. 4.5). The treatment of outliers in FA analysis is important as well (Pison et al., 2003). Here, we attribute outliers to analytical artifacts, usually from contamination as a result of sampling and processing. Outliers were initially identified in the combined data set (July 1995 and Sept 1996 Massachusetts Bays, July 1996 GOM) as those values that exceeded 3 times the standard deviation of means. However, observations from three samples (DI from July 1995, and the surface samples from MB15 and MB16 Sept 1996) met this criteria consistently among many co-variables (i.e., relatively high values among many of the metals) and these data were thought to represent Boston Harbor water and are not considered as true outliers. Thus, six observations were treated as outliers and removed (Table 4.4).

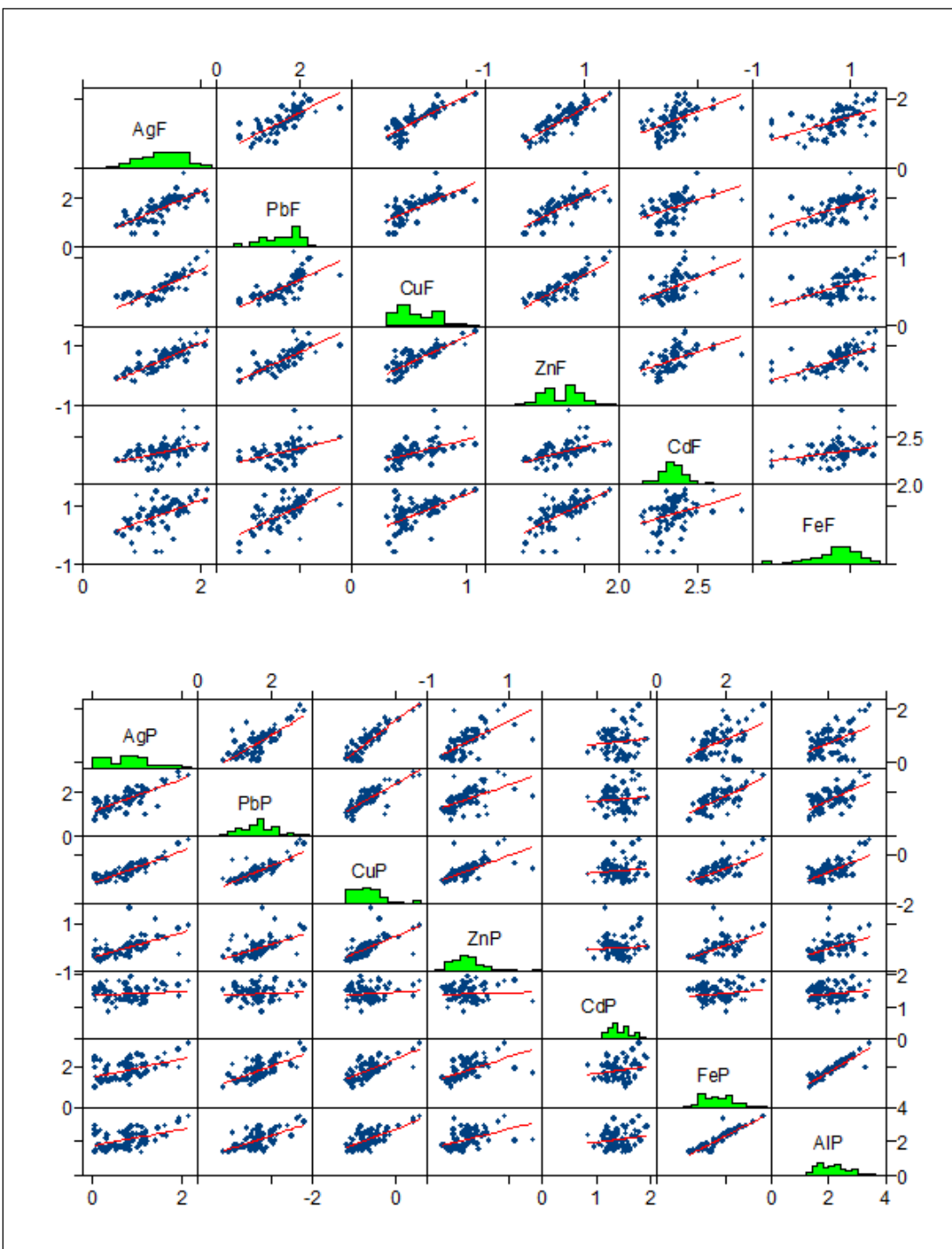


Figure 4.8. Summary matrix plot of combined filtered and particulate metals (Me_F and Me_P) log concentrations (as listed in Chapter 3) for Massachusetts Bay water samples collected during July, 1995, July 1996, and Sept 1996. Distribution histograms are shown along the matrix diagonal. Least squares regression lines are also shown in red.

Table 4.4. Observations treated as outliers in the combined data set.

Survey	Sample	Depth (m)	Analyte
1995 July 31	SA1	1	Pb _F
	SA3	1	Cd _F
	MAN1	1	Zn _P
1996 July 18	GOM3	60	Cd _P
1996 Sept 11	MB7	1	Ag _F
	MB14	2	Fe _F

Data visualization is an important early step in developing multivariate models. The frequency distribution of each of the 17 parameters (see Table 4.1) for each cruise was plotted (Appendix B.3) and those that exhibited non-normal distributions were transformed following procedures presented in Singer and Willett (2003). Summary statistics and the types of transformation on each variable are also presented in Appendix B.5. For those variables that showed little improvement with transformation ($p < 0.05$, Kolmogorov-Smirnov Goodness of Fit) or were near-normally distributed, the data were not transformed prior to model runs. It may be important to note each individual survey data set had elements that may reflect “real” shorter-term processes or un-resolvable sources that contribute to bi- or multi-modal distributions (e.g., incomplete mixing of contaminated Boston Harbor water in the Massachusetts Bay data sets or localized upwelling observed in the data from the southwestern Gulf of Maine survey; previous work-Ch. 3). In fact, most of the multi-modal distributions observed in individual survey data are masked by merging into a single data set, presenting a generally uni-modal distribution - consistent with the 3-end member mixing hypothesis presented earlier (see Fig. 4.2). One Boston Harbor sample (DI) from the July 1995 Massachusetts Bay survey and the surface observations from Station MB 15 and 16 of the

Boston Harbor – Massachusetts Bay mixing survey (Sept. 1996) were removed prior to conducting EFA as measure to improve the multivariate normal distribution of the individual and merged data sets. In addition, the 16 parameters (with the exception of salinity) had median seawater concentrations ranging over several orders of magnitude; from 0.6 ng L^{-1} (for Ag) to 0.5 mg L^{-1} (for TSM). To render the observed variables more amenable for direct comparison, the transformed data were standardized as z-scores (mean = 0, SD = 1).

4.4 Results and discussion

Factor solutions in FA are very sensitive to *a priori* decisions about (1) the variables and samples to include in the analysis, (2) the number of factors extracted, and (3) the rotation methods employed. EFA was performed on each individual data set then again on the combined data using the 17 variables listed in Table 4.1. As discussed above as measure to improve the multivariate normal distribution of the data, the Boston Harbor samples from the 1995 and 1996 Massachusetts Bays surveys were omitted and the data identified as outliers were ignored.

The water quality parameters listed in Table 4.1 were selected to help understand the processes important in the observed distribution of trace metals in the coastal waters of the Massachusetts Bays system. As demonstrated in previous work (Chapter 3), most of the Ag in Massachusetts Bay originates from wastewater discharges associated with metropolitan centers in the adjacent watersheds. For our FA, we treat Ag as a marker characterizing the importance of wastewater loading in the Massachusetts Bay system and as an estimator for the portion of wastewater-borne co-analytes of the data sets. Particulate Al serves as our tracer of crustal

weathering, Chl *a* as a measure for the importance of biological processing, salinity for freshwater sources, and POC and TSM to highlight the importance of particulate quality in the speciation, transport, and fate of metals in the coastal waters of the Massachusetts Bays system. As will be shown below, Cd loadings were characteristically strong in some of the factors that emerged from the exploratory FA, and serves as a possible tracer for organic particle formation/degradation because of its association with soft tissue of marine plankton (Millero, 2006) or due to unique reversible sorption of Cd (Hatje et al., 2003) relative to the other trace metals investigated.

To assist the selection of the number of important factors for each survey, we performed preliminary PCA each data set. Screeplots results, which show the percent variance explained by principle components, for each of the three individual survey data sets, are shown in Fig. 4.9. According to Cattell's scree test, all factors can be omitted after the factor where the percent variance explained rapidly begins to level off, or what Cattell (1966) refers to as the elbow in a curve generated from screeplot results. The possibility for bias introduced by subjectivity in identifying the screeplot elbow was minimized by identifying the number of principal components that had significant loadings; those that exist beyond the upper 99% confidence interval derived from step-wise least squares regression, beginning with the lowest (noise) principal components. These regressions and the number of significant "factors" are illustrated in Fig. 4.9. The PCA results generally point to a 2 or 3 factor solutions for each of the three individual survey data sets.

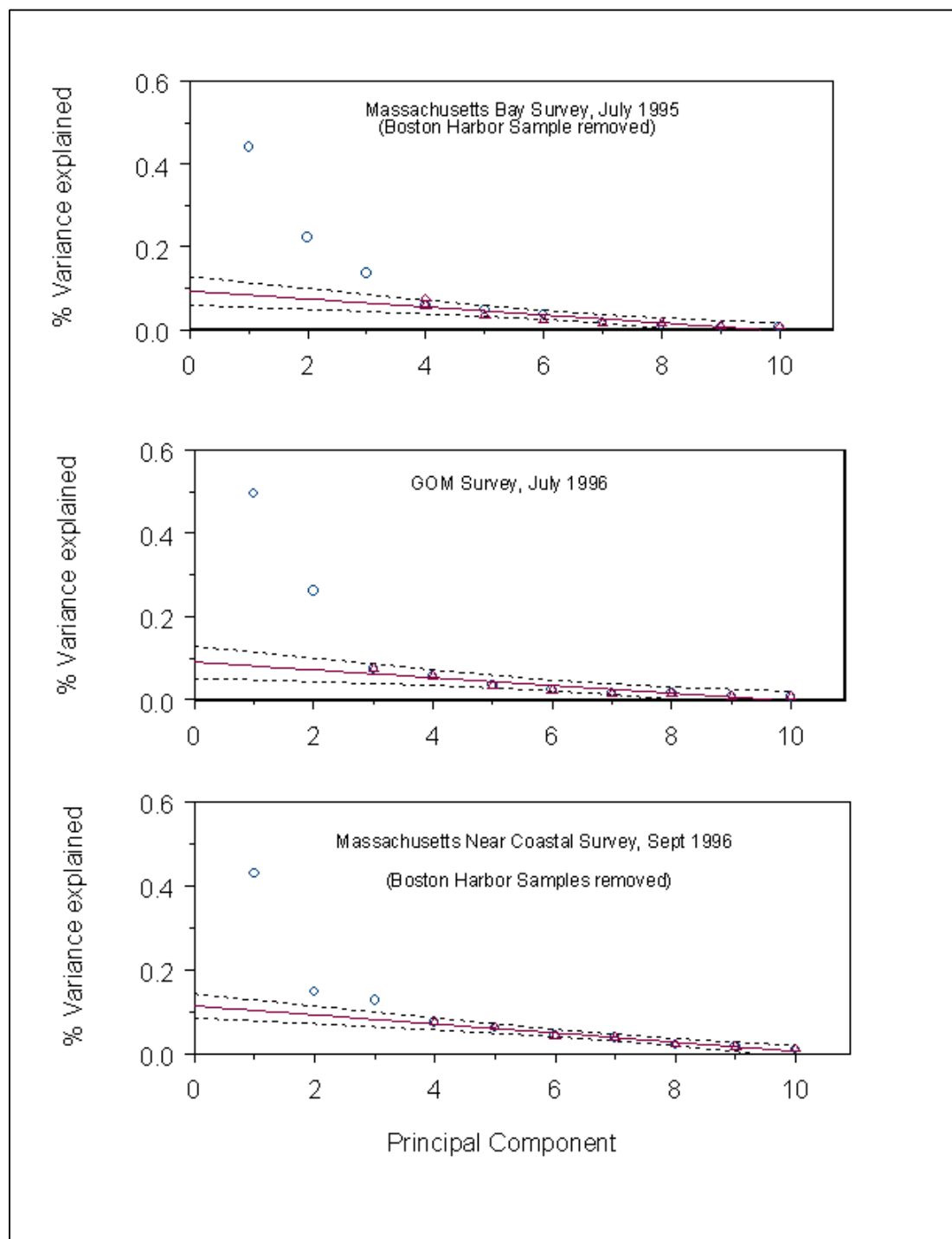


Figure 4.9. Screeplots from provisional Principal Components Analyses of observations and surveys listed in Table 4.1 Superimposed are the least squares regression (with 99% confidence intervals) of the less important principal components used to estimate the number of factors for exploratory factor analyses.

Factor loadings are indeterminate when the covariance matrix of the variables does not have a unique solution. This is often the case in natural scientific data sets (e.g., Reimann et al., 2002; Stanimirova et al., 2004). Therefore, any factor solution can be arbitrarily rotated in the q dimensional “space”. Varimax rotation (Kaiser, 1958) is commonly used in many FA (Reimann et al., 2002). This method is an iterative process that rotates the factor solution such that there are a minimum number of large loadings while maximizing as many near-zero loadings as possible and was initially applied to the factor solutions. Oblique rotations were performed when correlation among the variables were important. Oblique rotation will produce a better estimate of the true factors (Fabrigar et al., 1999) when the factors are correlated and provide a more simple structure than will an orthogonal rotation. The oblimin oblique rotation — which relies on an initial varimax solution and fixes a value to control factor correlation— was performed (Jennrich and Sampson, 1966) and compared to the initial varimax rotation to evaluate the importance of factor correlation. If comparison between orthogonal and oblique rotations were then orthogonal rotation is justified and its solution is presented.

Finally, EFA was conducted on the combined set of K_D , along with the ancillary parameters (Salinity, TSM, POC, and Chl a concentrations) as means of developing a conceptual model on the comparative biogeochemistry of the selected metals in coastal marine systems. Samples from three stations with a strong “Boston Harbor” signal (elevated metal concentration near the entrances of Boston Harbor) in the combined data set were also removed (DI, July 1995; MB-15 and MB-16, July 1996) to reduce the influence of bimodal distribution among the parameters (beyond the perceived resolution of the model) and improve the multivariate normal fitness of the data (See Appendix B.4).

4.4.1 Massachusetts Bay survey, July 1995

The solution for a three-factor EFA with varimax rotation is shown in Table 4.5.

Squared factor loadings represent the proportion of the variance of the variable (x_i) that is accounted for by that factor (Manly, 1994). For simplicity, only moderate to strong factor loadings (> 0.4) are shown. Oblique rotation gives similar solutions to the varimax rotation because these factors are not significantly correlated (Table 4.6).

Table 4.5. July 1995 Massachusetts Bay Survey
exploratory factor analysis, 3-Factor solutions, varimax
rotation. Boston Harbor sample (DI) removed.

Variable	Factor 1	Factor 2	Factor 3
Ag _F		0.776	-0.425
Pb _F		0.931	
Cu _F	0.532	0.775	
Zn _F	0.434	0.756	
Cd _F		0.610	
Fe _F	0.547		
Ag _P	0.657	0.546	
Pb _P	0.868		
Cu _P	0.687	0.457	
Zn _P	0.779		
Cd _P			0.497
Fe _P	0.961		
Al _P	0.841		
Sal			-0.639
TSM	0.576		
POC	0.740		
Chl <i>a</i>	0.469		0.659

Table 4.6. Factor (F) correlation matrix after oblique (oblimin) rotation and angle (below diagonal) relative to varimax rotation.

	F1	F2	F3
F1	1.00	-0.28	-0.07
F2	108°	1.00	0.18
F3	84°	84°	1.00

The 3-factor solution with varimax rotation explained 70% of the total variance. Factor 1 represents 35% of the total variance and is dominated by strong positive loadings of particulate variables, most notably Al, Fe, Pb, Zn, and POC. Because of the strong loadings of Al_P and Fe_P, this factor is thought to be representative of crustal weathering processes that include riverine and atmospheric sources and, by extension, the importance of crustal weathering processes to the loadings of Pb_P, Cu_P, and POC loadings. The relatively high loadings of POC and Chl *a* in Factor 1 may represent a composite of crustal weathering and biological mediation. The amount of organic carbon associated the particles (POC) are the result of a broad range of biological processes. For coastal waters, these types of processes vary considerably in time and space, and by the relative contributions from allochthonous and autochthonous processes. If atmospheric stimulation is considered negligent, the POC variable could be tested as aquatic biological marker and explored as a potential correction for atmospheric Pb with confirmatory models. The moderate loading of Ag_P may indicate that Factor 1 is complex and may represent related but distinct anthropogenic processes (e.g., wastewater discharge, contribution from the Merrimack River, atmospheric deposition, or sediment resuspension) that contribute collectively to the covariance of this portion of the data. Factor 2 represents 24% of the total variance. With the exception of Fe_F, Factor 2 is dominated by the filterable metals and to a lesser extent the particulate metals: Ag_P and Cu_P.

Because of the moderate-strong loadings of Ag, this factor is considered to represent the influence of anthropogenic sources. Factor 3 is comprised of a strong negative loading for salinity, strong positive loading for Chl *a*, and a moderate loading of Cd_p. Cadmium is linked with planktonic Cd/Ca and associated with the soft tissue of living and dead organisms in uncontaminated seawater (Millero, 2006). However, after relatively rapid adsorption of Cd to particles, Cd was remobilized and showed increased desorption over time in estuarine waters (Hatje et al., 2003) possibly the result of chlorocomplexation and competition with major cations (e.g., Ca²⁺, Mg²⁺). Thus, this factor is interpreted to represent the influence of organic particulate matter formation and/or reversible adsorption from suspended matter. Factor 3 accounts and additional 11% of the total variance.

The distribution of variables in 3-factor space is shown in Fig. 4.10. An important region is suggested, where particulate Cd, filterable Ag and Zn, and low salinity loadings occur along the pollution and organic particle formation gradients (Factor 2 and 3, respectively). Because the loading of Chl *a* is somewhat removed from this area, a greater portion of organic material may be allochthonous. In this region, particulate organic matter may have origins from wastewater discharges and/or sediment resuspension rather than from riverine sources.

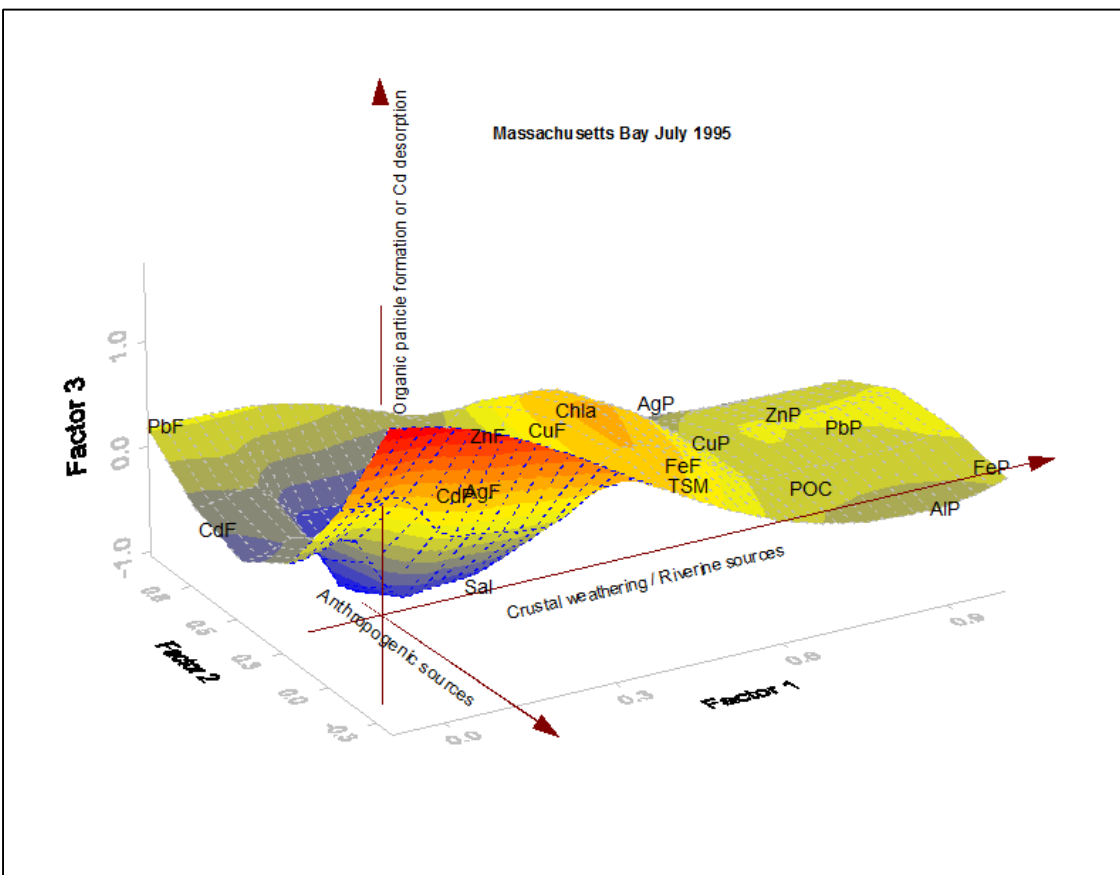


Figure 4.10. The factor loading surface projected in 3-Factor space using varimax rotation for the July 1995 Massachusetts Bays survey (Boston Harbor sample removed) using Z-normalized data. The locations of variables (see Table 4.1) are also shown.

During our July 1995 sampling, much of the region was in an extended drought (cf. Chapter 3) and thus freshwater loading to Massachusetts Bay especially low. It is therefore likely the importance of wastewater metal loadings to the Bay was more significant during this period relative to other freshwater sources (i.e., precipitation, rivers). Overall, these results may highlight the relative importance of contaminant loading to crustal weathering/riverine sources, the potential for biological mediation and the processes associated with organic particulate genesis as controls on speciation, transport, and fate of selected trace metals in this region of coastal Massachusetts waters.

4.4.2 Southwestern Gulf of Maine survey, July 1996

The southwestern Gulf of Maine survey was conducted to assess the Gulf of Maine boundary conditions for metal loading (more specifically, Ag) to Massachusetts Bay. The location of the GOM transect was selected to minimize the affect of Boston Harbor and the Merrimack River metal signatures. In addition, some parameters determined were near the method detection limits (especially Cu_p and Ag_p). Not unexpectedly, most of the other parameters monitored resulted in substantially lower concentrations than observed for Massachusetts Bay waters given the relatively “pristine” water quality of the open Gulf of Maine (Larsen, 1992, Wallace, unpublished data). The 2-Factor solution as suggested by the preliminary PCA (see middle panel, Fig. 4.9) with varimax rotation for the July 1996 survey is shown in Table 4.7. Neither factor shows significant loadings for Ag. Assuming Ag as a tracer for wastewater supports the reasoning that wastewater is not important to the covariance structure of the 1996 GOM data.

The 2-Factor, varimax rotated model for the Gulf of Maine survey explained 52% of the total variance. Factor I explained about 35% of the variance in the model and was dominated by strong positive loadings from particulate metals thought to represent the “crustal” signature (Al_p and Fe_p). Factor 1 is also characterized by positive Pb_p loading (similar to the Factor 1 derived from the 1995 Massachusetts Bay survey), and a moderate positive loading of salinity. However, the GOM Factor 1 is moderately negative with respect to the loading of the biological variables (i.e., POC and Chl *a*) and thus different from the positive loadings that characterizes the 1995 MB Factor 1. The high loadings of Al_p and Fe_p may reflect a mixture of processes that include localized upwelling of metal-enriched Gulf of Maine coastal deep water where the

Table 4.7. GOM July 1996 Survey exploratory factor analysis, 2-Factor solution, varimax rotation.

Variable	Factor 1	Factor 2
Ag _F		
Pb _F		0.514
Cu _F		0.540
Zn _F	0.458	
Cd _F	0.783	
Fe _F	0.575	
Ag _P		
Pb _P	0.940	
Cu _P	0.791	0.454
Zn _P	0.515	
Cd _P		
Fe _P	0.992	
Al _P	0.996	
Sal	0.524	-0.526
TSM		0.572
POC	-0.457	0.890
Chl <i>a</i>	-0.727	0.561

concentration of Al_P and Fe_P were much higher than the overlying mixed layer and inorganic detrital crustal loading from atmospheric sources. The moderate positive loading of salinity and the strong negative loading of POC in the GOM Factor 1 suggest mixing along a salinity gradient and one or more sources enriched in metal relative to organic carbon. The moderate negative loading of Chl *a* may be more biogeochemically consistent with the shallow coastal upwelling process scenario (greater Al_P:Chl *a* ratio below the mixed layer) and remains consistent with mixing along a salinity gradient. Factor 2 is dominated by loadings from filterable Pb and Cu, POC, and characterized by a moderate negative loading of salinity. If Factor 1 reflects ocean-dominated processes, it could be that Factor 2 is a representative of processes associated with riverine input. Factor 2 explained 16% of the total variance.

Factor 2 may represent anthropogenic sources of contaminants because of the co-occurrence of Pb_F and Cu and the moderate negative loading of salinity associated with freshwater input to the near coastal region of the southwestern Gulf of Maine. Factor 2 may also be influenced by changes in metal speciation due to biogeochemical processes associated with primary productivity (moderate-to-high positive loadings of POC and Chl *a*). Figure 4.11 illustrates the variable loadings along the two factors. Sources containing crustal material (whether from coastal sediment resuspension, local upwelling, or atmospheric deposition) appears to be the main factor contributing to the distribution of metals during the 1996 survey in the southwestern Gulf of Maine (explaining approximately 35% of the variability in the data set) relative to riverine sources that may contribute to part of the variability captured in Factor 2 (i.e., moderate negative loading of salinity). Biological mediation is more important to the loading of Factor 2. The absence of silver in the 2-Factor solution can be interpreted to reflect the negligible importance of sewage-derived contaminants on the observations from the 1996 GOM survey.

4.4.3 Boston Harbor – Massachusetts Bay mixing zone, Sept. 1996

The September 1996 Massachusetts Bay survey targeted the mixing zone of Boston Harbor and Massachusetts Bay along the eastern coast of Massachusetts and to the south of Boston Harbor (Signell and Butman, 1992). To some extent, this survey serves as a validation of EFA since we expect a significant contribution from wastewater to the metal distribution in the southwestern portion of Massachusetts Bay (see Chapter 3). The results from the 3-Factor oblimin-rotated model for the Sept. 1996 survey are given in Table 4.8.

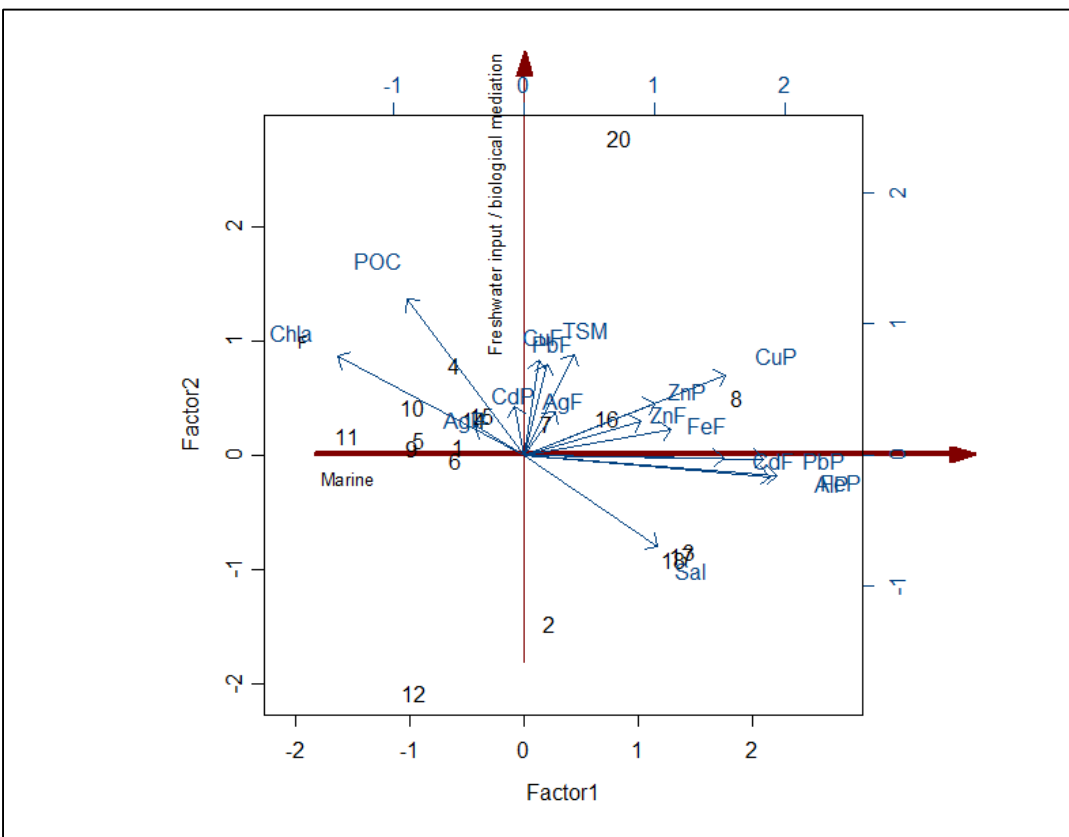


Figure 4.11. Biplot of a 2-Factor, varimax rotated FA solution using the Gulf of Maine 1996 survey data (Table 4.1) showing hypothetical marine gradient and cumulative freshwater biological gradients. Number indicate the presence of individual samples.

Oblique rotation (oblimin) produced a different solution from the varimax rotation because the Factors were moderately correlated (Table 4.9). The oblimin-rotated Factor 1 is dominated by the loadings from Ag, Cu, and Zn (both filterable and particulate), and Pb_p, with strong loadings from TSM and Chl *a*. Factor 1 explains 33% of the variance. Because of the high loadings from Ag, we interpret Factor I as the anthropogenic factor. Factor II is dominated by moderate – high loadings from the particulate metals. Either this factor represents a source contribution from the Merrimack River (not supported by the absence of salinity), which occasionally enters

Table 4.8. Sept 1996 Mixing-zone survey, Boston Harbor-Massachusetts Bay exploratory factor analysis, 3-Factor, oblimin-rotated solution.

Variable	Factor 1	Factor 2	Factor 3
Ag _F	0.828		
Pb _F	0.513		
Cu _F	0.964		
Zn _F	0.834		
Cd _F			0.471
Fe _F			
Ag _P	0.704	0.411	
Pb _P		0.659	
Cu _P	0.652	0.583	
Zn _P	0.821		
Cd _P		0.506	-0.409
Fe _P		0.859	
Al _P		0.873	
Sal		(-0.337)	
TSM	0.833		
POC			
Chl <i>a</i>	0.750	-0.428	

Table 4.9. Sept. 1996 Mixing-zone survey, Boston Harbor-Massachusetts Bay. Factor (F) correlation matrix after oblique (oblimin) rotation and angle (below diagonal) relative to varimax rotation.

	F1	F2	F3
F1	1.00	-0.28	-0.07
F2	107°	1.00	0.18
F3	94°	80°	1.00

into Massachusetts Bay (Xue et al., 2000) or is representative of processes associated with short term particle dynamics as contaminated Boston Harbor water mixes with Massachusetts Bay. However, the strong factor loading of “crustal weathering” indicators (Al_P and Fe_P) and absence of any significant salinity loading suggests processes may be associated with resuspension of contaminated sediments rather than freshwater related. The oblimin rotated solution identified a 3rd Factor that is dominated by moderate loadings of Cd. Particulate Cd is loaded equally relative to filterable Cd but it is negative. Cadmium undergoes fractionation (relative to phosphate) during biologically-mediated particle formation in marine waters (Elderfield and Rickaby, 2000). That is, Cd is preferentially taken up relative to phosphate and incorporated in the soft tissues of phytoplankton. Because Cd_P loads negatively, one hypothesis is that Factor 3 represents organic particulate degradation. However, the negligible loading of organic particle traits (i.e., Chl *a* or POC) may indicate the influence of Cd desorption from particles as chlorocomplexation or competition for active sites by major cations become more important to Cd speciation in marine waters (Paalman et al., 1994). Factor 3 represents 6% of the explained variance. The variables and the factor loading surface when presented in three-factor space (Fig. 4.12) is used to present a possible map of wastewater dispersion and the relative roles of metal sources; one group source that includes crustal sources-whether from sediment resuspension, atmospheric deposition, or riverine transport and another that is anthropogenically elevated. It is important to note that salinity was only moderately loaded (<0.4) and negative on Factor 2 and contributes nothing to our understanding of Factor 1 which we consider to represent “pollution” and limits speculation of a solely wastewater factor.

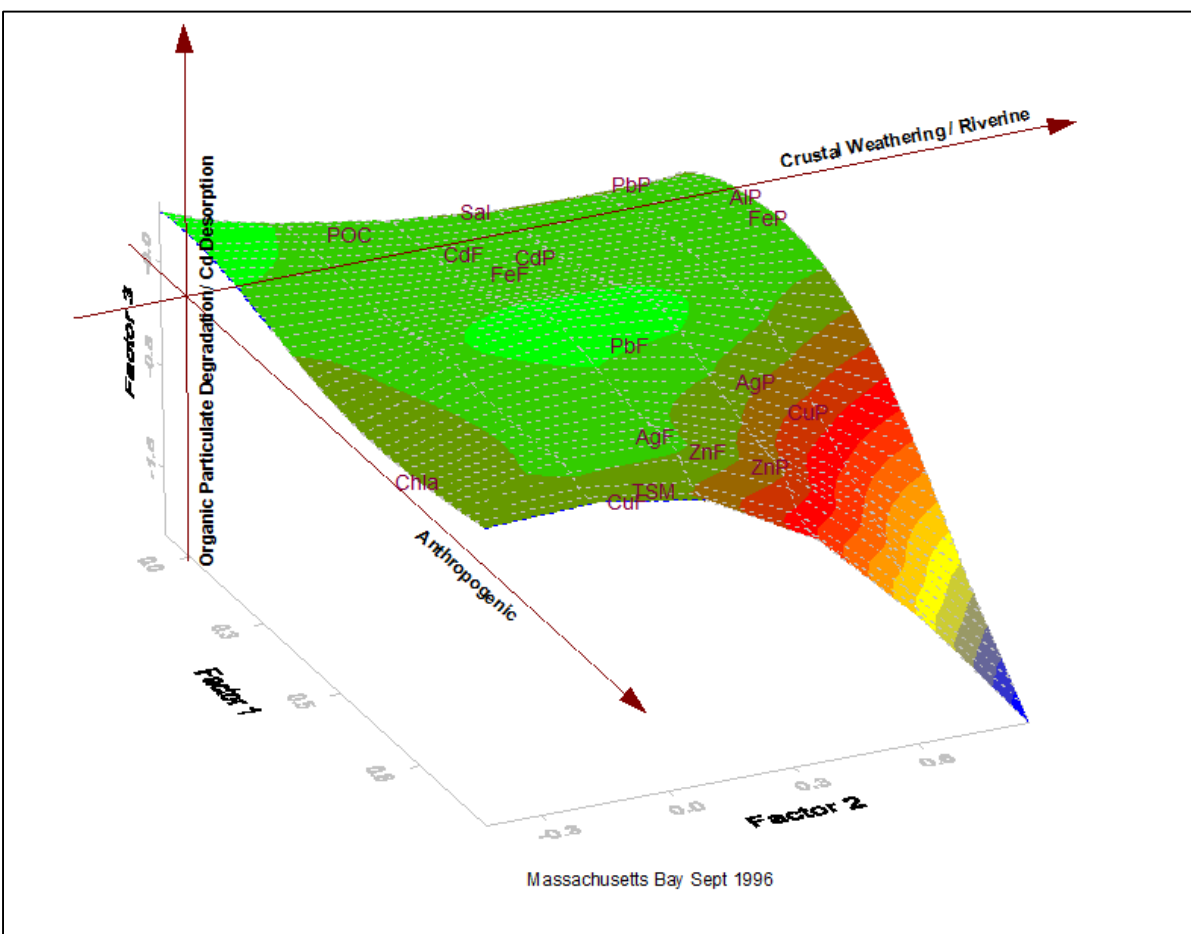


Figure 4.12. The factor loading surface projected in 3-Factor space using oblimin rotation for the Sept 1996 Mixing-zone survey, Boston Harbor-Massachusetts Bay (Boston Harbor samples removed) using Z-normalized data. The locations of variables (see Table 4.1) are also shown.

4.4.4 Comparative biogeochemical analyses, combined data set from three cruises

Consideration of the dimensionality of the data sets on the stability of results from FA is often neglected. Different rules have been suggested regarding the “sufficient” number of samples needed in FA for a given set of parameters monitored. When discussed in the context of FA the number of samples needed can vary from simply ensuring a greater number of samples relative to the parameters monitored to more stringent requirements; e.g., # samples $> p^2 + 3p + 1$, where p represents the number of parameters (see references in Reimann et al., 2002). By combining data sets from the three sampling events, the number of observations

increased from ~20-30 to 76. As mentioned earlier, the combined data set was manipulated to minimize multimodal characteristics in the distributions of data among the suite of parameters monitored and thus distinguished three “Boston Harbor” stations (4 samples). These samples were considered to be in disequilibria relative to the processes being explored in the combined data set and were eliminated from the combined data set. Here we perform EFA to evaluate (1) the characteristics of potentially important general factors controlling the distribution patterns of trace metals in the Massachusetts Bays system and (2) the comparative biogeochemistry of trace metals by using computed $K_{D-Crust}$ with the suite of indicators: Al_p for crustal weathering, $Chl\ a$ for biological processes, and particulate material quality (POC) and quantity (TSM). We use the visual observation of the scree plot (Fig. 4.13) generated from a provisional PCA analysis (S-Plus 2000) of the combined data set to help determine the number of factors to be considered for EFA.

From Fig. 4.13 (upper panel), a three-factor EFA on the primary variables was considered for the Massachusetts Bays system - which includes the “stage-setting” nature of the Gulf of Maine, the role of riverine discharges to periodic conditions in Massachusetts Bay, the role of wastewater loading and dispersion on trace metal distributions, and atmospheric loading on the transport and fate of metals in coastal Massachusetts waters. Oblique rotation (using oblimin) was performed because of the covariance of factors in the varimax solution. Oblimin rotation strengthened the loading of Ag in Factor 1, separated the crustal component to Factor 2, and identified Factor 3 as biologically-mediated (strong positive loading of $Chl\ a$). The oblimin-rotated, 3-factor solution explained 60% of the total variance (Table 4.10). Factor 1 we interpret as the wastewater factor, which is dominated by both filterable and particulate metals

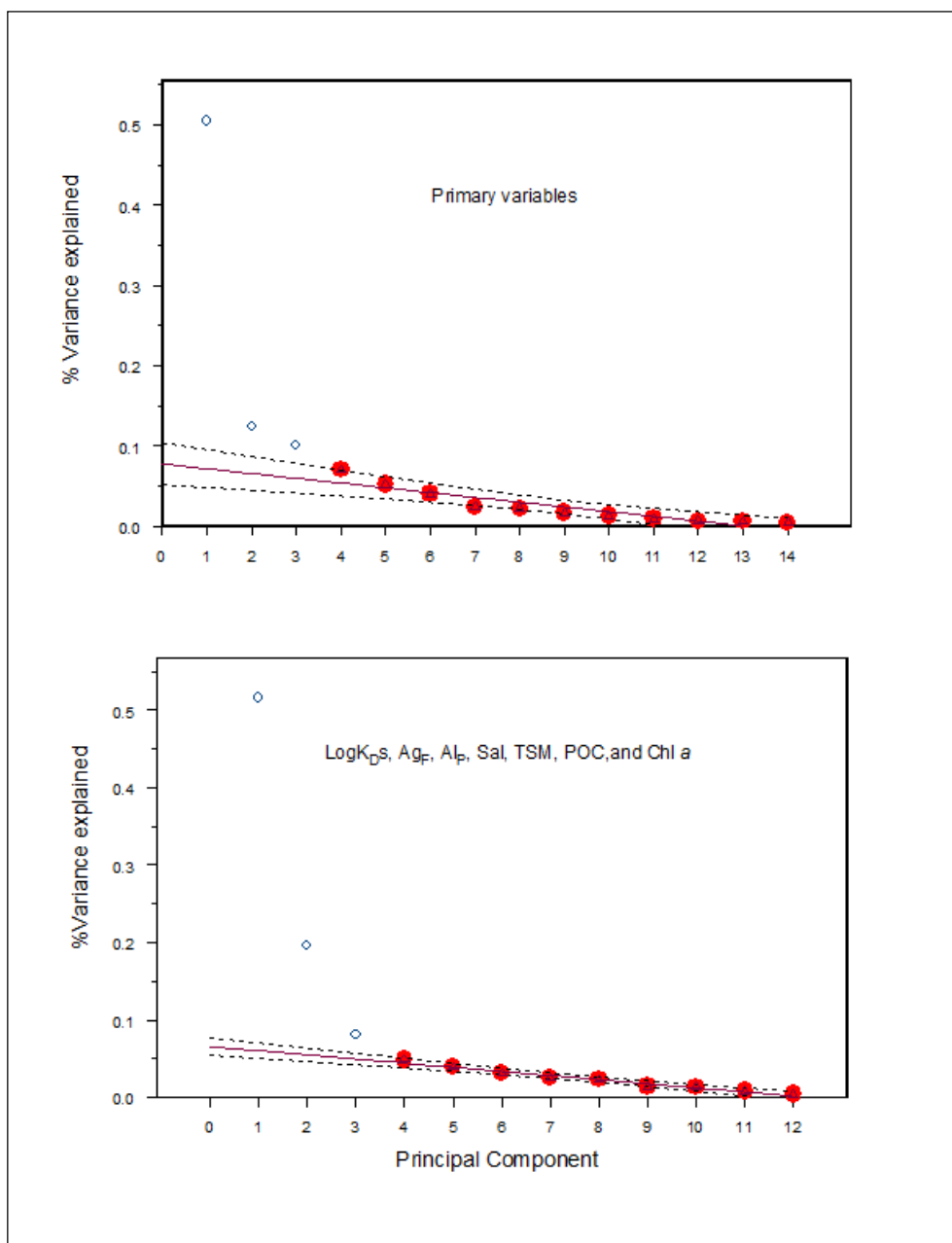


Figure 4.13. The screeplot results from Principal Components Analysis of combined z-score data (Boston Harbor samples removed) from three surveys to determine # of important Factors. Upper panel PCA includes the primary variables (filterable and particulate metals, salinity, TSM, POC, Chl *a*). Linear regression of the minor components (red dots) and 99% confidence intervals are superimposed. Bottom panel includes the conditional partition coefficients (log K_D) along with the variables that are thought to represent wastewater (Ag), organic particulate decomposition (Cd), crustal weathering processes (Al_P), biological mediation (Chl *a*) and measures of particle quantity and quality (TSM, POC).

Table 4.10. Combined z-score data set of variables from the July 1995, July 1996 and Sept1996 surveys in coastal waters near Massachusetts, USA. 3-Factor, oblimin-rotated solution.

	Factor 1	Factor 2	Factor 3
Ag _F	0.915		
Pb _F	0.818		
Cu _F	0.744		
Zn _F	0.813		
Cd _F	0.462		
Fe _F	0.585		
Ag _P	0.881		
Pb _P	0.815		(-0.303)
Cu _P	0.863		
Zn _P	0.637		
Cd _P			(-0.276)
Fe _P		0.832	
Al _P		0.877	
Sal	-0.408		(-0.325)
TSM		0.474	0.442
POC	0.454		0.403
Chl <i>a</i>			0.877
% Variance	38%	12%	10%

(except Cd_P, Fe_P, and Al_P) and moderate loading of POC. This factor is also characterized by moderate negative salinity. Overall, wastewater processes remain the leading candidate for controlling the latent structure of metals distribution in the Massachusetts Bay waters sampled, explaining nearly 40% of the total variance. It is important to note that these processes were targeted for specifically in one of the surveys and provides for some sampling bias in the combined data.

Factor 3 is characterized by moderate – high loadings of POC, TSM and Chl *a* and appears to have little importance on trace metal distribution for the Massachusetts Bays system.

The weak loadings for Cd_p and Pb_p may reflect the degree of uptake and incorporation in biogenic particles.

Lastly, an effort to better understand the biogeochemical nature of Ag speciation and the important processes controlling speciation of metals in the Massachusetts Bays system was performed using a 3-Factor analysis (see Fig. 4.13, lower panel) on the apparent metal distribution coefficients ($\text{Log } K_D$) with the parameters: Ag_F , Al_p , salinity, TSM, POC, and Chl *a*. Here we explore whether Ag can be used to assess the role of pollution on trace metal speciation. The results from a 3-Factor, oblimin rotation solution are presented in Table 4.11. The three factors collectively explained 68% of the total variance but was limited in the ability to discern differences among the trace metals studied (Ag, Pb, Cu, Zn, Cd, Fe) and their partitioning between particles and filtered seawater.

Table 4.11. Factor loadings (> 0.4) after oblimin rotation from combined z-score metal $\text{Log } K_D$ and water quality data from July 1995, July 1996 and Sept 1996 surveys in coastal waters near Massachusetts, USA. Three Factors considered

Variable	Factor 1	Factor 2	Factor 3
Al_p			0.868
Sal		-0.684	
TSM	-0.893		
POC		0.785	
Chl <i>a</i>	-0.413	0.584	
$Ag \text{ Log } K_D$	0.850		
$Pb \text{ Log } K_D$	0.686	(-0.341)	
$Cu \text{ Log } K_D$	1.054		
$Zn \text{ Log } K_D$	0.693		
$Cd \text{ Log } K_D$	0.755		
$Fe \text{ Log } K_D$	0.469	-0.451	
Ag_F		0.734	
% Variability	38	20	10

Factor 1 included significant positive K_D loadings for all the metals studied. Factor 1 is further characterized by a strong and moderate negative loading for TSM and Chl *a*, respectively.

Factor 2 is characterized by a strong positive loadings from Ag_F and POC, strong negative loading of salinity, moderate loading of Chl *a*, and a moderate negative loading of Fe Log K_D .

Because of the strong loadings for Ag_F (positive) and salinity (negative), Factor 2 represents the wastewater gradient. Factor 3 is solely dominated by a strong loading for the crustal tracer: Al_p .

The representation of factor loadings in 3-Factor space for the analysis of conditional partition coefficients are shown in Fig. 4.14. The crustal and wastewater loadings show little effect on the distribution of metal K_D s which cluster near the positive end of an unexplained “partitioning” factor with the metal K_D order observed earlier (see Fig. 4.7) preserved

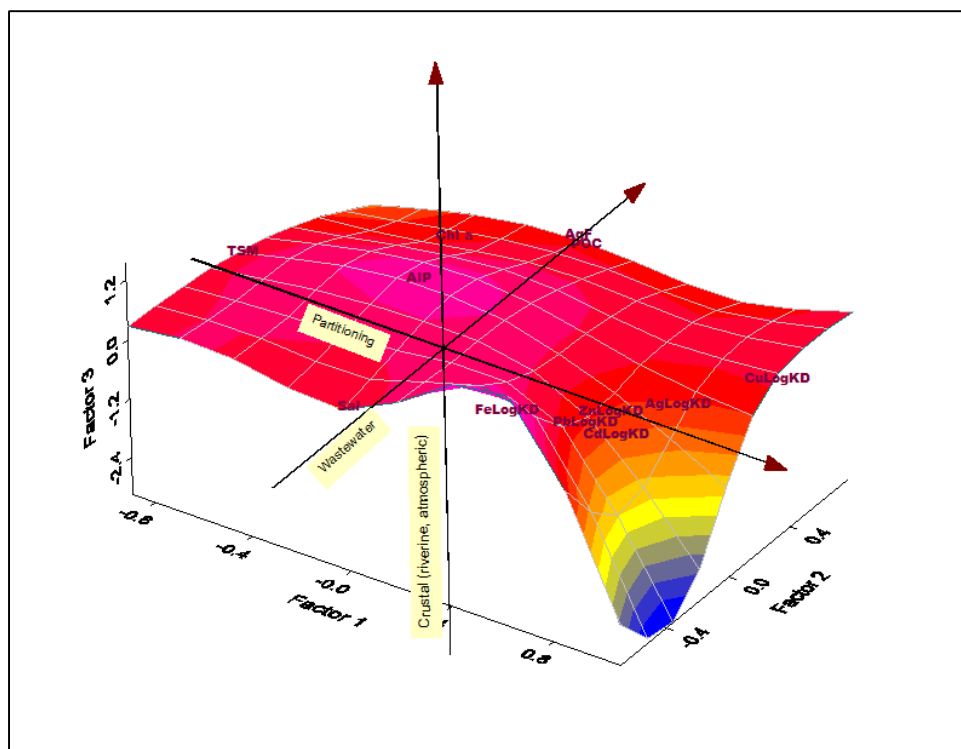


Figure 4.14. The factor loading surface projected in 3-Factor space using oblimin rotation for the combined Z-normalized data sets and variables listed in Table 4.1. Boston Harbor samples removed.

It is important to note that the sampling designs included in this analysis was not random and had, in part, a design to distinguish wastewater distribution in coastal waters that presents challenges to formulating general biogeochemical hypotheses on the controlling factors to chemical speciation. The potential for different moieties in the filtrate also cannot be overlooked when interpreting the temporal and spatial distribution of apparent K_D , especially in waters burdened by extensive loading of wastewater. Colloids, inorganic ligands, and thiol compounds have been identified as important metal-complexing components of natural waters and enriched in meta-stable sulfide ligands in waters where wastewater discharges occur (Shafer et al., 1998 and 2004; Adams and Kramer, 1999; Smith et al., 2002). The moderate loading of Fe $\text{Log}K_D$ on Factor 1 and negatively in Factor 2 (with a weak Pb $\text{Log}K_D$) may be more indicative of the changing nature of filterable metal species, both space (GOM and Mass. Bays) and time (1995-1996). Both colloids and important dissolved ligands are ephemeral in nature (Benoit et al., 1994; Tang et al., 2000; Wells et al., 2000), and can have profound effects on the apparent K_D and thus the solutions provided by EFA. The inverse loading of TSM with the significant $\text{Log}K_D$ loadings in Factor 1 may be a combination of the increasing importance of the components contributing to the filtrate (and thus lower K_D values, eq. 1), and increasing abundance of inorganic detrital phase that contributes to lower metal sorption affinity of the particulate pool. Clearly this analysis can benefit from characterizations that include the amount and types of colloids, and knowledge about the nature and character of NOM, biogenic ligands, and soluble chelators important to trace metal speciation in aquatic systems (e.g., Shine and Wallace, 1995; Tang et al., 2000). Further, our interpretation of the results must consider the bias inherent with assigning process indicators to parameters within the data sets used in the EFA analyses above.

4.5 Summary and conclusions

The primary objective of this analysis was to provide insight on the important factors controlling the biogeochemical fate of silver and other selected metals in the coastal waters of Massachusetts. Data from three surveys conducted in 1995-1996 in unique compartments of the Massachusetts Bays system were analyzed and included a Massachusetts Bays surface water survey; targeted sampling of the mixing zone between Boston Harbor (a highly-contaminated urban estuary) and Massachusetts Bay, and a nearshore survey in the southwestern portion of the Gulf of Maine –beyond the northern boundary of Massachusetts Bay. Apparent K_D s for metals showed distinct differences among the compartments of the Massachusetts Bays system.

Apparent K_D values were generally lower in the region near Boston Harbor (Sept. 1996 survey) relative to those observed for Massachusetts Bay proper (July 1995) and from the southwestern Gulf of Maine survey (July 1996). The K_D values observed do not distinguish between potentially important ephemeral components that may have contributed to the filterable fraction used in our empirical derivation. Important components like colloids and sulfur-rich ligands, other soluble organic ligands, or greater contribution from crustal derived material can have pronounced affect on K_D values and subsequently on the stabilization, transport, and fate of metals in aquatic systems. When viewed in the context of the larger scale mixing processes deemed important to the Massachusetts Bays system, the data were interpreted to be consistent with mixing of water from a large contaminated urban estuary and waters from the Gulf of Maine with Massachusetts Bay. Exploratory factor analysis was used to evaluate among contaminant loading sources (e.g. wastewater, riverine, and crustal weathering) and important

processes (biologically-mediated, particle quality and quantity) on trace metal speciation and ultimate fate in the coastal waters near Massachusetts, USA. R-mode EFA (with either orthogonal or oblique rotations) models were developed to conceptualize roles of important processes, both in the sub-compartments of the Massachusetts Bays system and in the general speciation of Ag and other selected metals. For the Gulf of Maine, deeper water upwelling and sediment resuspension, riverine, and/or atmospheric inputs were hypothesized as import processes for further confirmatory FA. The role of sediment resuspension as a potentially important process influencing metal speciation in the coastal waters but not discernable from the parameters contained in this exploratory analysis. For Massachusetts Bay, wastewater loads appeared to be important, especially for the targeted survey in Sept. 1996, where focused sampling was conducted in the mixing zone between Boston Harbor and Massachusetts Bay. Wastewater water contributed to the loading of factors in both of the Massachusetts Bays survey and was noticeably absent from the Gulf of Maine survey. A third factor identified in the targeted Boston Harbor – Massachusetts Bay mixing survey was characterized by inverse loadings of Cd_F and Cd_P and considered as representing a gradient in biogenic or organic particulate dynamics, Cd desorption from particles, or reflect the importance of resuspension to metal speciation in coastal waters.

Two “wastewater” factors were identified from the July 1995 data set that were distinguished by particulate and soluble metals, respectively. The ability to resolve the wastewater component of these factors was aided, in part, by the extensive drought conditions that preceded our July 1995 survey and may have enhanced the significance of wastewater to the freshwater loading to Massachusetts Bay. The use of FA in exploratory exercises must be viewed as non-confirmatory because of the potential for parsimony and interpretability of the

results is subjective to investigator-interpretation. The FA uses the following candidates for consideration as process indicators: Al_p as a “tracer” for crustal weathering, Ag as our tracer for wastewater dispersion, and possibly Cd in delineating important organic particle formation and degradation in the water column. Clearly, important aspects of metal speciation are not accommodated here because of the lack of appropriate “indicators”. It is possible the determinations of colloids, sulfhydryl ligands, ligand classes, free metal ion, and nutrient concentrations would further the understanding of metal speciation in these coastal waters. EFA appears to be a promising technique for understanding the structure of geochemical data sets. More robust methods for FA are emerging and, coupled with recent analytical advancements in the marine chemistry for colloids and ligand chemistry, may aid in the understanding of trace metal speciation in aquatic systems and provide direction for more confirmatory investigations on trace metal biogeochemistry using these techniques.

Finally, Ag appears to be intermediate with respect to particle reactivity when compared to the metals observed for this study and consistent with observations of Ag speciation in coastal and open ocean systems. EFA revealed similar behavior of Ag to that of Cu and Zn, which we attribute loosely to our understanding for preferential complexation with reduced sulfur ligands in the water column.

CHAPTER 5

ANALYTICAL METHODS

5.1 The determination of silver and other metals in natural waters and in certified reference waters from the National Research Council of Canada

5.1.1 Introduction

Silver in the aquatic environment has received considerable attention in recent years due in part to recent advances in analytical capabilities and the application of these techniques to the understanding of the fate and transport of silver contamination in the aquatic environment (Rutherford and Church, 1975; Martin et al., 1988; Sañudo-Wilhelmy and Flegal, 1992; Flegal et al., 1995; Duarte et al., 1999; Ndung'u et al., 2001; Zhang et al., 2001; Sañudo-Wilhelmy et al., 2002; Ranville and Flegal, 2005; Smith and Flegal, 2005). For the determination of silver in natural waters, few detailed comparisons of analytical results of common samples among different analytical methods exist due to the lack of suitable water reference material.

This section presents the results of standard additions of silver, zinc, copper, iron, lead, and cadmium to acidified (pH 1.5 - 2) National Research Council of Canada (NRCC) certified reference materials: CASS-3 (coastal), and NASS-4 (open ocean). Quantitative analysis were further evaluated from the recoveries of metals in samples from the Merrimack River, Boston Harbor, Massachusetts Bay and Gulf of Maine seawater spiked with metals at levels that are typically expected for these waters. Pre-concentration of metals in natural water is usually

required prior to detection for methods that employ GFAAS or inductively coupled plasma-mass spectrometry (ICP-MS). We utilized a liquid/liquid extraction technique described in Wallace et al., (1983) and similar to those described earlier (Kinrad and Van Loon, 1974; Danielson et al., 1978; Bruland et al., 1979) in which dithiocarbamates of heavy metals are formed in water samples and extracted into an immiscible liquid organic solution. The APDC/DDDC extraction technique described below has been modified such that quantitative extraction of silver can be included with the extraction of Zn, Cu, Cd, Ni, Fe, and Pb.

5.1.2 Experimental

5.1.2a Cleaning procedures.

Polycarbonate sample collection bottles (2l, Nalgene) were initially cleaned with Micro[®] detergent (Cole-Parmer Instrument Co.) and rinsed with 0.2 μm -filtered deionized water, sonicated at 80⁰C for 1 hour each with 4N HCl and 0.2 μm -filtered deionized water, rinsed with DI water and stored for greater than one week in 0.2 μm -filtered DI water acidified to near pH 2 with Suprapur HCl. Large polycarbonate carboys (22l - Nalgene) were washed with Micro[®], rinsed with 4N HCl, and stored with 0.2 μm -filtered DI water acidified to pH 2. Plastic bottles (low density polyethylene) in which samples were stored for later processing were processed in a similar manner as the 2l polycarbonate bottles but were additionally sonicated with 4N HNO₃ and stored with acidified sub-boiled quartz-distilled de-ionized water (Q water) to a pH 2 (Optima HNO₃). Polysulfone filtration apparatuses (Nalgene) were cleaned with Micro[®], rinsed with filtered DI, sonicated for one hour at 60⁰C in 4N HCl and then with 0.2 μm -filtered DI water, rinsed with Q water, and dried in a class 100 laminar-flow clean air bench.

5.1.2b Sampling.

River and coastal water samples were collected with a peristaltic pump (American Sigma Streamline Series 700) through acid-cleaned silicon tubing in pre-cleaned and sample-rinsed 2L polycarbonate bottles (Nalgene). Sub-samples (500 - 1000 ml) were vacuum-filtered (<10 psi) through 0.4 μm polycarbonate filters (Poretics Corp.) in a laboratory clean room equipped with a filtered air supply and class-100 clean benches. Samples were acidified with pre-screened ultra-pure HNO_3 (Optima, Seastar Chemicals, Inc.) to pH 2 (1 μl concentrated HNO_3 ml^{-1} sample) and stored in 500 ml polyethylene bottles for later analysis. Details on the collection of CCRC certified reference materials can be found in McLaren et al. (1995).

5.1.2c Reagents.

Dithiocarbamate solution. A 1% (w/v) solution of ammonium 1-pyrrolidinedithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) was prepared and purified as follows. In a pre-cleaned Teflon separatory funnel, dissolve 2.0 g each of APDC and DDDC in 200 ml of Q water. Add purified ammonium acetate buffer (see below) to the chelate solution until pH ~4 is attained. Add 10 ml of chloroform (Burdick and Jackson High Purity stabilized with 1% ethanol), shake vigorously for 2 min. After 10 min. for phase separation, the chloroform fraction is drained. Add 10 ml of sub-boiled distilled freon (1,1,2-trichlorotrifluoroethane, Burdick and Jackson, Cat. 358-1), double-bag the separatory funnel and place on a shaker for 1 to 2 hours. Repeat until acceptable blank levels are attained. After adequate purification, add 2 ml of NH_4OH (Ultrex).

Ammonium acetate buffer. In a teflon separatory funnel add 90 g of CH_3COOH (Baker Instra-Analyzed[®]) to 170 g Q water. Slowly add 38 g NH_4OH ((Baker Instra-Analyzed[®]) while

swirling. Allow to cool to room temperature. Purify by repeated extraction with 1.5 ml of previously purified dithiocarbamate chelate solution and 10 ml chloroform. Repeat until acceptable blank levels are attained.

5.1.2d Liquid/liquid extraction of metals.

The APDC/DDDC back extraction technique was developed as a modification the organic extraction methods of Danielsson et al. (1978) and Kinrade and Van Loon (1974). An aliquot of sample (between 200 - 300 g) is transferred to a 250 ml Teflon separatory funnel and buffered to pH 4 with 3 ml of purified ammonium acetate solution. 1.5 ml of APDC/DDDC solution is added and shaken to homogenize. Five ml of chloroform is added next and shaken vigorously for 2 min. After allowing 10 minutes for phase separation, the chloroform is drained into a 30 ml threaded Teflon vial (Savillex). A second and third extraction of the chelated species is performed by shaking for 1 min each followed by a 10 min. phase separation; each time combining the chloroform fractions together with the first. Any aqueous phase that is carried over with the chloroform is carefully removed via pipette and discarded. 100 μ l of concentrated HNO_3 (Optima) is added to degrade the dithiocarbamate complexes. The vial is capped and vigorously shaken for 30 sec. After 10 min. for phase separation, the aqueous phase is removed to a pre-cleaned 2.0 ml polyethylene sample cup (Elkay Products, Inc.). 900 μ L of Q water is added to the remaining chloroform, vigorously shaken for 30 sec., and allowed to separate for 10 min. The Q water is then quantitatively removed and combined with the previous aqueous phase such that the final volume in the sample cup is 1.00 ml. This procedure allows for a 200-300:1 concentration of Ag, Zn, Cu, Cd, Ni, Fe, and Pb.

5.1.2e Graphite furnace atomic absorption (GFAAS) analysis.

Silver, zinc, cadmium, copper, iron and lead were analyzed by GFAAS. A Perkin-Elmer Zeeman/5000 spectrometer equipped with a HGA 500 graphite atomizer was used. All metals were analyzed utilizing pyrocoated graphite tubes fitted with L'vov platforms. All absorbance observations were measured in the peak area mode with Zeeman background correction. A mixed-matrix modifier of differing mass loadings of Pd and Mg were used for Ag, Cd, and Pb analyses. Table 5.1 lists the conditions used in GFAAS analysis. The absorbances at 328.1 nm (for Ag) during pyrolyzation for different Ag concentrations (in 10% HNO_3) are shown in Figure 5.1.

Table 5.1. Instrument settings and conditions for GFAAS

	Ag	Pb	Cu	Zn	Fe	Cd
λ (nm)	328.1	283.3	324.8	213.9	248.3	228.8
Slit width (nm)	0.7 low	0.7 low	0.7 low	0.7 low	0.2 low	0.7 low
Injection Vol (μ l)	35	35	20	10	10	10
Matrix Modifier	0.1 μ g Pd 0.02 μ g Mg	0.13 μ g PO ₄ 0.003 μ g Mg				0.22 μ g PO ₄ 0.006 μ g Mg
Step 1						
Temp (°C)	140	120	140	140	140	120
Ramp(sec)	1	1	1	1	1	1
Hold (sec)	30	35	20	10	10	15
Step 2						
Temp (°C)	200	200	200	200	200	200
Ramp(sec)	1	1	1	1	1	1
Hold (sec)	5	5	5	5	5	5
Step 3						
Temp (°C)	700	800	1200	700	1200	700
Ramp(sec)	5	5	10	5	10	5
Hold (sec)	15	15	15	15	15	15
Step 4						
Temp (°C)	2000	1800	2400	2000	2500	1600
Ramp(sec)	0	0	0	1	0	0
Hold (sec)	5	6	6	5	6	5
Internal Gas						
Flow (ml min ⁻¹)	0	0	30	120	120	20
Step 5						
Temp (°C)	2700	2400	2700	2500	2700	2400
Ramp(sec)	1	1	1	1	1	1
Hold (sec)	4	3	3	3	3	3
Step 6						
Temp (°C)	20	20	20	20	20	20
Ramp(sec)	1	1	1	1	1	1
Hold (sec)	20	15	20	15	20	15

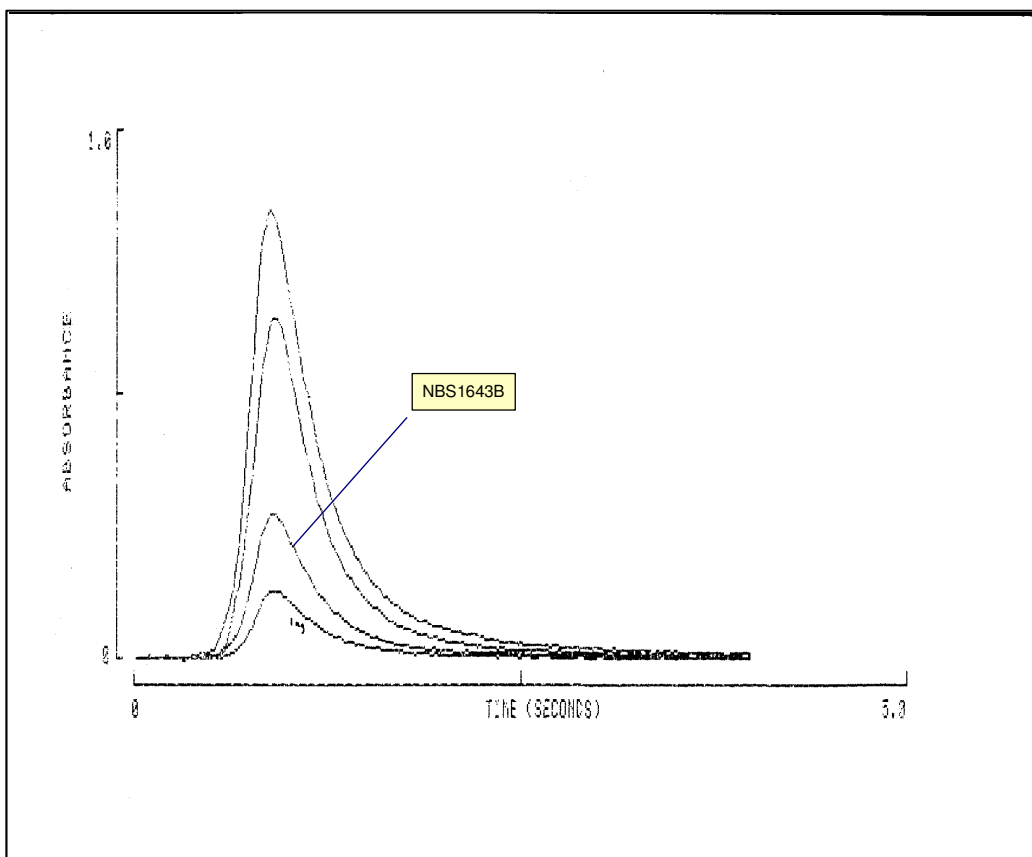


Figure 5.1. Typical absorbance trace at 328.1 nm beginning one second prior to atomization by GFAAS for Ag standards (2-8 ng Ag mL⁻¹ in 10% HNO₃) and Standard Reference Material 1643B (trace metals in water) from the U.S. National Bureau of Standards (NBS). 0.1 µg Pd and 0.02 µg Mg matrix modifier added.

5.1.3 Results and discussion

5.1.3a pH dependence of extraction.

Seawater used to investigate the extraction of Ag, Zn, Cu, Cd, Fe, and Pb as a function of pH was collected from the eastern portion of Massachusetts Bay (42° 13.2'W, 70° 25.3'N). Approximately 20L of filtrate was collected by pumping seawater through a pre-cleaned, pre-rinsed 0.2 µm pleated capsule filter (Gelman) and collected in a pre-cleaned 22L polycarbonate carboy. A 2L subsample of the filtered seawater was spiked with 36 ng Ag, 108 ng Zn, 270 ng

Cu, 36 ng Cd, and 2700 ng Fe. Aliquots (260 ml) of the spiked sample were transferred to Teflon separatory funnels, their pH adjusted, and extracted using the APDC/DDDC procedure.

The variation in absorbances of Ag, Pb, Zn, and Fe, as a function of pH, is shown in Fig. 5.2. It is apparent from this technique there is a wide range in pH over which most metals may be adequately extracted. If iron is to be analyzed along with the other metals, the extraction should be carried out at pH 4 - 5.

The results shown in Fig. 1 are similar to a dithiocarbamate extraction study by Kinrade and Van Loon (1974) in which most metals demonstrated plateaus in absorbance between pH 3 and 6. Their method used methyl isobutyl ketone (MIBK) as the organic solvent and a 1.2M solution of sodium citrate as a buffer. When the extraction was carried out using an acetate buffer, Kinrade and Van Loon (1974) report the formation of metal-acetate complexes which may ultimately affect the ability of certain metals (especially Pb and Ag) to be extracted into the MIBK phase.

Although the results in Figure 5.1 are similar to the observations of Kinrade and Van Loon (1974), there are distinct differences. The formation of metal-acetate complexes is not an important factor when extraction occurs with chloroform as the organic solvent. The differences in dithiocarbamate extraction techniques may reflect varying degrees in the solubility of the metal-dithiocarbamate complexes with solvent type (Sandell and Onishi, 1977). Freon is also used in solvent extraction methods because of high immiscibility with aqueous solutions. The use of Freon for the pre-concentration of Ag from natural water samples was inconsistent with respect to quantitative yields. Thus, chloroform was selected as the organic solvent, even though it is less superior to Freon in terms of immiscibility and had the tendency

to form emulsions with samples of high organic content.

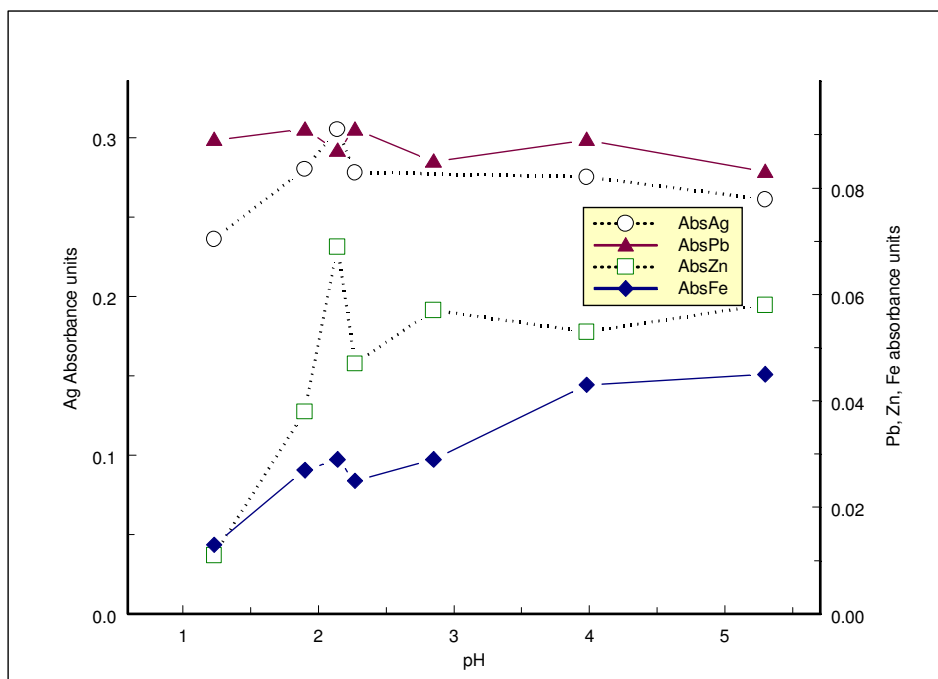


Figure 5.2. The peak integrated absorbance of seawater samples as a function of extraction pH from Massachusetts Bay (collected July 31, 1995, at HUM6, 42° 13.642'N 70° 25.529'W,) spiked with Ag, Pb, Zn, and Fe.

5.1.3b Recovery of metals from spiked seawater samples.

Samples collected from Boston Harbor were transferred in duplicate to separatory funnels. To one set, Ag, Pb, Cd, Zn, Fe and Cu were added such that the concentrations of these metals were approximately 50% greater than ambient concentrations. A subset of Boston Harbor samples was pre-screened to determine ambient metal concentrations. These results were used in creating a mixed spiking solution of selected metals (in 10% HNO₃). 100 µl of the

spiking solution was added to each replicate as a matrix-spike and extracted along with the original. A 10-fold dilution of the spiking solution was saved for comparative analysis.

The extractions of Ag, Pb, Cd, Zn, Cu and Fe from spiked seawater samples show recoveries close to 100% (Table 5.2). Recoveries are calculated by

$$(1) \quad \% Rcvy = \left[\frac{\left[\frac{MS - SC}{M_{MS}} \right] - \left[\frac{S}{M_S} \right] + SC}{SC} \right] * 100$$

where S and MS are the mass (in ng) of metal extracted from the sample and matrix spike, respectively, SC is the mass of metal added to MS, and M_S and M_{MS} are the mass of sample extracted.

Table 5.2. Recovery of metals from seawater samples collected from Boston Harbor, Massachusetts, USA.

Sample	Ag	Pb	Cd	Zn	Cu	Fe
BH7	102.6	99.2	99.9	103.5	92.3	96.6
BH15	102.4	102.7	100.0	102.8	96.2	112.7
BH22	100.1	97.8	99.3	98.6	96.5	96.7
Mean:	101.7	99.9	99.7	101.6	95.0	102.0
STDS:	1.4	2.5	0.4	2.7	2.3	9.3

Samples collected 11 June 1996. BH7, BH15 and BH22 from 42° 21'N 71° 1'W, 42° 18'N 71° 2'W and 42° 17'N 70° 56'W, respectively. Salinities ranged from 27.9 to 29.9 PSU.

5.1.3c Silver in Certified Reference Materials (CRMs) by standard comparative analysis.

In order to evaluate potential matrix affects in the GFAAS – solvent pre-concentration and back extraction method used to determine silver concentration in natural samples Massachusetts coastal waters, standard addition analytical response curves were generated using National Research Council of Canada certified reference coastal (CASS3) and open-ocean

(NASS4) samples and compared to results generated from external standards that were prepared in ultra-pure 10% HNO₃. Six aliquots (~260 mL for CASS3; ~350 mL for NASS4, determined gravimetrically) from each sample were transferred to trace-metal clean Teflon separatory funnels. Varying amounts of Ag (in ultra-pure 10% HNO₃) was added to each aliquot, ranging from 0 – 5 ng, (0 to 2.5 ng Ag for NASS4), such that the concentrations of these metals were approximately 50% greater than ambient concentrations. A subset of the CRM sample was pre-screened to determine apparent metal concentrations. These results were used in creating a spiking solution of Ag (10% ultrapure HNO₃). Aliquots (50 - 400 µl) of the spiking solution were added to each replicate as a matrix-spike and extracted along with an aliquot of the original sample. A 10-fold dilution of the spiking solution was saved for comparative analysis. The concentration Ag in each sample was determined from the analytical response of Ag from the extracted sub-samples by linear extrapolation. In order to remove any matrix artifacts, the extraction volume is held constant for all sub-samples (V_{ex}) and the analysis is reduced to determining analyte mass. This analytical method relies on the property that the GFAAS analytical signal (A) is proportional to the analyte (x) mass in the sample (m_x). Thus,

$$(2) A_x = k m_x$$

First the analytical signal (A_x) is measured for the unknown sample with V_{ex} . Next, a known amount of analyte (standard) is added to the unknown solution. The analytical signal, A_{x+S1} is measured:

$$A_{x+S1} = k(m_x + m_{S1})$$

Thus the ratio of the responses in equations (2) and (3) are used to estimate the mass of analyte in the original sample.

$$m_x = A_x / (A_{x+s_n} - A_x)$$

where s_n denotes various standards added

As a measure of precision this process is repeated with varying amounts of analyte added to subsamples. Standard additions linearization consists of plotting the ratio of mass determined by spectroscopy to the mass added of each sub-sample. Thus, the y-intercept gives estimates the mass of the analyte in the sample as well as precision. The concentration of analyte [X] is:

$$[X] = m_{x,y-int} / V_{ex}$$

Figure 5.3 shows the analytical results for standard additions to NASS3 CRM. The concentrations of Ag determined for CASS3 and NASS4 are given in Table 5.3. These values agree with batch Ag results (corresponding to the surveys reported in Chapter 3) generated by analysis of external standards (in 10% HNO₃) and show no significant seawater matrix effect for Ag. Table 5.4 list the batch metals results of CRM analyzed during surveys in Massachusetts Bay and the Gulf of Maine. Concentrations in

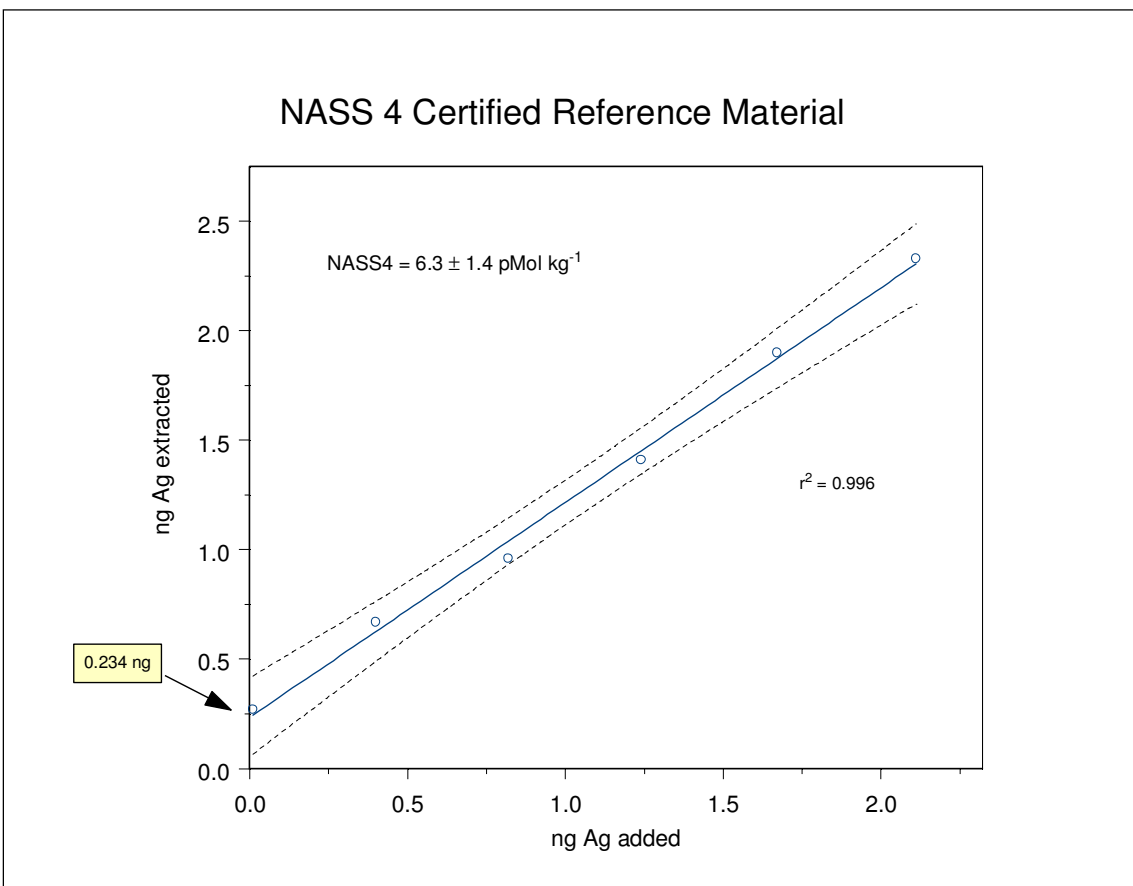


Figure 5.3. Standard additions of Ag (0 - 2.5 ng) to National Research Council of Canada ocean water certified reference material: NASS4. Average mass extracted = $0.343 \pm 0.001 \text{ kg}$.

Table 5.3. Silver concentrations in NRCC certified reference material.

Sample	Ag (pmol kg^{-1})	r^2 (n=6)
NASS4	6.3 ± 1.3	0.996
CASS3	57.4 ± 16.8	0.998

Standard error estimates of silver concentration predicted from simple linear regression.

Table 5.4. Canadian National Resource Council Standard Reference Material Analyses.

Analytical Batch	SRM	Ag	Pb	Cu	Zn	Cd	Fe
		pmol kg ⁻¹	pmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	pmol kg ⁻¹	nmol kg ⁻¹
95 Feb.	CASS3	58.3	30.9	8.09	18.9	186	129.3
		61.4	36.3	8.22	19.5	197	21.1
95 Jul.	CASS3	55.0	NA	NA	NA	NA	15.6
		40.7	NA	NA	NA	NA	NA
		37.4	NA	NA	NA	NA	NA
June96	CASS3	69.0	44.6	7.26	18.6	280	8.8
96 Sept.	CASS3	63.7	51.5	7.09	22.2	271	20.0
	CertVal	NA	58±19	8.14±0.98	19.0±3.8	267±44	22.6±13.0
96 Jul.	NASS4	6.05	37.8	3.69	2.48	162	0.03
		5.34	32.9	3.39	2.54	154	1.93
	CertVal	NA	63±24	3.59±0.17	1.76±0.28	142±27	1.88±0.3

86% of seawater CRMs analyzed for Cd, Zn, Cu, and Fe fell within 2 SD of the certified values. The accuracy was poor for Fe analysis and high values reflect the ease at which samples can be contaminated for Fe. Extremely low recoveries for Fe in two of seven trials remains unexplained. Except for one occasion (one of two CRM extractions accompanying the analysis of the Sept. 1996 samples), the analyses for Pb in CRM seawater was generally low and just outside the lower (95%) confidence intervals for both NASS4 and CASS3. Both seawater CRMs have relatively large uncertainties for certified Pb concentrations (~20% RSD). If the lower confidence interval is considered, our Pb-“recoveries” would be consistently near 90%. There has been some suggestion that organic ligands present in these seawater CRMs can effectively compete with metal chelating complexation during solvent-liquid extraction (Ndung’u et al., 2003). Recoveries in metal extraction techniques that use solvent-extraction preconcentration methods may be improved when water samples are pre-treated with ultraviolet (UV) irradiation and potentially competing organic matter is broken down. Ndung’u et al.

(2006) report that UV radiation may be necessary for adequate extraction and preconcentration of Ag from natural waters with high natural organic matter concentrations if using chelating resin column partition (CRCP)-ICP-MS.

No certified reference material exists for Ag in natural waters. However, the analyses of Ag in the National Research Council of Canada CRMs conducted with the analyses of Massachusetts coastal waters are in good agreement with those values reported in the peer-reviewed literature (Table 5.5).

Table 5.5. Silver analysis of Canadian National Council Seawater Reference Material for this work and compared to values reported in peer-reviewed literature

	Reference	Ag (pM)	SD	Analytical Method
CASS 2				
	Barriada et al., 2007	62.2	2.4	APDC/ICPMS
CASS 3				
	This Work	60..4	2.7	APDC/GFAAS
CASS 4				
	Ndung'u et al., 2001	56.6	8.3	APDC/ICPMS
	Yang and Sturgeon, 2002	50.2	0.7	AER/ICPMS
	Ranville and Flegal, 2006	101	2.6	UV-Digest/AER/ICPMS
	Ndung'u et al., 2006	78.6	18.2	APDC/ICPMS
	Flegal, pers. com., 2008	60.6	8.4	APDC/GFAAS
		64.6	7.6	UV-Digest/AER/ICPMS
NASS 2				
	Rivera-Duarte et al., 1999	6.3	1.5	APDC/GFAAS
NASS 4				
	Rivera-Duarte et al., 1999	12	1.5	APDC/GFAAS
	This Work	7.3	1.8	APDC/GFAAS

APDC – Dithiocarbamate solvent extraction

ICPMS- Inductively-coupled plasma mass spectrometry

GFAAS-graphite furnace atomic absorption spectrometry

AER-anion exchange resin

UV-digest- UV digestion prior to preconcentration and analysis

5.1.4 Conclusions

The liquid/liquid extraction of metals from natural waters modified allows for the detection of silver with other metals in filtered seawater. No matrix effect is apparent in the GFASS analysis of silver in marine waters as there is good agreement between standard addition analyses and results generated from external standard responses. In order to maximize the quantitative recovery of co-extracted metals, metal-chelation and extraction into the organic phase should occur at $\text{pH} > 4$. Chloroform was the preferred organic phase because of superior extraction efficiencies compared to the other organic liquids evaluated. Removal of the concentrated HNO_3 in the first aqueous fraction of the back extraction procedure was critical for consistent recoveries of Ag. The quantitative assessment of Pb, Cu, Zn, Cd, and Fe concentrations in natural waters are also capable with the modifications developed here.

5.2 Method for particulate organic carbon and nitrogen analysis

Methods for particulate carbon and nitrogen follow those described by Hedges and Stern (1984). Particulate matter collected on pre-combusted glass fiber filter (Whatmann GF/F) is subjected to vapor acidification to remove inorganic carbon (CaCO_3). This is accomplished by placing the “wetted” sample in a 50 x 9 mm tight-fit Petri dish (Falcon No. 1006, Fisher Sci. Cat. # 08-757-105). Filters are “wetted” using organic free water (Q HOH: sub-boiled, quartz-distilled, deionized water). A drop of organic-free concentrated HCl is placed in the Petri dish, away from the filter and sealed. The filter containing the sample is exposed to HCl vapor for 24-48 h at room temperature. The acidified sample is air-dried on a Class 100 clean bench and analyzed by high temperature (925°C) combustion. A Perkin-Elmer 2400 CHN Elemental Analyzer is used in this analysis. Carbon, nitrogen, and hydrogen in the particulate material are

converted to simple gases (CO₂, H₂O, and N₂). These gases are quantified by the analyzer using gas chromatographic column and thermal conductivity detection. Analytical blanks are carried throughout the procedure from wetting, vapor acidification, air drying, and analysis.

5.3 Fluorometric determination of Chl *a* and phaeo-pigments (UMB ver. 2.3b)

(The procedure, detailed below, is adapted mainly from Strickland and Parsons – A Practical Handbook of Seawater Analysis, pp185-194 and pp. 201-203.)

5.3.1 *Sample collection*

Water samples are collected employing standard sampling techniques. Typically, discrete seawater samples are collected in Niskin or Go-Flo bottles at depth over the water column. A subsample is collected from the Niskin bottle and stored in a 2L polycarbonate bottle. For field filtration, a sample of about 50-100 mL is syringe-filtered through a glass-fiber filter (2.4 cm Whatman GF/F). The filter is removed, carefully folded in aluminum foil and frozen for later analysis. Samples that are not filtered in the field are stored in a cool dark place and processed within 8 hours of collection.

5.3.2 *Lab filtration* (performed under low light conditions to minimize artifacts):

Water samples may be passed through a 300 :m mesh sieve (if necessary to remove large material/zooplankton) into a 200 mL filtration funnel loaded with a 2.4 cm Whatman GF/F glass fiber filter.

The sample is filtered through the glass fiber filter, taking care not to exert too much pressure. (Pressure above 55 mm Hg may rupture cells and allow material to pass through the filter).

Using forceps, remove filter and associated retained material and place in a extraction vial. (A capped 20 mL KIMAX test tube serves this purpose well.) Record sample and test tube #. If samples are to be extracted at a later date, wrap test tube/filter in aluminum foil and store at or below 0°C (in freezer).

5.3.3 Extraction

Under a low-light regime, add 10 mL of 90% acetone (10% DI HOH) v/v to the test tube/filter and shake vigorously. Save an aliquot of the 90% acetone for a reagent blank. Sample procedural blanks are performed by filtering a representative “sample” volume (50-200 mL, estuarine-Mass. Bays samples) using DI HOH, through two filters loaded in the filtration apparatus. Procedural blanks are performed on the most downstream filter. (In the past, DI HOH have given high blanks due to the microbial buildup in our DI system. Obviously, this would be an inappropriate procedural blank. Typical blank values should read between 0.0-0.1 units on the most sensitive setting.) Store test tubes with the extracting sample in the dark at 0°C (in freezer) for 12 – 24 hrs.

5.3.4 Fluorometry

Under a low light regime, remove extraction samples from the freezer, keeping them covered under an aluminum tent. Allow samples to equilibrate to near room temperature. (Most fluorescent materials have significant temperature coefficients. Since standards are prepared at room temperature, it is recommended that samples and blanks all be determined at room temperature.)

Turn instrument (Turner Designs, Model 10 Series Fluorometer) on and allow and allow 5-10 minutes for warm-up. Check instrument zero with a fresh aliquot of 90% acetone. (Prepare

fluorometric standards while the instrument is warming up and samples are equilibrating to room temperature.)

For coastal samples, the following settings are recommended:

1X-100X sensitivity knob should be set to 1X.

Range switch set to “auto”.

Shake sample and fill cuvette (13x100 mm culture tube) with extract.

Insert cuvette into the instrument holder and record the relative intensity as **R_b** (*read only from the 0-10 scale* regardless of scale factor – this is accounted for in the equations listed in § V.)

Add 2 drops of 5% v/v HCl to cuvette and take a 2nd reading approximately 30 s later. Record this value as **R_a**.

5.3.5 Calculations

Convert the measured fluorescence relative intensities to chlorophyll and phaeo-pigments concentrations using the following equations:

$$\text{Chl } a \text{ (ug L}^{-1}\text{)} = 10 \times [(F_d \times (t/t-1))] \times [((R_{b \text{ samp}}/\text{Scale}_{b \text{ samp}}) - (R_{a \text{ samp}}/\text{Scale}_{a \text{ samp}}))/\text{Samp. Vol (mL)}]$$

$$\text{Phaeo-pigment (ug L}^{-1}\text{)} = 10 \times [(F_d \times (t/t-1))] \times [((R_{a \text{ samp}}/\text{Scale}_{a \text{ samp}}) - (R_{b \text{ samp}}/\text{Scale}_{b \text{ samp}}))/\text{Samp. Vol (mL)}]$$

where:

$$t = (\text{mean } R_{b \text{ std}} / \text{mean Scale}_{b \text{ std}}) / (\text{mean } R_{a \text{ std}} / \text{mean Scale}_{a \text{ std}})$$

$$F_d \text{ (door factor)} = \text{Fluorescence Standard Conc. (ug L}^{-1}\text{)} / (\text{mean } R_{b \text{ std}} / \text{mean Scale}_{b \text{ std}})$$

The fluorescence standard is made by quantitative dilution (typically 1/50) of the spectrophotometric standard. The spectrophotometric standard is determined by reading absorbances at 630, 647, 664, and 750 nm. The concentration of the spectrophotometric standard is calculated by:

$$\text{Chl } a \text{ (mg L}^{-1}\text{)} = 11.45 (\text{Abs}_{664} - \text{Abs}_{750}) - 1.54(\text{Abs}_{647} - \text{Abs}_{750}) - 0.008(\text{Abs}_{630} - \text{Abs}_{750})$$

5.3.6 Standard preparations

A. Stock Standard

In a 100 mL volumetric flask, add approximately 2 mg of commercially available chlorophyll *a* ($\text{C}_{55}\text{H}_{72}\text{MgN}_4\text{O}_5$, available from Sigma, product # C-5753) and dilute to mark with acetone.

Wrap volumetric flask with aluminum foil and store at 0°C.

B. Spectrophotometric Standard:

In a 100 mL volumetric flask, quantitatively add 5 mL of stock standard and dilute to mark with acetone solution (approximate concentration $\sim 1 \text{ mg L}^{-1}$). Prepare fresh daily.

C. Fluorometric Standard:

In a 100 mL volumetric flask, quantitatively add 2 mL of spec. standard and dilute to mark with acetone solution.

Note: All solutions should be at room temperature (ideally at 20°C) to allow for quantitative dilutions.

5.4 Total suspended matter (TSM) analytical protocol

5.4.1 Field collection

Aliquots of TSM samples are obtained from the 2L polycarbonate bottles filled in the field.

5.4.2 Processing equipment

Nalgene® polysulfone filtration apparatus (Fisher Cat. # 09-740-23D)

Top reservoir = 500 mL

Filtrate receiver can be either 500 mL or 1000 mL

Filters (47 mm, 0.4 μ m Poretics® polycarbonate membranes), pre-weighed

[Filters for TSM are pre-weighed by placing filters in a dessicator for a minimum of three (3) days prior to weighing on the Perkin-Elmer microbalance next to the CHN analyzer. Tared weights (M_i) are recorded to the nearest 1/1000th milligram. Typical tared weights are between 13-17 mg. Tared filters are stored in disposable Falcon® Petri dishes (Fisher Cat. # 08-757-105) with their tared weight recorded on the Petri dish cap in permanent marker.]

Forceps

Filter apparatus holder

Vacuum pump with vacuum gauge

Q HOH in squirt bottle.

Graduated Cylinders, 250 mL, 500 mL, and 1000 mL

5.4.3 Sample preparation procedure

Set up filtration apparatus/apparati on lab bench in holder. Connect Teflon fitting, for vacuum, to one of the ports on the top of the filtrate receiver. Using forceps, remove a tared polycarbonate filter from Petri dish and place onto the analytical plate (the two-piece white/off-white support bed) of the filtration apparatus. Save Petri dish with tared weight recorded on the

cap for later storage of processed sample. Place top of filtration apparatus on and screw down finger tight. *Make sure at least one of the black (sometimes clear) silicone plugs (there are three) from the screw cap on the top reservoir is removed before filtering* -This allows for air to enter, preventing the formation of a vacuum and potentially rupturing the filter.

Now you are prepared to process samples. Add a “reasonable” amount of sample to be filtered for TSM measurement. For example:

Boston Harbor water -- ~200 mL (sometimes more depending on season, i.e. winter)

Gulf of Maine open water – up to 2 L on occasion

Coastal waters – between 500-1000 mL

The goal is to load the filters sufficiently to measure the mass of particulates (~0.3-0.6 mg) without causing artifacts due to clogging (pore size changes) during processing. Add additional sample in 25 – 50 mL increments until filtration slows down. This will be noticed by a substantial slowing in the rate of filtration as the filter begins to clog. During last incremental filling, swirl sample to prevent loss of particulate material to the side of the apparatus. After sample has been completely filtered, remove vacuum and decant filtrate through one of the ports on the filtration receiver into an appropriate graduate cylinder (500 mL for coastal waters, 1-2L for open ocean samples) and measure the amount of filtrate. Record this volume (V_f). After obtaining the filtrate volume, close port, re-apply vacuum and rinse filter with 10 – 20 mLs of QHOH, using the squirt bottle and rinsing all of the filter and sides of the apparatus, to ensure complete particle collection and to remove residual saltwater from filter. Residual saltwater trapped in the filter pore spaces may add a substantial amount of mass if allowed to dry with captured particulates. Following the QHOH rinse, remove top portion of apparatus away from receiver, taking care not to disturb filter. This is easiest if the vacuum is left on while removing the top portion of filtration apparatus. Turn off vacuum now, and remove filter by using forceps and return

processed filter to original Petri dish. Place filter with particulate matter open with cap underneath base, in a dessicator, and allow to dry for a minimum of three (3) days prior to weighing. After filters have been desiccated, weigh filters on the CHN microbalance, recording to the nearest $1/1000^{\text{th}}$ mg (M_s).

Blanks are processed in the same manner, using 50 mLs of QHOH. Sometimes QHOH may be contaminated with particles and a better measure of “blanks” are obtained from re-weighing “control” filters-those that were not subjected to any filtration processing. It is important to re-weigh at least three (3) “control” filters since changes in relative humidity can cause a significant artifact in the determination of TSM. As a control of relative humidity, three (3) pre-weighed filters are reserved for re-weighing at the time of sample weighing. On occasion, these filters will be consistently higher or lower (~ 0.01 mg) than when originally weighed. Use the mean value (M_b) to correct sample weights for effects of relative humidity.

Clean filtration apparatus (just the top, with a small amount of laboratory soap and gently wiping with Kimwipes® (UNLESS you are using the filtrate for dissolved constituents – like nutrients- BUT NOT METALS-see trace metal protocol for dissolved metals), followed by substantial rinses of QHOH. Use either QHOH or deionized water for rinses.

5.4.4 Calculations

TSM are calculated as follows

$$[(M_s - M_t) - M_b]/(V_f)$$

where:

M_s is the mass of filter *plus* sample in mg

M_t is the mass of filter (*tared wt.*) in mg

M_b is mean blank value in mg

V_f is the filtrate volume (in liters)

Note:

When processing large batches of samples (10-20) guestimate which ones are the “cleanest”.

(i.e., have the lowest TSM content). DO THESE FIRST. “Dirtiest” last. One strategy is to process the blanks after processing a few of the very “clean” samples (like Mass. Bay, Gulf of Maine); or run them at the very beginning. A minimum of 3 blanks should be processed, and 10% of the samples should be replicated.

Table 5.6. Past TSM observations.

Blanks	Ftr Tare	Ftr Mass	Delta
	(mg)	(mg)	(mg)
1	15.604	15.609	0.005
2	15.783	15.797	0.014
3	15.913	15.929	0.016
5	15.690	15.702	0.012
6	15.808	15.834	0.026

LOD: 0.07 mg L⁻¹
(3 * STD, based on
350 mL sample
vol.)

Table 5.7. Past TSM replicates.

Sample	mg L ⁻¹
MB16-1	2.68
MB16-1R	2.97
WE6	2.18
WE6 (Rep)	2.28
28.2 A	1.00
28.2 B	1.02

CHAPTER 6

SUMMARY

Human well-being requires a balance of human impacts with prosperity. This balance includes the preservation of or restoration to “healthy” ecosystems. Ecosystem health is often defined in terms management targets based on the quality of ecosystem forms and functions. Environmental quality has been linked to human well-being (e.g., WHO, 2005). Best ecosystem management strategies and implementation rely on knowledge from relevant and available information and, if needed, further monitoring and research to inform inherent management re-evaluation.

The global human population profile, where nearly 50% live within 150 km of the coast, places coastal ecosystems at the forefront of environmental risks because of threats from land-based human activities (UNOA, 2010). These activities—habitation, industry, transportation, and agriculture, recreation—contribute to the milieu of land-based pollution. Among the effects of land-based coastal pollution are those caused by the delivery of contaminants and nutrients. These materials are delivered by rivers and streams, industrial effluents, atmospheric deposition, storm water runoff, and groundwater discharges. Enrichment of nutrients in coastal ecosystems can result in eutrophication which leads to shifts in ecosystem function that are often considered deleterious to environmental quality. Over half (64%) of the estuaries and coastal embayments evaluated by the U.S National Oceanic and Atmospheric Administration were considered nutrient-impaired (Bricker et al., 2007). The Pew Oceans Commission’s State of the Oceans

report (2003) listed pollution and coastal development in 3 of 10 major threats to the environment. Clearly, coastal pollution management is important to human well-being and environmental quality.

This dissertation examines the forms and distribution of Ag along with Cu, Zn, Pb, Cd, and Fe in the coastal waters in and near Massachusetts Bay, a relatively shallow embayment in the southwestern portion of the Gulf of Maine. The Massachusetts Bays System is comprised of Boston Harbor—a highly urbanized estuary, Massachusetts and Cape Cod Bays, and an open Gulf of Maine boundary along the north and west of Massachusetts Bay. For the Massachusetts Bay System, wastewater dispersion and fate are important considerations for coastal management (Dolan, 2004). There are known (e.g., Mallin et al., 2007.) and unknown impairments imposed by contaminants associated with wastewater. Understanding wastewater dispersion can inform environmental management decisions that seek to balance impacts with ecological and economical benefits. In this work, Ag in the coastal waters of the Massachusetts Bays System is evaluated as a biogeochemical tracer for coastal pollution because of the role of wastewater discharge in contaminant loading to the study area (Alber and Chan, 1994; Menzie-Cura, 1996; Bothner et al., 1994 & 2002; Hunt et al., 2006).

Oceanic observations report pM concentrations for Ag (Murozumi, 1981; Martin et al., 1983; Sañudo-Wilhelmy and Flegal, 1992; Flegal et al., 1995, Rivera-Duarte et al., 1999; Zhang et al., 2001; Ndung'u et al., 2001; Sañudo-Wilhelmy et al., 2002; and Randville and Flegal, 2005) while concentrations in wastewater effluents can be 2 – 4 orders-of-magnitude higher (Adams and Kramer, 1999b). For the study period (1994-1996), the Boston municipal wastewater treatment facility to Boston Harbor was a major source (3-10 kg d⁻¹) of silver to the coastal zone. Water column surveys conducted in Boston Harbor, Massachusetts and Cape Cod

Bays, and the southwestern Gulf of Maine near coastal region occurred during the period when wastewater management for the Boston Metro area was undergoing significant changes.

Treatment programs were implemented to meet violated water quality standards in the mid 1980's. Direct discharge of sewage sludge to the Harbor ended in 1991. New primary treatment for Boston wastewater began in 1995, and by 2001, a new wastewater discharge relocated to deeper waters (30 m) in Massachusetts Bay was online.

Silver concentrations in both particulate and filtered ($<0.4\ \mu\text{m}$) fractions ranged from <3 to $211\ \text{pmol kg}^{-1}$ in the Massachusetts Bays system, averaging 103 and $117\ \text{pmol kg}^{-1}$ for Boston Harbor, 34 and $10\ \text{pmol kg}^{-1}$ in western Massachusetts Bay, and 11 and $7\ \text{pmol kg}^{-1}$ in the central portion of Massachusetts Bay, respectively. Average Ag concentrations for filtered and particulate fractions in southern Gulf of Maine coastal waters were 10 and $2\ \text{pmol kg}^{-1}$, respectively. While almost half of the silver existed in particulate form in Boston Harbor and the Merrimack River (42 and 47% , respectively), nearly 80% of the silver in Massachusetts Bay, Cape Cod Bay, and the southeastern Gulf of Maine occurred in the filterable fraction. The potential for Ag as a tracer of contaminated water mixing in coastal waters is evident by conservative mixing of Ag in Boston Harbor water with near coastal Massachusetts Bay water observed during a transect from Boston Harbor to the eastern edge of Massachusetts Bay (August, 1994). Apparent freshwater endmember metal concentrations predicted from Ag concentrations in low salinity (<31.6 psu) samples were comparable with MWRA effluent characterizations for the study period. Overall, coastal water surveys revealed non-conservative Ag behavior which is likely the result of incomplete mixing of three or more water masses with unique conservative Ag signatures (e.g., Merrimack River, Boston Harbor, surface and intermediate Gulf of Maine waters).

Using the results from the 1994-1996 surveys in the Massachusetts Bays system and from the southeastern Gulf of Maine Survey (July 1996), quasi-steady state mass balance approaches estimate most of the silver entering into the Massachusetts Bays system was the result of municipal wastewater discharge to Boston Harbor (84-93%). Input from the Gulf of Maine (which includes, on occasion, sources from the Merrimack and the western Gulf of Maine coastal current) was a distant second. The role of the Merrimack in the *annual* flux of Ag to Massachusetts Bay was estimated to <1% but important seasonally during periods of high watershed runoff (spring). The Massachusetts Bays model presented in this work is unable to capture wind events, which can be locally important to transport mechanisms (Jiang and Zhou, 2004; Jiang et al., 2007; Jiang and Zhou, 2008; Tian et al., 2008). The roles of the Merrimack River and the western Gulf of Maine coastal current to mass transport to Massachusetts Bay remain uncertain; the relatively low contribution of these sources to Ag loading is, at a minimum, within the uncertainties presented in recent hydrodynamic models (Jiang et al., 2007).

Recent advances in wastewater treatment have reduced metal levels in the Boston municipal wastewater and the outfall was relocated from Boston Harbor to Massachusetts Bay. While Ag from direct wastewater discharge has been reduced overall by two orders of magnitude since this study period, anthropogenic sources of Ag to the Massachusetts Bay may still be formidable as sources, especially when considering the legacy of contaminants in Boston Harbor sediments (Wallace et al., 2006; Li et al., in press).

Multivariate analyses were conducted to evaluate fundamental controls on the distribution and fate of Ag in Massachusetts coastal waters. More specifically, the analyses were structured to identify relationships among metal distribution with biological,

weathering/sediment resuspension, and anthropogenic tracers. Metal partitioning data were examined separately to characterize and compare biogeochemical behavior among trace metal observations. The results of observations from water samples collected during two Massachusetts Bays surveys (July 1995 and Sept 1996) and a survey conducted in the nearcoastal region of southwestern Gulf of Maine (July 1996) show that Ag is intermediate with respect to particulate reactivity when compared to the metals observed for this study and consistent with observations of Ag speciation in coastal and open ocean systems. Apparent distribution coefficients (K_D) were generally lower in the region near Boston Harbor (Sept. 1996 survey) relative to those observed for Massachusetts Bay (July, 1995) and from the southwestern Gulf of Maine survey (July 1996).

Exploratory factor analysis was used to evaluate the presence of potential underlying structures in the data sets. The use of factor analysis for exploring latent structures to the data sets has been controversial since its emergence as an analytical tool in multivariate analyses (Nesselroade, 1994; Reimann et al., 2002). The more common approach has been to use factor analysis to confirm, or refute, hypotheses that have been developed *a priori*. The distinction between exploratory and confirmatory factor analysis is often muddled as may be the case here by assigning processes or source identification to selected variables (e.g., Al as continental weathering/sediment resuspension, Ag as wastewater source) before examining the data for latent structures. Further, factor analysis remains challenging with respect to defining true relationships, since finding a unique rotation in component hyperspace is often illusive. It is in this context that factor analyses using 2- or 3- factors models were conducted for 17 variables (including K_D s) to evaluate metal sources, loadings, and partitioning in Massachusetts coastal waters.

The results from factor analyses could not fully distinguish between chemical speciation processes and trace metals loading but did indicate wastewater factors that were characterized by moderate to strong positive loadings from silver fractions and moderately negative loadings from salinity. Wastewater factors were identified for both Massachusetts Bay survey data and found absent from the Gulf of Maine survey data. Exploratory factor analysis revealed behavior of Ag similar to that of Cu and Zn, and may reflect complexation potential and preference to similar ligand classes in the water column. The potential use of Cd phases (filterable and particulate) as a tracer for biogenic or biodegradation of particles emerged from exploring both Massachusetts Bays surveys. The factor analyses presented in this research shows the importance of the types of variables that can be used to explore the relative contributions of processes and sources controlling biogeochemistry, transport, and fate of trace metals in aquatic systems. It is possible that including additional variables, such as ligand characterization, colloid and nutrient concentrations, may contribute to the utility of factor analysis for understanding these controls.

The analysis of silver content in the central portion of Cape Cod Bay from data provided by the U.S. Environmental Protection Agency's National Coastal Condition Assessment ("Northeast Regional Pages) demonstrate the importance of organic phases to metal transport and fate in coastal waters. This importance has been recognized previously (e.g., Hunt, 1979; Wallace et al., 2006). Highly correlated distribution among sediment bound metals with fine grained, organic rich sediment indicate their importance as sinks in the Massachusetts Bays system. Extrapolating the observations from Cape Cod Bay to areal estimates of the distribution of fine grain, organic rich sediments of the Massachusetts Bays system estimates the majority of Ag retained in sediment occurs in Stellwagen Basin (44-59%).

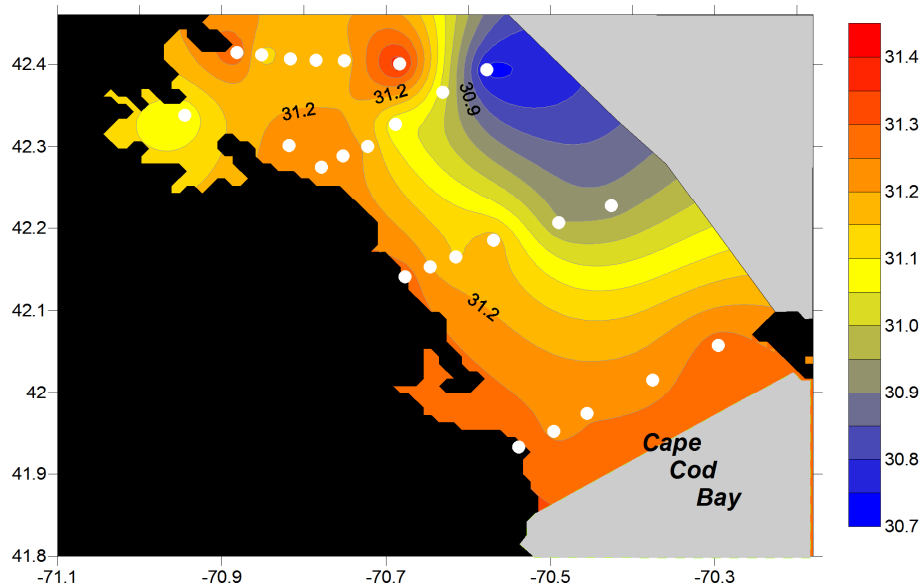
Understanding the transport and fate of trace metals in marine systems is complicated by the number and variability of contributing factors. The use of markers for processes and loadings has been demonstrated as a tool for identifying latent factors among geochemical data sets. For instance, Ag has served as anthropogenic tracer in coastal systems where wastewater discharge is a significant source of contamination has been shown (e.g., Sañudo-Wilhelmy and Flegal, 1992) and demonstrated as a wastewater tracer in the coastal waters of the Massachusetts Bays system. Evaluating the role of sediments as sources and sinks for contaminants needs further evaluation, especially for the potential from historically contaminated sediments of Boston Harbor. Because of relatively low background Ag levels in natural waters, Ag could also be an elegant tracer for further understanding the biogeochemical behavior of similar soft (B-type) metals, complexation with similar (soft) ligands including those that are either wastewater borne or biogenic and limit toxic exposure in aquatic organisms.

APPENDIX

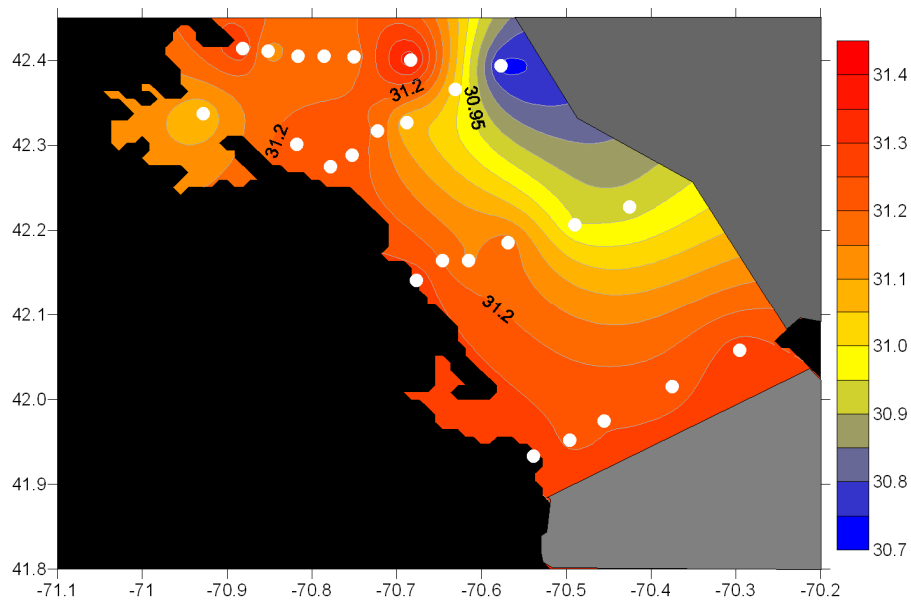
A. CHAPTER 3

a.1 Comparison of salinity (psu) contour plots using data obtained by CTD hydrocasts and data derived from discrete samples.

Data from July 1995 Massachusetts Bays Survey



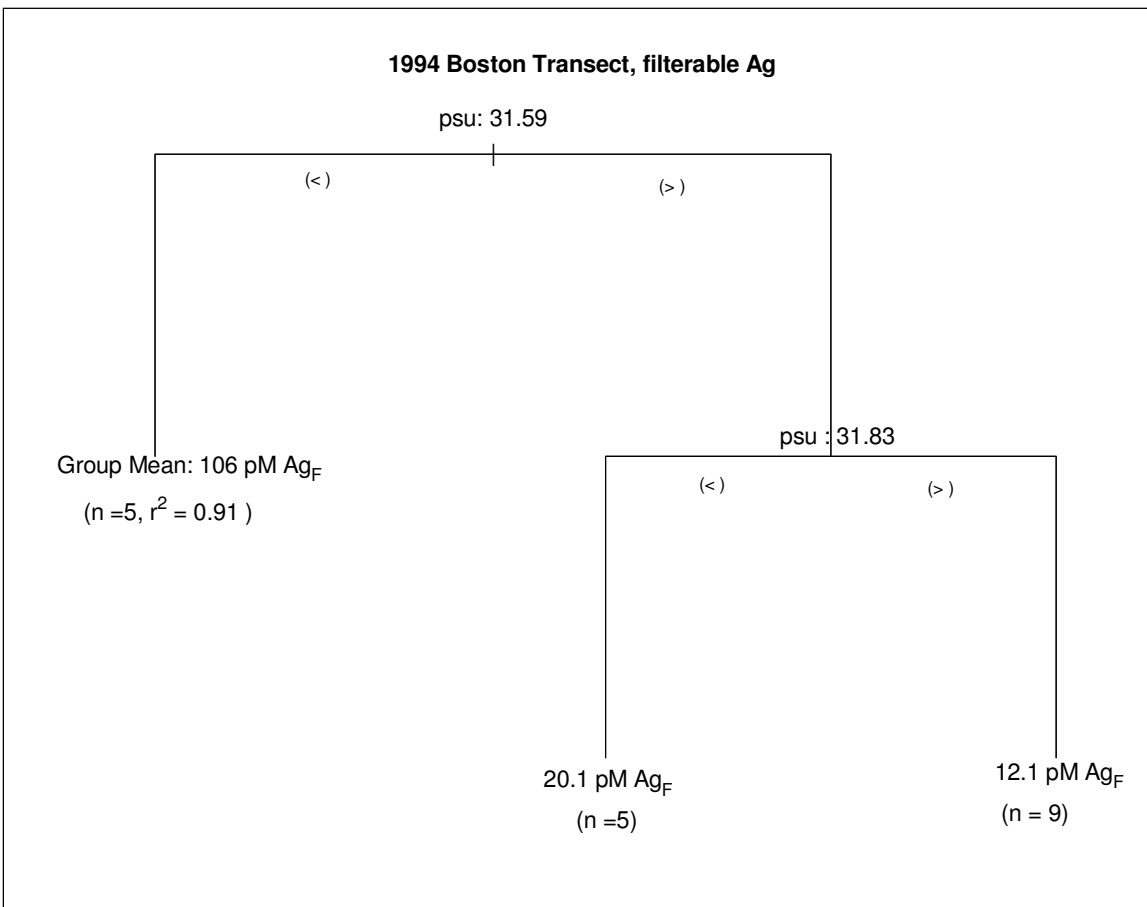
Data from CTD hydrocasts (Hydrographic stations indicated by white dots)

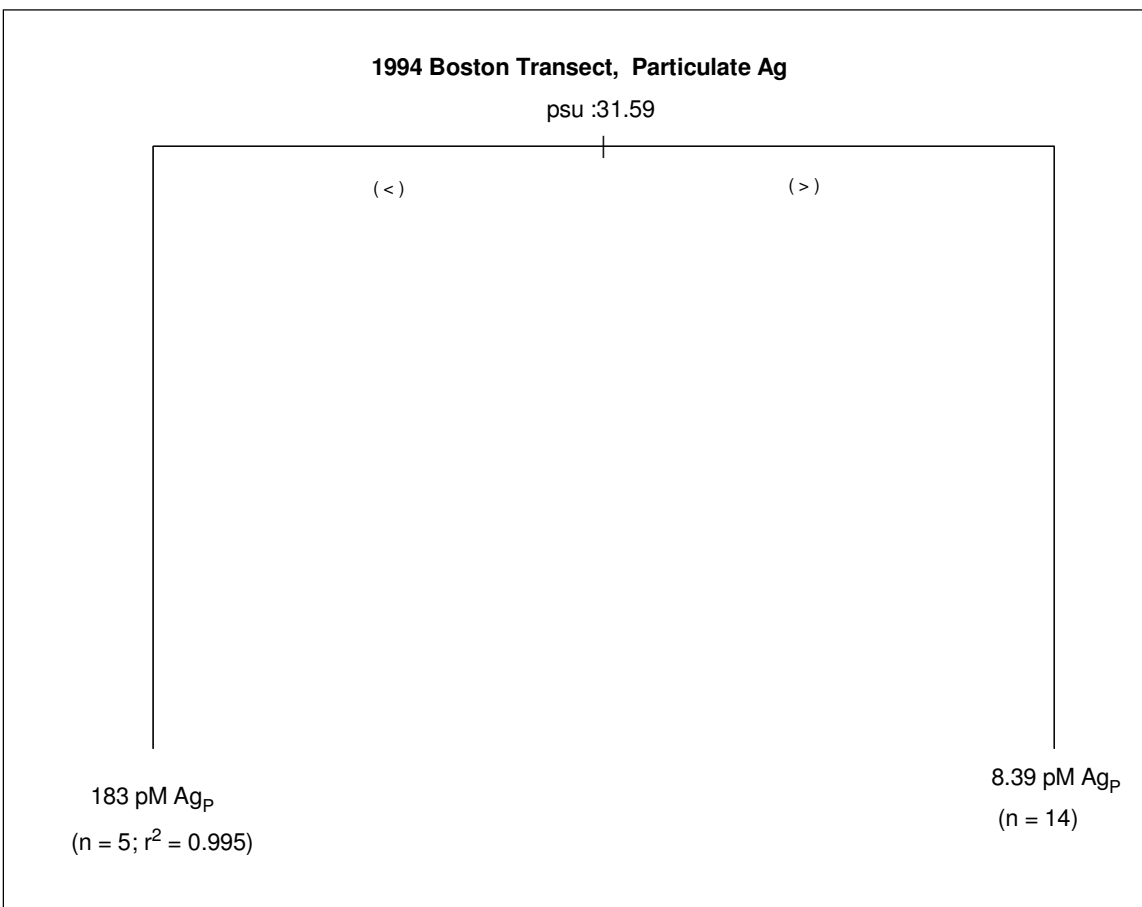


Data from discrete surface water samples (indicated by white dots)

a.2 Regression tree model results for Ag – salinity (psu) during the 09 Aug 1994 Boston transect survey.

Group means, sample size, and where appropriate, linear regression coefficients, are shown at the terminus of each branch.



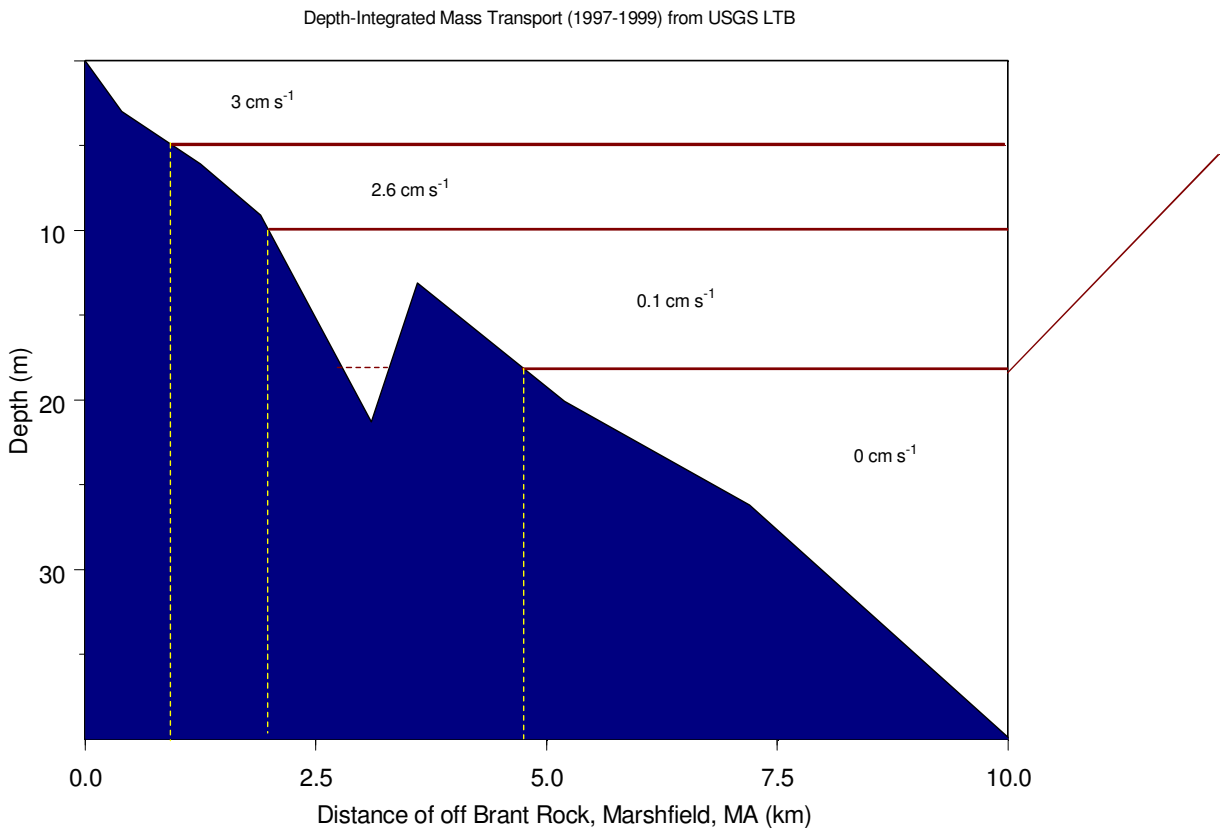


a.3 Sampling period fresh water exchanges to Boston Harbor and Mass. Bay

Date	Deer I. m ³ d ⁻¹	Nut I. m ³ d ⁻¹	Charles R. m ³ d ⁻¹	Nep.R. m ³ d ⁻¹	Other BH m ³ d ⁻¹	Mer. R. m ³ d ⁻¹
July 1994	7.68E+05	3.07E+05	1.73E+05	7.43E+04	4.67E+04	5.70E+06
Aug. 1994	8.74E+05	3.63E+05	1.73E+05	7.43E+04	4.67E+04	5.70E+06
Feb. 1995	9.27E+05	4.62E+05	8.64E+05	3.72E+05	2.33E+05	1.57E+07
June 1995	7.80E+05	3.41E+05	2.59E+05	1.11E+05	7.00E+04	7.95E+06
July 1995	7.42E+05	3.03E+05	1.73E+05	7.43E+04	4.67E+04	4.15E+06
Aug. 1996	7.65E+05	3.79E+05	2.59E+05	1.11E+05	7.00E+04	6.39E+06
Sept. 1996	8.74E+05	4.58E+05	6.05E+05	2.60E+05	1.63E+05	5.44E+06

A.4 Advective flux cross-section, western Mass. Bay into Cape Cod Bay. (corresponding to the Duxbury transect, 11 Sept 1996).

Application of summary currents (cm s^{-1}) from USGS LTB mooring observations.



a.5 Sediment inventory of silver in the top 2 cm of Cape Cod Bay. Grain size and Ag sediment concentration data from EPA's National Coastal Assessment (2000 – 2005).

Sediment density (g cm^{-3}) was linearly interpolated among Ag concentration contours corresponding to 0.1 – 0.65 after evaluating the distribution of “mud” and Ag in Cape Cod Bay (see Figure 3.54).

Contour	Total AREA (m ²)	delta Area	Vol (m ³)	Ag ug/g dw	Density g cm ⁻³	ug Ag cm ⁻³	kg Ag m ⁻³	kg Ag
0	1.55E+09	1.94E+08	3.88E+06	0	1.75	0.00	0.00E+00	0
0.5	1.35E+09	1.87E+08	3.74E+06	0	1.75	0.00	0.00E+00	0
1	1.17E+09	1.49E+08	2.97E+06	0	1.75	0.00	0.00E+00	0
1.5	1.02E+09	1.44E+08	2.88E+06	0.05	1.75	0.09	8.75E-05	252
2	8.75E+08	1.15E+08	2.30E+06	0.10	1.75	0.18	1.75E-04	402
2.5	7.60E+08	1.07E+08	2.13E+06	0.15	1.62	0.24	2.43E-04	519
3	6.53E+08	1.05E+08	2.11E+06	0.20	1.48	0.30	2.96E-04	624
3.5	5.48E+08	9.20E+07	1.84E+06	0.25	1.34	0.34	3.35E-04	617
4	4.56E+08	8.36E+07	1.67E+06	0.30	1.20	0.36	3.60E-04	602
4.5	3.72E+08	9.10E+07	1.82E+06	0.35	1.06	0.37	3.71E-04	676
5	2.81E+08	1.01E+08	2.02E+06	0.40	0.92	0.37	3.68E-04	744
5.5	1.80E+08	1.34E+08	2.68E+06	0.45	0.78	0.35	3.51E-04	941
6	4.58E+07	4.38E+07	8.75E+05	0.50	0.64	0.32	3.20E-04	280
6.5	2.06E+06	2.06E+06	4.13E+04	0.55	0.50	0.28	2.75E-04	11
Total Ag in upper 2 cm of CCB sediments:								5667

Quartz = 2.65 cm^{-3}
Bulk sandy = 1.75 g cm^{-3}
High HOH content mud = 0.5 g cm^{-3}

Area encompassed by individual Ag concentration contours were computed using ArcView 9.3 (ESRI)

a.6 Constants used for box model Ag flux calculations.

			Reference:	
Boston Harbor		Area (km ²)	108	Stolzenbach and Adams (1998)
		Mean Depth (m)	4.9	Signell and Butman (1992)
		Mean Vol (x 10 ⁸ m ³)	6.4	Stolzenbach and Adams (1998)
		Intertidal Vol (x 10 ⁸ m ³)	2.9	
		Long term Depositional Area (km ²)	49.2	
		Sed. Acm. Rt (cm y ⁻¹)	0.2	
		Ag _{Particulate} (pM)	163 (161)	This work (SD, n=7)
		Ag _{Filterable} (pM)	108 (57)	
		Ag _{Sediment} upper BH (µg g ⁻¹ dry wt.)	1.7	Bothner et al. (1993), and Bothner (1997)
		Ag _{Sediment} lower BH (µg g ⁻¹ dry wt.)	4.7	
Massachusetts Bay		Area (km ²)	3550	Signell et al. 2000
		Mean Depth (m)	35	
	Northeastern (Stellwagen Basin)	Area (km ²)	2800	
		Mean Depth (m)	40	
		Long term Depositional Area (km ²)	1960	
		Sed. Acm. Rt (cm y ⁻¹)	0.1	
		Ag _{Particulate} (pM)	2 (2, n=20)	Gulf of Maine, 1996 (SD)
		Ag _{Filterable} (pM)	10 (5, n=24)	
		Ag _{Sediment} (µg g ⁻¹ dry wt.)	0.23	Bothner et al. (1993), and Bothner (1997)
	Western	Area (km ²)	750	Knebel and Circé, 1995
		Mean Depth (m)	20	
		Long term Depositional Area (km ²)	22	
		Sed. Acm. Rt (cm y ⁻¹)	0.15	Intermediate rate
		Ag _{Particulate} (pM)	9 (6)	Sept. 1996 (SD, n=16)
		Ag _{Filterable} (pM)	40 (26)	
		Ag _{Sediment} (µg g ⁻¹ dry wt.)	0.04 - 0.1	Bothner et al. (1993), and Bothner (1997)

a.6 Constants used for box model Ag flux calculations (continued).

Cape Cod Bay	Area (km ²)		1450	Knebel et al., 1996
	Mean Depth (m)		25	Anraku (1966)
	Long term Depositional Area (km ²)		783	Knebel et al., 1996
	Sed. Acm. Rt (cm y ⁻¹)		0.1	
	Ag _{Particulate} (pM)		5 (2)	July 1995 (Std)
	Ag _{Filterable} (pM)		20 (5)	
	Ag _{Sediment} (µg g ⁻¹ dry wt.)		0.51	Bothner et al. (1993), and Bothner (1997)
Overall:	Bulk solids density		0.5 g cm ⁻³	Stolzenbach and Adams (1998)
	MWRA Ag load	1994- 1996	2110 kg y ⁻¹	M. Hall, MWRA
		2000- 2002	377 kg y ⁻¹	
Gulf of Maine	Area (km ²)		9.3x10 ⁴	

B. CHAPTER 4

b.1 Difference in means among surveys for $K_{D, \text{-Crust}}$

Variable: $K_{D, \text{Crust}}$

Grouping variable: Date (7/95=1, 7/96=2, 9/96=3)

Box Plot:

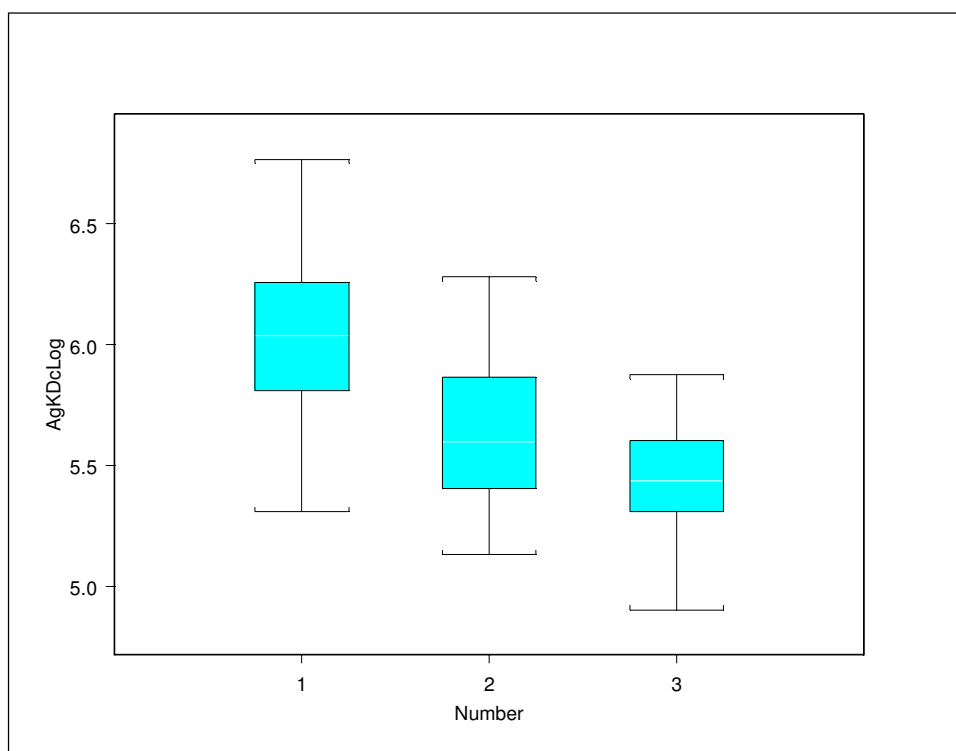
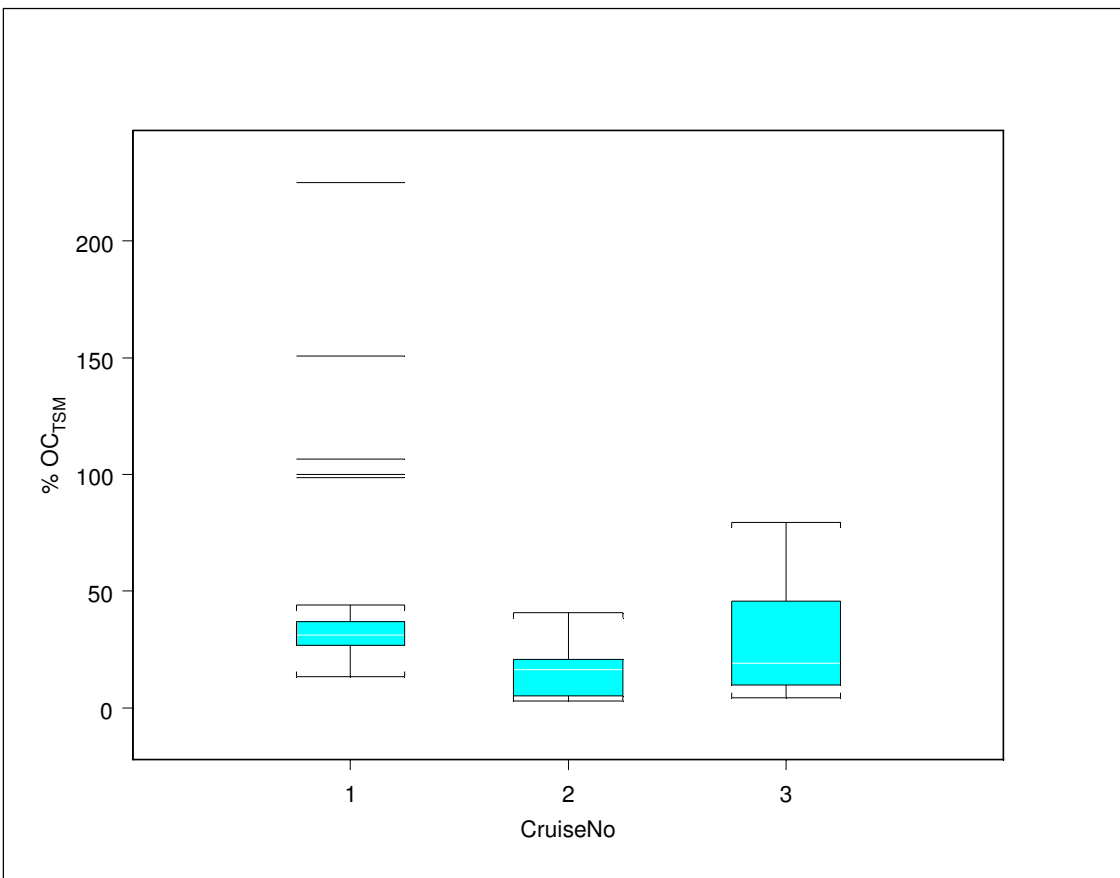


Table B.1. One-way ANOVA:

	Df	Sum of Sq	Mean Sq	F Value	P-value
Number	1	4.49	4.49	48.06	1.3 e-9
Residuals	74	6.92	0.09		

A significant difference exists within the data sets of 1,2,3

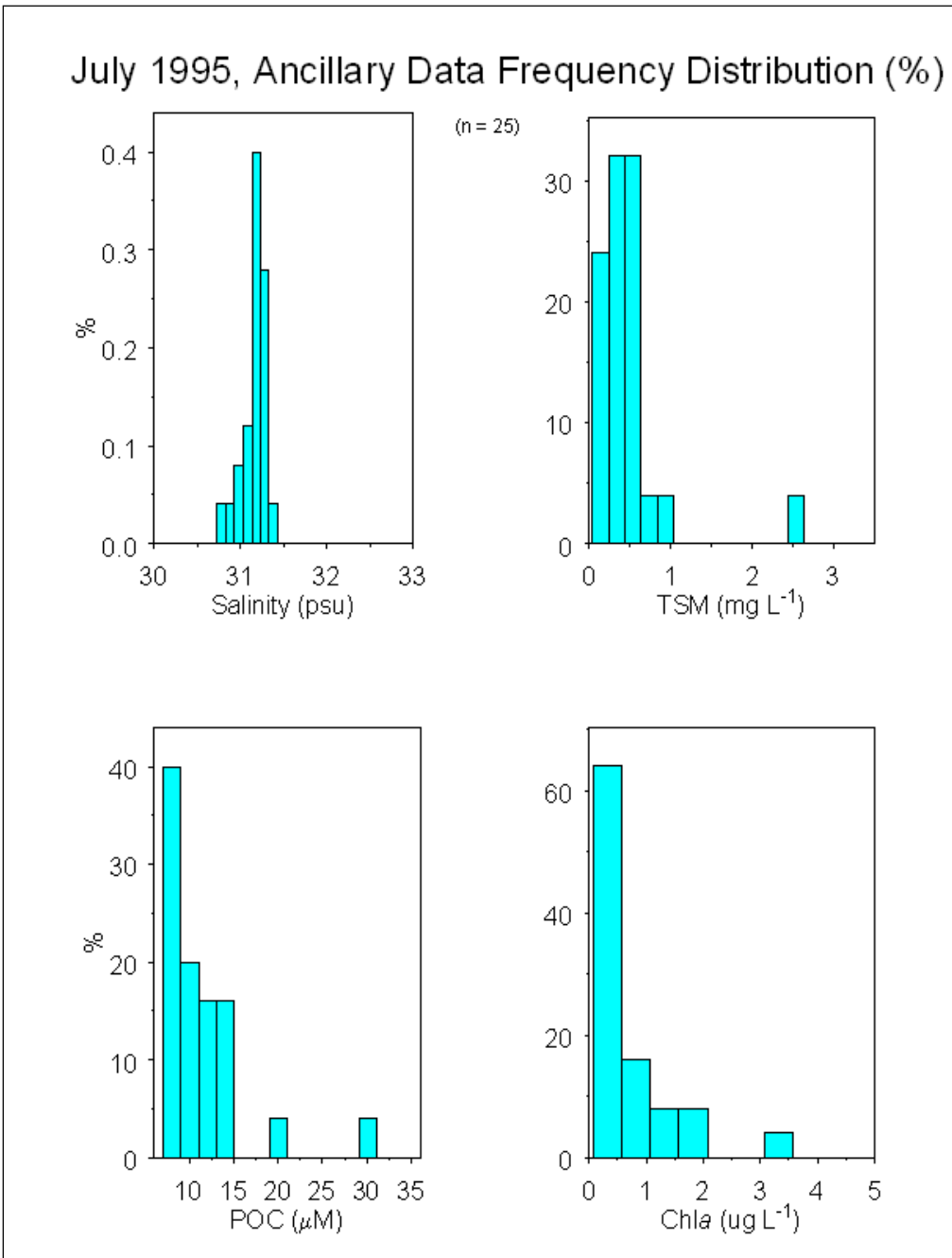
b.2 Box-whisker plot of particulate organic carbon observed for July 1995 (1), July 1996 (2), and Sept. 1996 (3).



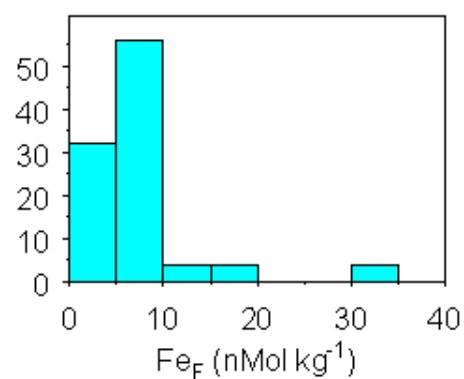
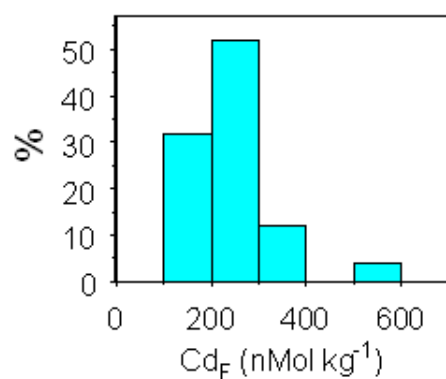
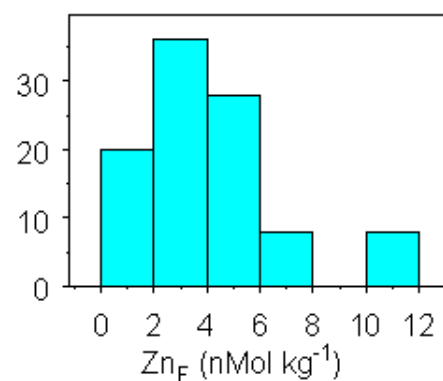
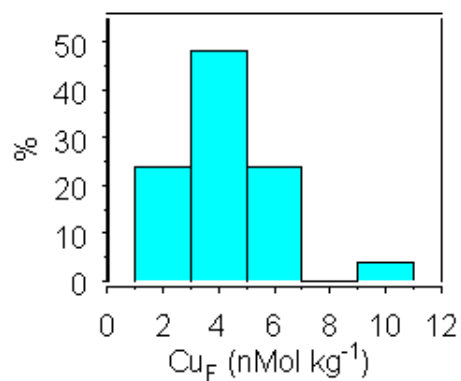
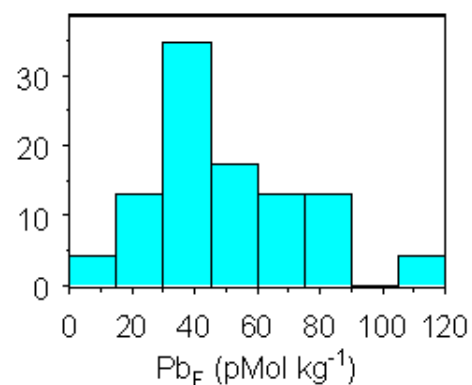
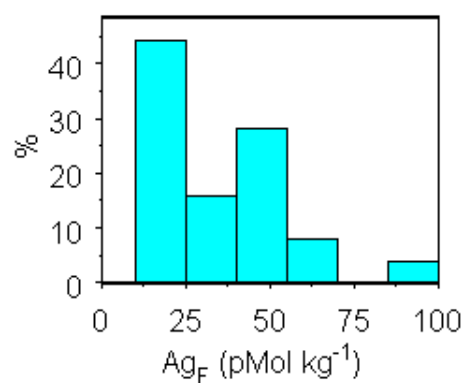
Box-whisker plots of % organic carbon July 1995 (1), July 1996 (2), and Sept. 1996 (3). Very low POC estimates resulted in outliers (> 100%) from the July 1995 survey.

b.3 Frequency distributions of data surveys: 7/95, 7/96, and 9/96

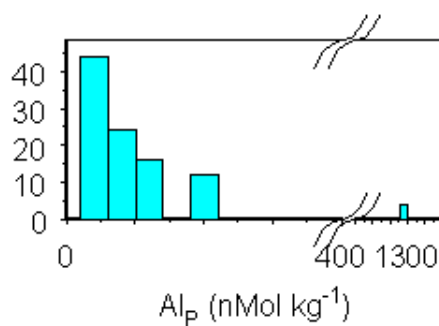
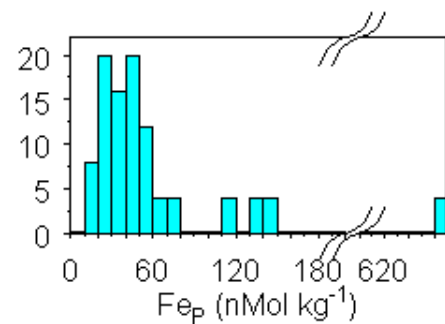
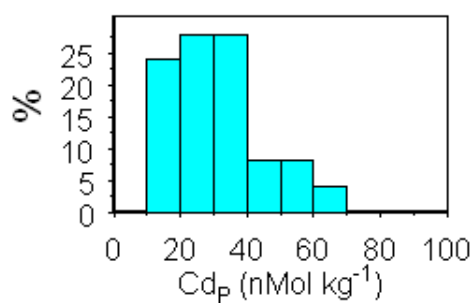
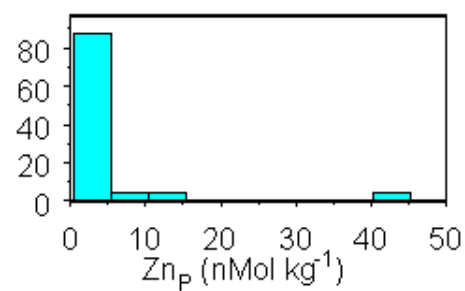
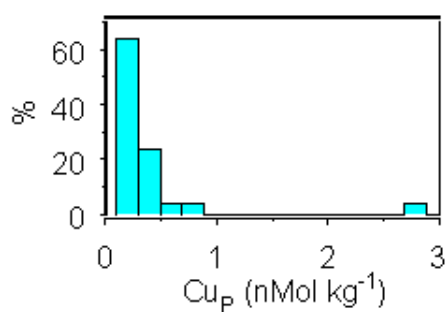
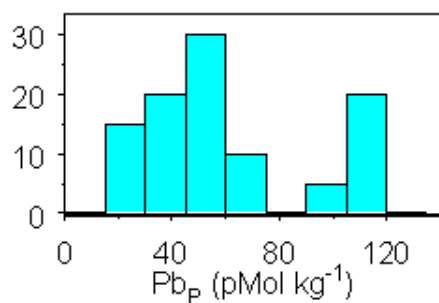
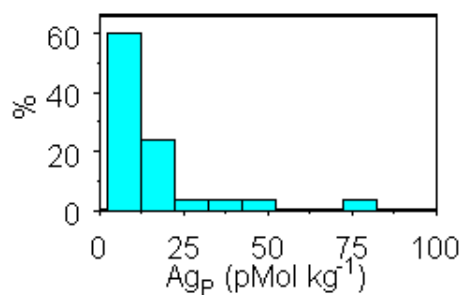
b3.1 July 1995 Massachusetts Bay survey



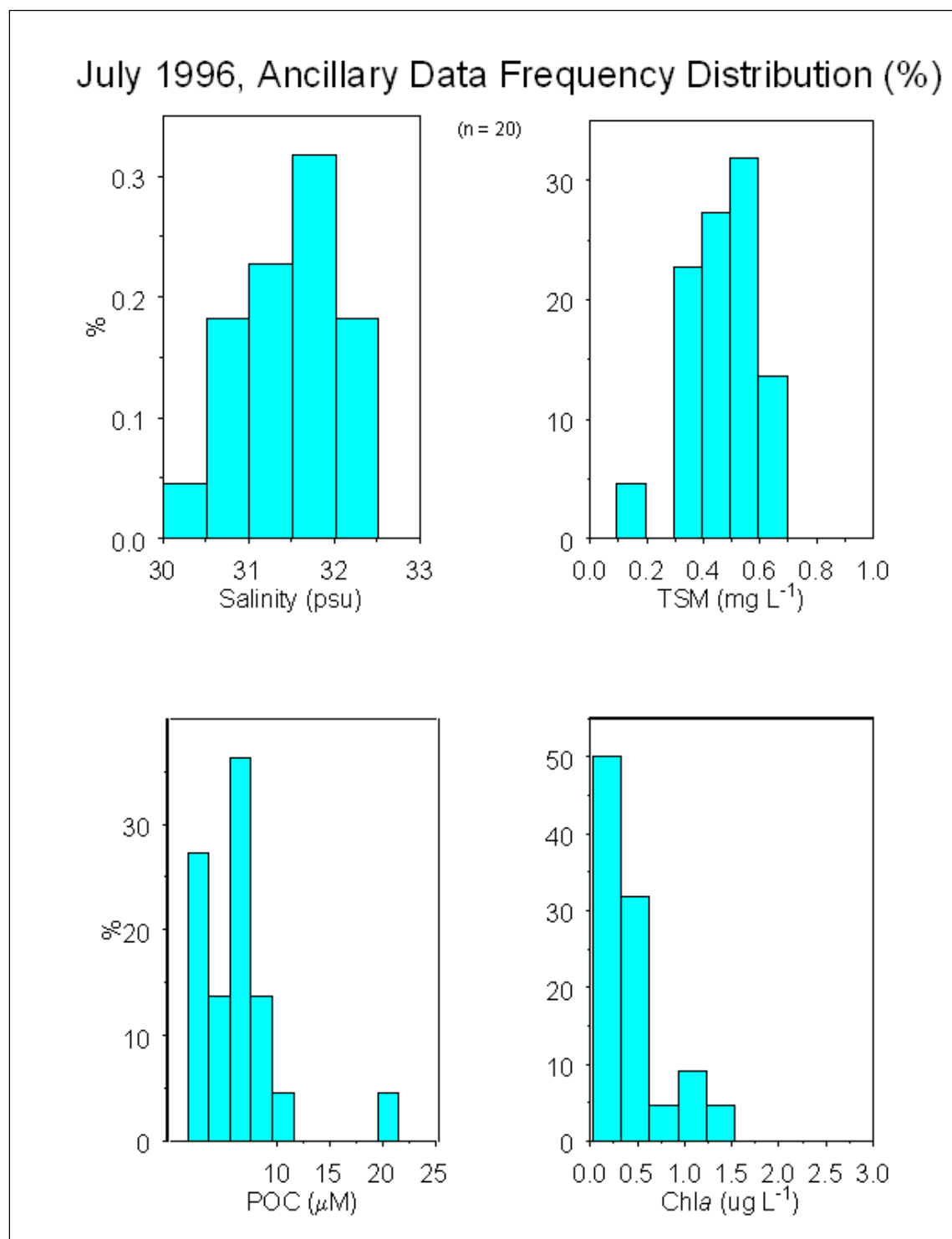
July 1995 Filtered Metals Frequency Distribution (%)



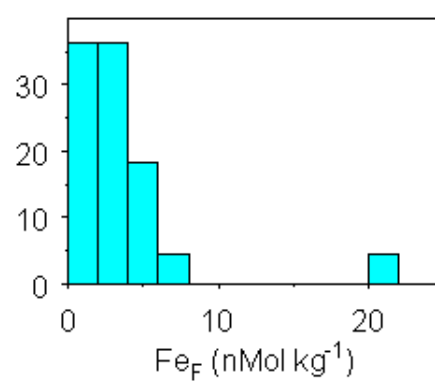
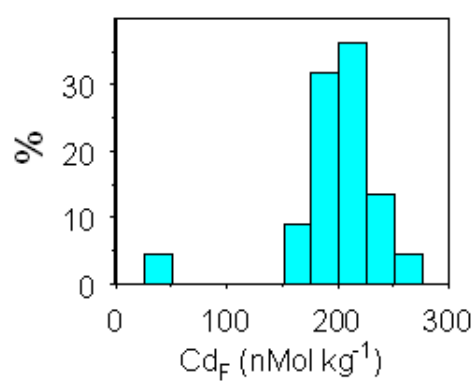
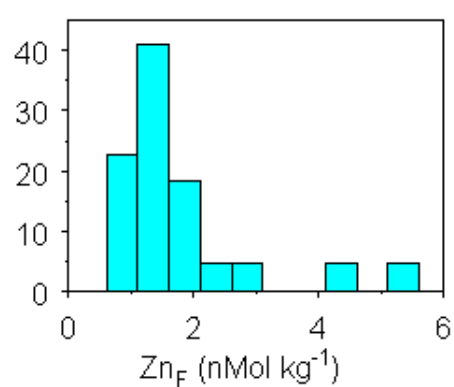
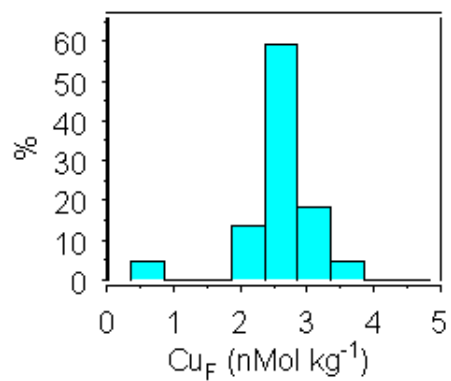
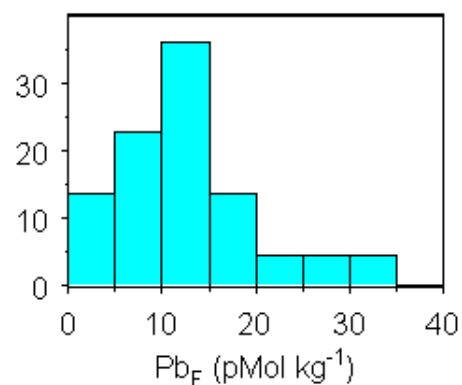
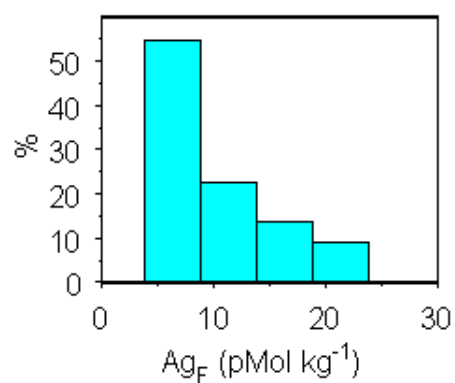
July 1995 Particulate Metals Frequency Distribution (%)



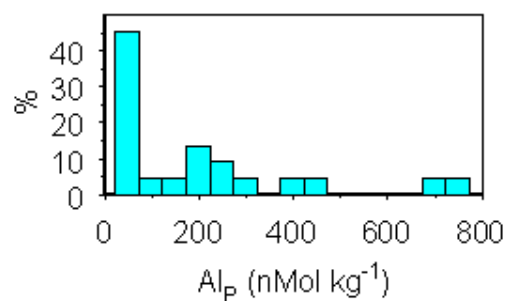
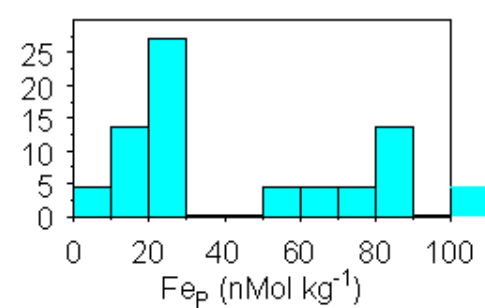
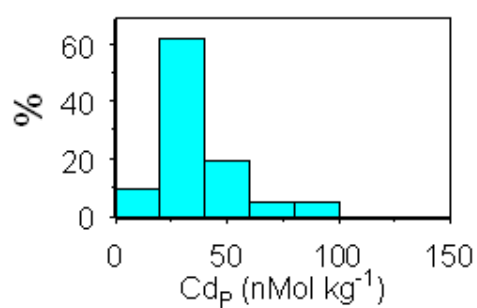
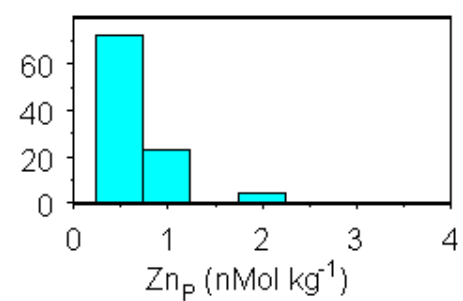
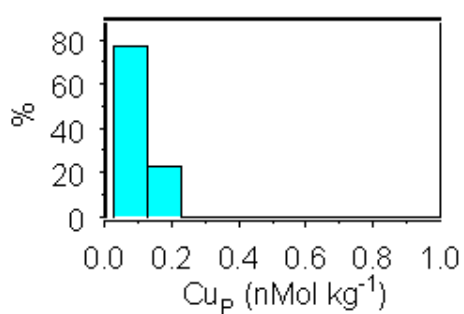
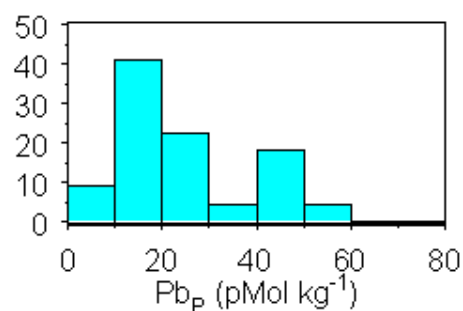
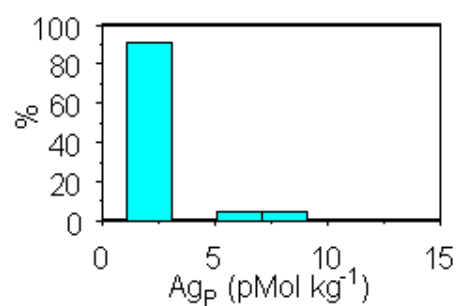
b3.2 July 1996 southwestern Gulf of Maine survey



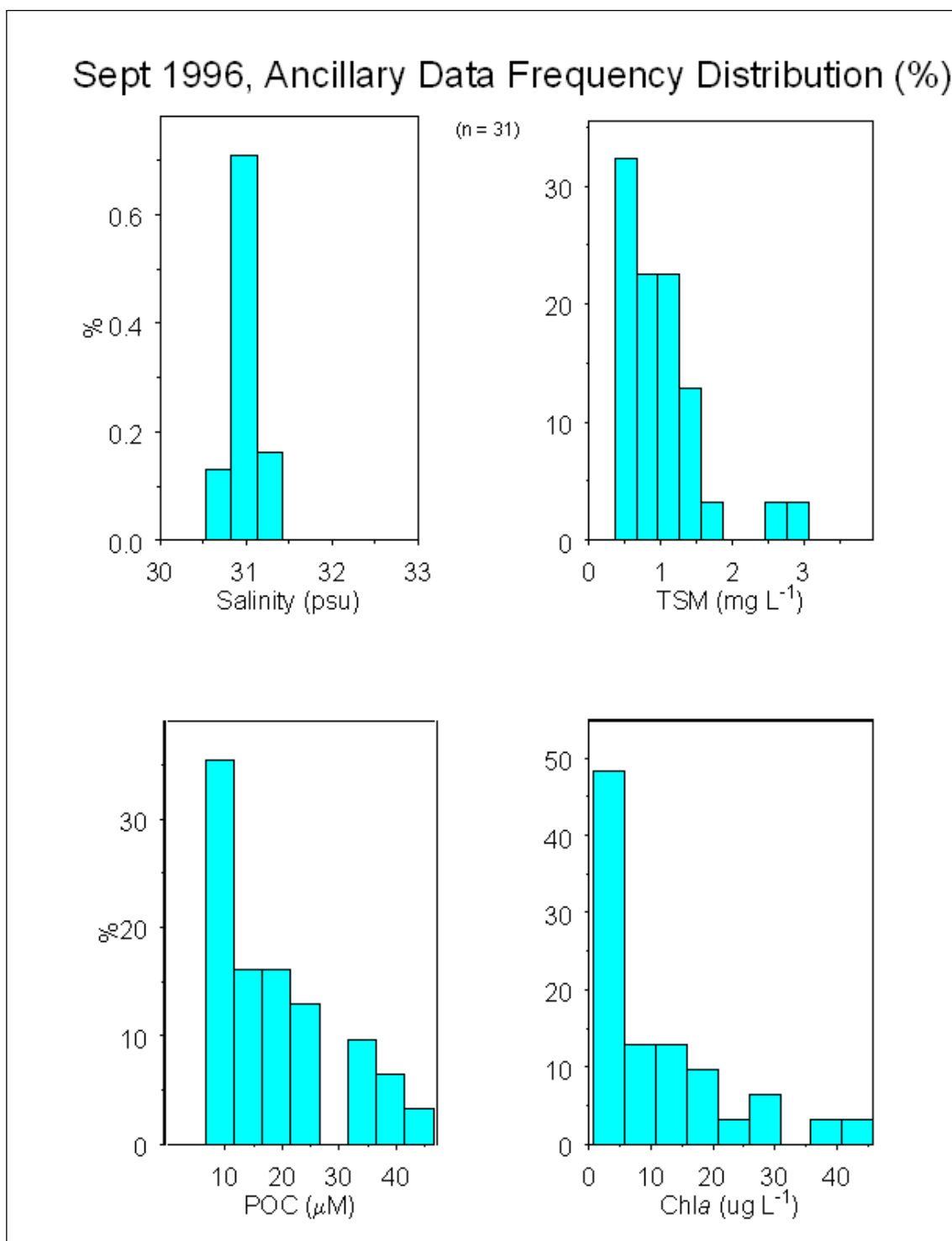
July 1996 Filtered Metals Frequency Distribution (%)



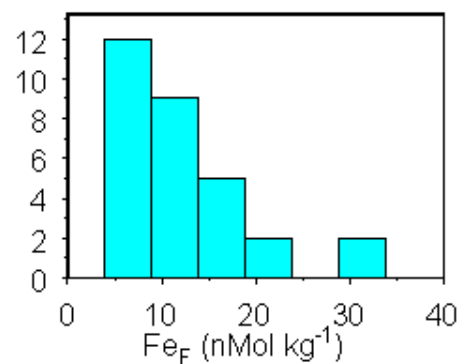
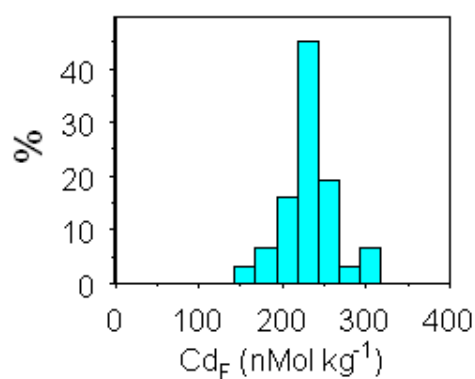
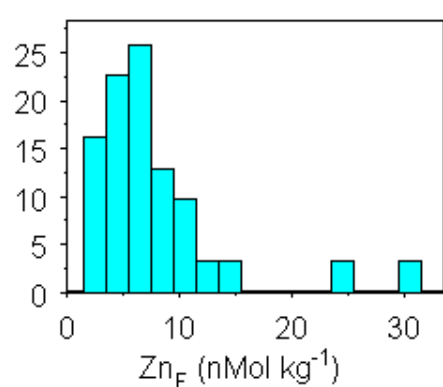
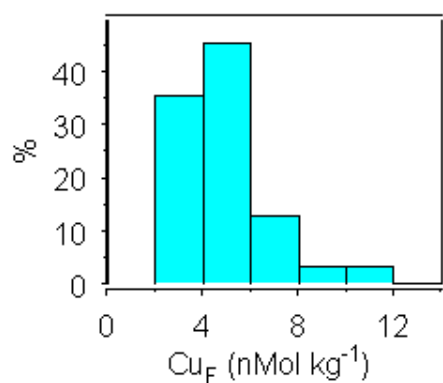
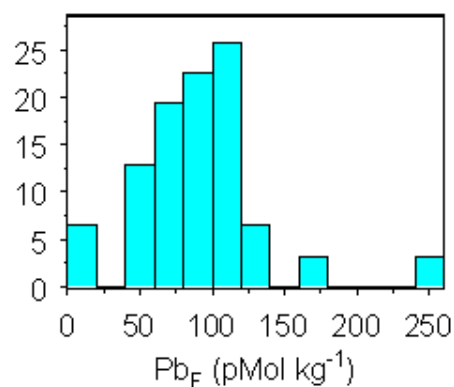
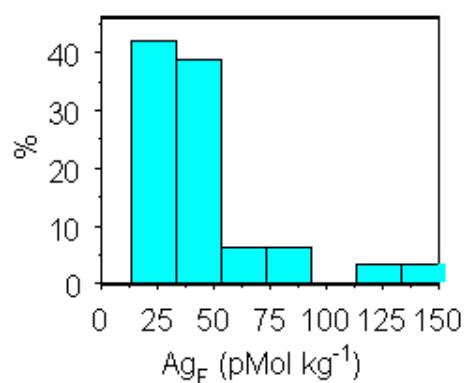
July 1996 Particulate Metals Frequency Distribution (%)



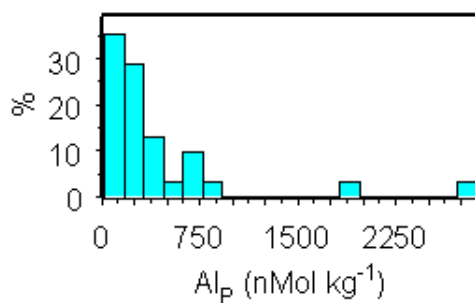
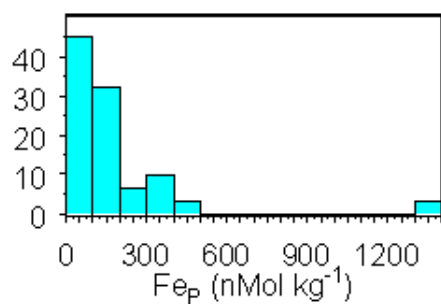
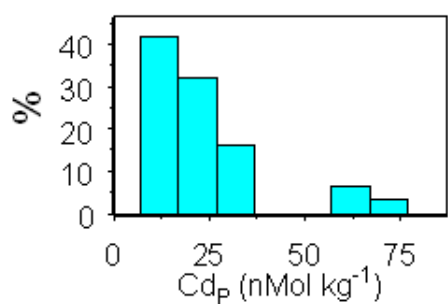
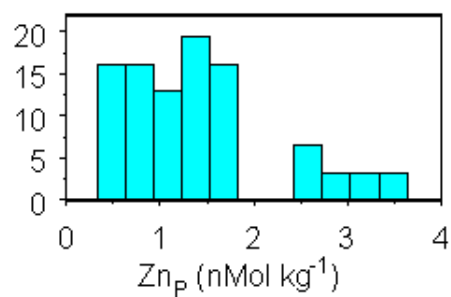
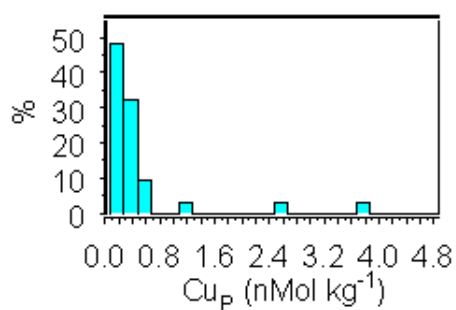
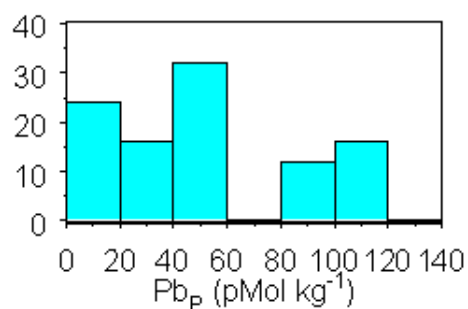
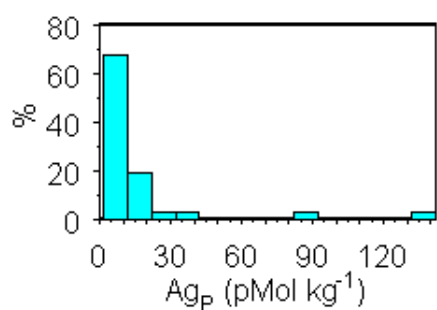
b3.3 Sept 1996 Boston Harbor - Massachusetts Bay mixing zone survey



Sept 1996 Filtered Metals Frequency Distribution (%)

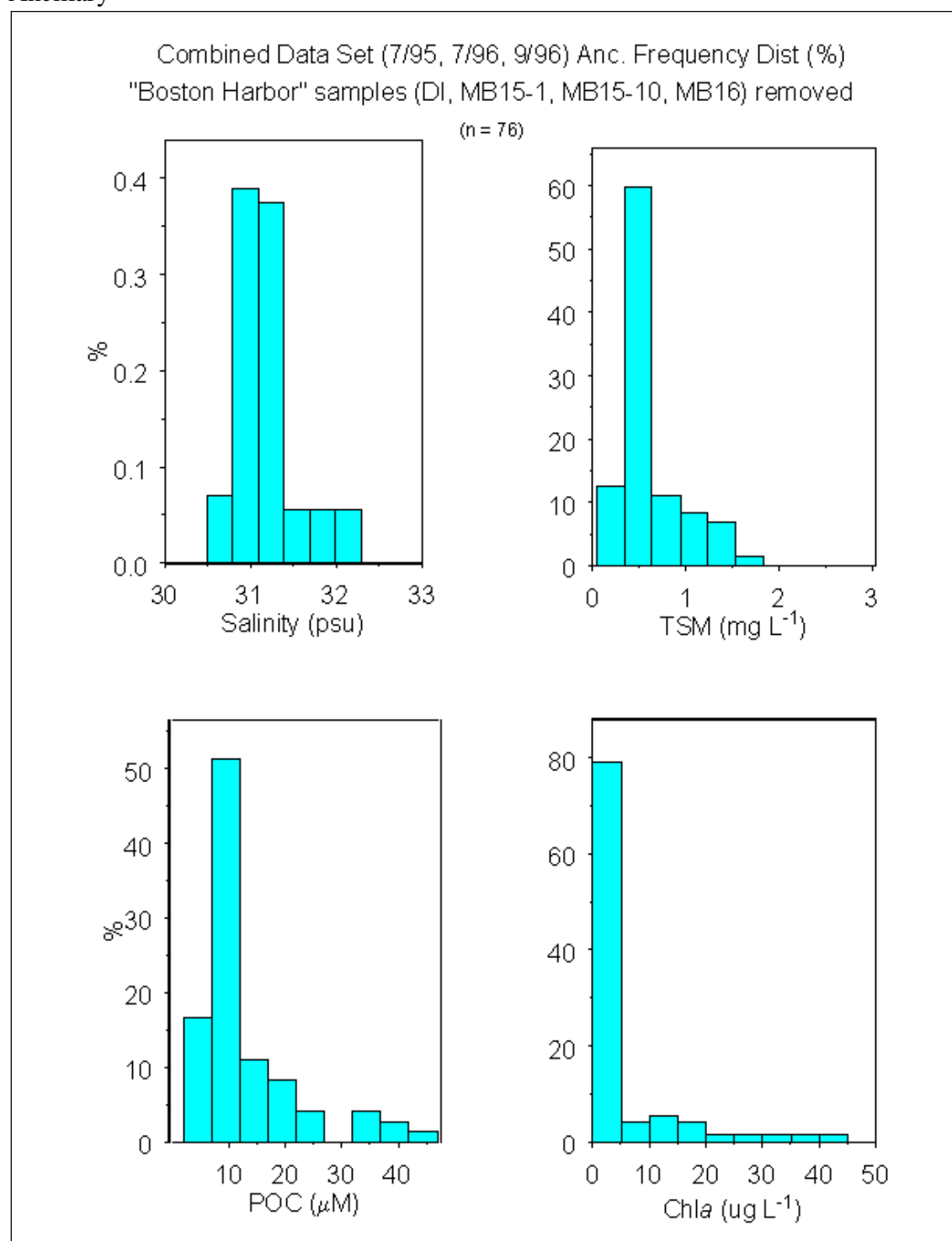


Sept. 1996 Particulate Metals Frequency Distribution (%)

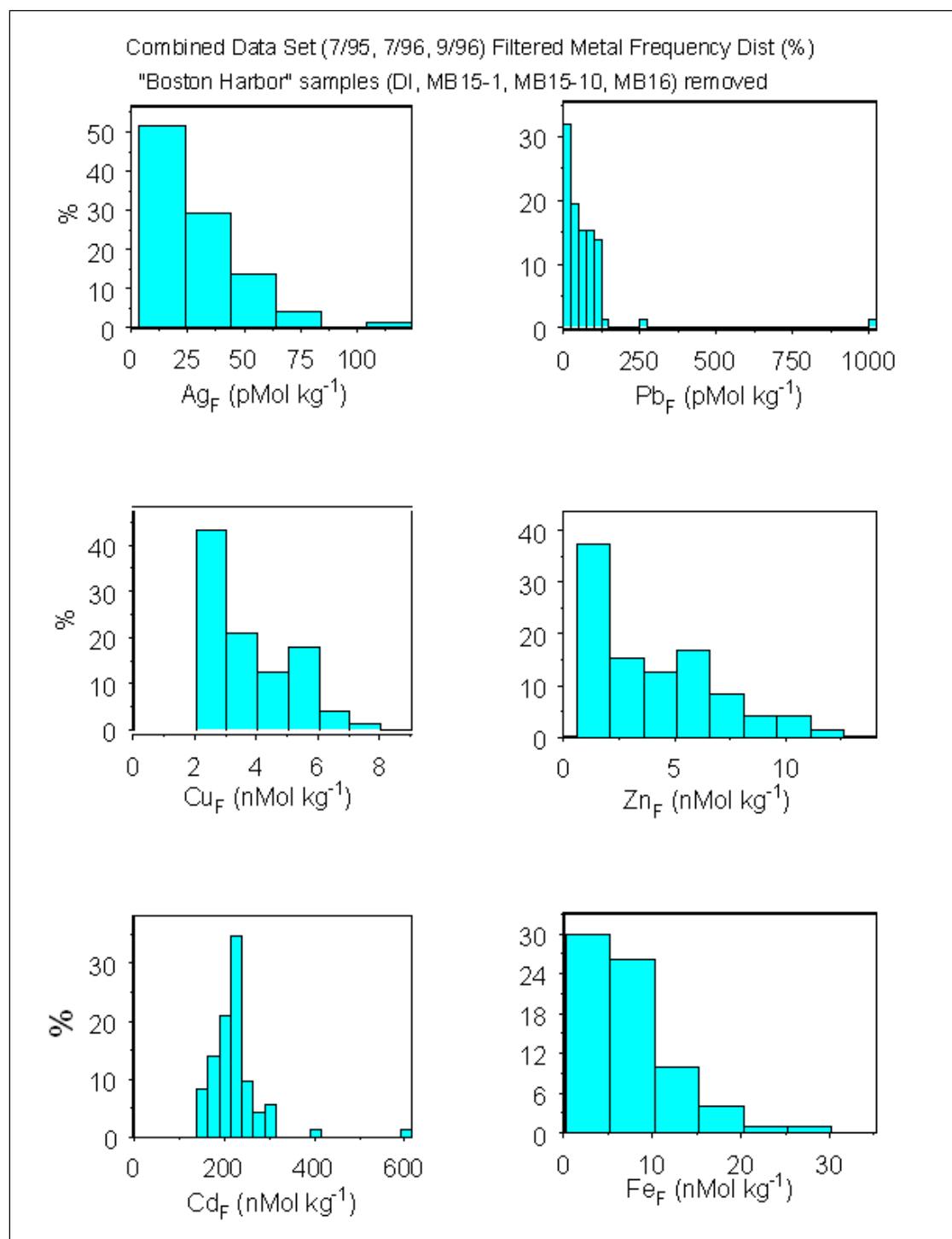


b3.4 Combined data set (7/95, 7/96, 9/96) with "Boston Harbor" samples removed

Ancillary

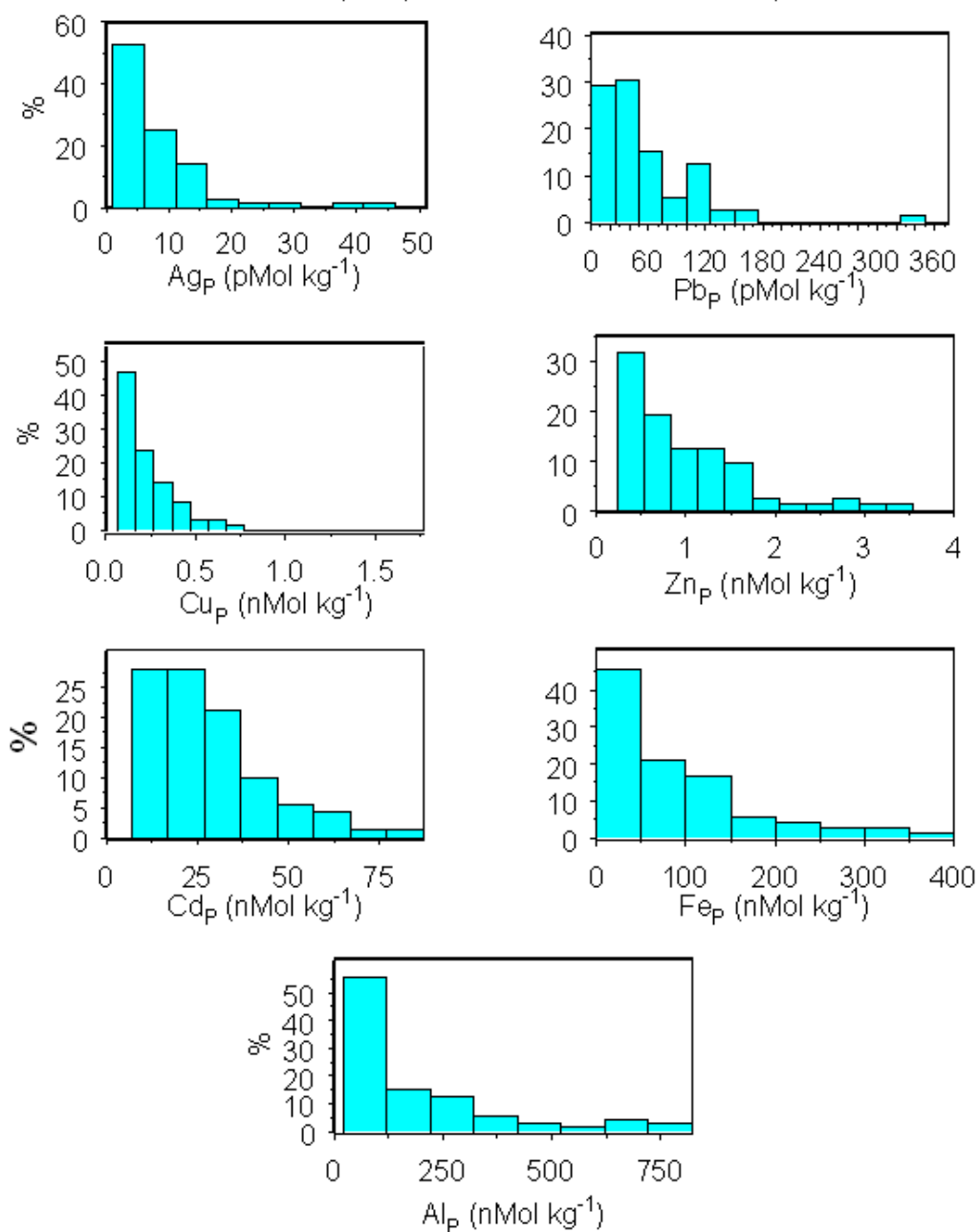


Filtered Metals



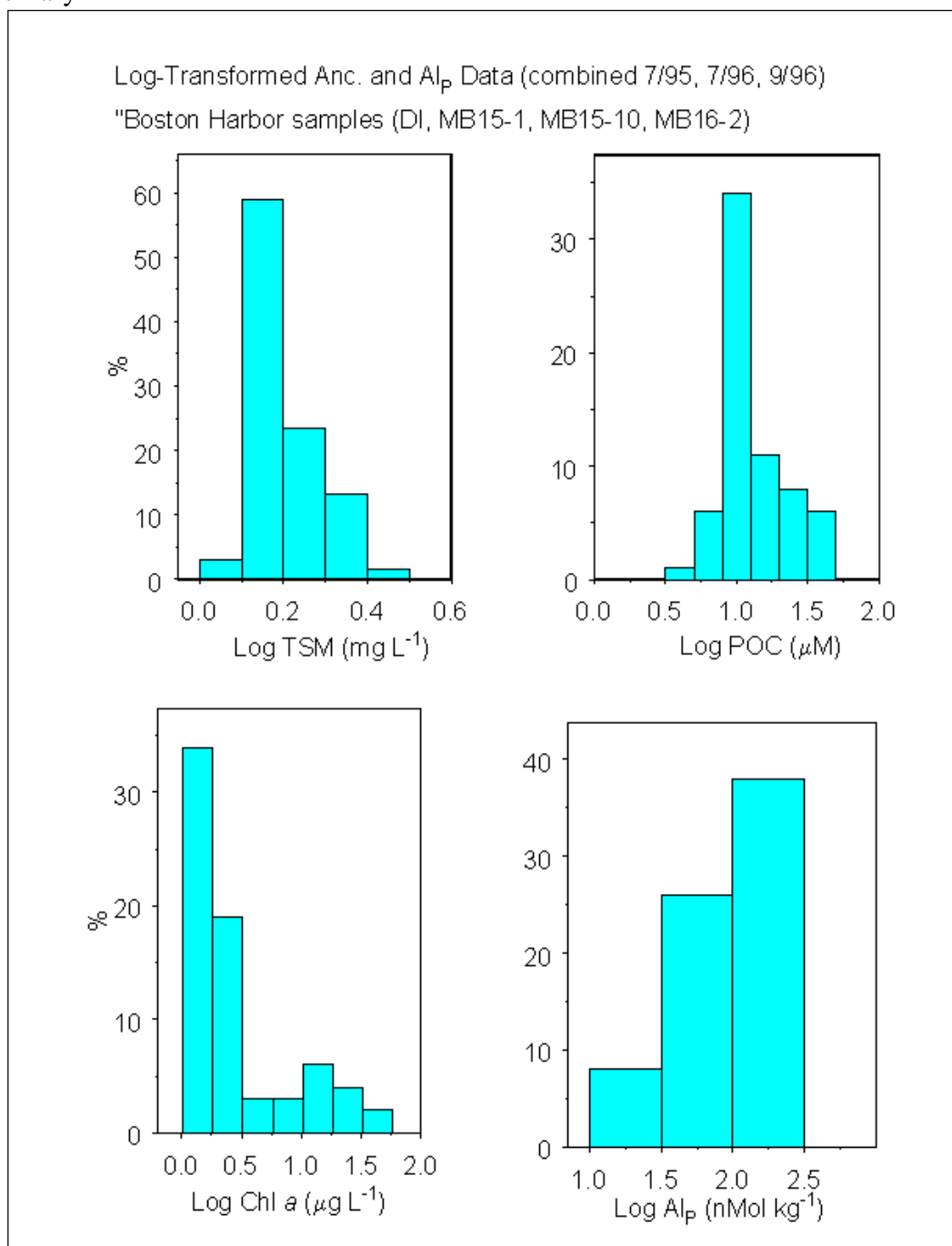
Particulate Metals:

Combined Data Set (7/95, 7/96, 9/96) Particulate Metal Frequency Dist (%)
 "Boston Harbor" samples (DI, MB15-1, MB15-10, MB16) removed

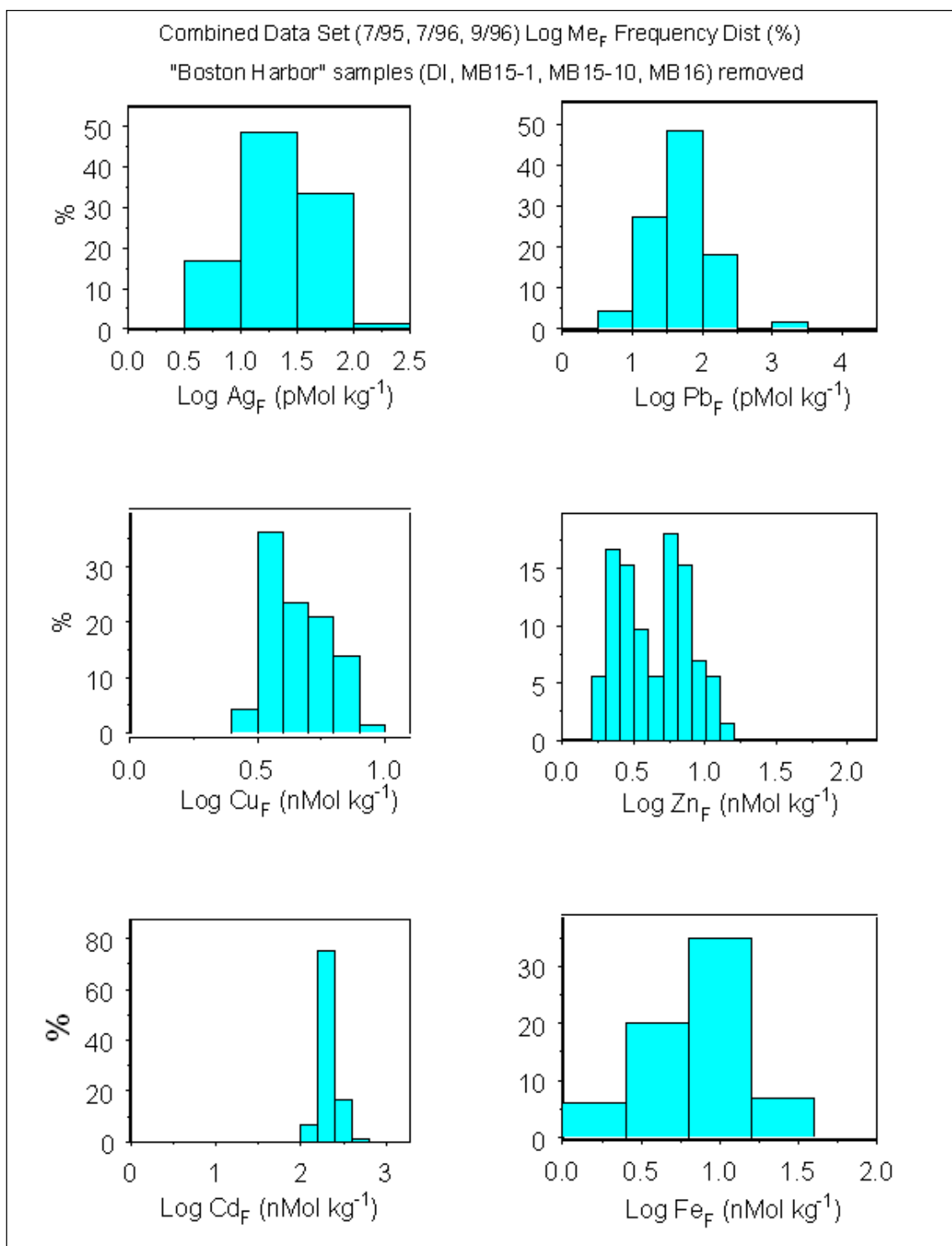


b.4 Log-transformed data.

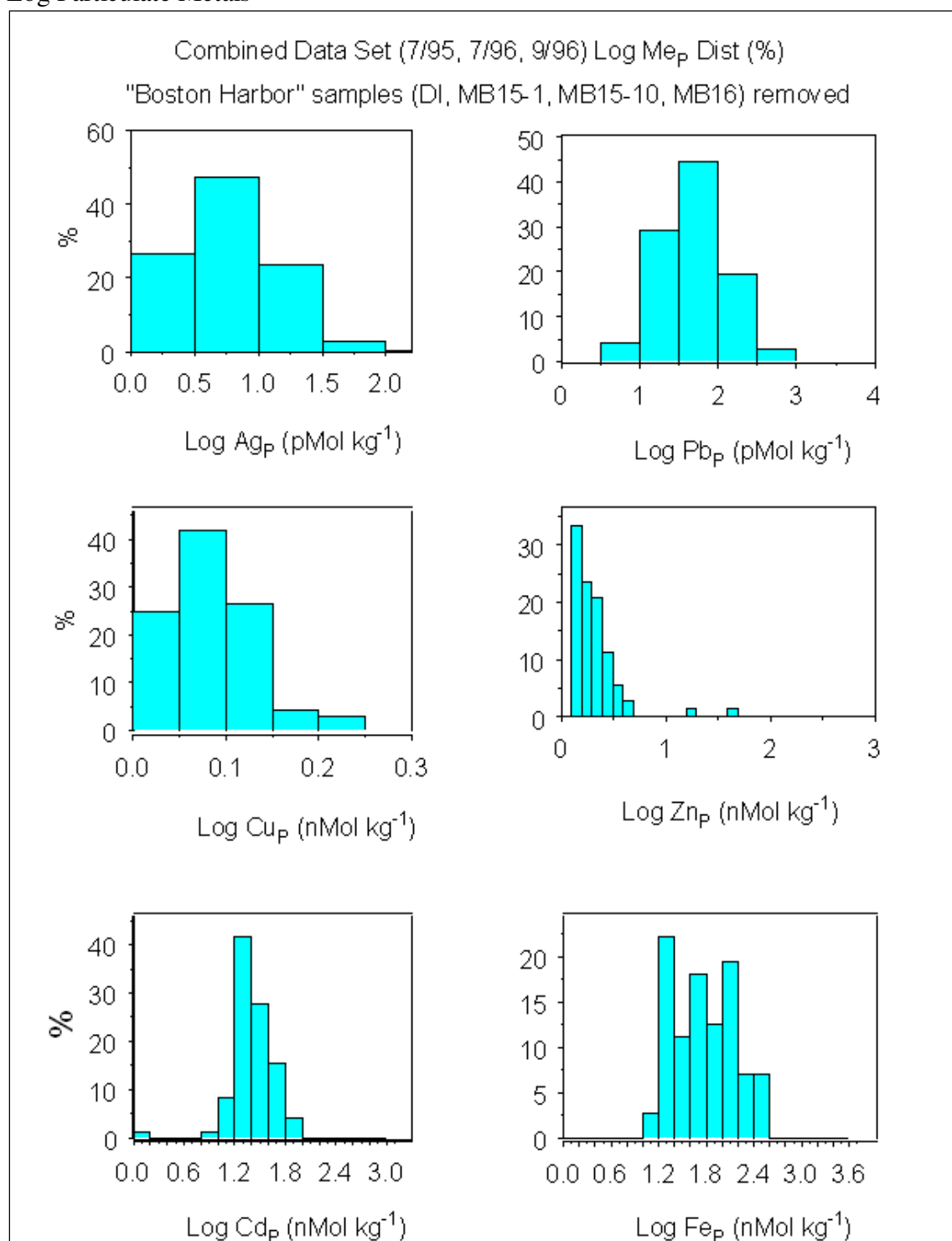
Log Ancillary



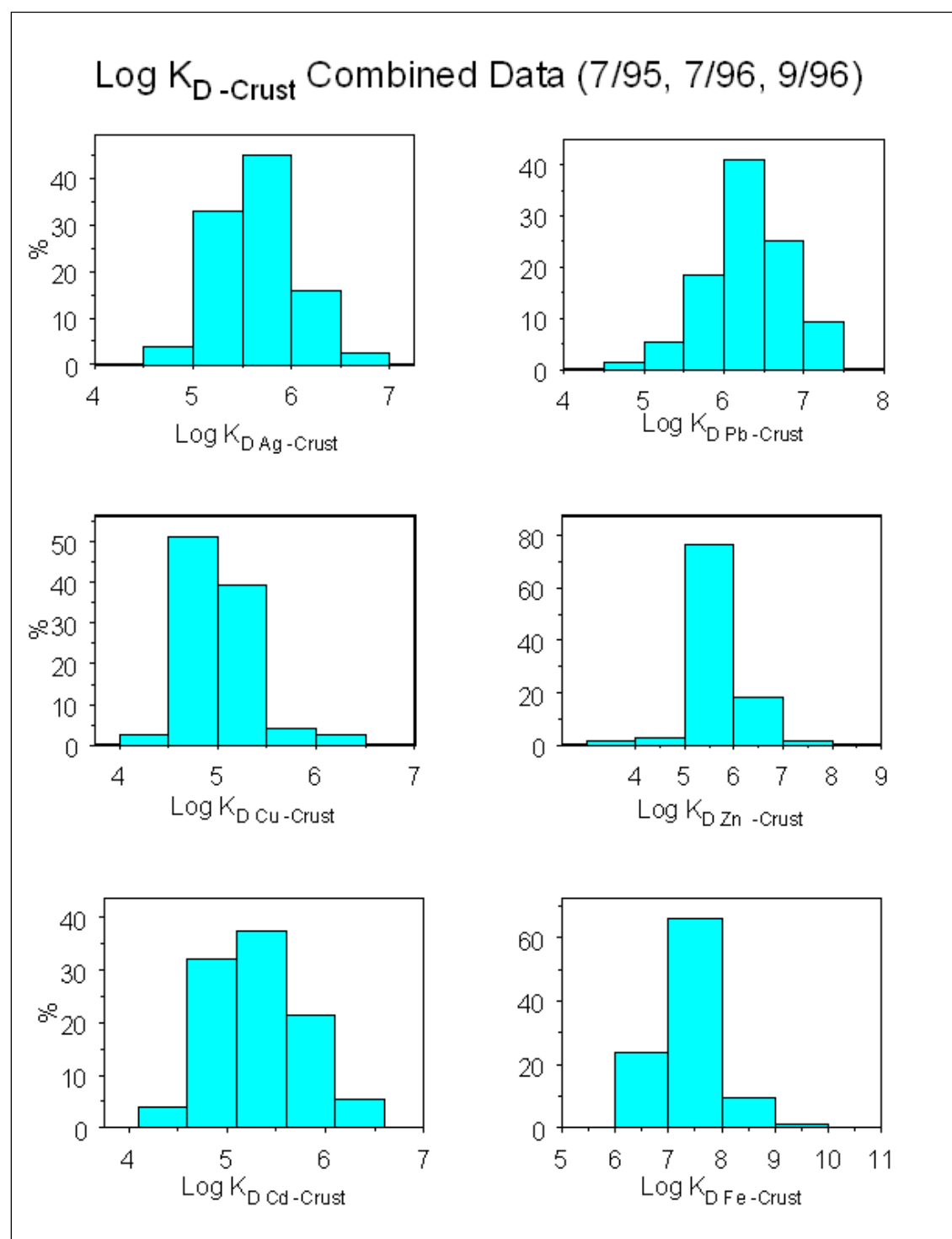
Log Filtered Metals



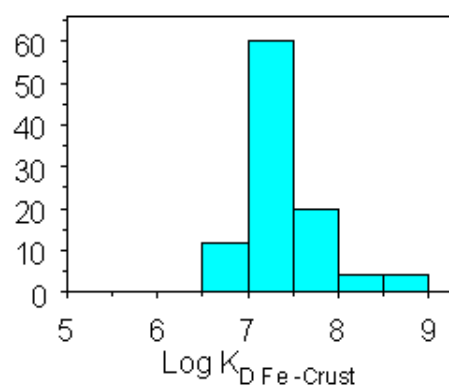
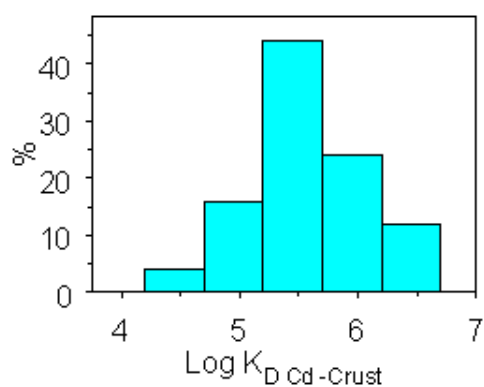
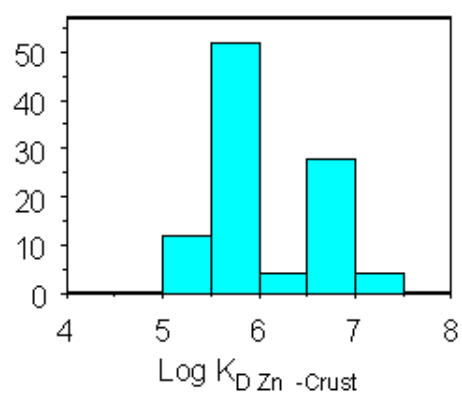
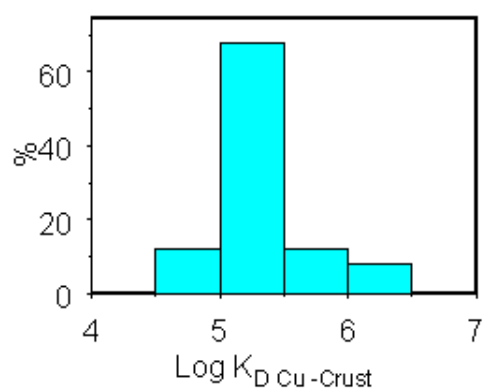
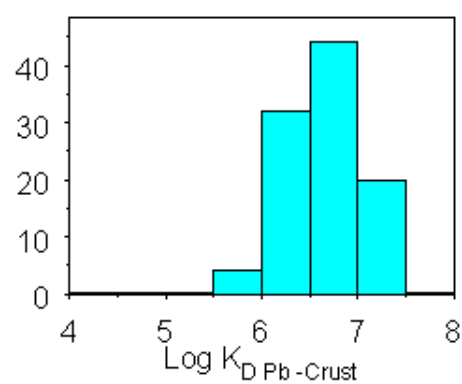
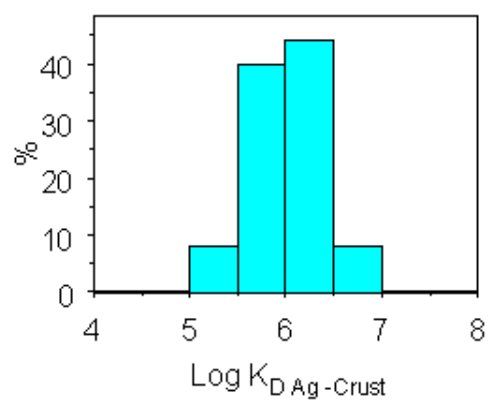
Log Particulate Metals



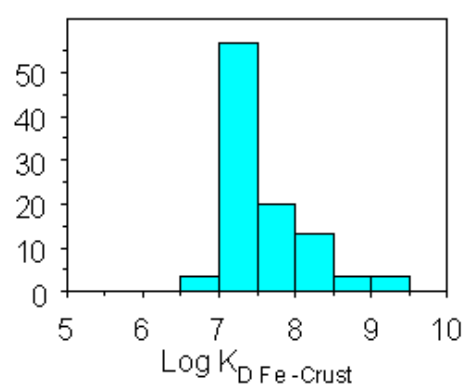
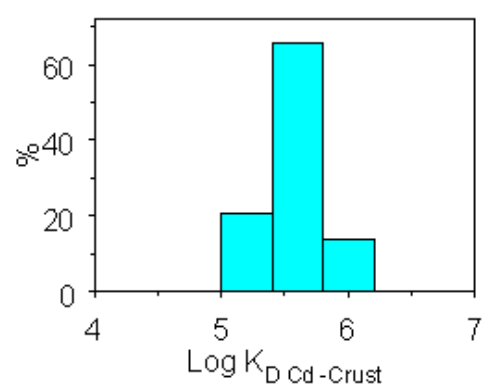
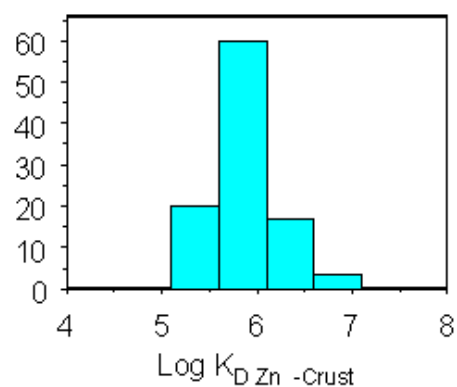
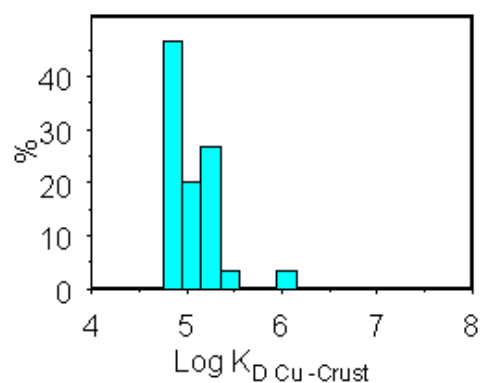
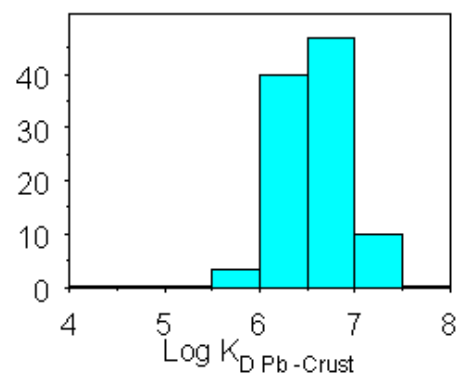
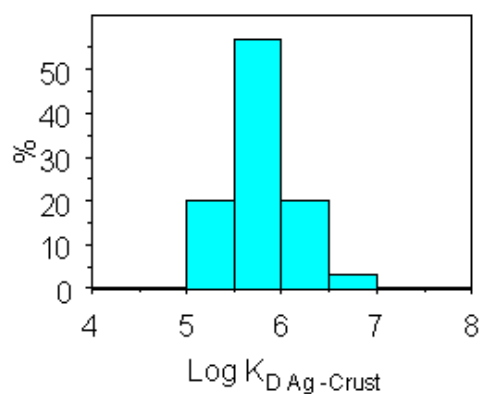
Log $K_{D,-Crust}$



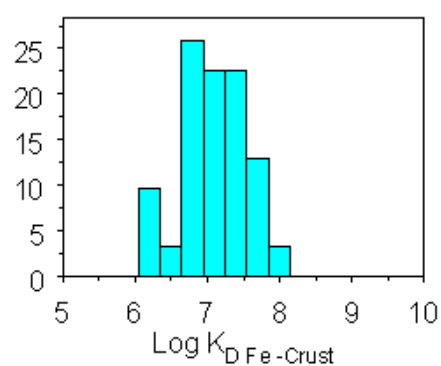
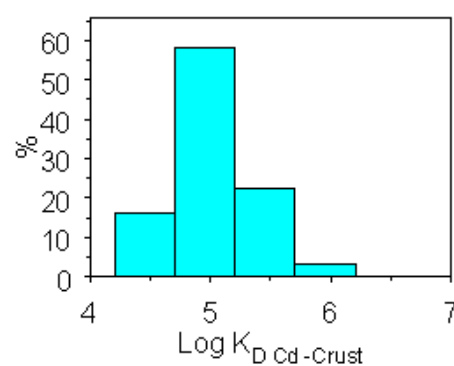
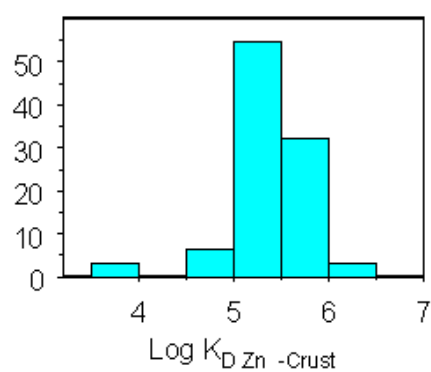
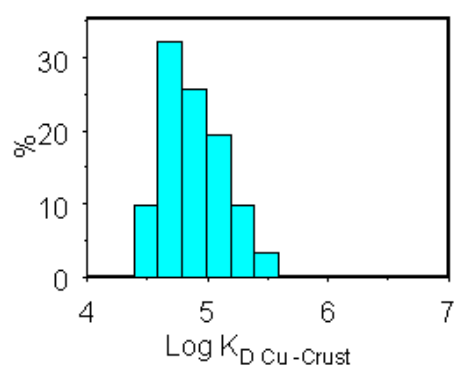
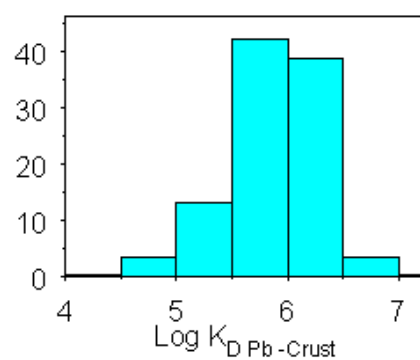
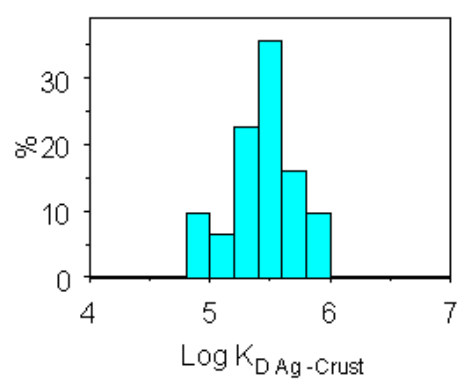
Log K_D -Crust July 1995 Data



Log K_D -Crust July 1996 Data

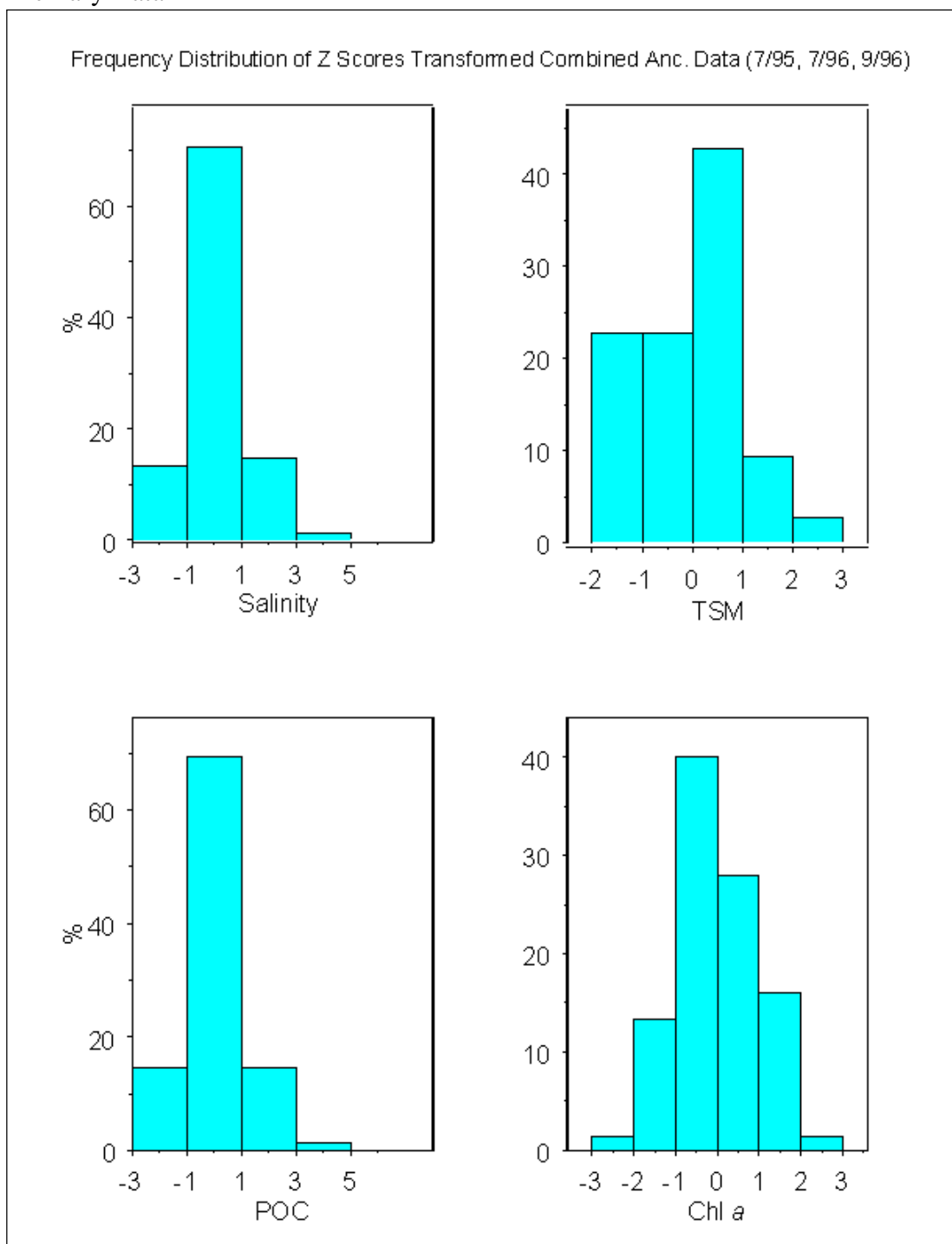


Log K_D -Crust Sept. 1996 Data

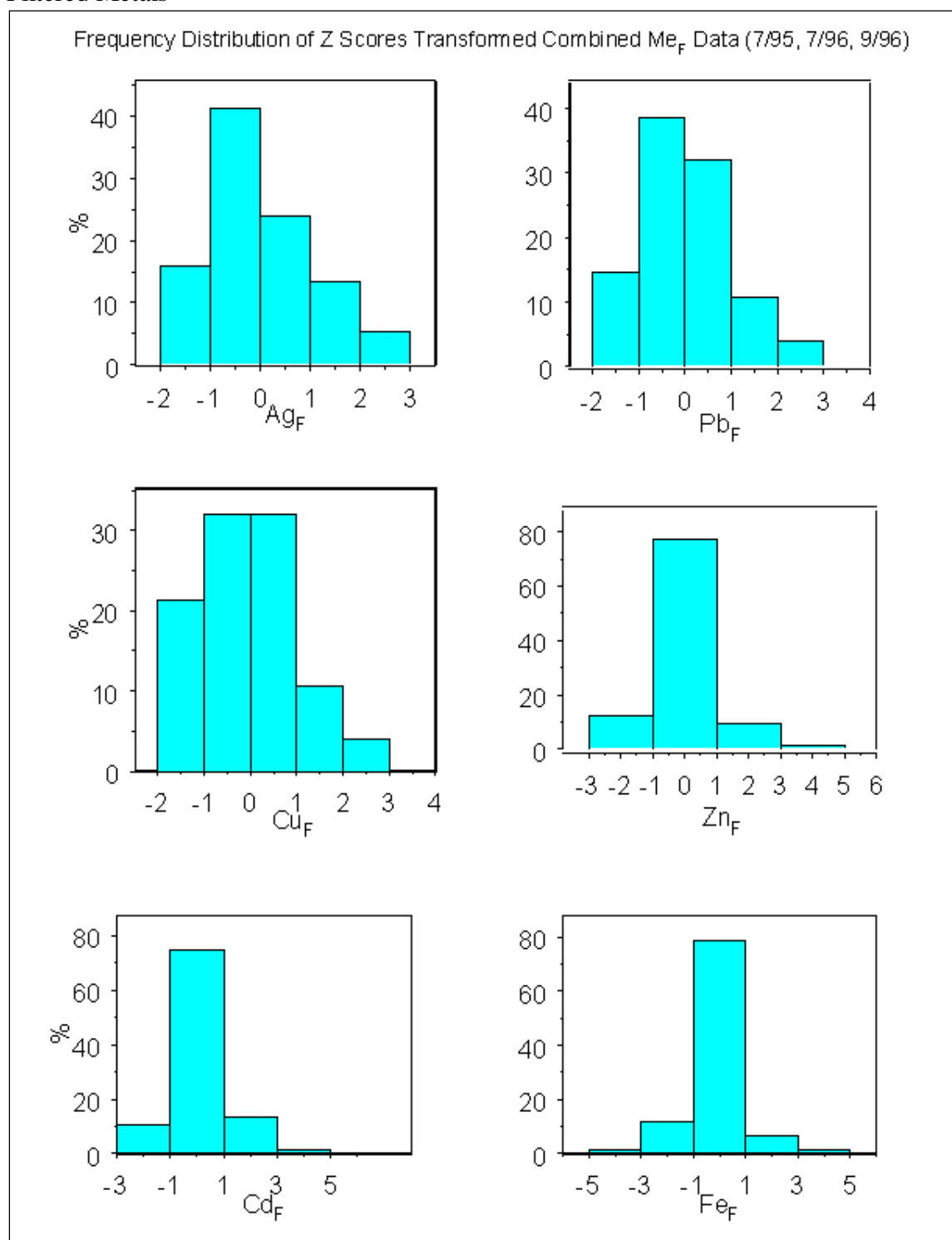


b.5 Frequency distribution of Z scores of transformed combined data (7/95, 7/96, 9/96)

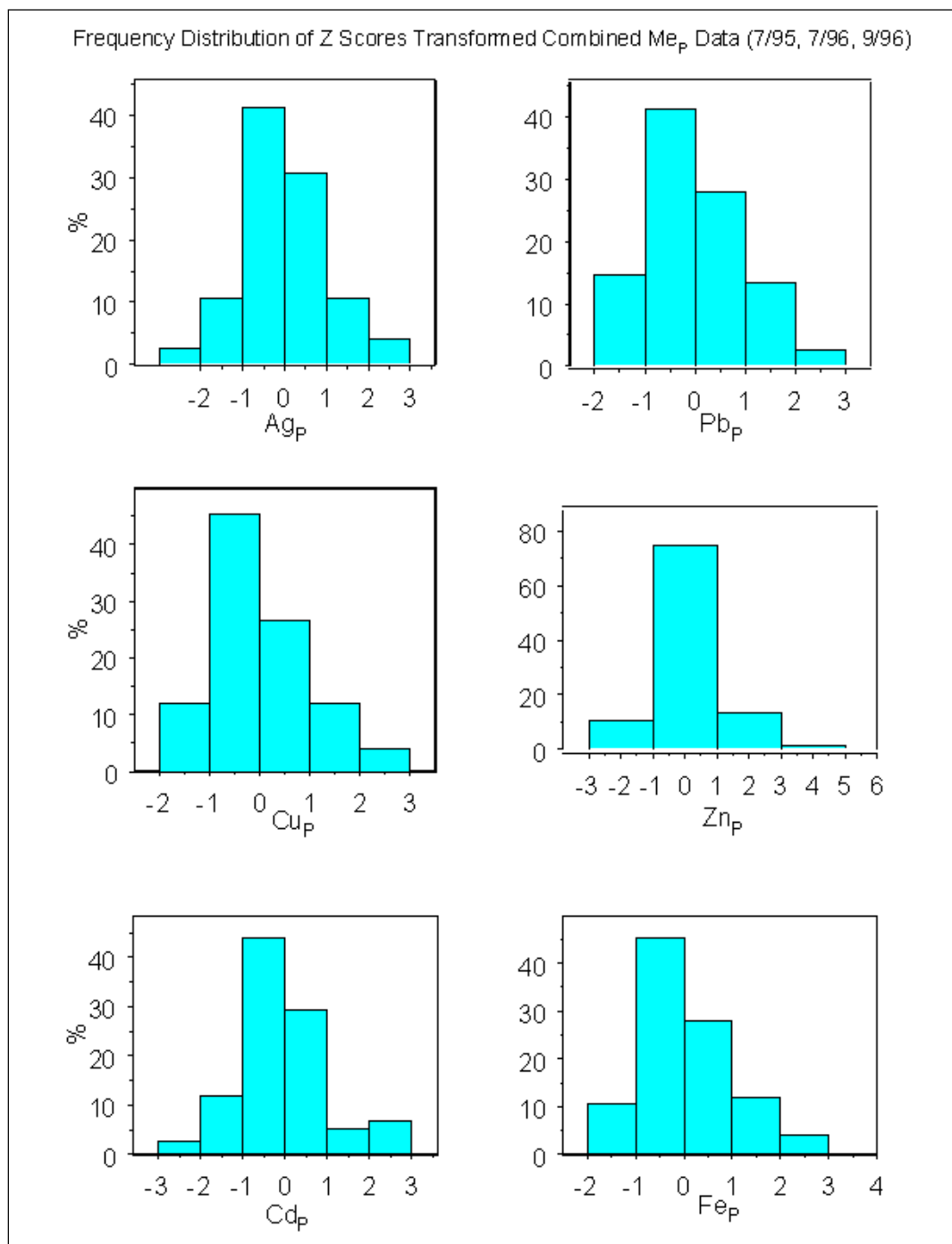
Ancillary Data



Filtered Metals



Particulate Metals



b.6. Summary statistics for each survey

July 1995 Massachusetts Bay Survey								
	Min:	Mean:	Median:	Max:	n	NA's	Skewness:	Kurtosis:
Sal	30.733	31.162	31.191	31.392	250	0	-1.4	2.6
TSM	0.04	0.47	0.41	2.61	250	0	3.5	14.9
POC	7.1	11.2	10.3	29.3	250	0	2.5	7.6
Chl.a	0.2	0.8	0.5	3.5	251	1	2.4	6.6
Ag _F	9.9	33.5	27.4	87.7	250	0	1.1	1.0
Pb _F	10	55	48	183	251	1	2.1	6.3
Cu _F	2.47	4.08	3.56	9.64	250	0	1.9	5.6
Zn _F	1.10	4.00	3.10	11.00	250	0	1.4	1.7
Cd _F	140	243	216	598	250	0	2.1	5.8
Fe _F	1.1	7.0	6.0	30.7	250	0	3.0	11.0
Ag _P	2.2	14.6	6.9	80.7	250	0	2.8	8.6
Pb _P	23	109	59	784	251	1	3.8	15.3
Cu _P	0.09	0.36	0.21	2.74	250	0	4.4	20.8
Zn _P	0.34	3.30	0.83	41.00	250	0	4.2	18.5
Cd _P	13	30	24	65	250	0	0.8	0.0
Fe _P	12	74	44	663	250	0	4.4	21.0
Al _P	21	129	64	1268	250	0	4.6	22.3

July 1996 SW Gulf of Maine								
	Min:	Mean:	Median:	Max:	n	NA's	Skewness:	Kurtosis:
Sal	30.496	31.466	31.679	32.136	200	0	-0.4	-1.3
TSM	0.34	0.49	0.50	0.62	200	0	-0.1	-1.5
POC	1.9	6.2	6.1	21.1	200	0	1.9	5.7
Chl.a	0.0	0.4	0.3	1.3	200	0	1.1	0.3
Ag _F	3.8	9.8	7.9	22.3	200	0	1.2	0.5
Pb _F	4	14	12	34	201	1	1.2	1.7
Cu _F	2.15	2.73	2.74	3.82	200	0	1.3	3.6
Zn _F	0.61	1.75	1.39	5.59	200	0	2.2	4.8
Cd _F	153	204	203	257	200	0	0.1	-0.5
Fe _F	0.3	3.4	2.4	21.1	200	0	3.4	13.2
Ag _P	1.1	2.0	1.5	7.4	200	0	2.8	7.4
Pb _P	5	24	19	51	200	0	0.6	-1.0
Cu _P	0.07	0.11	0.10	0.16	200	0	0.4	-1.1
Zn _P	0.24	0.61	0.47	1.91	200	0	2.1	5.0
Cd _P	16.1	37.7	33.7	84.5	201	1	1.6	3.3
Fe _P	9	83	40	263	200	0	1.1	-0.2
Al _P	23	195.97	88.05	735	200	0	1.5	1.6

b.6. Summary statistics for each survey (cont.)

Sept. 1996 Boston Harbor – Mass. Bay mixing zone								
	Min:	Mean:	Median:	Max:	Total	NA's	Skewness:	Kurtosis:
Sal	30.527	30.983	30.977	31.307	31	0	-0.5	0.5
TSM	0.36	1.01	0.92	2.83	31	0	1.6	3.1
POC	6.5	18.7	16.3	43.7	31	0	0.9	-0.2
Chl.a	0.8	10.4	5.9	42.7	31	0	1.4	1.4
Ag _F	13.1	42.2	35.2	134.0	31	0	1.9	3.8
Pb _F	12	91	91	252	31	0	1.3	4.3
Cu _F	2.04	4.80	4.84	11.89	31	0	1.3	2.8
Zn _F	1.5	7.7	6.4	31.3	31	0	2.5	7.1
Cd _F	143	230	228	311	31	0	0.1	1.7
Fe _F	0.7	11.8	11.6	32.4	31	0	1.2	1.7
Ag _P	2.0	15.9	6.9	138.0	31	0	3.6	13.7
Pb _P	7	101	54	599	31	0	2.8	7.9
Cu _P	0.07	0.50	0.27	3.84	31	0	3.5	12.9
Zn _P	0.33	1.61	1.26	8.12	31	0	3.3	14.1
Cd _P	7	24.3	20.3	76.8	31	0	2.1	4.4
Fe _P	17	167	108	1305	31	0	4.0	18.9
Al _P	23	409	245	2785	31	0	3.1	10.6

b.7 Factor analysis details

b.7.1 Data manipulations

Table B.7.1. Normalization procedures by analyte for each survey

Parameter	Jul-95	Jul-96	Sep-96	Combined
Ag _D	log	none	log	log
Pb _D	none	none	none	log
Cu _D	none	none	none	none
Zn _D	log	none	log	log
Cd _D	log	none	none	log
Fe _D	none	log	log	log
Ag _P	log	1/x	log	log
Pb _P	log	none	log	log
Cu _P	log	none	log	log
Zn _P	log	log	log	log
Cd _P	log	none	log	log
Fe _P	1/x	none	log	log
Al _P	1/x	none	log	log
Sal	1/x	none	none	none
TSM	none	none	log	log
POC	1/x	none	log	log
Chl a	log	none	log	log

Table B.7.2. Normalization procedures for K_Ds

Parameter	
Ag K _D , -Crust	log
Pb K _D , -Crust	log
Cu K _D , -Crust	log
Zn K _D , -Crust	log
Cd K _D , -Crust	log
Fe K _D , -Crust	log

b.7.2 Standardization

z scores: $z = (X_i - \mu)/\sigma$

b8 Summary statistics, multiple factor analyses

Table B.8.1. Summary Statistics for z-score Factor analyses data from July95, July96, and Sept96 survey data as manipulated in Table A.1. mle = maximum likelihood estimates for # of Factors

Factors	mle p values for # of Factors				% Variance explained (principal)			
	1	2	3	4	1	2	3	4
July95	.000	.000	.016	.076	31	19	12	11
July96	.000	.030	.106	NR	27	25	12	NR
Sept96	.000	.000	.004	.078	29	21	12	5

b.9 Factor analysis report results

b.9.1 Massachusetts Bays survey, July 1995

3-Factor, varimax rotation

*** Factor Analysis ***

Importance of factors:

	Factor1	Factor2	Factor3
SS loadings	5.9848624	4.0742492	1.8336094
Proportion Var	0.3520507	0.2396617	0.1078594
Cumulative Var	0.3520507	0.5917124	0.6995718

The degrees of freedom for the model is 88.

Uniquenesses:

	AgF	PbF	CuF	ZnF	CdF	FeF	AgP
	0.0668052	0.08241246	0.1169619	0.2403562	0.5542486	0.5963965	0.1494599

	PbP	CuP	ZnP	CdP	FeP	AlP	Sal
	0.08860176	0.3138056	0.1446317	0.7291618	0.05276517	0.2829484	0.4391884

	TSM	POC	Chla
	0.5885572	0.3975821	0.2634097

Loadings:

	Factor1	Factor2	Factor3
AgF	0.388	0.776	-0.425
PbF		0.931	0.226
CuF	0.532	0.775	
ZnF	0.434	0.756	
CdF		0.610	-0.264
FeF	0.547	0.135	0.293
AgP	0.657	0.546	0.347
PbP	0.868	0.342	0.201
CuP	0.687	0.457	
ZnP	0.779	0.310	0.391
CdP	0.152		0.497
FeP	0.961		0.154
AlP	0.841		
Sal	0.206	0.331	-0.639
TSM	0.576	0.281	
POC	0.740	0.208	-0.108
Chla	0.469	0.286	0.659

b.9.2 Southern Gulf of Maine survey, July 1996

2 Factor, varimax rotation

*** Factor Analysis ***

Importance of factors:

	Factor1	Factor2
SS loadings	5.9600274	2.8093185
Proportion Var	0.3505898	0.1652540
Cumulative Var	0.3505898	0.5158439

The degrees of freedom for the model is 103.

Uniquenesses:

AgF	PbF	CuF	ZnF	CdF	FeF	AgP
0.9222885	0.7279966	0.7054753	0.7552772	0.3867587	0.649354	0.937338

PbP	CuP	ZnP	CdP	FeP	AlP	Sal
0.1160428	0.1688032	0.647289	0.9231131	0.0002089526	0.05101393	0.4491279

TSM	POC	Chla
0.6347439	4e-010	0.1563593

Loadings:

	Factor1	Factor2
AgF	0.125	0.249
PbF		0.514
CuF		0.540
ZnF	0.458	0.188
CdF	0.783	
FeF	0.575	0.142
AgP	-0.189	0.165
PbP	0.940	
CuP	0.791	0.454
ZnP	0.515	0.295
CdP		0.275
FeP	0.992	-0.122
AlP	0.966	-0.126
Sal	0.524	-0.526
TSM	0.196	0.572
POC	-0.457	0.890
Chla	-0.727	0.561

b.9.3 Boston Harbor - Massachusetts Bay mixing zone survey, Sept 1996

3 Factor, oblimin rotation

*** Factor Analysis ***

Importance of factors:

	Factor1	Factor2	Factor3
SS loadings	6.0854591	2.7359284	1.8607597
Variable Index	0.3579682	0.1609370	0.1094565
Cumulative Index	0.3579682	0.5189051	0.6283616

The degrees of freedom for the model is 88.

Uniquenesses:

	AgF	PbF	CuF	ZnF	CdF	FeF	AgP
	0.8570287	0.430876	0.3890612	0.737306	0.2684492	0.1593434	0.5399286

	PbP	CuP	ZnP	CdP	FeP	AlP	Sal	TSM
	0.1058191	0.1684098	0.6031051	0.8266577	4e-010	0.05100988	0.400231	0.6333002

	POC	Chla
	4e-010	0.06769317

Loadings:

	Factor1	Factor2	Factor3
AgF	0.112		0.368
PbF		0.746	
CuF		0.779	
ZnF	0.453		0.201
CdF	0.792	0.173	-0.203
FeF	0.581	0.551	-0.399
AgP	-0.205	-0.302	0.576
PbP	0.946		
CuP	0.774	0.268	0.381
ZnP	0.502		0.400
CdP			0.411
FeP	1.002	-0.150	
AlP	0.975	-0.146	
Sal	0.546	-0.569	-0.103
TSM	0.172	0.380	0.407
POC	-0.497	0.679	0.510
Chla	-0.759	0.250	0.510

Component/Factor Correlations:

	Factor1	Factor2	Factor3
Factor1	1.000	-0.056	0.078
Factor2	-0.056	1.000	0.081
Factor3	0.078	0.081	1.000

b.9.4 Combined data sets (MB95, GOM96, MB96)

3-Factor, oblimin rotation

Primary variables

*** Factor Analysis ***

Importance of factors:

	Factor1	Factor2	Factor3
SS loadings	6.5064939	2.0795415	1.6297713
Variable Index	0.3827349	0.1223260	0.0958689
Cumulative Index	0.3827349	0.5050609	0.6009298

The degrees of freedom for the model is 88.

Uniquenesses:

AgF	PbF	CuF	ZnF	CdF	FeF	AgP
0.1595288	0.2273325	0.2660843	0.160045	0.7793772	0.5288606	0.2325259

PbP	CuP	ZnP	CdP	FeP	AlP	Sal
0.2914926	0.1614682	0.2270599	0.8623457	4e-010	0.07108648	0.6259743

TSM	POC	Chla
0.5455132	0.5124357	5.357472e-007

Loadings:

	Factor1	Factor2	Factor3
AgF	0.915	-0.157	
PbF	0.818	0.171	
CuF	0.744	0.231	
ZnF	0.813	0.121	0.154
CdF	0.462	-0.147	
FeF	0.585	0.241	
AgP	0.881	-0.131	
PbP	0.815	0.189	-0.303
CuP	0.863	0.157	
ZnP	0.637	0.335	0.217
CdP	-0.165	-0.276	
FeP	0.376	0.832	
AlP	0.226	0.877	
Sal	-0.408	0.225	-0.325
TSM		0.474	0.442
POC	0.454	-0.116	0.403
Chla	0.203	0.148	0.897

Component/Factor Correlations:

	Factor1	Factor2	Factor3
Factor1	1.000	-0.054	0.278
Factor2	-0.054	1.000	0.354
Factor3	0.278	0.354	1.000

Metal LogKDs, AgF, AlP, POC, TSM Chl *a*, and salinity 3-Factor, oblimin rotation

*** Factor Analysis ***

Importance of factors:

	Factor1	Factor2	Factor3
SS loadings	4.5771931	2.4563636	1.14499656
Variable Index	0.3814328	0.2046970	0.09541638
Cumulative Index	0.3814328	0.5861297	0.68154611

The degrees of freedom for the model is 33.

Uniquenesses:

	AgF	AlP	Sal	TSM	POC	Chla	AgKDLog
	0.3842249	0.1873259	0.4751322	0.1016854	0.3434868	0.3371856	0.2860152

	PbKDLog	CuKDLog	ZnKDLog	CdKDLog	FeKDLog
	0.2639189	0.008611647	0.4007658	0.2089837	0.3531671

Loadings:

	Factor1	Factor2	Factor3
AgF	0.734	0.316	
AlP	-0.173	0.868	
Sal	-0.684	0.200	
TSM	-0.893	0.241	
POC	0.785		
Chla	-0.413	0.584	
AgKDLog	0.850		
PbKDLog	0.686	-0.341	0.132
CuKDLog	1.054	0.296	0.133
ZnKDLog	0.693	-0.167	
CdKDLog	0.755	-0.233	-0.181
FeKDLog	0.469	-0.451	0.333

Component/Factor Correlations:

	Factor1	Factor2	Factor3
Factor1	1.000	-0.314	-0.094
Factor2	-0.314	1.000	-0.028
Factor3	-0.094	-0.028	1.000

C. ANALYSES OF BLANKS FOR PARAMETERS MONITORED DURING CHAPTER 3 SURVEYS

Definition of Blanks:

- a. *Filtration Blank*: the contribution to the analyte signal resulting from the process of filtration. Potential sources of contribution to blank values from filters, filtration apparatus, and processing. Determined by analyzing filtered sub-boiled, quartz-distilled, deionized water (QHOH) and compared with non-filtered QHOH
- b. *Reagent Blank*: the contribution to the analyte signal resulting from trace impurities in reagents used for extracting soluble (filtered) metals from natural waters. Determined by analyzing trace impurities from reagents added to previously extracted natural samples.
- c. *Filter blank*: the contribution to the analyte signal resulting from trace impurities associated with pre-cleaned filters. Determined by analyzing cleaned unused filters after batch digestion with particulates collected from natural water samples. These serve as procedural blanks for particulate metal determination of natural waters.
- d. *Others*: Other blanks were conducted to monitor the potential contribution from steps within the soluble extraction (funnel blanks, back-extraction blanks, beaker blanks) as a measure of ensuring trace metal clean conditions prior to batch sample extraction. All *other* blanks were less than either than the filtration, reagent, or filter blanks described above.

Table C.1. Blanks for each survey reported in Chapter 3. Filtration Blanks (ng):

Date	Ag	Pb	Cu	Zn	Cd	Fe
94Aug09	0.29	1.97	16.2	9.8	0.38	78.7
	0.18	2.34	14.9	15.7	0.26	80.2
	0.34	1.66	11.1	8.6	0.20	44.0
95Feb23	0.25	0.51	4.6	NA	0.08	110
	NA	0.51	4.0	NA	0.12	175
95Jul31	0.21	1.03	2.6	NA	0.40	0.0
	0.19	0.68	4.8	NA	0.40	8.3
	0.21	0.88	5.6	NA	0.46	51.7
95Sept	0.16	0.09	1.7	6.5	0.12	37.5
	0.13	0.09	2.4	4.4	0.31	36.3
	0.13	0.46	1.7	5.8	0.19	30.3
96Jul18	0.14	0.28	2.9	8.1	0.01	25.6
	0.09	0.24	3.4	7.1	0.08	(267)
	0.09	0.45	1.7	8.1	0.08	61.7
96Sept11	0.06	1.00	4.1	14.0	0.19	20.6
	0.05	0.39	1.2	9.4	0.15	19.5
	0.05	0.35	1.8	9.4	0.00	30.7

Table C.2. Reagent Blanks (ng)

Date	Ag	Pb	Cu	Zn	Cd	Fe
94Aug09	0.24	0.34	2.7	4.7	0.07	10.8
	0.20	5.54	1.4	0.9	0.00	16.2
	0.20	6.59	0.7	1.0	0.01	21.6
95Feb23	0.38	0.11	1.6	NA	0.12	20
	0.17	0.22	1.5	NA	0.08	62
	0.07	0.57	1.0	NA	0.00	25
	0.18	0.11	2.3	NA	0.12	29
	0.11	0.00	1.4	NA	0.12	(236)
95Jul31	0.10	0.23	1.1	14.1	0.17	37.6
	0.10	0.00	0.0	0.2	0.00	59.0
	0.10	0.09	0.5	3.5	0.09	22.4
	0.12	0.09	0.7	1.2	0.09	25.4
95Sept	0.07	0.04	0.3	0.5	0.04	20.6
	0.06	0.15	1.0	1.4	0.24	20.6
	0.07	0.00	0.5	0.0	0.03	14.6
96Jul18	0.07	0.28	1.7	3.5	0.01	12.0
	0.07	0.24	2.0	4.1	0.08	13
	0.07	0.21	1.7	4.3	0.08	7.1
	0.06	NA	2.5	4.1	0.08	10.3
96Sept11	0.05	1.35	2.3	22.6	0.24	(237)
	0.07	0.70	8.9	13.3	0.00	42.4
	0.09	1.00	2.7	13.8	0.01	37.1
	0.06	0.35	1.5	5.8	0.05	15.3

Table C.3. Filter Blanks (ng):

Date	Ag	Pb	Cu	Zn	Cd	Fe	Al
94Aug09	NA	0.93	6.9	9.0	NA	NA	217
	NA	0.93	8.6	7.3	NA	NA	282
	NA	2.50	8.3	12.5	NA	NA	299
95Feb23	0.20	(8.89)	NA	8.3	NA	150	506
	0.17	1.82	NA	7.5	NA	79	605
95Jul31	0.10	1.03	5.3	15.3	0.97	117	103
	0.08	0.68	3.4	3.2	0.65	70	145
	0.04	0.68	5.7	4.8	0.79	137	74.5
95Sept	0.16	0.71	4.4	6.5	0.77	(345)	47.8
	0.13	0.59	4.4	4.4	0.50	177	43.5
	0.13	0.53	2.8	5.8	0.40	186	NA
96Jul18	0.03	0.22	2.2	3.9	0.52	47	40.1
	0.00	0.15	1.9	2.6	0.45	33	14.0
	0.01	0.00	1.3	1.2	0.39	53	8.6
96Sept11	0.04	0.64	1.9	3.5	0.54	146	25.1
	0.04	0.48	1.4	2.4	0.35	102	17.0
	0.06	0.64	1.9	3.4	0.35	171	36.4

Table C.4. Determination of Limits of Detection (LOD): Analysis of Blanks.

Analysis of 14 Extracted Blanks from 96Jul							
	mass (kg)	Ag ng	Pb ng	Cu ng	Zn ng	Cd ng	Fe ng
QRB1	0.07058	0.069	0.106	14.445	8.17	NA	135.25
QRB2	0.10934	0.075	0.451	31.979	7.974	NA	131.17
QRB3	0.15335	0.068	0.244	12.133	5.357	NA	50.06
QRB4	0.19834	0.172	0.794	66.086	10.395	NA	107.83
QRB5	0.24491	0.099	0.451	38.242	12.096	NA	111.33
QRB6	0.29249	0.111	0.382	30.149	6.339	NA	47.73
RBA	0.21308	0.135	0.278	1.723	3.498	0.009	11.97
RBB	0.21783	0.087	0.244	2.040	4.058	0.078	12.60
RBC	0.21171	0.093	0.210	1.723	4.282	0.078	7.08
RBD	0.21338	0.087	0.244	2.515	4.058	0.078	10.34
FB1	0.26400	0.068	0.347	2.884	8.105	0.009	25.55
FB2	0.25002	0.068	0.278	3.365	7.123	0.078	267.2
FB3	0.26358	0.072	0.451	8.375	8.105	0.078	61.73
QHOH	0.26545	0.064	0.176	1.727	7.385	0.078	68.15
Mean:		0.091	0.333	2.282	6.925	0.061	74.86
STDs:		0.031	0.171	0.656	2.518	0.032	71.69
		pM	pM	nM	nM	pM	nM
FB	LOD250	0.9	5.0	0.6	0.1	4.3	4.9
QR	LOD250	4.4	13.5	3.7	0.5	NA	7.3
All	LOD250	3.4	9.9	3.6	0.5	3.4	15.4

QRB: Q HOH extracted

RB: Previously-extracted HOH

FB: Filtration Blank, processed with QHOH

QHOH: sub-boiling, quartz-distilled, dionized water

LOD250: Molar Limit of detection based on extraction volume = 250 mL

Analysis of 9 Extracted Blanks from 96SEP							
		Ag	Pb	Cu	Zn	Cd	Fe
mass (kg)		ng	ng	ng	ng	ng	ng
QRB1		0.049	1.348	22.640	2.271	0.151	237.525
QRB2		0.070	0.696	13.284	8.908	-0.090	42.375
QRB3		0.091	1.000	13.796	2.723	0.006	37.057
QRB4		0.056	0.347	5.828	1.516	-0.042	15.255
FB1		0.063	1.000	14.015	4.081	0.054	20.573
FB2		0.049	0.391	9.410	1.215	0.006	19.510
FB3		0.056	0.347	9.410	1.818	-0.138	30.677
QHOH		0.028	0.696	9.849	1.215	-0.042	71.089
		pM	pM	nM	nM	pM	nM
FB	LOD250	0.8	21.1	0.5	0.3	10.7	1.3
QR	LOD250	2.1	24.7	1.3	0.1	11.1	3.1
All	LOD250	2.0	21.2	1.0	0.2	7.2	6.1

QRB: Q HOH extracted

FB: Filtration Blank, processed with QHOH

QHOH: sub-boiling, quartz-distilled, dionized water

LOD250: Molar Limit of detection based on extraction volume = 250 mL

Summary of LODs for filterable metals (Me_F)

CRUISE	Ag	Pb	Cu	Zn	Cd	Fe
	pM	pM	nM	nM	pM	nM
94 Aug.	3.1	11	0.1	0.1	10	1.2
95 Feb.	5.6	13	0.1	0.3	5	13.6
95 Jul.	1.3	19	0.2	0.1	4	1.0
95 Sept.	2.3	13	0.1	0.2	10	0.8
96 Jul.	0.4	7	0.6	0.1	4	0.5
96 Sept.	0.8	21	0.5	0.3	11	1.3
Mean:	2.3	14.0	0.3	0.2	7.2	3.1
%RSD:	85.2	37.2	84.5	51.9	45.3	168.3

LOD adjusted assuming 250 mL sample volume used in extractions

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