A Review and Summary of Toxic Contaminants in Boston Harbor and Massachusetts Bay: 1990 to 2005

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A REVIEW AND SUMMARY OF TOXIC CONTAMINANTS IN BOSTON HARBOR AND MASSACHUSETTS BAY:

1990 TO 2005

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EXECUTIVE SUMMARY

This report is one in a series of reviews on toxics contaminant issues in the Boston Harbor and Massachusetts Bay region produced for the Massachusetts Water Resources Authority (MWRA). Past toxics issue reviews have addressed topics such as contaminant discharges by MWRA, multimedia fate models, potential impacts from contaminant discharge, analytical methods and contaminant trends in lobster, and an evaluation of mussel contingency plan threshold exceedances.

This review has two major goals: 1) to present an integrated approach to understanding the sources, fate and transport of historical and current chemical contamination to the Boston Harbor/ Massachusetts Bay system, and 2) to address the questions of whether the infrastructure improvements associated with the MWRA's "harbor clean-up" project have resulted in water and sediment quality improvements in Boston Harbor or degradation near the new discharge site in Massachusetts Bay. In so doing, five topics are discussed 1) the factors affecting the transport, fate, and bioavailability of contaminants, 2) current understanding of contaminant loadings into the Bays system, 3) trends in sediment contaminants, 4) trends in contaminants in tissue from winter flounder, lobster, and blue mussels, and 5) emerging chemical contaminants of concern.

MWRA marked a major milestone in 2005 with the passage of five years since its wastewater treatment plant discharges to Boston Harbor ended with the start-up of the outfall diffuser system in Massachusetts Bay in September 2000. Consistent with predictions made in the Supplemental Environmental Impact Statement for the Massachusetts Bay outfall (EPA 1988), contaminant related impacts have not been detected in the coastal environment from the diversion of effluent into Massachusetts Bay. Moreover, although influence of the outfall on nearby sediments has been found, the effluent has not caused substantive changes in the quality of the environment near or far from the outfall location nor has the discharge acutely impacted marine life in the vicinity of the outfall and Bay at large.

The key findings in this report are:

- contaminants in Boston Harbor and Massachusetts Bay have a historical legacy but are responding to regulatory actions;
- MWRA source reduction efforts and facility improvements have measurably reduced contaminant loading to the system over the past ten years;
- source reduction actions have demonstrably decreased contaminant levels in surface sediments of Boston Harbor;
- improvements in tumor incidence and bioaccumulation of contaminants in fish and shellfish taken from the Bays have been documented;
- contaminant transport, fate and bioavailability processes in this system are becoming sufficiently understood to make better judgments about the future response;
- emerging contaminants are a potentially important issue and should be understood in anticipation of potential regulatory actions over the next decade; and
- the present (through 2003) knowledge base is sufficient to allow future reductions in monitoring.

MWRA has successfully and effectively implemented major facility improvements that have dramatically reduced the loading of contaminants under its control to coastal Massachusetts. The reductions over the past decade have demonstrably improved the quality of sediment in Boston Harbor while exerting minimal impact to the sediments of Massachusetts Bay. Continued changes and improvements can be expected in Boston Harbor as natural biogeochemical processes continue to modify and bury contaminants, making them less accessible for bioaccumulation by organisms. The improved sediment quality of Boston Harbor is evident in the recovery of the health of major living resources (e.g. winter flounder) and general reductions in contaminant levels in fish and shellfish resources in the system.

Unlike a generation ago, when the Deer Island Treatment Plant (DITP) discharge was a major source and conduit of contaminants to Boston Harbor and Massachusetts Bay, DITP effluent in the early twenty-first century plays a much smaller role in the loading of contaminants to the system. Source control is a key to continuing to ensure that MWRA discharges have only minimal toxic contaminants. MWRA must continue its vigilance in controlling industrial, commercial, and household contaminant sources and input to its wastewater collection system and to ensure its treatment plant operations continue to provide the most effective contaminant removal possible. This is important for both traditional contaminants and emerging chemicals of concern such as endocrine disruptor compounds, hormonally active agents, and brominated flame retardants. Significant future reduction of contaminant loadings to coastal Massachusetts will result from decreasing loadings from storm runoff and air.

Monitoring and research on sediment quality changes in Massachusetts Bay is warranted even though only minor changes in sediment quality near MWRA's outfall have been observed through 2004. For example, additional understanding of the role of the outfall on mercury methylation in Massachusetts Bay sediments and the potential for bioaccumulation is needed. Such understanding will significantly help to understand an apparent increase in mercury in flounder sampled from the vicinity of the outfall. Such monitoring coupled with selected bioaccumulation monitoring, either with caged mussels or the national Mussel Watch program, should provide sufficient information to address potential risk from MWRA derived contaminants to humans and natural resources.

1 INTRODUCTION

Since its creation in 1985, the Massachusetts Water Resources Authority (MWRA) has worked to end long-standing violations of the Clean Water Act and to minimize the effects of wastewater discharge on the marine environment. Steps to minimize effects of effluent discharge have included source reduction to prevent pollutants from entering the waste stream, improved treatment before discharge, and better dilution once the effluent enters the marine environment.

MWRA's industrial pretreatment and pollution prevention program is designed to minimize toxic contaminant discharge into the sewer system. Source reduction has included projects to lessen household hazardous waste disposal to sewers, and to minimize mercury discharges from hospitals and dental offices. In addition, best management practices are employed at sewer facilities to mitigate accidental discharge of pollutants. Operator training programs and process control and maintenance tracking systems are also in place. Improvements to the treatment processes are ongoing today and continue to improve the effluent quality.

In 1991, MWRA ended discharge of municipal sludge into Boston Harbor. Improved treatment began in 1995, when a new primary treatment plant at Deer Island (DITP) was brought on line, and disinfection facilities were completed. The first and second batteries of secondary (biological) treatment went on line in 1997 and 1998. In 1998, discharge from the Nut Island Treatment Plant into Quincy Bay ceased, ending effluent discharge to the southern part of the harbor; all wastewater was conveyed to Deer Island for treatment. In September 2000, the Massachusetts Bay outfall went on line, allowing dechlorination of the effluent. The third and final battery of secondary treatment became operational in 2001.

The new outfall achieved better dilution by diverting the effluent discharge from the shallow waters of Boston Harbor to a new diffuser system located on the sea floor 9.5 miles from DITP in Massachusetts Bay (Figure 1-1). The outfall site was selected because it had a water depth that would promote effective dilution and the ocean current patterns were the least likely of the alternative sites evaluated to affect sensitive resources, and it was feasible to construct an outfall tunnel to the location.

Moving the effluent outfall from the harbor to Massachusetts Bay, raised some concerns about potential environmental impacts, which were expressed as general questions:

- Is it safe to eat fish and shellfish?
- Are natural/living resources protected?
- Is it safe to swim?
- Are aesthetics being maintained?

These questions are the basis of MWRA's monitoring program, which is a requirement of its National Pollutant Discharge Elimination Permit issued jointly by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (MADEP) in 2000. Among many other comprehensive requirements, the permit requires MWRA to monitor the effluent and the ambient receiving waters for compliance with permit limits and in accordance with a monitoring plan (MWRA 1991, 1997) developed in response to the EPA Supplemental Environmental Impact Statement (SEIS, EPA 1988).

EPA and MADEP require monitoring to ensure compliance with the permit, to assess whether the outfall has effects beyond the area identified in the SEIS as acceptable, and to collect data useful for outfall management. MWRA began some studies during 1989-1991, and implemented a broad baseline-monitoring program in 1992. In 2000, monitoring of the discharge effects of the new outfall began, and is ongoing.

Over the past 15 years, MWRA has periodically published reviews on toxics contaminant issues in the Boston Harbor and Massachusetts Bay region. These reports provided information to support planning that MWRA regularly conducts and to inform the public and state and federal regulators on topics of interest or concern. Previous MWRA toxic issues reviews focused on predicting or projecting possible changes or potential impacts that could result from the outfall diversion and facility upgrades and addressed topics such as contaminant discharges by MWRA (Shea 1993), multimedia fate models (Shea 1995), potential impacts from contaminant discharge (Mitchell *et al*. 1997), analytical methods and contaminant trends in lobster (Lefkovitz, *et al*. 2001), and an evaluation of mussel contingency plan threshold exceedances (Hunt *et al*. 2002a).

2005 marked the completion of five years of discharge data collection, since the new bay outfall went on line. This report summarizes and interprets the extensive monitoring data on toxic contaminants in Boston Harbor and Massachusetts Bay. Consistent with predictions made in the Supplemental Environmental Impact Statement for the Massachusetts Bay outfall (EPA 1988), the effluent has not caused substantive changes in the quality of the environment near or far from the outfall location nor has the discharge acutely impacted marine life in the vicinity of the outfall and bay at large (Werme and Hunt, 2005).

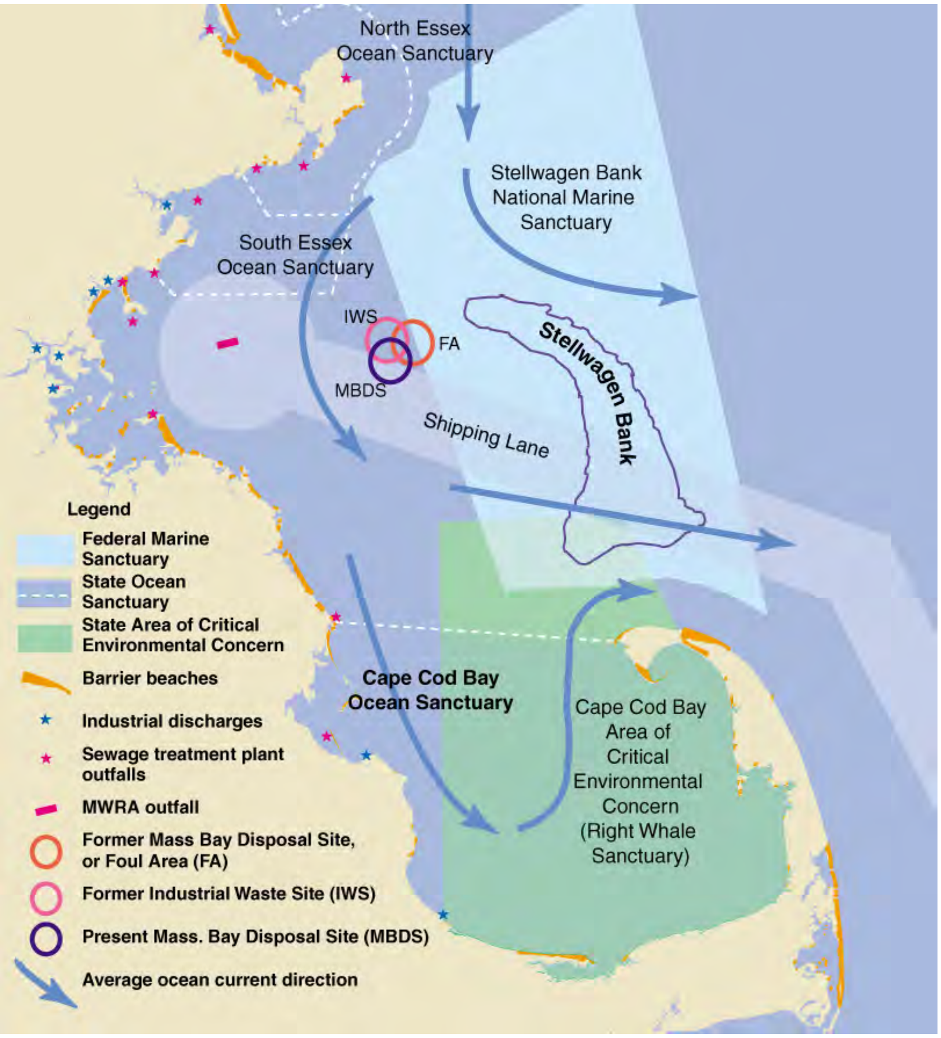

Figure 1-1. Map of Massachusetts and Cape Cod Bays showing the location of the MWRA and other point sources to Massachusetts Bay.

1.1 Background

Historically, contaminant levels began to increase in the environment near the end of the Civil War and are attributed to growing industrial development. The published literature often cites atmospheric and direct discharge as the major vectors for transferring the contaminants from the sources to lakes and the coastal zone. The literature also indicates the development of sewers in the towns and cities was a major factor in the transfer of contaminants to the coastal zone (Bricker *et al*., 1989). Contaminant inputs grew as the industrial revolution continued and as anthropogenic activities mobilized metallic contaminants and discovered new materials (e.g., petroleum) and created chemicals (e.g., PCBs, pesticides, etc.).

Like other urbanized coastal embayments in the Northeast United States, Boston Harbor has a long history of use as a repository for domestic and industrial wastes. As early as the seventeenth century, sewers funneled household wastes and stormwater runoff to numerous discharge locations in the harbor. In 1833 local ordinances allowed human waste to be discharged into the evolving combined sewer system (Dolin, 1990). During this same period, widescale filling of the harbor's tidal areas inhibited the transport of these wastes away from the near-shore waters of the harbor. In response to a severe cholera epidemic in the 1860's, the sewer system was upgraded by centralizing stormwater and untreated domestic and commercial waste, and discharging the mixture off Moon Island at the mouth of Quincy Bay on the outgoing tide. The success of this project led to the expansion of sewer services to neighboring communities and to the building of pumping stations and discharge pipes at the mouth of Boston Harbor at Deer Island in 1895, and at Nut Island in 1904. Waste generated by a burgeoning coastal population and the impacts of industrialization throughout the first half of the twentieth century increasingly stressed Boston Harbor, as it did many urbanized coastal areas (Stolzenbach and Adams 1998). Boston's sewage treatment facilities were upgraded to state-of-the-art (for the times) primary treatment plants; Nut Island in 1952 and Deer Island in 1968 (Havens and Emerson/Parson Brinkerhoff 1983). However, digested sludge, a byproduct of wastewater treatment, with its associated contaminants, was discharged at the mouth of the harbor. In the 1970's and 1980's the outdated facilities fell into disrepair, making them even less effective—pumping failures caused substantial discharges of raw sewage from the combined sewer overflow (CSO) outfalls that rimmed the harbor; CSOs also discharged to tributary rivers.

Federal legislation was passed in the early 1970's mandating wastewater facilities to upgrade to secondary treatment, which would provide substantially greater removal of solids and chemical contaminants. The state of Massachusetts applied for a waiver from secondary treatment for the Boston treatment plants, which ultimately was denied. MWRA was created in 1985 with a court-ordered mandate for short-term and long-term remediation activities to decrease anthropogenic contaminants discharge into the harbor. MWRA was placed on a schedule for constructing secondary treatment facilities. During the late 1980's MWRA began to rigorously enforce regulations limiting toxic contaminants entering the wastewater system from industry; ended sludge scum discharge into the harbor; and provided more reliable chlorination of wastewater discharge. In December 1991, a major milestone was met as all sewage sludge discharge into the harbor ended. In the 1990's pumping capacity at the Deer Island Treatment Plant (DITP) increased and more combined sewage flows were pumped to the newly improved DITP, thereby reducing CSO discharges. The first batteries of secondary treatment came on line in late 1997 and early 1998. In July, 1998, the inter-island tunnel was completed so that flows from the south system, which had been treated at the Nut Island treatment plant, were sent to DITP. At this time, most of greater Boston's wastewater received secondary treatment (Figure 1-2), and the discharge of sewage effluent into southern Boston Harbor ended. All treatment plant discharges to Boston Harbor ended in September 2000 as the new 9.5-mile-long outfall was opened offshore in Massachusetts Bay. Wastewater quality improved more when the third battery of secondary treatment came on line in March 2001. Also, corrosion control in the water supply system reduced copper and lead leaching from water supply pipes, and programs implemented with dental and medical facilities reduced mercury discharges to the sewer system. Federal regulation of toxic chemicals and banning of contaminants like PCBs and DDTs in the 1970's and 1980's led to a continued reduction in toxic discharges. These improvements have resulted in a five fold decrease in wastewater solids discharge since the early 1990's (Figure 1-3). Since many contaminants readily bind onto particles, the magnitude of the solids reduction is mirrored for most chemicals of concern in the MWRA effluent (Figure 1-4). Improvements to other MWRA facilities have also resulted in smaller contaminant loadings from the MWRA waste collection system.

The legacy of past chemical discharges to Boston Harbor and its watershed is captured in the sediment and can be understood through collection and analysis of undisturbed sediment cores. A recent example in the Boston area is analysis of sediment cores collected from Upper Mystic Lake, the headwater of the Mystic River that flows into Boston Harbor (Rauch and Hemond 2003). Data from this core suggest that chromium in the sediment increased gradually beginning in the latter part of the 1800's, peaked in the 1955 to 1970 period and decreased to nineteenth century levels by 2002. Arsenic and lead show similar patterns; although the lead peak at the turn of the twentieth century is attributed to industrial activity and a second peak in the mid-1980s is attributed to remobilization of contaminated deposits and use of leaded gasoline. A sharp decrease in lead concentration was reported after the mid-1980's and reflects, as is typically observed in coastal sediments from around the United States, the change from leaded to unleaded gas. Interestingly, platinum, a metal used in automobile exhaust-system catalysts only increased modestly from 1870 until 1975, but has since risen dramatically. These data demonstrate that while technology can address past known threats to the environment, it continues to create new sources of concern.

Sediment data from Boston Harbor also demonstrate that lead input to the harbor gradually increased from the latter half of the nineteenth century, peaked in the post World War II era, and has decreased by half since (Bothner *et al.*, 1998). Diminished use of lead in gasoline beginning around 1973 contributed to the recent decreases in lead concentrations. These authors also report the level of other metal contaminants in Boston Harbor decreased substantially between 1977 and 1993. The decease was documented through analysis of trace metals in surface sediments from four stations in the outer portions of Boston Harbor, sediment cores collected in depositional areas of the harbor, and a compilation and analysis of historical data from the harbor. A decrease of 46% ± 12% in background corrected lead levels in the upper two centimeters (cm) of core samples was observed and similar decreases in chromium, copper, mercury, silver, and zinc were also reported. Bothner *et al.* (1998) suggest these decreases are due to cessation of sewage sludge discharge to the harbor in 1991 by MWRA, source reduction efforts by industry, and improved wastewater handling and treatment by MWRA.

The improvements in wastewater treatment, ongoing reductions of inputs into the system, and increasingly accurate analytical measurements of contaminants in the effluent (Leo *et al.* 1993) have resulted in most contaminant loadings into Massachusetts Bay being well below those projected by the EPA's Supplemental Environmental Impact Statement of 1987 (EPA 1988) written to support the outfall location decision. During the same period, research provided a better understanding of the MWRA's discharge impact (Stolzenbach *et a*l. 1993). These authors concluded that for most of Boston Harbor (excluding the President Roads and Nantasket Roads areas), the heaviest fraction of particles associated with waste discharges probably deposit within 100 to 1000 meters (m) of the point of entry and that at least half of the particle load to the inner harbor is retained in semi-enclosed reaches such as Fort Point Channel. They further conclude that about 80 percent of the harbor is depositional in nature, which coupled with efficient dispersion in the harbor, make attribution of contamination to specific sources difficult (i.e. the Harbor is an effective mixing bowl). Thus, only major changes in the strength of loading from a particular source or in the total loading to the Harbor are likely to be detected and then only after several years. Such information led Leo *et al.* (1993) to conclude that "cleanup" of the harbor (as measured by sediment quality) will take many years and depend on factors such as the amount of organic material reaching the sediments, the rate of new sediment burial (e.g. sedimentation rate), and the biological succession that brings benthic organisms that can live in and deeply mix the sediments of the harbor. The role of organic matter is important to the retention of contaminants in sediments because organic matter can enhance the processes that sequester contaminants, especially metals, in sediments

(DiToro, 2001). This in turn can affect the bioavailability and ultimately the toxicity and bioaccumulation of contaminants in living resources such as fish and shellfish.

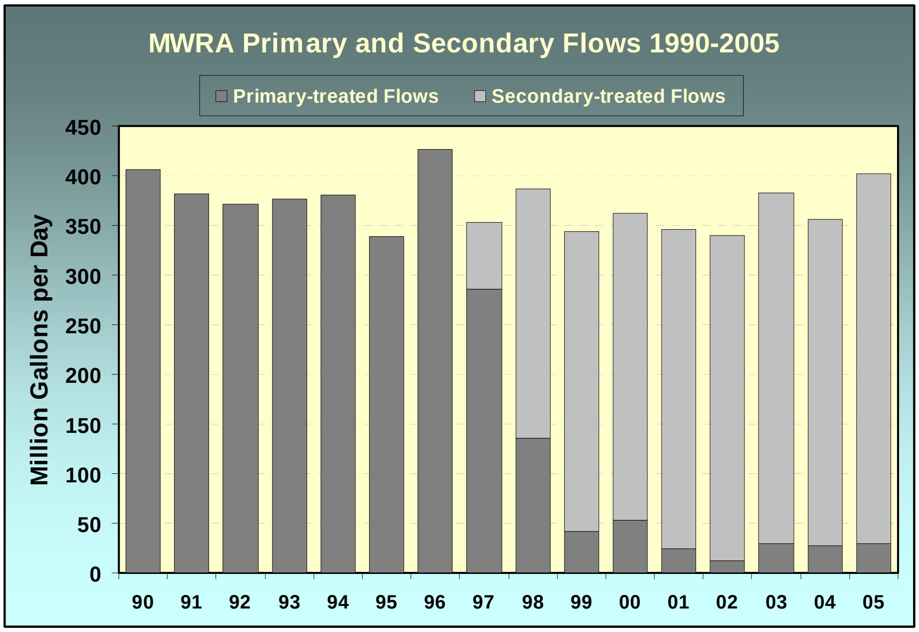

Figure 1-2. MWRA improvements to wastewater treatment since 1990.

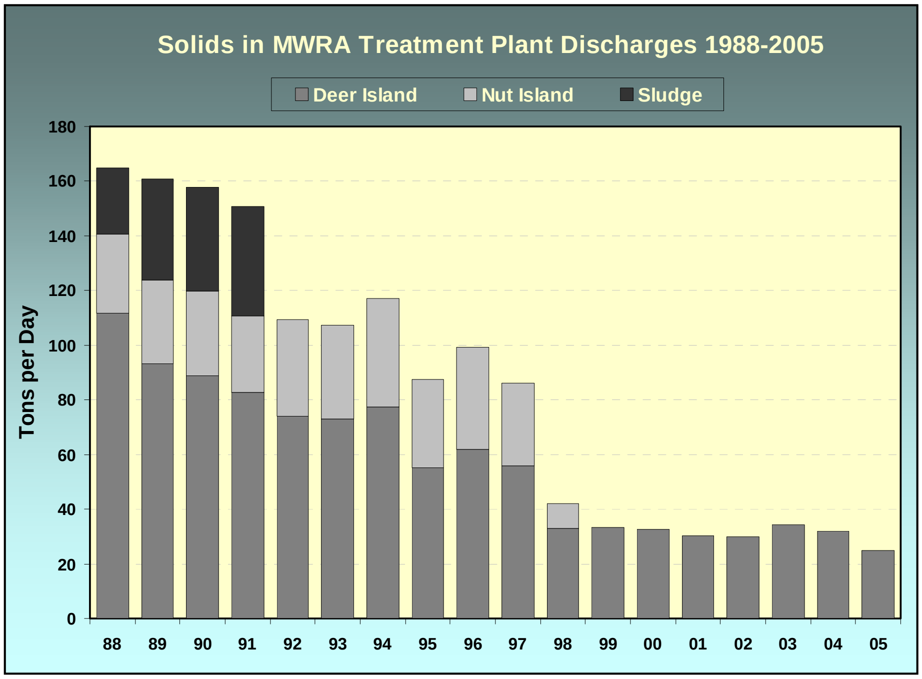

Figure 1-3. Reduction in solids loadings from treatment plants since 1988.

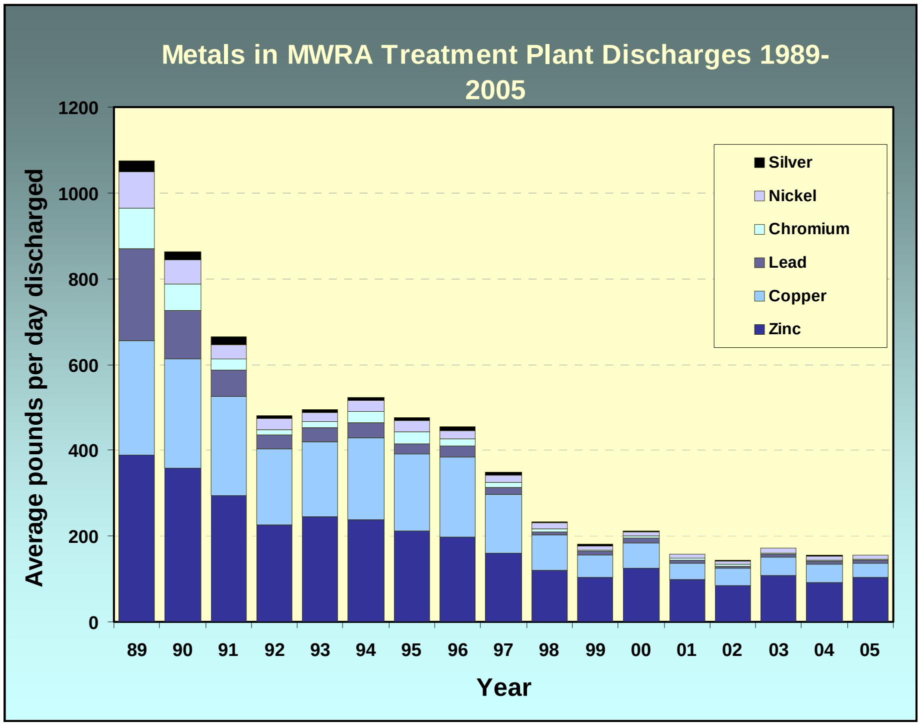

Figure 1-4. Changes in metals loading to the Massachusetts Bay system from the MWRA effluent since 1989.

1.2 Report Objectives

The primary purposes of this review are to: 1) provide information to support MWRA's planning, 2) inform the public of past and present chemical contaminant inputs, current contaminant levels and sediment quality in Boston Harbor and Massachusetts Bay and improvements thereto, 3) discuss the current understanding of bioaccumulation in the indicator organisms monitored by MWRA in the bays and the role of the MWRA effluent in this, and 4) describe potential emerging contaminant issues (e.g., endocrine disruptors). It is also the intent of the review to convey information on how chemical contaminants have responded in the sediments and tissue in the four years following the diversion of effluent from Boston Harbor to Massachusetts Bay. Toxic contaminants are less of a concern in the water column; outfall dilution verification studies of 2001 (Hunt *et al*. 2002b; 2002c) and continuing effluent monitoring strongly indicate that water quality criteria are not violated by the discharge of effluent in Massachusetts Bay (Werme and Hunt 2005). Moreover, good agreement between effluent dilution simulations of the early 1990s and post-discharge water quality monitoring data have been documented (Signell in Bothner and Butman 2005). The following topics are addressed:

1) the current status of contaminants in the system and how the sediments reached this point;
2) a brief review of factors affecting the distribution and concentrations of contaminants (a process story) to set stage for discussion of potential future responses and concerns;
3) an understanding of present contaminant inputs to the system and how they have changed since the Boston Harbor "cleanup" started;
4) the response of harbor sediments to "cleanup" and changes in Massachusetts Bay since the diversion in 2000;
5) the transport and fate of contaminants in Massachusetts Bay and future implications;
6) the response of contaminants in fish and shellfish tissues since effluent diversion; and
7) expected future responses relative to contaminants and the MWRA effluent and emerging chemicals of concern.

2 FACTORS AFFECTING THE TRANSPORT, FATE, AND BIOAVAILABILITY OF CONTAMINANTS

This section overviews the general characteristics of the sources and sinks of chemicals in the coastal region; describes in general terms the processes that influence the transport, distribution, and fate of chemicals in the system; and conveys the primary factors that affect bioavailability. The information is presented to provide context for considerations presented in subsequent sections of this review.

The sources, transport processes, and fate of contaminants in Boston Harbor/Massachusetts Bay/Cape Cod Bay are presented schematically in Figure 2-1. The schematic shows seven major external sources of contaminants to the Massachusetts Bay system: atmospheric, rivers, nonpoint, outfalls, CSOs, ground water, and the ocean boundary. The major sinks for contaminants are burial in sediments, weathering and degradation (chemical and bacterially mediated) to other compounds, and export from the system. Water is primarily exported from the system near the tip of Cape Cod. The diagram also illustrates that contaminants enter the system in two major forms: dissolved and particulate. There are also a number of internal physical, chemical, and biological processes that affect where contaminants are found in this system. These include sediment resuspension, exchange of contaminants from particulate to dissolved phase within the sediments under changing reducing and oxidizing conditions, and in some cases remobilization and diffusion of contaminants back into the water column.

The transport and fate of contaminants entering coastal systems is influenced by many chemical and biological factors that control the partitioning between dissolved and particulate forms. Physical factors also affect the transport and fate of contaminants. Physical factors include the type and size of particles, the rate that the particles settle, water depth, cohesiveness (e.g., stickiness) of the sediment, advective processes such as resuspension (by biology or physical processes, such as waves and currents) and water movement (currents and waves), and proximity to sources. Adsorption processes (both biological and chemical) and biogeochemical processes, such as remineralization or degradation, which are often mediated by microbial communities, also influence the transport and fate of contaminants. Microbial processes that consume organic matter and oxygen are particularly important in the marine environment. Chemical processes such as photolysis, oxidation, and hydrolysis also degrade organic contaminants.

In general, the potential bioavailability of contaminants is influenced by whether they are sequestered on particulate phases (less available) or found in the dissolved state (more available). The major factors that influence where and how a contaminant may or may not be sequestered are: proximity to the source, concentration in the source and rate of input, the strength of the association with particles (both inorganic and biological), the rate of particle deposition, water depth and currents, water residence time, and the potential for areas to be erosional or depositional. These factors interplay to set the balance between reducing and oxidizing sediments through a complex series of biogeochemical reactions involving organic matter, sulfate, and metal oxides.

Many of these concepts are considered more comprehensively for Boston Harbor in Stolzenbach and Adams (1998) who conclude that Boston Harbor acts as a sink for most contaminants. Particularly noted by these authors is the concept that regions close to sources and with weaker transport functions (e.g., lower energy input, less bottom shear stress, faster particle settling rates) tend to retain particles and associated contaminants. Areas in the harbor that are typically depositional in nature are the shallow enclosed regions with limited advective movement and low potential for dispersion of the sediments. Conversely, areas that have stronger transport functions, such as the erosional areas located in the entrance channels of the outer harbor, are less likely to be the final repository of contaminants. Sediments may also scavenge particles from the water column depending on micro topographic and compositional characteristics (e.g., grain size, total organic carbon (TOC)). In addition to these physical and chemical processes, many benthic organisms actively remove particles from the water column to the sediments and visa versa.

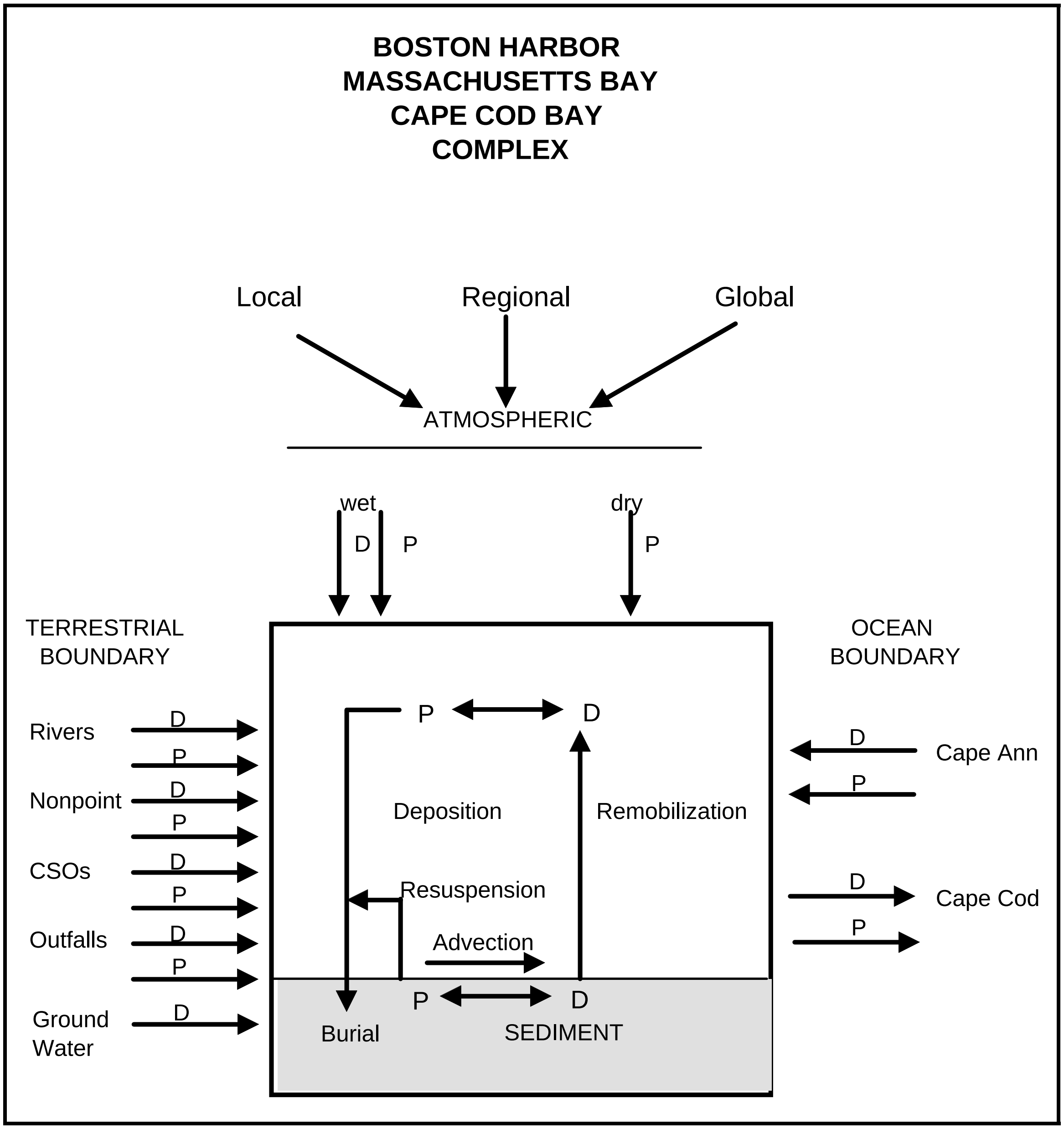

Figure 2-1. Schematic diagram depicting the major sources and sinks and transfer processes between dissolved (D) and particulate (P) phases of contaminants in coastal ecosystems.

The form or species of a chemical also influences the composition of the dissolved and the particulate phases throughout the system. For example, a dissolved metal may enter the system as the free metal ion (e.g., Cu^{2+}), as an inorganic chemical species (e.g. $CuOH^{+}$), or associated with many types of dissolved organic matter (e.g., proteins, amino acids, fulvic acids, humic acids, etc.) These associations, known as organic complexes ($Cu\text{-}org^{+}$), occur over a large concentration range and are affected by a range of water characteristics (e.g., pH, salinity, etc.). Contaminants may also enter a system associated with colloidal material or associated with a range of particle types (e.g., clay, minerals, organic detritus, iron and manganese oxides, etc.) and sizes. Similarly, organic contaminants may enter the system as unassociated dissolved forms or associated with various forms of dissolved organic carbon.

Both metal and organic contaminants may be transported in association with particulate matter. These contaminants may be occluded within the particulate phase (i.e., in the crystalline structure of clay minerals or within organic detritus), sequestered within combustion products (e.g., soot), or adsorbed to the surface of inorganic or organic matter (Gobas and Zhang 1994, Newman and Jagoe 1994).

The many factors that influence the manner and strength of the association of contaminants between the dissolved components (i.e. ligands) and particulate matter are well understood (see for example Hammelink *et al.* 1994, DiToro 2001). These factors are most often described using thermodynamic equilibrium theory or reaction kinetics and lipid (fat) solubility concepts. The rate that an equilibrium is reached can be fast (microseconds) or slow (hours to years) and is strongly influenced by the temperature. Thermodynamic equilibrium among the chemical species should not to be confused with steady state concepts. Steady state denotes that the rate of input and the rate of loss for a system is the same, resulting in an unchanging (steady) concentration within the media (i.e., a water body, an organism, an organ, etc.).

For metals, where the free metal ion (not bound to any ligand) is a cation (positively charged atom), several factors influence its chemical speciation and therefore, its fate, transport, and bioavailability. Among these factors are pH, the type and concentration of anions (negatively charged ligands such as chloride [Cl^-], hydroxide [OH^-}, or forms of sulfur [S^{2-}, $SO4^{2-}$]), organic ligands (org-), and whether the media is oxidizing or reducing (REDOX status). Similarly, factors such as the octonol/water partitioning coefficient (K_{OW}) or organic carbon partitioning coefficient (K_{OC}) affect how much an organic contaminant will associate with particles, sediments, or the tissue of organisms. While each ligand is important, the organic carbon content is often the most important. This influence is apparent whether the partitioning is between water and sediment, water and organisms, or particles and organisms. For the purposes of normalizing contaminants to carbon levels in these matrices, the lipid content of the solid phase (e.g., tissues) or total organic carbon are used.

Recently, investigators have demonstrated that combustion-derived “black carbon” (soot, chars, etc.), a minor component of the organic matter in sediments, exerts a major influence on the partitioning of hydrophobic organic compounds (e.g. PAHs, PCBs, etc.) through their very high affinity for the “black carbon” (Accardi-Dey and Gschwend 2002, 2003 and references therein). This strong affinity is now considered critical for accurate estimates of mobility and bioavailability of PAHs, PCBs, and other hydrophobic organic compounds (Lohmann *et al.* 2005). Moreover, the association of metals with organic matter is sufficiently strong that changes in the metal content of sediment between 1991 and 1998 at two Boston Harbor stations could be correlated with changes in organic matter content of sediments (Zago *et al.* 2001). These changes may also be associated with other factors as considered below.

It is well established that oxidation of organic matter through bacterially mediated processes can completely consume available oxygen. This creates reducing conditions that result in the reduction of electron acceptor compounds in the order of oxygen (O_2), nitrate (NO_3^-), manganese oxide (MnO_2), iron oxy-hydroxides (FeOOH), and sulfate ($SO_4{}^{2-}$). Carbon dioxide (CO_2), ammonium (NH_4^+), Mn^{+2}, Fe^{+2}, hydrogen sulfide ion (HS^-) are generated over this sequence of reactions. The sulfides react rapidly and strongly with some reduced metals, such as Fe, to create solid phases (i.e., iron sulfide). Other reduced metals, such as manganese, do not form sulfide complexes or do so only slowly. Notably dissolved Fe^{+2} and Mn^{+2} concentrations may increase in pore water and diffuse or be advected towards the overlying water. If the reactions occur near the sediment water interface, these and other metals (depending on reaction kinetics and thermodynamic properties) may enter the water overlying the sediments. Regardless of where the reducing zone is in the sediment or overlying water, the reduced iron and manganese rapidly oxidize on contact with oxygen and precipitate iron and manganese oxides at the redox interface. Other metals may co-precipitate with these two major sediment phases and interact with other compounds (i.e. organic matter), increasing concentrations at the redox interface (Hunt, 1983a, b). In highly reducing sediments in some areas of Boston Harbor, this redox interface may be at the water-sediment boundary.

Formation of sulfides is especially evident in marine systems due to the high concentration and nearly infinite supply of sulfate in sea water. Other metal sulfides are also highly insoluble (depending on the speciation in the solid phase) and stay sequestered within the sediment unless released by physical processes (e.g., bioturbation, sediment resuspension, advection). Such processes return reduced species to aerobic environments where they are oxidized and released from the sulfide compound(s) to form complexes with other ligands or adsorb to particles. The cycle is repeated once these chemicals reenter the aerobic geochemical cycle and are transported and redeposited. The stability of the complexes formed by transition metals in the environment is generally predicable and follows the Irving-Williams order for stability of complexes (Stumm and Morgan 1981). The Irving-Williams order of stability is $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ (Stumm and Morgan 1981). This means that Cu^{2+} binds more tightly with humic materials than does Ni^{2+}, which binds more tightly than does Co^{2+}, etc. Other stability sequences (e.g. with organic ligands or hydroxide) are possible.

Since organic matter is actively consumed (oxidized) by bacteria, a supply of organic matter is needed for the sediments to remain in a reducing state. Changes in the rate organic matter is supplied to the sediments or in the rate of oxidation, which typically occurs as seasonal temperatures increase and decrease, can result in changes in the redox status of the sediments and release (or sequester) contaminants from sediments. Mesocosm experiments set up to evaluate the response of contaminated sediments to removal of external sources of contaminants and organic matter loading suggests that some metals may be preferentially released from the sediment (Hunt and Smith 1983). In these studies isolation of the sediments from the high carbon loads resulted in rapid deepening of the redox discontinuity from the sediment-water interface in the most contaminated sediments to more than 1.5 cm below the water-sediment interface within 18 months of isolation. In that same period more than 50% of the cadmium inventory in the sediment was exported from the mesocosm while <3% of the lead and copper was lost. Manganese was imported to the mesocosm, most likely through oxidation and retention at the sediment surface. The data support chemical speciation and thermodynamic theory that reduction of organic matter input to sediments may result in release of contaminants from the surface sediments. Release of organic compounds may also occur as the primary phase holding these compounds in the sediments decreases.

An important consideration in the biogeochemical cycle of contaminants is the role of bioturbation and irrigation (movement of water through sediments by biological activity) by benthic organisms. Bioturbation is the physical turning over of sediments by organisms that live and borrow through sediments and actively move (irrigate) overlying water through the sediments as part of their life cycle. The importance of bioturbation on chemical distributions in sediments, particularly those that are redox sensitive (Aller 1982) has been evident for many years. This in part is related to the transport of oxygenated water to depth in the sediments, which in turn modifies the balance between organic matter oxidation and sulfide formation. Moreover, it is known that such organisms are less abundant in areas that are highly impacted by organic matter loading (Person and Rosenberg, 1978; Rhodes *et al*., 1978). It stands to reason and has been demonstrated that the relative abundances of organisms that irrigate and mix sediments affect the rates that the processes occur and ability of sediments to sequester chemicals. Conversely, the process may release elements bound in sulfides to the overlying water column as a system recovers from organic loading.

The importance of these processes may be best demonstrated from the mercury cycle in Boston Harbor which has recently been reported by Benoit *et al*. (in press). Mercury is a highly toxic element that is known to bind strongly with sulfide ($K_D \sim 10^{54}$). It has been known for many years that methyl mercury production is associated with sulfate reducing bacteria in sediments (Benoit *et al*., in press and references therein). It is now known that the zone in sediments where methyl mercury is produced is bounded by the penetration of oxygen into the sediments (no sulfate reduction) and sulfur inhibition (sulfide production is greater than the available metals to bind it, creating excess free sulfide). As a result methyl mercury production and accumulation tends to occur near the sediment-water interface in a restricted zone in the sediment. The size of this zone and its ability to accumulate methyl mercury depend greatly on the balance between the supply of oxidants (e.g., oxygen) and rate of sulfate reduction, which is known to be affected by infauna. The role of infauna and bioturbation in the production and accumulation of methyl mercury in Boston Harbor was tested by Benoit *et al.* (in press) who found that increased densities of infaunal borrows produced deeper peaks in methyl mercury concentrations by providing oxidants that decrease sulfide buildup (relaxed sulfide inhibition on the bacteria), and increased the size of the zone where mercury methylation occurs. However, the inventory of methyl mercury was lowest where infauna abundances were either high or low. In the latter case, inhibition by high sulfide levels due to a smaller methylation zone was causative. For the former case, increased release of methyl mercury to the overlying water column through advective processes associated with bioturbation is likely. These findings have implications relative to availability and potential bioaccumulation of methyl mercury by higher trophic level organisms in the harbor, the latter case being of the most concern as the system adjusts from large areas of intense carbon loading, where sulfide inhibition may dominate the methylation process, to areas of intermediate and high infaunal abundance, where release of the mercury to the water column may occur. Similarly, if carbon loading to sediments near the outfall in Massachusetts Bay increases, higher potential for methylation and bioavailability may come about. Whether these processes are sufficient to create a net loss of mercury from the sediments is unknown. Depending on the chemical and biochemical reactions involved, some elements, such as manganese, may build up in the surface sediments, while others decline.

Chemical reactions and bacteriologically mediated processes in sediments can also degrade organic compounds such as PAHs, PCBs, and pesticides such as DDTs or increase release to the overlying water as discussed for the mercury cycle. Changes in the congener pattern or in the parent chemical structure provide evidence of these processes. This topic area is the subject of extensive studies too numerous to summarize in this short synopsis. Suffice it to say that these processes act in concert with physical processes such as sediment transport (deposition, resuspension, and burial) to alter the levels of contaminants in coastal sediments. These transport processes are especially important to understand in Boston Harbor and Massachusetts Bay. In the harbor, the transport process may help redistribute or bury contaminants depending on the energetics of the local environment. Understanding where these processes are occurring helps determine the best locations for monitoring sediment quality changes. In Boston Harbor, which is now receiving lower contaminant loads than in the past (see discussion in Section 3 of this report), these processes may result in decreased contaminant concentrations that mimic the load reductions. These can be confounded, however, by the deposition in some locations. Ascribing the changes to load reductions versus transport or burial is thus important to the overall understanding of the harbor's response to the cleanup. Such changes are considered in Section 4.

In contrast, the offshore environment near the outfall in Massachusetts Bay is now receiving more direct contaminant inputs from the outfall diversion which may alter the local contaminant signature. The Bay is also subject to significant storm events which can resuspend and transport sediments to more quiescent environments, for example from near-shore to deeper waters. Thus, it is important to have the ability to monitor for local and distant changes over time. Changes in Massachusetts Bay in the initial two years since outfall startup are considered in Section 4.

An important aspect of sediment geochemistry and production and loading of organic matter to coastal areas is the availability of contaminants to interact with organisms. For toxic effects to occur, metals and organic contaminants must be in phases that are available for uptake by organisms. For metals, this is generally considered the free metal ion. As considered previously, many ligands influence the amount of "free" metal (ionic form) in waters and sediments. In oxygenated waters dissolved organic matter can bind free metals, reducing their availability to cause toxicity. In contrast, excess organic ligands can over sequester key "nutrient' metals leading to poor growth due to micronutrient limitations. This area has been the subject of extensive research and is not further reviewed here. Analogous to the water column, in sediments, the acid volatile sulfide (AVS) and organic matter interact to sequester the metals making them unavailable (DiToro 2001). When the molar capacity for the AVS in the sediments to sequester the metals is exceeded, toxicity to benthic organism is observed. Recent findings regarding the role of "black carbon" in reducing availability of the hydrophobic chemicals plays an analogous role for hydrophobic organic compounds and reduces bioavailability of these chemicals (Lohmann *et al*. 2005).

Other recent research invokes a concept known as the biotic ligand model which quantifies the bioavailability of certain metals to aquatic life. Detailed information on the biotic ligand model can be found in *Integrated Approach to Assessing the Bioavailability and Toxicity of Metals in Surface Waters and Sediments* (EPA-822-E-99-001). The biotic ligand model is based on the theory that toxicity is related to metal complexes and interactions at the site of action (biotic ligand). Thus, not only the form of the metal but the type of receptor is important. Research is now showing that for metals, mortality occurs in aquatic organisms when the concentration of metal bound to the biotic ligand (e.g., fish gill) exceeds a certain threshold concentration.

As a past major contributor of chemicals to the Boston Harbor/Massachusetts Bay complex, it is important to understand how MWRA actions have reduced loading of contaminants to the harbor and to the Bay system. Moreover, it is important to understand where and how the harbor is responding to the actions, and where the areas of concern remain. Lastly, an important issue for MWRA is the potential availability of chemicals for interactions with biota and whether MWRA's activities are reducing the potential for contaminant impacts. The following sections address these issues primarily using MWRA data, but incorporating recent research findings and other available studies.

3 CONTAMINANT INPUT TO THE BOSTON HARBOR AND MASSACHUSETTS BAY SYSTEM

Contaminants are introduced to Boston Harbor and Massachusetts Bay by many pathways. Past studies of contaminant loading to Boston Harbor (Menzie *et al*. 1991; Alber and Chan 1994) developed estimates of loadings for sources such as the MWRA effluent, CSOs, stormwater, other NPDES-permitted discharges, tributaries, and groundwater, as well as runoff from Logan airport and atmospheric input. Alber and Chan (1994) found that loadings in the early 1990s (1990 through 1993) were substantially lower (20 to 60 percent depending on the contaminant) relative to the pre-1988 estimates developed by Menzie *et al*. (1991). A major factor in this estimated load reduction was the ending of sewage sludge discharge to the harbor in 1991 as evident in Figure 1-4. Source reduction efforts, reduction in groundwater inflows to sanitary and stormwater systems, and better estimates of contaminants in the sources also accounted for some of the decrease. It was anticipated harbor loadings would decrease substantially as secondary treatment came on line and as effluent was transferred offshore. Alber and Chan (1994) also suggested minor reduction in loading estimates for some metals introduced via CSOs over this time period, but did not report significant reduction estimates for the other sources.

A comprehensive estimate of contaminant loadings to Massachusetts Bay has not been completed since these studies were published nor since the MWRA discharge was moved offshore in 2000. However, recent updates for atmospheric inputs (Golomb *et al*. 1997a; Golomb *et al*. 1997b) and MWRA effluent and CSO loading are available. Stormwater flow data for the entire Boston area (MWRA, 1997b) and contaminant concentrations measured by the US Geological Survey for stormwater in the Charles River Basin (Breault *et al*. 2002) provide the data necessary to estimate current stormwater contributions to the harbor. Also available is a comprehensive examination of changes in nutrient loadings to Boston Harbor from 1995 through 2003 (Taylor 2005). Contaminant loading estimates based on the above citations are compared in this section to historic estimates made for the environmental impact analysis for the outfall relocation (EPA 1988), revised loading estimates from the early 1990s (Alber and Chan 1994), pilot studies of the effectiveness of the secondary treatment (Hunt *et al*. 1995; Butler *et al*. 1997), and loading estimates based on MWRA discharge monitoring data.

Effluent. The most recent MWRA estimates for contaminant loading from treated effluent discharged into Massachusetts Bay are shown in Table 3-1 for an 18-month period from early 2004 to mid-2005. The MWRA loading estimates in this table are based on a period where annual flows were nearly those used in the SEIS (400 million gallons per day (mgd) compared to the 390 mgd assumption used in the SEIS). Pilot-scale secondary effluent treatment effectiveness studies conducted in the mid-1990s (Hunt *et al*. 1995) and used by Coates (1995) to calculate the minimum time which would be needed to detect contaminant changes in the offshore sediments are also shown. Those data provide a comparison to the projected loads which were made when good quality secondary effluent data became available. Subsequent effluent studies reported in Butler *et al*. (1997) found slightly lower than projected secondary treatment contaminant removal efficiency. Contaminants loading estimates based on their study results and an annual flow of approximately 380 mgd were generally higher than the 1995 estimates except for tPAH and cadmium. Both the Butler and Hunt projections were based on best available estimates of flow and treatment efficiency at the time of the study, and thus are not as accurate as the fully operational plant loading estimates recently calculated by MWRA.

The loading estimates in the SEIS (EPA, 1988) were much higher, except for silver, than those estimated with data from the initial MWRA pilot treatment plant studies of the early-1990s (Hunt *et al*. 1995). Moreover, the latest MWRA effluent monitoring data indicate its contaminant loads to Massachusetts Bay are generally similar to, and often less than, those projected based on the mid-1990s pilot data (Butler *et al*. 1997), although lead, zinc, and tDDT loadings are higher. The recent MWRA data also show cadmium, silver, and mercury loading is as much as 50% lower than projected from the pilot treatment studies even though not all the effluent received full secondary treatment and flows were slightly higher than used for the mid-1990s projections.

Table 3-1. Loading Estimates for MWRA Effluent 1988 through 2005.

Contaminant	EPA[1] 1988 kg/yr	Coates[2] 1995 kg/yr	Butler *et al*. 1997 kg/yr	MWRA[3] Jan 2004 - Jun 2005 kg/yr
Cadmium	697	185	106	66
Chromium	3,517	735	4,031	697
Copper	11,945	5,730	8,184	6,835
Lead	4,961	900	1,074	1,261
Mercury	216	23	24	12
Nickel	8,926	1,650	2,557	1,526
Silver	299	520	310	216
Zinc	34,493	8,880	14,053	17,785
tPCB	50	1	9	3
4-4DDT	5	NA	NA	0.2
tDDT	28	5	0.1	1
PAH	NA	550	457	348
Heptachlor	10	NA	NA	0

1. SEIS
2. Based on Hunt *et al*. (1995)
3. Based on MWRA effluent monitoring data

Combined Sewer Overflows Over the past decade MWRA has also been implementing controls at a number of Combined Sewer Overflows (CSOs) discharging to the harbor. Combined sewer systems serve large parts of Boston, Cambridge, Chelsea, and Somerville. Combined sewer systems were designed to collect sewage and stormwater runoff and transport both to treatment facilities. During heavy rains, overflows from these combined systems discharge a mixture of sewage and storm runoff directly into local waters. As of early 2002, MWRA had completed 13 of the 25 projects proposed under MWRA's 1997 CSO Control Plan. These completed projects included, among others, the upgrading of five CSO treatment facilities (Fox Point, Commercial Point, Cottage Farm, Prison Point, and Somerville Marginal), two sewer separations, the closing of 21 CSO outfalls, the installation of floatable controls, and two hydraulic relief projects. These projects have, on a site-specific basis, decreased CSO discharges, reduced the discharge of floatable materials, or provided improved pathogen kill and dechlorination. Together with major sewer system conveyance improvements related to the Deer Island upgrades, these projects have reduced the quantity of CSO discharges system-wide (albeit with an increase in separate stormwater in some locations) and increased the amount of sewage that reaches treatment facilities during rainy weather. The overall effect of these ongoing improvements has been a decrease in average annual CSO discharge from approximately 3.3 billion gallons in 1988 to an estimated 1.0 billion gallons (MWRA 2006).

Much of the reduction in CSO flow has been to discharges into the freshwater reaches of the Charles River Basin, which can act as a sink for contaminant-laden solids before they reach the harbor itself. Therefore, it is unclear how much of the reduced CSO contaminant loading translates to a direct reduction in loading to Boston Harbor. The reduction tabulated below is loading to Boston Harbor and its tributary rivers, including the Charles, Mystic and Neponset.

MWRA CSO loadings estimates (Table 3-2) were made using the 1988-1992 5-year average flow of 2.5 billion gallons per year; the 2001-2005 estimates are based on a 5-year average of 1.25 billion gallons per year, thus the CSO loadings calculation assumes a 50% reduction in flow between the two 5-year periods. Contaminant concentrations used in the load estimates are from MWRA CSO discharge monitoring. These estimates indicate the CSO improvements have likely greatly reduced the loading of contaminants to Boston Harbor. For example, cadmium and mercury loadings from this source are estimated to have been reduced by more than 84 and 76 percent (6 and 4 fold), respectively. While not documented, reduction in loading of other contaminants associated with stormwater runoff (e.g. PAH) has likely occurred. Less impact on loading is expected for chemicals that are not associated with these discharges (e.g., pesticides and PCBs). Data from sediments near the major CSOs in Dorchester Bay (Lefkovitz et al. 2005) support some decrease in loading over the past decade, likely in response to the CSO system upgrades and from loading decreases from other sources such as the MWRA sewage effluent.

Table 3-2. Comparison of estimated late 1980's metals loading to Boston Harbor from CSOs to loadings of today.

	Cadmium kg/yr	Chromium kg/yr	Copper kg/yr	Lead kg/yr	Mercury kg/yr	Zinc kg/yr
1988-1992	14.2	75.9	569	758	2.6	1753
2001-2005	2.3	55.0	165	302	0.6	609
%reduction	84	28	71	60	76	65
Ratio	6	1	3	3	4	3

Atmospheric loading Atmospheric inputs of metals to Massachusetts Bay and Boston Harbor were updated using the atmospheric flux data published by Golomb *et al*. (1997a). The total loads were estimated by converting the published fluxes derived from data collected between September 1992 and September 1993. The fluxes were multiplied by the area of the harbor (108 km^2 used in Alber and Chan (1994) or Massachusetts Bay (3670 km^2) to estimate the annual atmospheric input (Table 3-3). These data update those of Alber and Chan (1994) who used data covering a shorter sampling period. While the longer data set gave similar loads, lead inputs were lower and copper higher than those reported in Alber and Chan (1994). This could be the result of averaging or the longer collection period.

Updating organic contaminant estimates is difficult since the atmospheric flux of the PAH compounds measured by Golomb *et al*. (1997b) at the two collection stations differed by several orders of magnitude and rendered calculation of a representative average for Massachusetts Bay difficult. If the flux estimates at the Nahant collection site are considered representative of the urbanized Boston Harbor, estimates of pyrene loading (Table 3-3) are two to three times that reported in Alber and Chan (1994), while benzo(a)pyrene loading is similar.

If it is assumed the atmospheric inputs have not changed since these flux data were obtained, the annual atmospheric metals load to Massachusetts Bay is considerably greater than from the outfall (compare Table 3-2 to Table 3-3). For Boston Harbor, atmospheric inputs for zinc, lead, and copper are within a factor of two of the most recent loading estimates for CSOs. In contrast, atmospheric inputs of cadmium and chromium appear to be much higher than the most recent estimate of CSO loads.

Table 3-3. Estimates of atmospheric input of contaminants to Massachusetts Bay and to Boston Harbor based on flux estimates of Golomb et al. (1997a; 1997b)

Metal	Flux ug/m2/yr	Load to Mass Bay kg/yr	Load to Boston Harbor kg/yr
Cadmium	405	1,486	44
Chromium	2,700	9,909	292
Copper	3,500	12,845	378
Nickel	7,200	26,424	778
Lead	2,700	9,909	292
Zinc	7,800	28,626	842
Pyrene	98	NA	11
Benzo(a)pyrene	30	NA	3

Stormwater There has never been a comprehensive review of total stormwater contaminant loadings into the harbor/Bays system. MWRA's CSO Facilities Plan (MWRA, 1997b) provides comparative CSO and storm-water flows to Boston's inner harbor and Dorchester Bays, and the rivers and tributaries which empty into this region. This report estimated that when CSO flows had dropped to current levels, approximately 1 billion gallons per year, the annual stormwater flows would be over 12 billion gallons. The USGS (Breuault *et al*. 2002) measured concentrations of metals in various types of stormwater entering the Charles River. Their data indicate that the concentrations of metals in stormwater are quite similar to concentrations measured by MWRA in its CSO discharges. Using this information, stormwater loads are conservatively estimated to be at least ten times the CSO loads.

The loadings of the five metals that have data for all four sources above are shown in Table 3-4. It must be stressed that loadings into the harbor/Bay system from other potentially important sources such as stormwater discharge from areas outside of Boston Harbor (and even stormwater flows from Boston's outer harbor regions like Hull and Hingham) and other NPDES permitted discharges are not included in this table. Also missing are minor sources like groundwater intrusion and the highly diluted contaminants from river discharges north of Boston (e.g Merrimack River). Even without the inclusion of these additional sources the MWRA loading contributions (CSO plus effluent) range from only a few percent for cadmium and chromium to approximately 32-34% for copper and zinc. The comparative loadings of these metals are likely representative of many contaminants which are ubiquitously found in the environment.

Table 3-4. Selected loadings to the Boston Harbor/ Massachusetts Bay system.

	MWRA effluent	CSOs	Atmospheric deposition	Storm water	Total	% MWRA Sources
Cadmium (kg/yr)	66	2	1,530	23	1,621	4
Chromium (kg/yr)	697	55	10,201	550	11,503	7
Copper (kg/yr)	6,835	165	13,223	1,650	21,873	32
Lead (kg/yr)	1,261	302	10,201	3,020	14,784	11
Zinc (kg/yr)	17,785	609	29,468	6,090	53,952	34

The loadings estimated in this report do not reflect very recent decreases in wastewater loadings from continuing secondary treatment process improvements at the Deer Island Treatment Plant. Moreover, planned CSO projects such as the storage and pump-back facilities in South Boston and the inner harbor will reduce CSO flows and contaminant loads even further. However, it is apparent from the discussion above that further major decline in contaminant loadings can only come from reductions in sources out of the jurisdiction of the MWRA.

Generally the reduction of contaminant inputs to Boston Harbor, as evidenced in the MWRA effluent and CSO data, should result in improved sediment quality and reductions of contaminant levels in biological receptors in the harbor over time. Moreover, the recent effluent data support the predictions of Coates (1995) of minor changes to sediment quality in Massachusetts Bay over long time periods. Note that the substantially lower silver and cadmium loads measured recently in the effluent increase the predicted time of detectable changes made in 1995 for sediments within 2 km of the outfall from approximately 1.5 and 1 year, respectively, to more than three years. Changes to sediment quality in Boston Harbor and Massachusetts Bay are explored further in Section 4.

4 CONTAMINANTS IN BOSTON HARBOR AND MASSACHUSETTS BAY SEDIMENTS

This section discusses the levels and patterns of sewage tracers and selected contaminants in surface sediments of Boston Harbor and Massachusetts Bay both historic and present. Temporal trends in these parameters since the onset of the MWRA facilities improvements are considered. Changes in the status of sediment quality as determined by comparison to Sediment Quality Guidelines (SQG) (Long *et al*. 1995; http://response.restoration.noaa.gov/book_shelf/121_sedi_qual_guide.pdf) are also presented[1].

4.1 Sewage tracers

Historically, anthropogenic contaminants entered Boston Harbor via sewage treatment plant effluent, direct industrial discharges, Combined Sewage Overflows, stormwater runoff, and atmospheric deposition. The signature of contaminants from these sources is readily captured in the sediments. Thus, understanding the response of sewage tracers in sediments to the harbor cleanup provides a means of evaluating how the system reacted when the intensity of sewage sources was reduced in the 1990s. One of the most commonly used tracers of sewage derived sources in marine systems is *Clostridium perfringens,* an anaerobic bacterium common to the intestinal tract of mammals. The changes in the level and distribution of the *C. perfringens* described in this section are used to set the stage for the discussion of contaminants in Section 4.2. Because the distribution of *C. perfringens* has been found to vary with the amount of fine grained sediments (Bothner *et al*. 1998), the concentrations are normalized to the percent fines in the sediments. This provides a more conservative means of interpreting the observed trends.

In the early 1990's, *C. perfringens* levels in Boston Harbor were high and variable (Figure 4-1). The highest values were found in the outer Harbor in the vicinity of the sludge discharge sites. With the cessation of sludge discharge in late 1991, *C. perfringens* levels dropped substantially in this region (Figure 4-1). Following subsequent facility upgrades (i.e. enlarged Deer Island primary treatment facility in 1995, first batteries of secondary treatment at Deer Island in 1997 and 1998, and in July 1998 the transfer of flow from the Nut Island treatment facility in the southern harbor to Deer Island) *C. perfringens* concentrations and variability further decreased (Figure 4-1). Overall, there was a statistically significant harbor-wide decrease in normalized abundances of *C. perfringens* from 1991 to 2004 (Maciolek *et al.* 2006). Further, decreasing trends were observed at all harbor stations, except T04, which is located in Savin Hill Cove and is considered to be a focus area for accumulation of sediment, and CO19, which is located in the inner harbor (Maciolek *et al.* 2006). There have been no substantial changes to *C. perfringens* abundances (normalized to percent fines) in Boston Harbor following diversion of effluent discharge from the harbor to the offshore outfall in September 2000, although the data suggest a continuing slow decline in all parts of the Harbor through 2004 (Figure 4-1).

In contrast to Boston Harbor, *C. perfringens* abundances (normalized to percent fines) in Massachusetts Bay ranged from 20 to ~230 cfu/g dw/% fines in the early 1990's through 1998 (Figure 4-2). The higher levels were similar to those measured in Boston Harbor just prior to diversion of the outfall into the Bay. Abundances in Massachusetts Bay typically decreased with distance from the harbor, with stations located more than 20 km from Deer Island Light in the mouth of the Harbor (which is close to the former outfalls from the treatment plant) displaying abundances below 50 cfu/g dw/% fines (Figure 4-2).

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[1] Maps showing the station locations are provided in Appendix A.

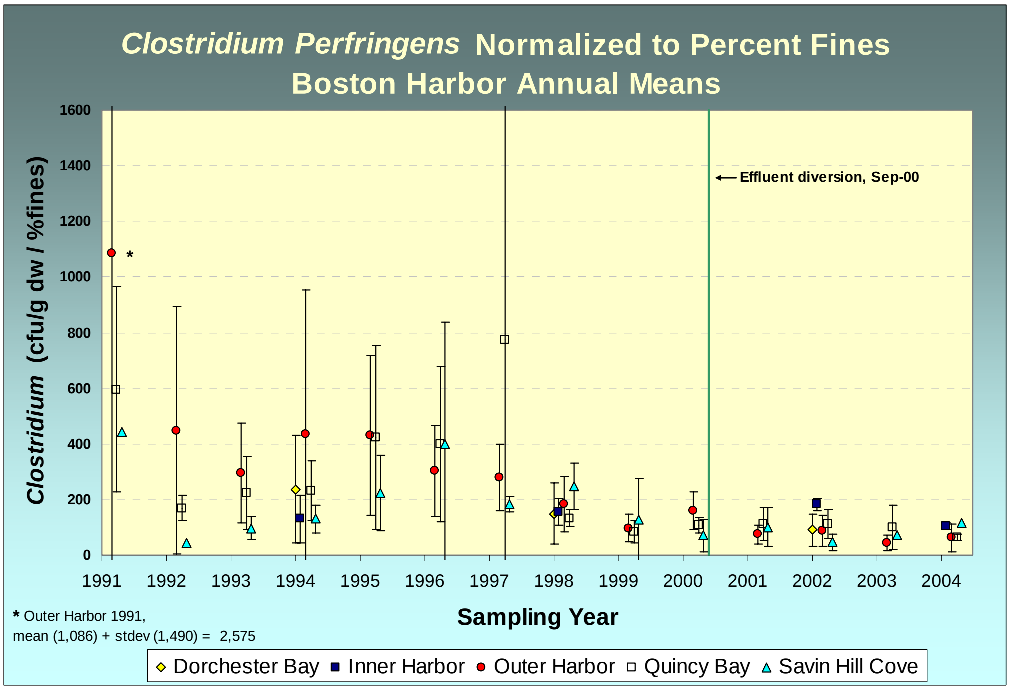

Figure 4-1. Yearly mean abundances of Clostridium perfringens, normalized to percent fines, in Boston Harbor from 1991 to 2004; August surveys only. Error bars represent one standard deviation. Dorchester Bay includes stations DB01, DB03, DB06, DB10, and DB12; inner harbor includes station CO19; Outer Harbor includes stations T01, T02, T03, T05A, and T08; Quincy Bay includes stations T06 and T07; and Savin Hill Cove includes station T04.

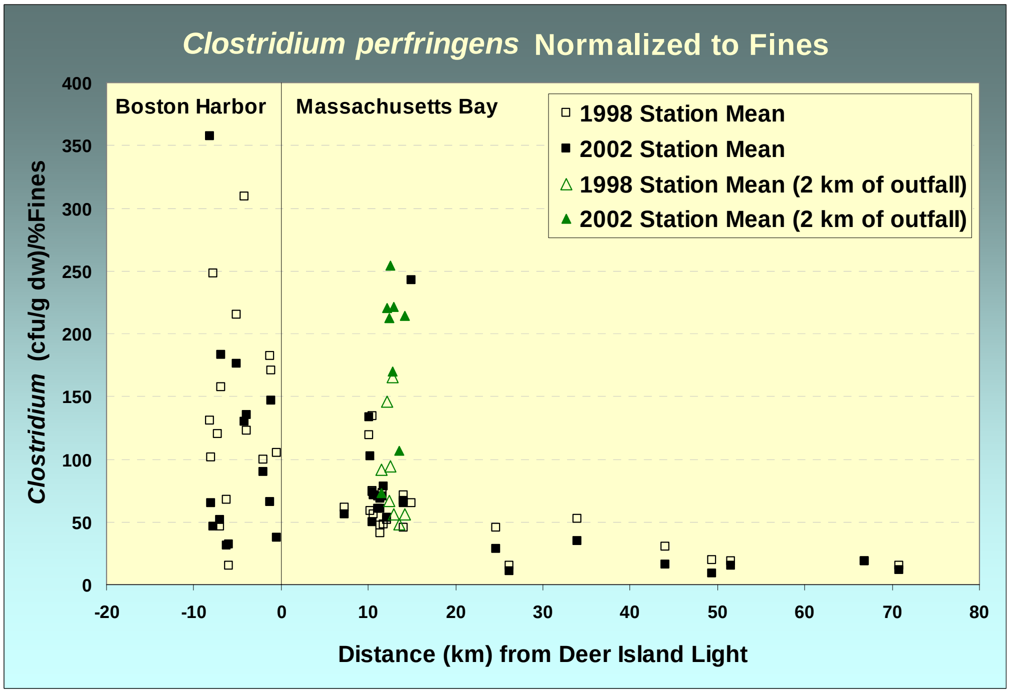

Figure 4-2. Station mean abundances of *Clostridium perfringens*, normalized to percent fines, as a function of distance from Deer Island Light; August surveys only. The 1998–2000 station mean values are the average of all replicates from 1998 to 2000, by station. The 2001–2003 station mean values are the average of all replicates from 2001 to 2003, by station.

Prior to effluent diversion, *C. perfringens* abundance in the transition area between the Outer Harbor and outfall location in Massachusetts Bay was generally higher and more variable compared to areas further offshore in Massachusetts and Cape Cod Bays (Figure 4-3). Since the diversion, this transition area has shown a slight decrease (Figure 4-3) and in 2004 approached the low abundances observed in the Farfield.

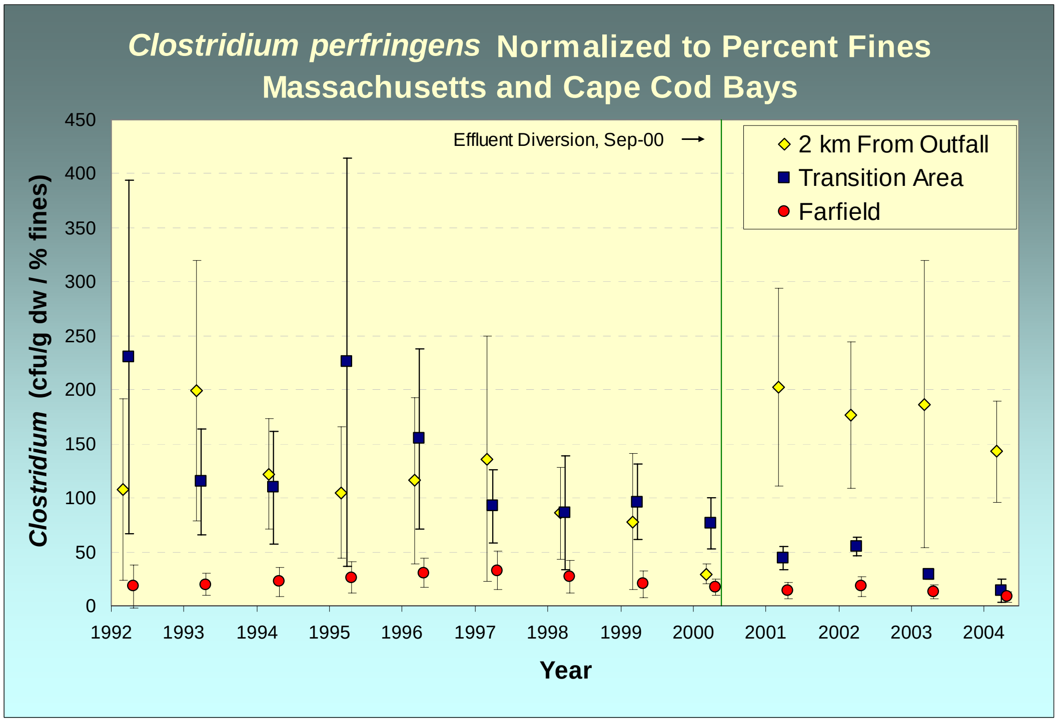

Figure 4-3. Yearly mean abundances of *Clostridium perfringens*, normalized to percent fines, in Massachusetts and Cape Cod Bays from 1992 to 2004; August surveys only. Error bars represent one standard deviation.

The post-diversion abundances of *C. perfringens* (normalized to percent fines) have not changed substantially at stations located more than 20 km from the offshore outfall. In contrast, there is clear localized, but modest, post-diversion increase in *C. perfringens* abundances (normalized to percent fines) at stations located within 2 km from the outfall (Figure 4-3). The increase at stations within 2 km of the outfall is comparable to *C. perfringens* levels observed in Boston Harbor between 1998 and 2000, when the harbor discharge was subjected to substantial secondary treatment. As seen in Figure 4-3, *Clostridium* abundance decreased in both the transition area and within 2 km of the outfall during the 1990s. The discharge signature seen within 2 km of the outfall increases only to levels seen at these locations in the early 1990s, when the locations were some 15 km away from the then inadequately treated plant discharge.

The *C. perfringens* data clearly trace the major improvements made in sewage treatment and discharge in Boston Harbor since 1991 and demonstrate that treatment plant effluent has less effect on sediments in Boston Harbor and in the transition area than it did before the Boston Harbor Project began. The data also indicate a clear signature of effluent discharge in the sediments near the outfall. The latter conclusion contrasts with those drawn by Bothner and Butman (2005) based on data from a single station that there was no significant increase in *C. perfringens* (and metals such as silver) at the 95% confidence level. The contrast is primarily related to spatial coverage provided in the MWRA program where sampling at 23 stations in the nearfield (western Massachusetts Bay) has enabled the program to capture the regional spatial variability and identify a fairly subtle effluent signature.

Further evidence of the limited field of influence from the offshore discharge is provided by sediment trap results presented in Bothner and Butman (2005). The USGS program has used sediment traps to collect particles falling through the water column at a location about 1 km south of the MWRA outfall since 1992. Because the rate of sediment collection depends on factors such as trap design, current speed, sediment fall velocity, as well as the frequency and magnitude of sediment resuspension, re-deployment of traps of the same trap design at a consistent location enabled comparison of concentrations of sewage tracers in trapped particles before and after the startup of the offshore outfall. Data from sediment traps placed as high as possible above the sea floor and a few meters below the seasonal pycnocline (~15m depth) minimized the entry of resuspended sediments into the traps and allowed the USGS to maximize the ability to detect recently discharged sewage particles. The USGS data shows that of the parameters measured, only *C. perfringens* and silver had a statistically higher concentration (significant increase >95 % level of confidence) in post-outfall samples. Concentrations of *C. perfringens* increased from a pre-diversion range of 1000 to 16,000 spores/g of sediment to a maximum of 73,000 spores/gram in the post-diversion data (Figure 4-4). Silver levels after discharge started were approximately twice those measured before the transfer (Bothner *et al.* in Bothner and Butman 2005). Bothner and Butman (2005) also calculate that the observed increase in silver concentrations represents a sewage contribution of about 2% in the trapped material. They conclude this is in reasonable agreement with modeled sewage dilution of about 1% at the trap location.

The temporal patterns in *C. perfringens* concentrations in the sediments collected within 2 km of the outfall (Figure 4-3) and sediment trap data (Figure 4-4) are remarkably similar. Together these data provide complementary evidence regarding the strength of the outfall signature in Massachusetts Bay and increase the confidence in the ability of the monitoring program to document the transport and fate of the effluent related contaminants discharged in Massachusetts Bay.

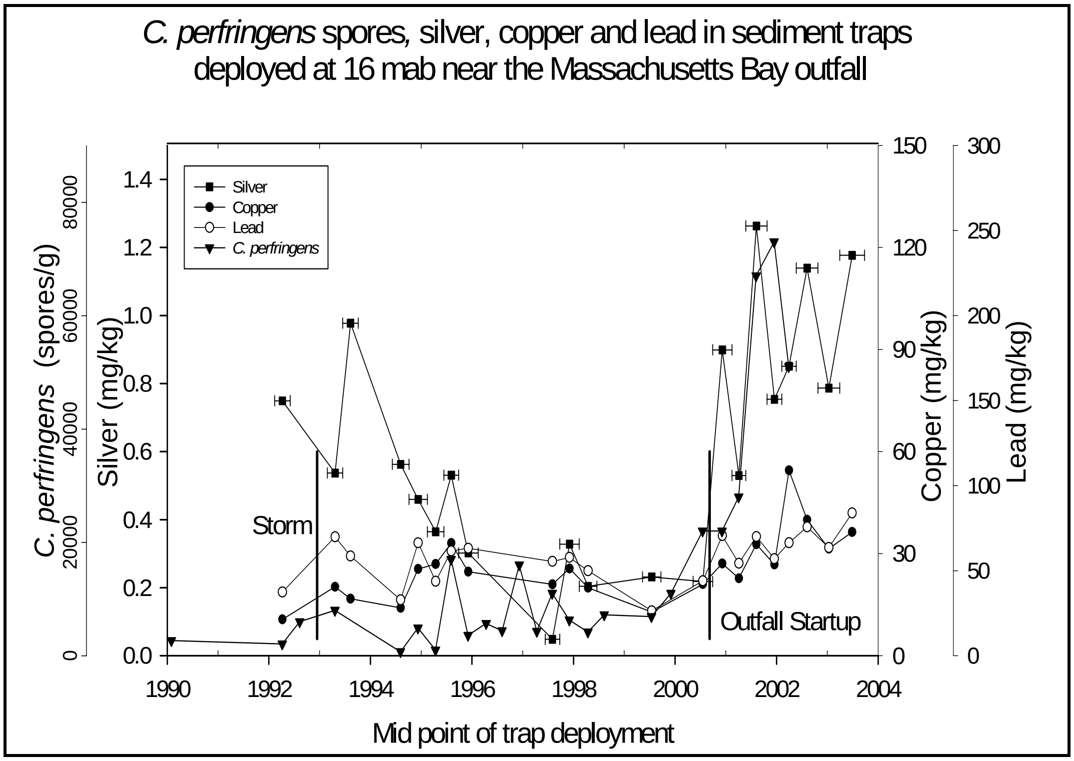

Figure 4-4. Trend in *C. perfringens*, silver, lead, and copper in trapped sediment from the USGS mooring in Massachusetts Bay (from Bothner and Butman 2005).

4.2 Chemicals

4.2.1 Regional Perspectives

Recent data for contaminant chemicals in the surface sediments (upper 2 cm) of Boston Harbor and Massachusetts Bay show large concentration ranges (Table 4-1). The range is greatest for the persistent organic chemicals and less for the metals. Of the organic chemicals, tPAH displays an 800 fold difference between the stations with the highest and lowest concentration. The ratio is 173 or lower for the other contaminants. Since, as is noted below, contaminants tend to have highest concentrations in the harbor and lower concentrations in offshore sediments, this ratio suggests PAH has a stronger inshore to offshore gradient than the other contaminants.

From a system-wide spatial perspective, contaminant levels are generally lowest in offshore Massachusetts and Cape Cod Bays and highest in the western areas of Boston Harbor (Figure 4-5, Figure 4-6, Figure 4-7, Figure 4-8, Figure 4-9, and Figure 4-10). Moreover, within major subregions (e.g. Dorchester Bay, outer Boston Harbor, nearfield area of the outfall), variability is high which often reflects differences in bulk sediment characteristics such as grain-size distribution and total organic carbon content. The variability caused by these factors is particularly evident in the stations located near the MWRA outfall in Massachusetts Bay, an area known to be highly heterogeneous and dynamic with respect to sediment properties. Variability in the Dorchester Bay area is also related to the physical properties of the sediments but is influenced by the large and variable inputs from CSOs and stormwater runoff discharges located along its shores.

Table 4-1. Range in contaminants concentration in surface sediments of Boston Harbor and Massachusetts Bay measured in 2002 under the MWRA HOM program.

Contaminant (unit)	**Measurable Concentration**		**Ratio (H/L)**
	Lowest	**Highest**	
tPAH (ng/g dw)	112	93,200	832
tPCB (ng/g dw)	1.18	204	173
tDDT (ng/g dw)	1.8	57.3	32
Lead (μ/g dw)	25.2	419	17
Mercury (μ/g dw)	0.041	1.09	27
Cadmium (μ/g dw)	0.0094	1.18	125
Copper (μ/g dw)	6.25	203	32

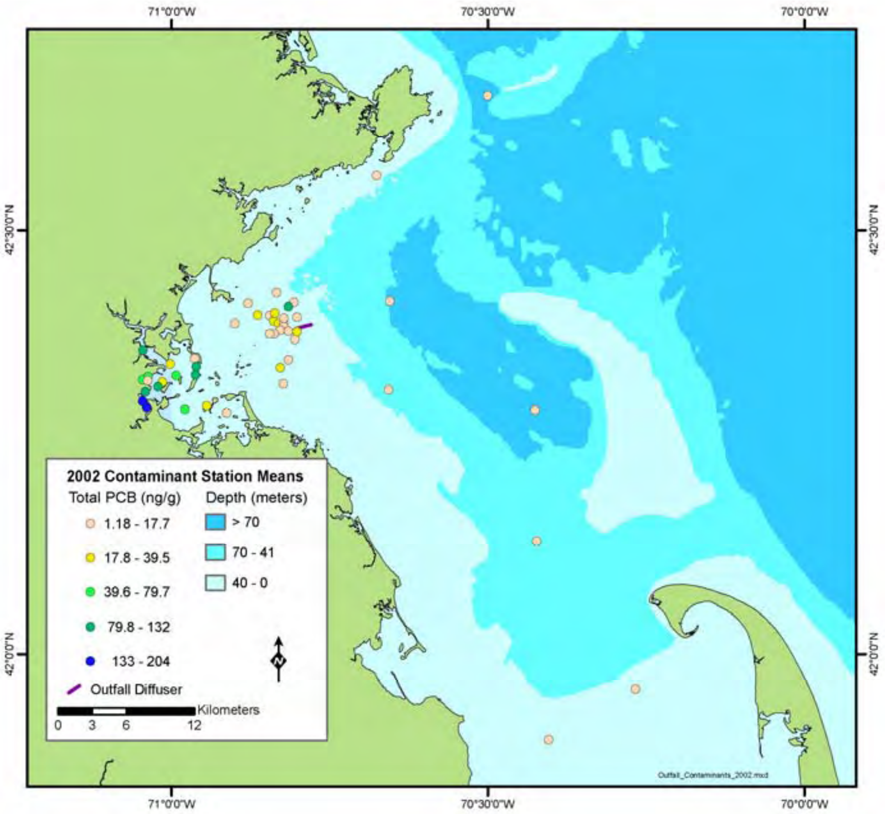

Figure 4-5. Sediment contaminant distribution map – tPCB 2002.

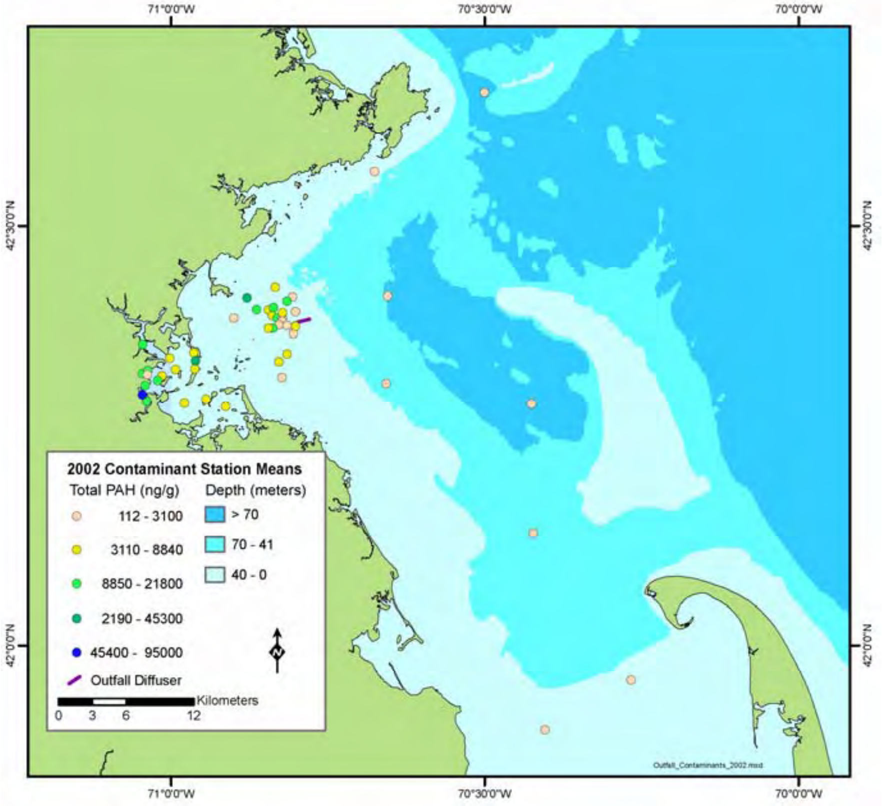

Figure 4-6. Sediment contaminant distribution map – tPAH 2002.

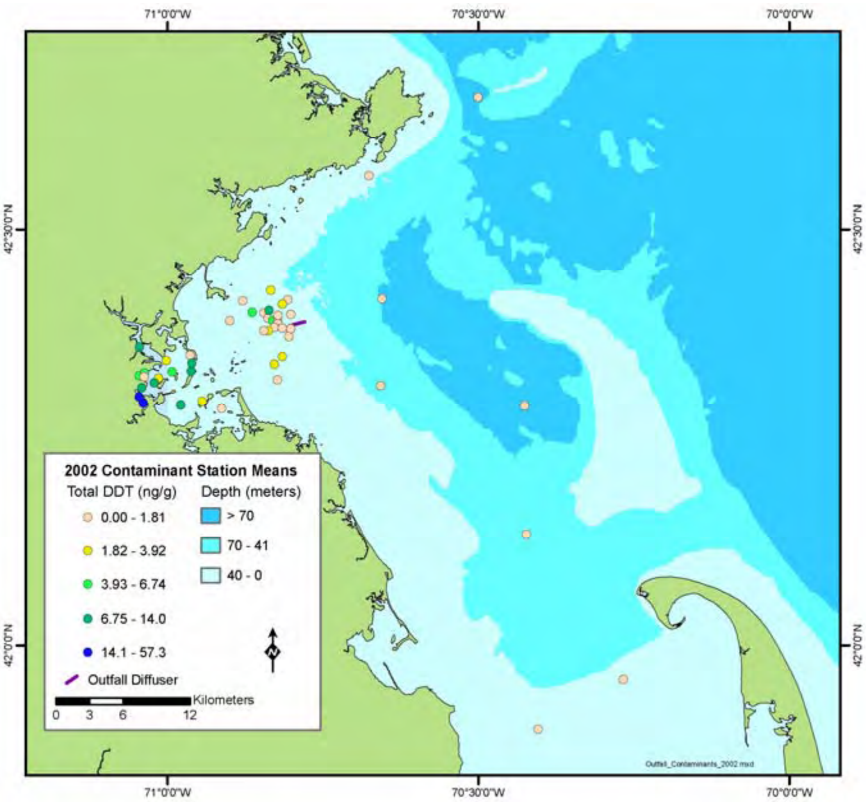

Figure 4-7. Sediment contaminant distribution map – tDDT 2002.

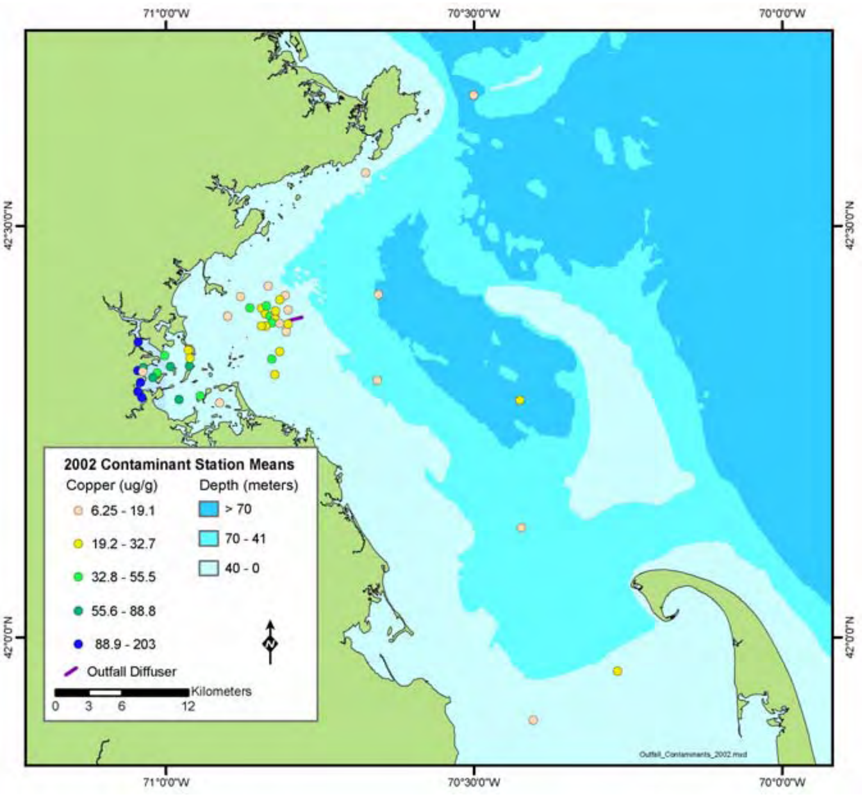

Figure 4-8. Sediment contaminant distribution map – Copper 2002.

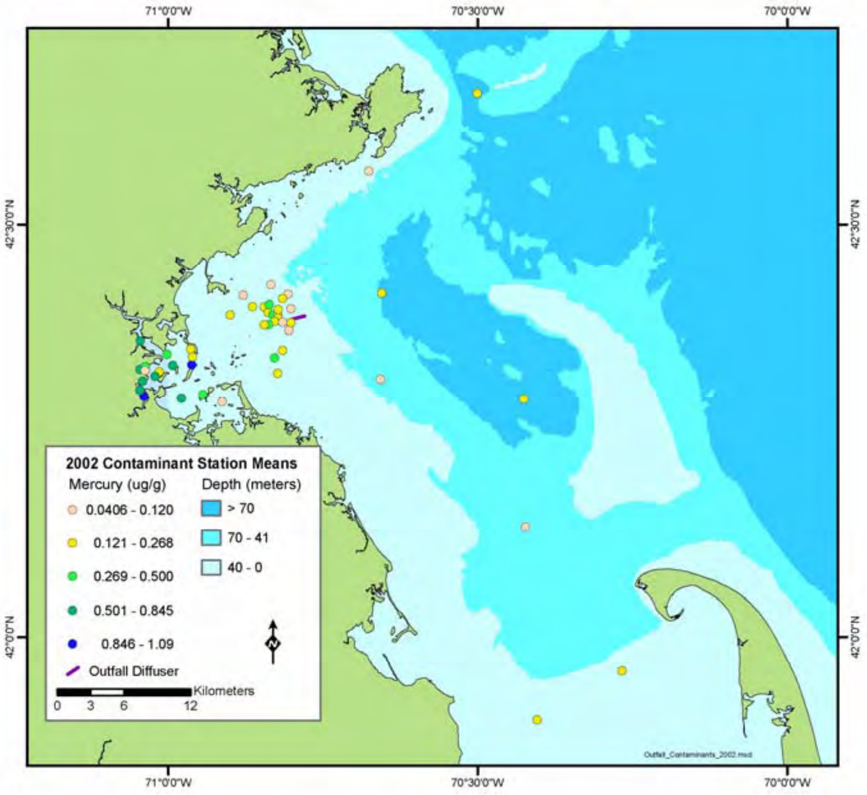

Figure 4-9. Sediment contaminant distribution map – Mercury 2002.

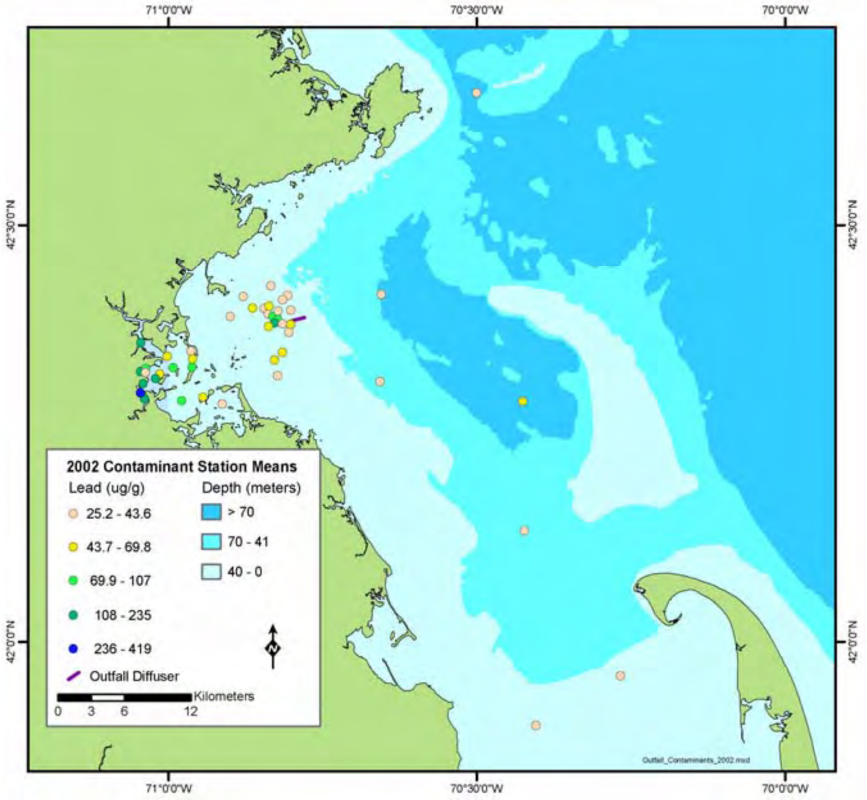

Figure 4-10. Sediment contaminant distribution map – Lead 2002.

4.2.2 Boston Harbor Trends: 1990 to 2004

As described in Section 1.1 and Section 3, contaminant concentrations and distributions in surface sediments of Boston Harbor and Massachusetts Bay are the result of more than a century of anthropogenic input. Since both regulatory actions (for example, the removal of lead from gasoline and banning of PCBs and some pesticides) and the implementation of the Boston Harbor Project have substantially reduced the loading of contaminants to this system over the past 15 years (Section 3), it is instructive to examine temporal plots at stations that have been consistently sampled and analyzed over this time frame to address whether the reductions are manifest in the sediment of the harbor, and if so where. To address this question, a series of plots were developed for selected areas from the harbor and Massachusetts Bay. Appendix B: TempOral tRends of contaminants in surface sediments of Boston harborincludes all of the figures developed; representative data are discussed below.

The data in these figures were collected using comparable field and laboratory methods. The data are discussed in detail in the MWRA Annual Harbor Benthic reports (see for instance Maciolek *et al*., 2005), Annual Outfall Benthic reports (see for example Maciolek *et al*., 2004), and the periodically produced MWRA CSO reports (see for example Lefkovitz *et al*., 2005). Each of these reports describes sediment results for a set of stations within its study domain. For the purposes of this discussion, the experimental design for each study was reviewed to determine those stations that had a consistent suite of parameters measured over the period of interest (1990-2004). MWRA has sampled 19 stations in the Harbor since 1990. Appendix C lists the stations and parameters by year. Several of the stations have been sampled every year for bulk sediment properties and sewage tracers; contaminant analyses were performed periodically on the stations considered most promising for evidence of a response to the cleanup.

Only Station T04, located in the Fox Point area (Figure 4-11), was sampled in each of the five years contaminant analysis was conducted (1990, 1994, 1997, 1998, 2002). However, only a subset of the entire suite of parameters measured by the MWRA over this period was measured in 1990, which limits the ability to comprehensively examine the data for trends. This subset of parameters includes TOC, %Fines, tPAH (24 compound total), tLAB, copper, mercury, lead, and cadmium. For this discussion, the yearly mean and standard deviation of representative parameters for each station was calculated and graphed. Examination of the information in Appendix C also shows that only Harbor stations T01, T02, T04, T08 and CO19 were sampled in 1994, 1998, and 2002 for the full suite of MWRA monitored parameters. Station CO19 was also sampled in 2004. Similarly, five stations (DB01, DB03, DB06, DB10, and DB12) were sampled in Dorchester Bay in 1990, 1994, 1998, and 2002. Thus, there are ten stations sampled by MWRA at four year intervals (T01, T02, T04, T08, CO19, DB01, DB03, DB06, DB10, and DB12). These ten stations provide the key stations from which contaminant trends across Boston Harbor can be evaluated.

In contrast to the contaminants, bulk sediment properties such as TOC, grain-size distribution, and selected tracers of sewage have been sampled every year since 1991, with the exception of T05A in August 1992. Samples for sediment properties were collected and analyzed twice annually between August 1992 and August 2002 and annually in August beginning in 2003 at stations: T01, T02, T03, T04, T05, T06, T07, and T08. This more highly resolved time series is first examined to set the stage for investigating trends in the contaminants data. Figure 4-12 shows the year to year changes in the percent fines in sediments from Station T04. These data suggest that the sediments at this station have undergone a general increase in the fraction of fine grained sediment (sediment grains less than 63 microns) over a fifteen year period of record. The contribution of fine sediments in the early 1990's was variable in the 70 to 80 percent range. This fraction increased systematically to over 95% by 1997 then decreased abruptly to ~78 percent in 1998. Note that the variability in the triplicate samples from this station also increased dramatically in 1998. This decrease was followed by a period of relatively stable fine grained sediment fraction at ~80 percent (1998-2000) and a sharp increase in the contribution of fine sediment to about 92 percent in 2001. The contribution of fine sediments has been relatively stable at ~92 percent fines since then.

An abbreviated grain size time series is included as Figure 4-13 to set the stage for the presentation of chemical data. When only data for the years that chemical contaminants were measured is graphed, there is an impression that the system incurred a spike in coarse grained material in 1998 but provides no information on when the sediment at this location rebounded to more than 90 percent fines. This observation when considered with similar observations for the total organic carbon below, suggests the temporal responses in the contaminant data could be confounded by the apparent dramatic, short-term change in bulk sediment properties in 1998.

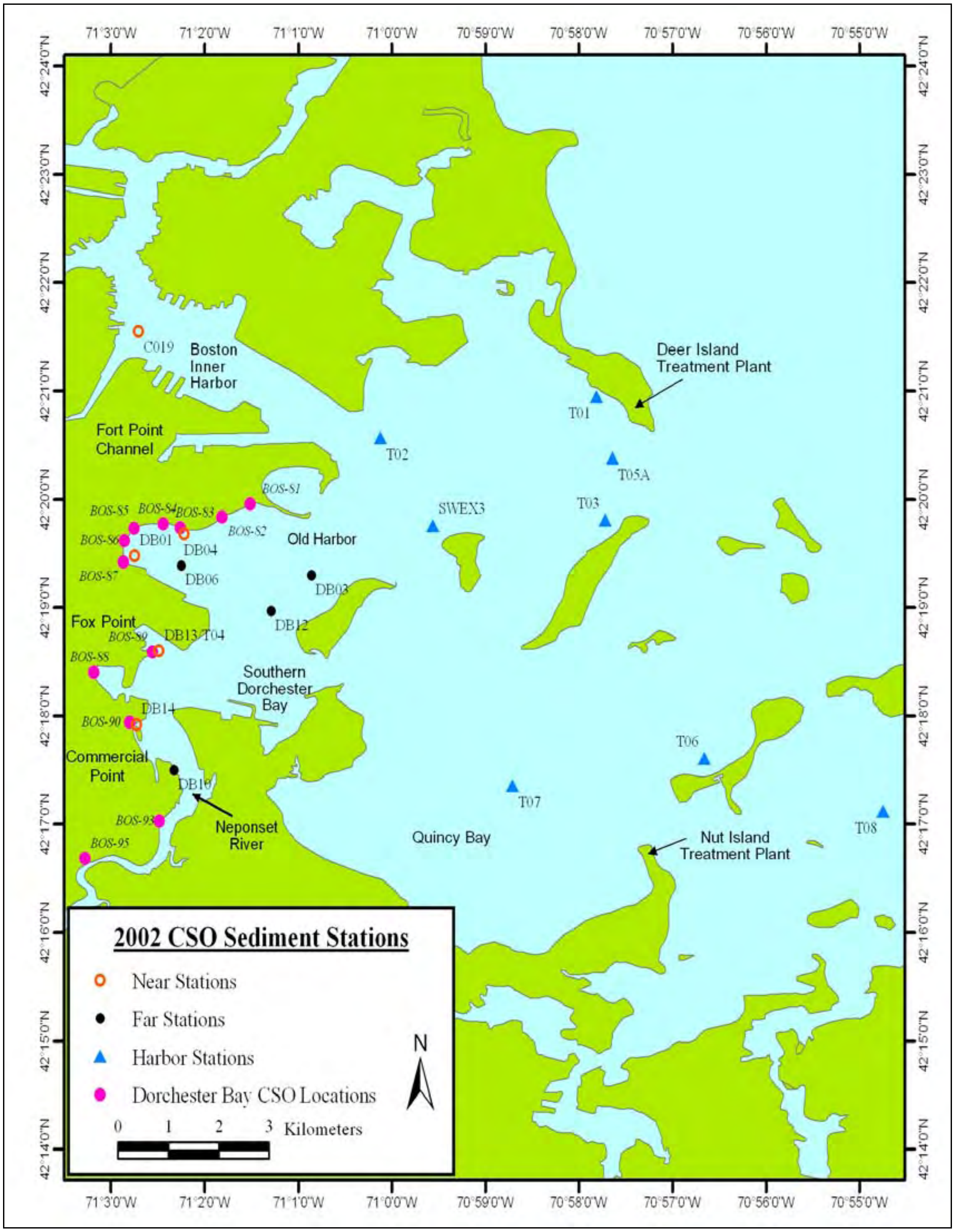

Figure 4-11. Location of stations sampled in Boston Harbor from 1990 to 2004.

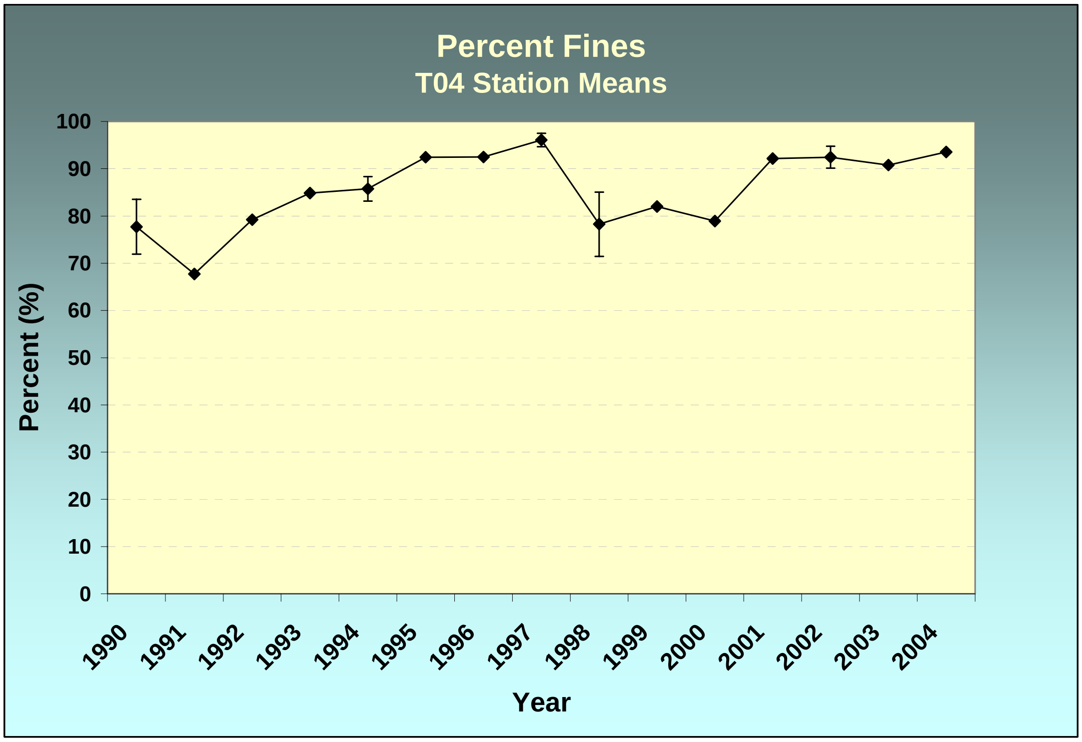

Figure 4-12. Annual variability in sediment grain size composition at Station T04, the station with the longest and most consistent sampling series from Boston Harbor.

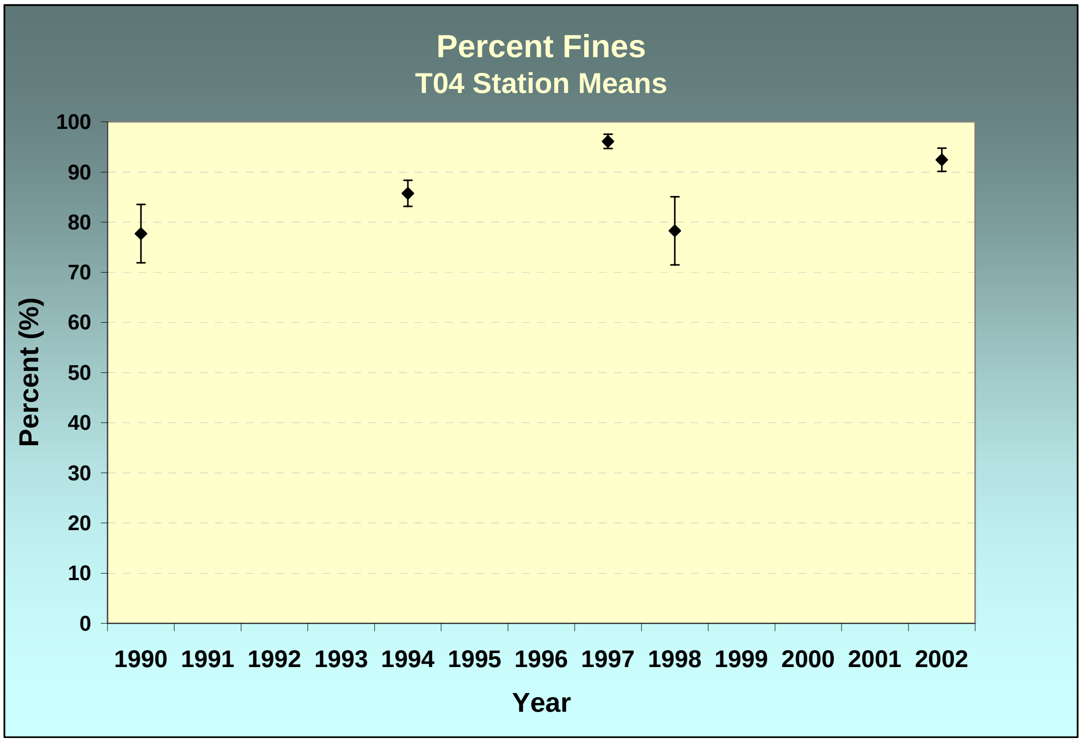

Figure 4-13. Variability in sediment grain size composition at Station T04 for the years chemical contaminants were collected.

The year to year pattern in sediment TOC (Figure 4-14) at Station T04 is slightly different from that of the grain size. These data suggest TOC decreased slightly from 1990 to 1994. A sharp increase from three to five percent appeared in 1995, followed by a consistent decrease through 1997. The station displayed an increase to at least seven percent TOC (although highly variable) in 1998, followed by a relatively sharp decrease through 2000 to levels observed in 1997. Since 2000 the TOC appears to have stabilized between 4.5 and 5 percent, although the 2003 and 2004 data suggest a slight increase after 2002, which had slightly lower TOC than in 2001. The slight dip in 2002 may have been due to the lowest spring runoff and stream flow recorded over the period of MWRA has monitored the harbor. As suggested for grain size, graphically displaying data for only five of these years (Figure 4-15) does not convey the dynamic nature of the sediment composition in this area, which is known to be affected by nearby CSO discharge (Lefkovitz *et a1*. 1999) and is considered to be a focus area for accumulation of sediment and contaminants entering Boston Harbor (Wallace *et al*. 1991; Stolzenbach and Adams 1998).

The contaminant data for T04 does not show a consistent trend among the variables. For example, the tPAH as calculated from the 24 common compounds in the data set (24PAH) is relatively constant at 10,000 to 15,0000 ng/g dry weight, except in 1998 when it jumped to 60,000 ng/g dry weight and became highly variable (Figure 4-16). This increase has been attributed to several potential causes (Lefkovitz *et al*. 2005) including a major storm and runoff event in June of 1998 and an unusually high density of the polychaete *Capitella capitata* (Maciolek *et al*. 2005) that may have influenced sediment retention or burial through biogeochemical and advective processes. During this same period, cadmium shows a variable but significant decrease (2.0 to 0.5 µg/g dw) between 1990 and 2002, with a spike in 1998 (Figure 4-17), whereas silver displayed a systematic decline from 5.6 µg/g dw in 1990 to 2.6 µg/g dw in 2002 (Figure 4-18). The other metals measured through time at this location do not display the dramatic decrease shown by cadmium; although slightly lower levels are observed when 1990 data are compared with 2002 data (see Appendix B). Moreover, metals in surface sediments from the Savin Hill subtidal area in 1986 (Wallace *et al*. 1991) were roughly equivalent to those reported by MWRA in 1990 (e.g., copper: 184 µg/g dw; lead: 230 µg/g dw; cadmium: 2.2 µg/g dw). The trend in tLAB levels in the sediment from T04 (Appendix B) was similar to the cadmium trend and not at all like the 24PAH trend.

Given the dynamic nature of the area represented by Station T04, it is difficult to identify a systematic change in the Harbor sediments in response to the cleanup, although some of the data suggest changes towards lower concentrations in this period of record.

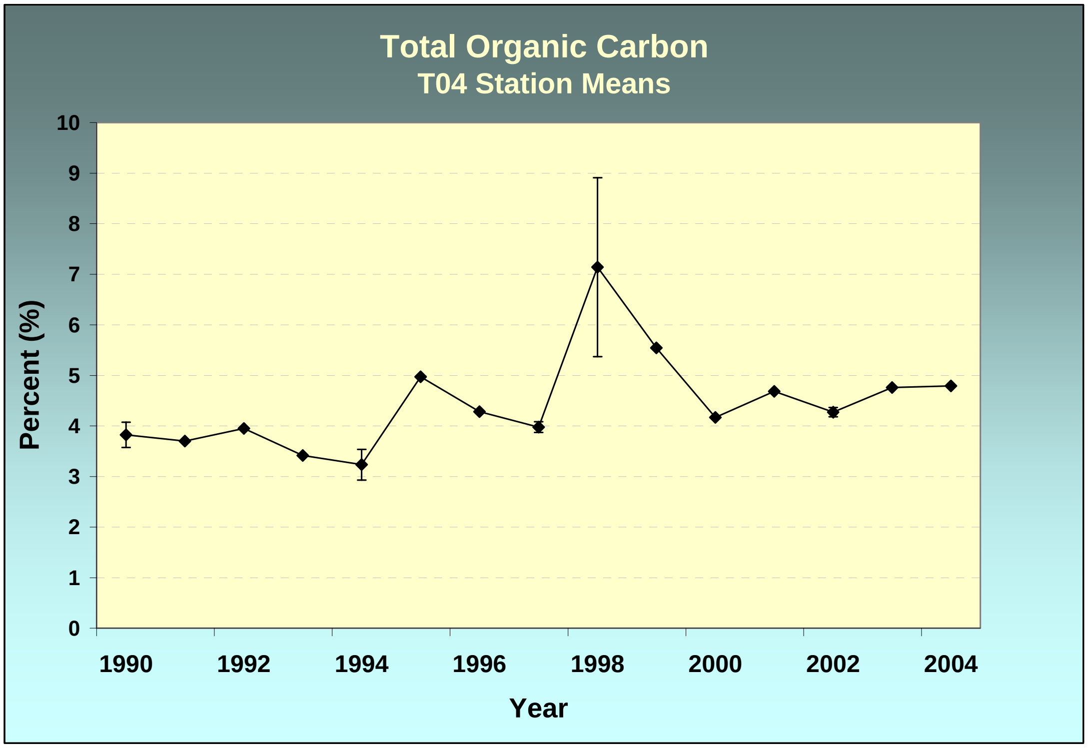

Figure 4-14. Annual variability in total organic carbon concentration at Station T04, the station with the longest and most consistent sampling series from Boston Harbor.

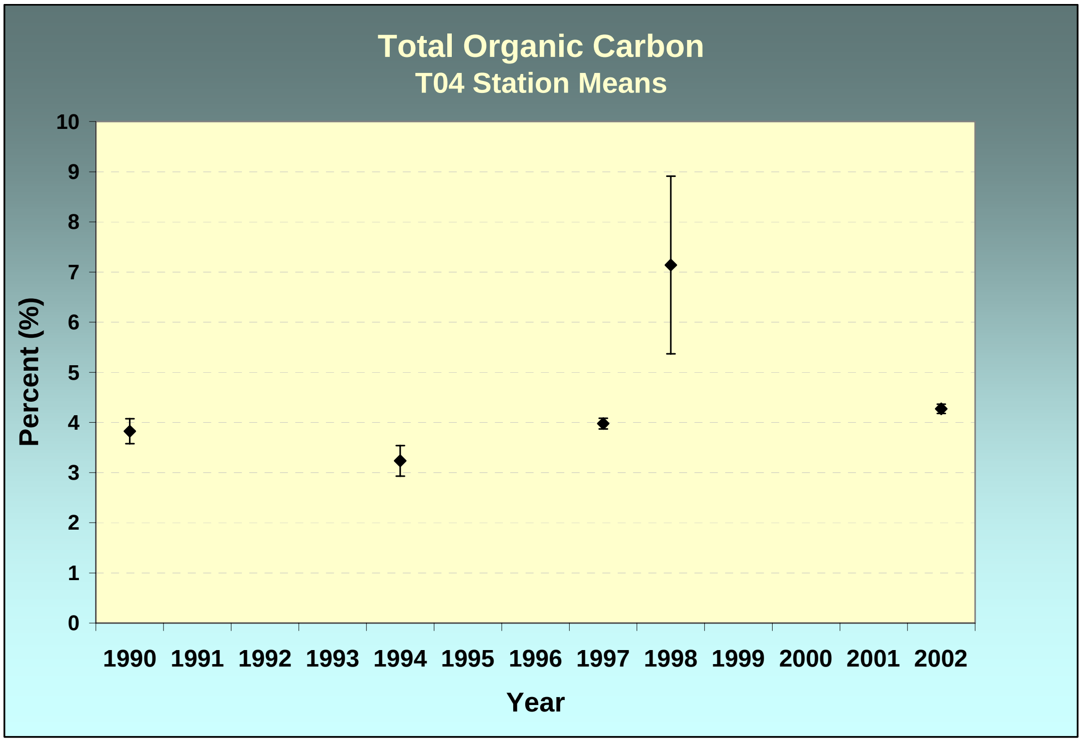

Figure 4-15. Variability in sediment total organic carbon composition at Station T04 for the years chemical contaminants were collected.

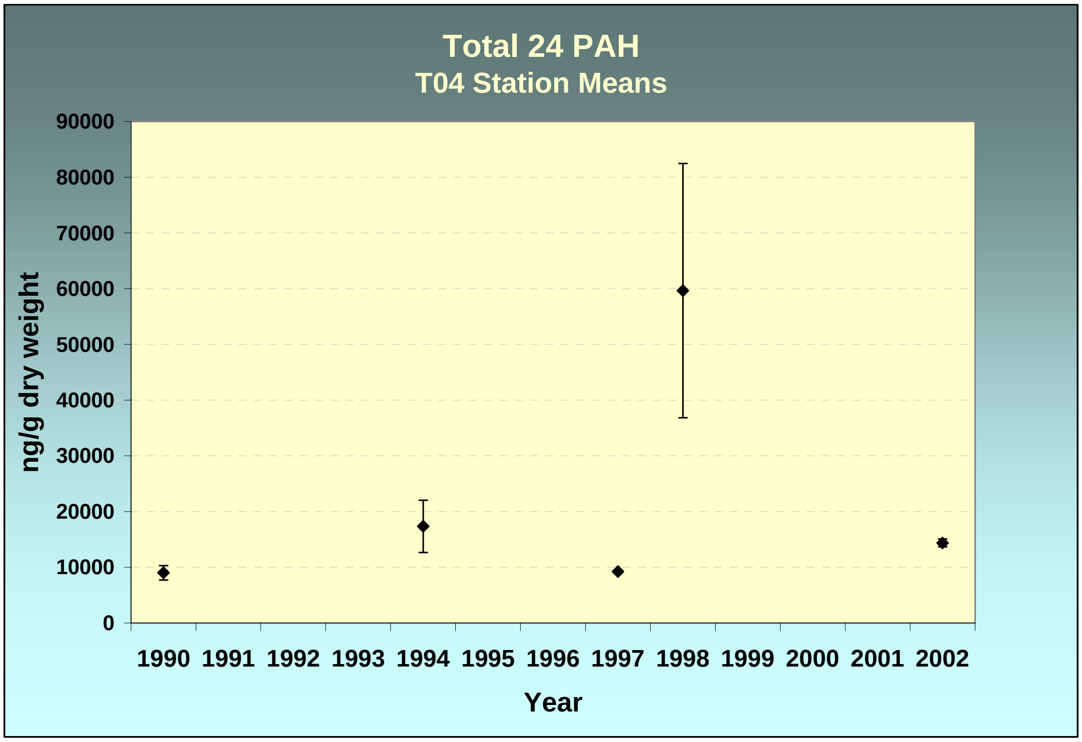

Figure 4-16. The tPAH (24 PAH) concentrations in surface sediments at Station T04 were relatively stable from 1990 to 2002.

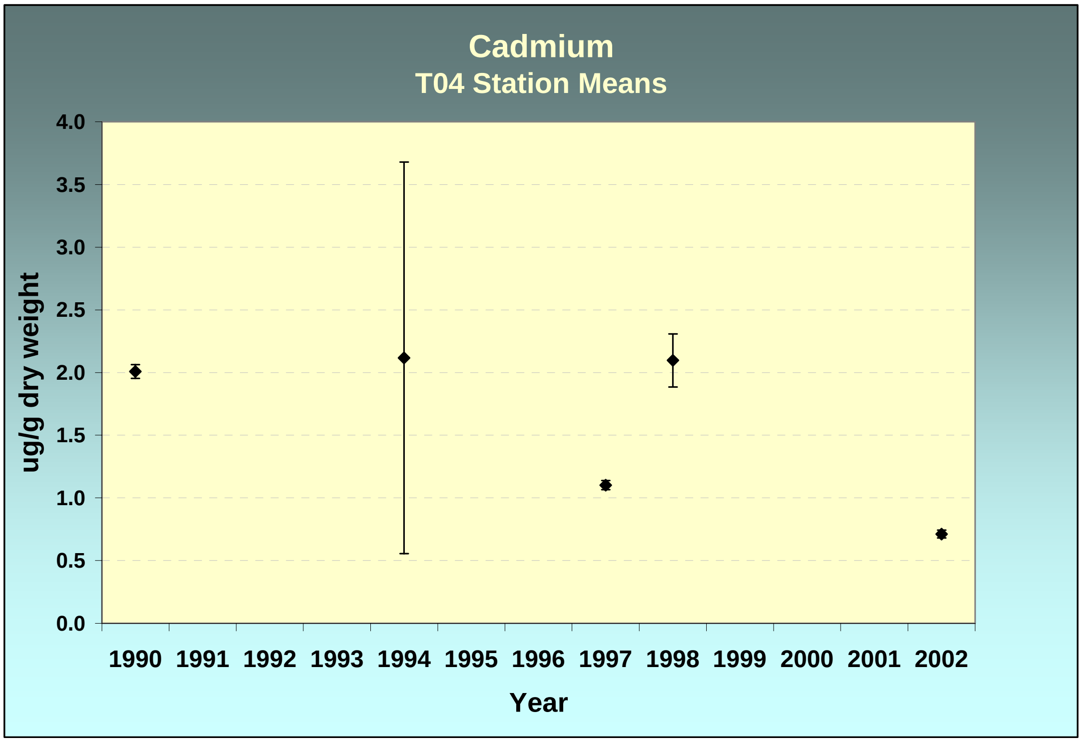

Figure 4-17. Cadmium concentrations in surface sediments at Station T04 appear to decrease since 1994.

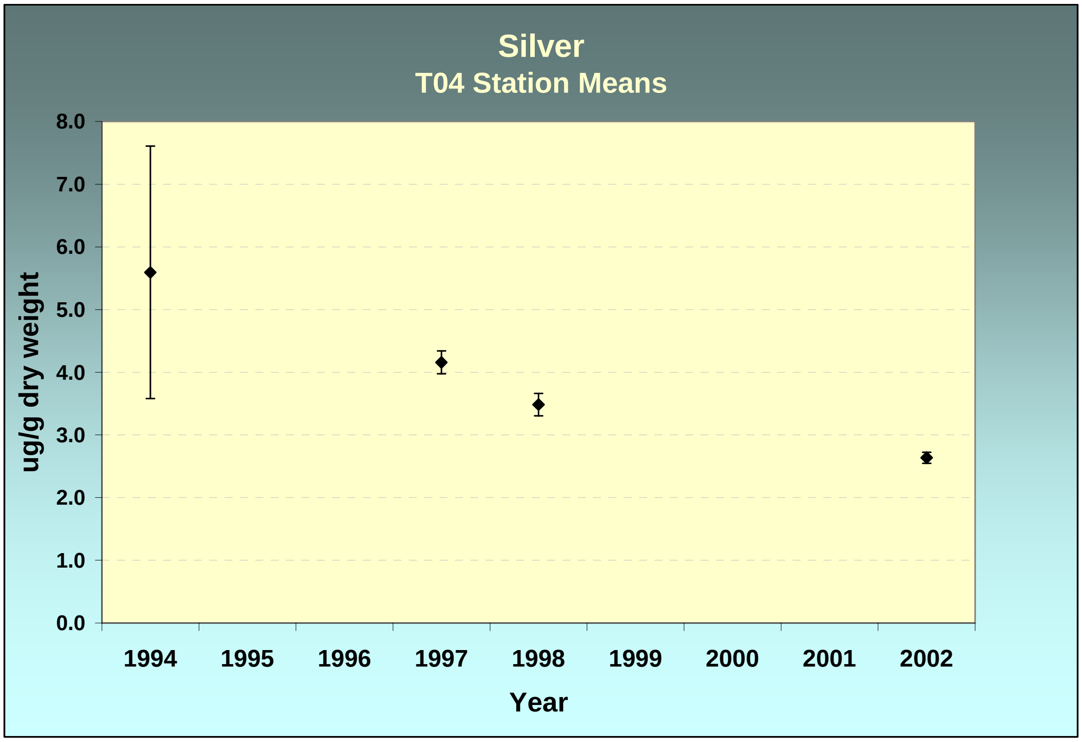

Figure 4-18. Silver concentrations in surface sediments at Station T04 appear to systematically decrease since 1990.

To gain a deeper understanding of changes in concentration over time in Boston Harbor, data from Dorchester Bay and the outer harbor were examined. MWRA data from stations located in these two areas were compiled for each of five years (1994, 1997, 1998, 1998, and 2002) and the average and standard deviation of each parameter by year calculated (Table 4-2 and Table 4-3). Dorchester Bay Stations DB01, DB03, DB06, DB10, and DB12 were used for the calculations; the outer harbor stations (defined for this analysis as stations east of Logan Airport sampled in each of the years being compared) were T01, T02, and T08[2]. Stations T04, DB04, and DB14 were excluded from these calculations due to their immediate proximity to CSO outfalls.

Comparison of the average concentration for selected contaminants from 1994 and 2002 reveals several patterns (see Appendix B). As reported in earlier publications and documents (Wallace *et al.* 1991), the Dorchester Bay area has consistently higher contaminant levels (compare Table 4-2 to Table 4-3) than other regions in the Harbor. These differences are consistent for both 1994 and 2002. Dorchester Bay had 2.5 to 5 times higher contaminant levels on average in 1994 than found in the outer harbor with tDDT and tPCB showing the largest difference. Total PAH, copper, lead, and cadmium were ~2.5 times higher in Dorchester Bay than the outer harbor. This pattern was still apparent in the 2002 data, although the range in the differences had increased (2.3 to 6.1) with tDDT showing the largest difference on average. Also apparent in these data is the relatively high variability shown in the magnitude of the standard deviation and the coefficient of variation (CV) which measures the relative variability. As seen in Table 4-2 and Table 4-3, the CV for the contaminants did not change substantially from 1994 to 2002, although there were reasonably large decreases in the yearly mean and standard deviation of several contaminants in both regions. Only lead and copper levels do not appear to have decreased in either region in the eight year period being compared. Average concentration changes for these two metals were less than five

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[2] Stations T03 and T05A were included in the outer harbor group for the sewage tracer analysis (Section 4.1) because data were available for all stations across all monitoring years, except T05A in 1992.

percent different and highly variable as seen in Figure 4-19 and Figure 4-20. In contrast, tPAH, tPCB, tDDT, mercury, cadmium and silver, each show substantial decreases between 1994 and 2002 on average (Table 4-2 and Table 4-3) in both the outer Harbor and in Dorchester Bay. Total DDT (tDDT) and cadmium in these two regions are compared in Figure 4-21 and Figure 4-22. While these chemicals appear to be decreasing in the Harbor, the variability in the data and limited number of samples from each area make the observed decrease statistically insignificant. Even so, tDDT, cadmium, and silver (Figure 4-23) appear to undergo a relatively consistent decline in concentration. As noted previously, systematic trends in the data are hard to detect due to the data variability and response to events such as storms, especially for contaminants most associated with run off, such as lead, cadmium, and tPAH. This probably explains the slight increase in the Dorchester Bay data from 1998 relative to the longer term trend.

Table 4-2. Comparison of changes in selected contaminant concentrations in outer Boston Harbor sediments between 1994 and 2002.

	Units	1994			2002			'94 to '02
		Mean	STD	%CV	Mean	STD	%CV	%Change
TOC	%	1.39	0.73	52.9	1.08	0.63	58.1	-22.2
Pct_Fines	%	21.2	15.9	75.3	32.1	22.2	69.1	51.7
Total PAH	ng/g dw	6042	2636	43.6	4780	2067	43.2	-20.9
Total DDT	ng/g dw	9.3	5.8	61.8	2.2	1.5	69.4	-76.5
Total PCB	ng/g dw	30.8	24.0	77.8	19.6	17.7	90.1	-36.4
Cu	µg/g dw	34.0	22.6	66.4	33.1	20.1	60.5	-2.5
Hg	µg/g dw	0.24	0.14	55.8	0.19	0.12	59.6	-20.7
Pb	µg/g dw	40.6	19.8	48.8	42.2	19.1	45.3	4.1
Cd	µg/g dw	0.30	0.19	64.4	0.14	0.10	74.6	-53.6
Ag	µg/g dw	1.31	1.05	80.2	0.82	0.59	72.0	-37.4

Table 4-3. Comparison of changes in selected contaminant concentrations in Dorchester Bay sediments between 1994 and 2002.

	Units	1994			2002			94 to '02
		Mean	STD	%CV	Mean	STD	%CV	% Change
TOC	%	2.18	1.54	70.6	2.35	1.57	66.9	7.9
Pct_Fines	%	46.8	34.7	74.1	52.7	40.0	75.9	12.7
Total PAH	ng/g dw	15405	10093	65.5	11130	8358	75.1	-27.8
Total DDT	ng/g dw	47.8	61.0	127.6	13.5	19.5	144.4	-71.7
Total PCB	ng/g dw	155.9	156.5	100.4	80.1	78.6	98.1	-48.7
Cu	µg/g dw	94.3	76.8	81.5	94.1	73.1	77.7	-0.18
Hg	µg/g dw	0.83	0.49	59.2	0.52	0.40	75.8	-37.2
Pb	µg/g dw	109.5	65.4	59.7	114.7	62.9	54.9	4.7
Cd	µg/g dw	0.79	0.66	83.9	0.44	0.32	73.7	-44.6
Ag	µg/g dw	2.70	2.00	74.1	1.70	1.10	64.7	-37.0

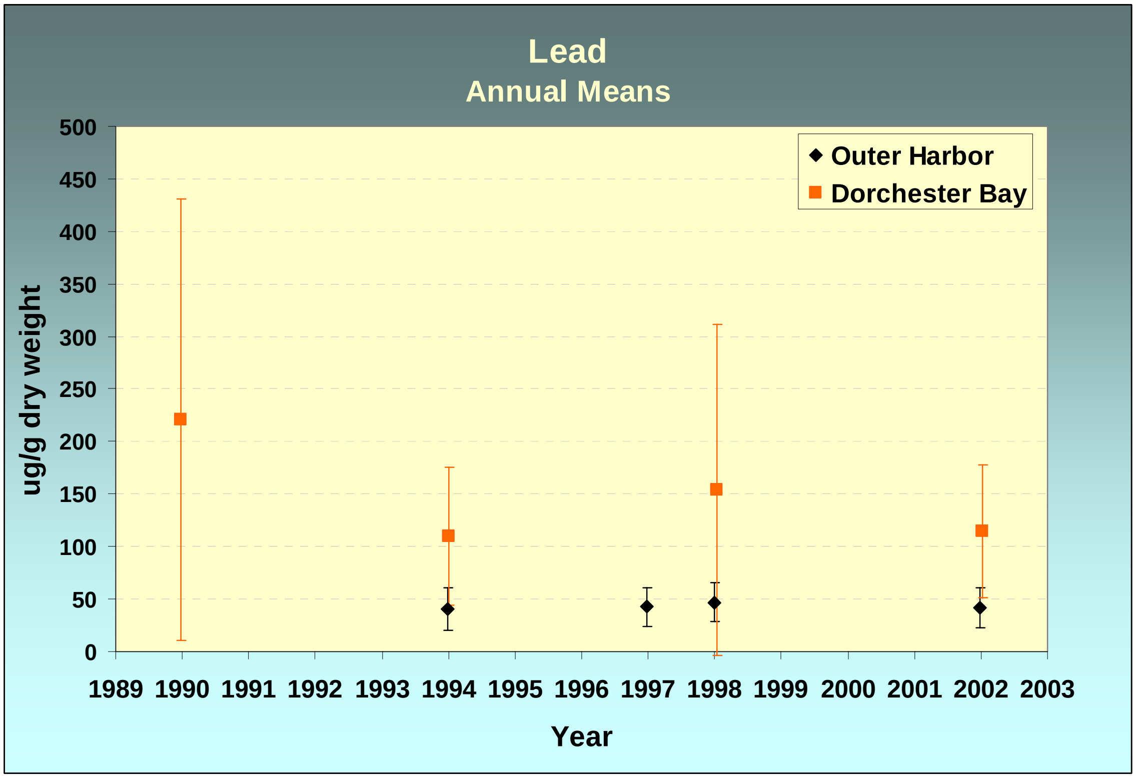


Figure 4-19. Temporal comparison of average lead concentrations in outer Boston Harbor and Dorchester Bay sediments.

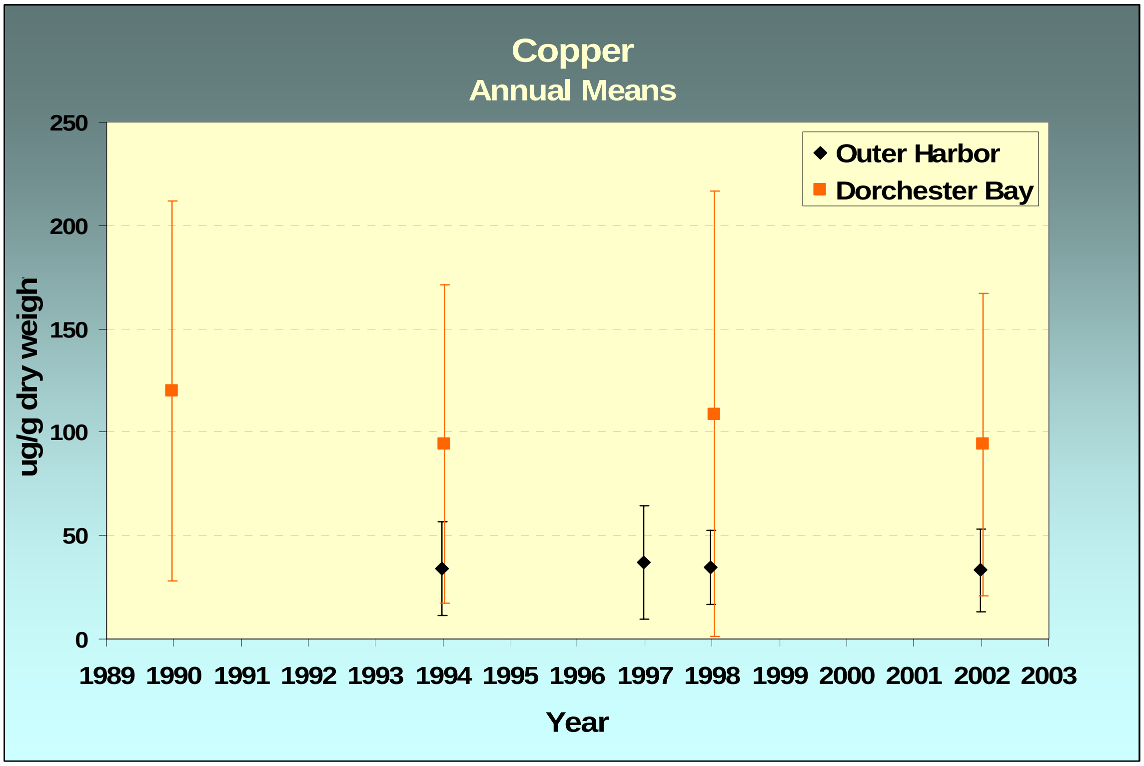


Figure 4-20. Temporal comparison of average copper concentrations in outer Boston Harbor and Dorchester Bay sediments.

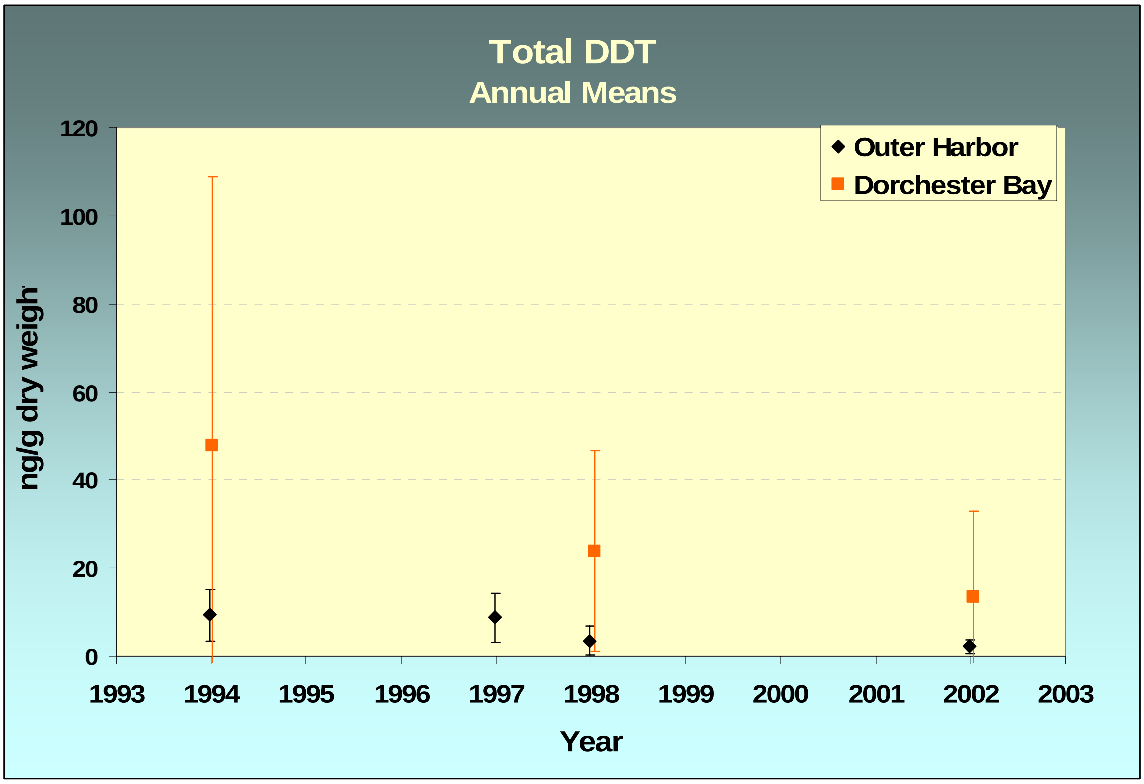


Figure 4-21. Temporal comparison of average tDDT concentrations in outer Boston Harbor and Dorchester Bay sediments.

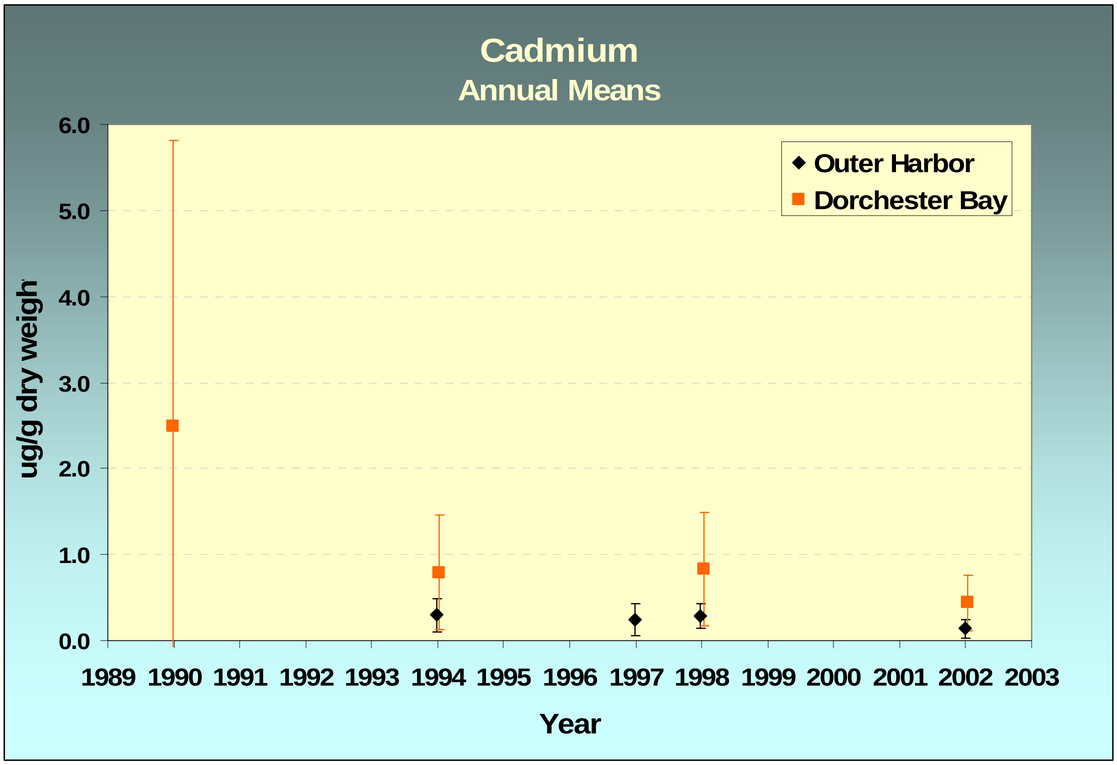


Figure 4-22. Temporal comparison of average cadmium concentrations in outer Boston Harbor and Dorchester Bay sediments.

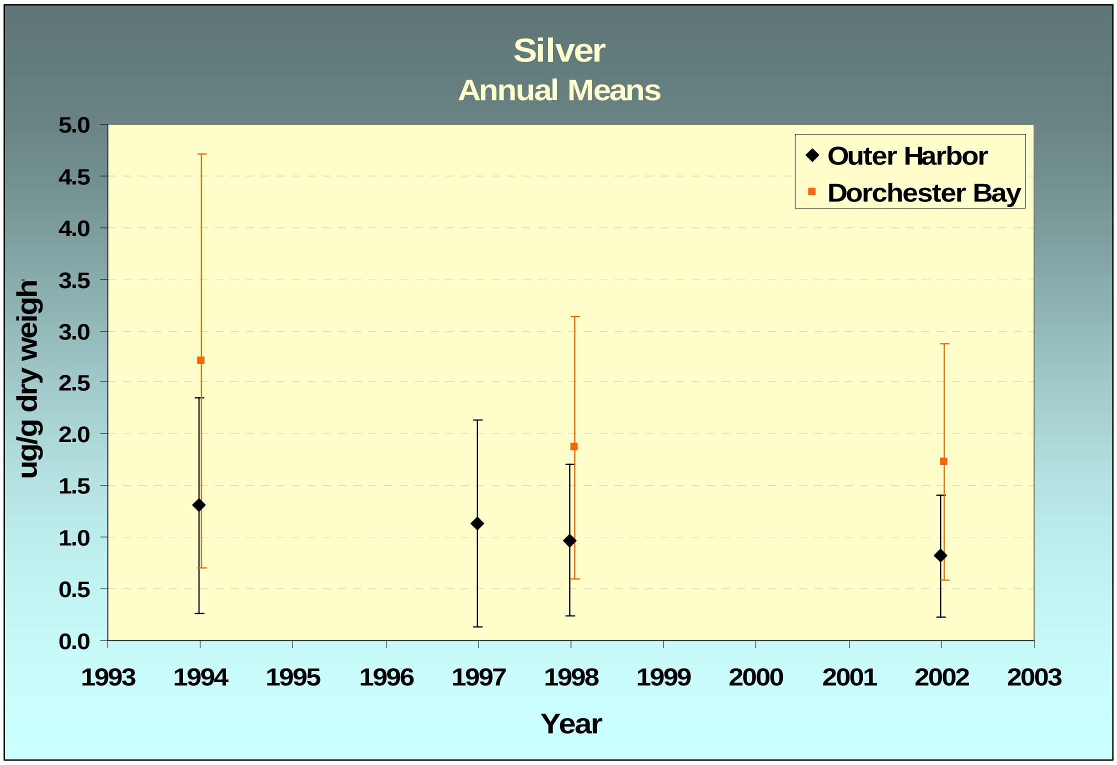


Figure 4-23. Temporal comparison of average silver concentrations in outer Boston Harbor and Dorchester Bay sediments

Temporal changes in the inner Boston Harbor are exemplified by the strong downward trend in silver at Station CO19 (Figure 4-24) where a systematic decease from 4.8 to 2.6 µg/g dw (50 percent) occurred between 1994 and 2004, similar to the decrease observed at station T04 (Figure 4-18). Other contaminants at CO19 displayed similar downward trends, but the decreases were not as consistent as seen in the silver data (see Appendix B for more plots). The percent decrease in contaminant levels from 1994 to 2002 was similar to those observed in the outer Harbor and Dorchester Bay. For example tPAH, tDDT, tPCB, cadmium, and silver decreased by 42, 77, 50, 48, and 33 percent, respectively.

Taken together, the observations from individual stations and for areas within Boston Harbor through 2004 suggest many contaminants in the harbor sediments continue to experience the downward concentration trend as reported by Bothner *et al.* (1998) through the mid-1990's. Cadmium, tDDT, and silver particularly display more systematic declines, while lead and copper do not appear to change substantially over the MWRA sampling record. Data reported in Bothner and Butman (2005) also indicate the decreasing trend has continued at the USGS station in Hingham Bay (Bothner *et al.* in Bothner and Butman 2005). These data show a linear decrease in silver, lead, and copper concentrations in the surface (0-0.5 cm) sediment that translate into an average decrease of about 50% since 1977.

While the decrease in the lead and copper levels reported by the USGS appears to be inconsistent with the MWRA data, a number of factors, including the depth of the sediment interval sampled and biogeochemical processes, may be invoked to explain the inconsistency. MWRA's program samples the top 2 cm of the sediment, while the long-term USGS program focuses on the top 0.5 cm. The very near surface sediments sampled by USGS tend to reflect the balance between near surface oxic and deeper anoxic sediment processes, and may be relatively quick to respond to changes in the rates of those processes. The thicker sediment horizon sampled by MWRA includes slightly deeper sediments that likely have experienced less oxic conditions than the very near-surface sediments sampled by USGS. As described in Chapter 3, the chemical speciation favored in lower oxygen environments favors tight coupling between metals and the ligands they are bound to, making them less likely to be released into the water column. Therefore, the slightly deeper samples collected by MWRA may be slower to indicate changes in sediment quality. It can be speculated that the observed differences among the metals may relate to their biogeochemistry and to the type and strength of the sources to the system. The good news is that the sediments of the harbor continue to move in the direction of higher quality.

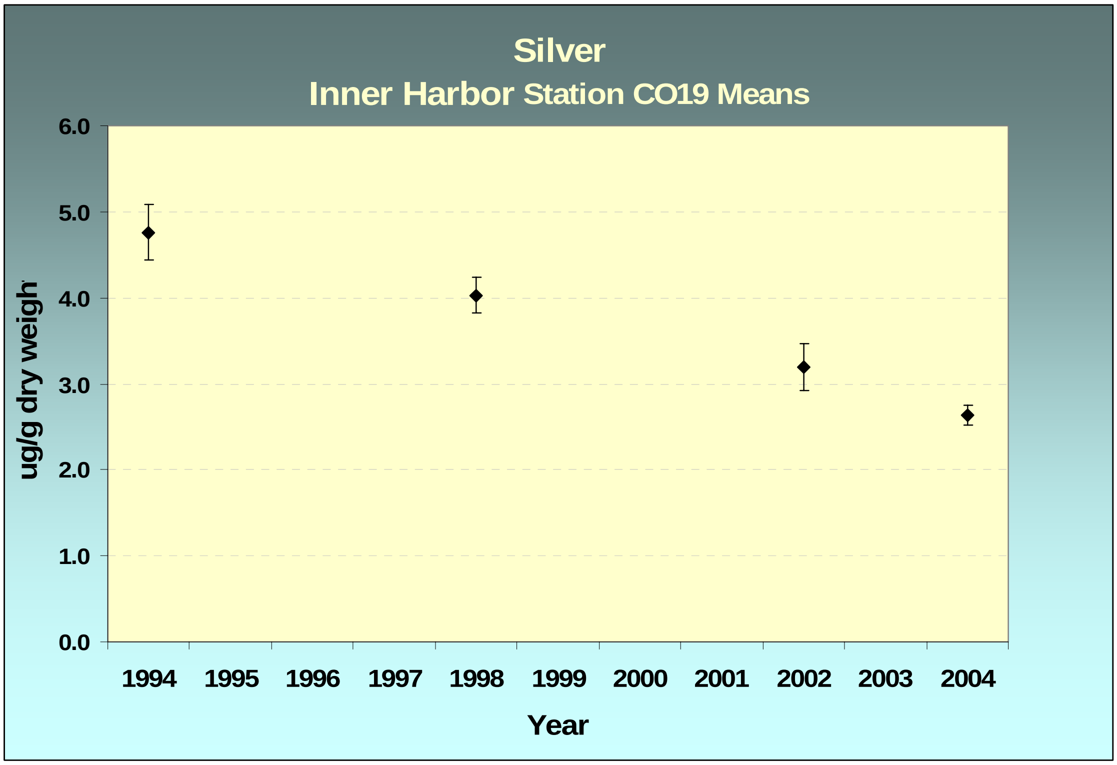


Figure 4-24. Temporal changes in silver in inner Boston Harbor sediments since the mid-1990s.

4.2.3 Pre- and Post-Diversion Comparison – Massachusetts Bay

Data from the Nearfield and Farfield areas of Massachusetts Bay were also examined for trends before and after the MWRA effluent discharge was moved offshore in 2000. The 1994 and 2002 data from the Nearfield (Table 4-4) and Farfield (Table 4-5) were compared. Unlike the Harbor, the changes in the average contaminant levels in the Nearfield and Farfield from 1994 to 2002 were generally small (<15%) and were not statistically significant. Exceptions are tPAH which increased by ~60% in both the Nearfield and Farfield, tPCB which decreased (~21%) in the Farfield and increased (~20%) in the Nearfield, tDDT which decreased in the Nearfield (~56%) and Farfield (~69%), and cadmium which decreased by ~40% in both regions.

Unlike Boston Harbor there are no clear temporal trends in the Massachusetts Bay data due in part to the lack of samples in the mid-1990s and in part to the large intra and inter-annual variability observed in the data sets (see for example Figure 4-25 [tDDT], Figure 4-26 [cadmium], and Figure 4-27 [silver]). This intra-annual variability (shown as standard deviation) reduces the confidence in any conclusion that Massachusetts Bay has undergone reduction in contaminant levels as the amount of change observed depends greatly on the years selected for comparison. For example, the cadmium changes reported above are based on the year with highest average concentrations (1994). Had other years been selected, the change would have been smaller. Regardless, comparison of the early 1990 data in the Farfield to the early 2000 data suggest slightly lower contaminant levels since the late 1990s which is consistent with observations (Figure 4-28) made by Bothner and Butman (2005) for a single station in Massachusetts Bay, located northwest of the MWRA diffuser system but sampled at a higher frequency and smaller sediment interval (0-2 cm vs 0-0.5 cm).

Table 4-4. Comparison of changes in selected contaminant concentrations in the Nearfield sediments of Massachusetts Bay between 1994 and 2002.

		1994			2002			94 to '02
	Units	Mean	STD	%CV	Mean	STD	%CV	% Change
Pct_Fines	%	35.9	27.7	77.2	37.5	21.9	58.4	4.5
TOC	%	0.79	0.55	70.5	1.02	0.65	64.1	29.9
Total PAH	ng/g dw	4435	3653	82.4	6954	11306	163	56.8
Total PCB	ng/g dw	15.21	11.86	78.0	18.23	23.48	129	19.9
Total DDT	ng/g dw	5.27	6.53	124	2.30	2.21	96.3	-56.4
Cadmium	µg/g dw	0.15	0.14	88.5	0.09	0.08	85.1	-40.6
Chromium	µg/g dw	86.8	44.6	51.4	78.9	32.4	41.1	-9.1
Copper	µg/g dw	22.8	12.5	55.0	25.1	11.6	46.3	10.0
Lead	µg/g dw	43.8	14.5	33.1	50.7	36.4	71.8	15.8
Mercury	µg/g dw	0.22	0.22	101.5	0.20	0.12	59.8	-7.0
Nickel	µg/g dw	17.0	7.5	44.1	17.2	6.6	38.1	1.7
Silver	µg/g dw	0.55	0.50	89.6	0.49	0.34	69.2	-12.1
Zinc	µg/g dw	56.9	23.7	41.6	64.2	20.9	32.6	12.7

Table 4-5. Comparison of changes in selected contaminant concentrations in the Farfield sediments of Massachusetts Bay between 1994 and 2002.

		1994			2002			94 to '02
	Units	Mean	STD	%CV	Mean	STD	%CV	% Change
Pct_Fines	%	54.7	28.6	52.3	51.3	26.9	52.6	-6.3
TOC	%	1.1	0.7	62.3	1.2	0.8	64.4	17.2
Total PAH	ng/g dw	3164	2841	89.8	5156	12108	235	62.9
Total PCB	ng/g dw	12.9	8.9	68.7	10.2	11.8	116	-21.2
Total DDT	ng/g dw	4.9	5.5	113	1.5	1.4	90.9	-68.9
Cadmium	µg/g dw	0.1	0.1	63.5	0.1	0.0	42.4	-42.7
Chromium	µg/g dw	87.8	39.1	44.5	76.2	28.5	37.4	-13.2
Copper	µg/g dw	19.5	10.9	55.5	19.7	10.3	52.6	0.7
Lead	µg/g dw	40.7	13.1	32.3	39.0	12.3	31.6	-4.1
Mercury	µg/g dw	0.2	0.2	129.1	0.2	0.1	73.1	-10.5
Nickel	µg/g dw	19.6	8.8	45.1	18.4	7.6	41.5	-6.2
Silver	µg/g dw	0.4	0.4	92.1	0.4	0.2	57.0	-16.0
Zinc	µg/g dw	65.2	25.6	39.3	69.1	22.9	33.1	5.9

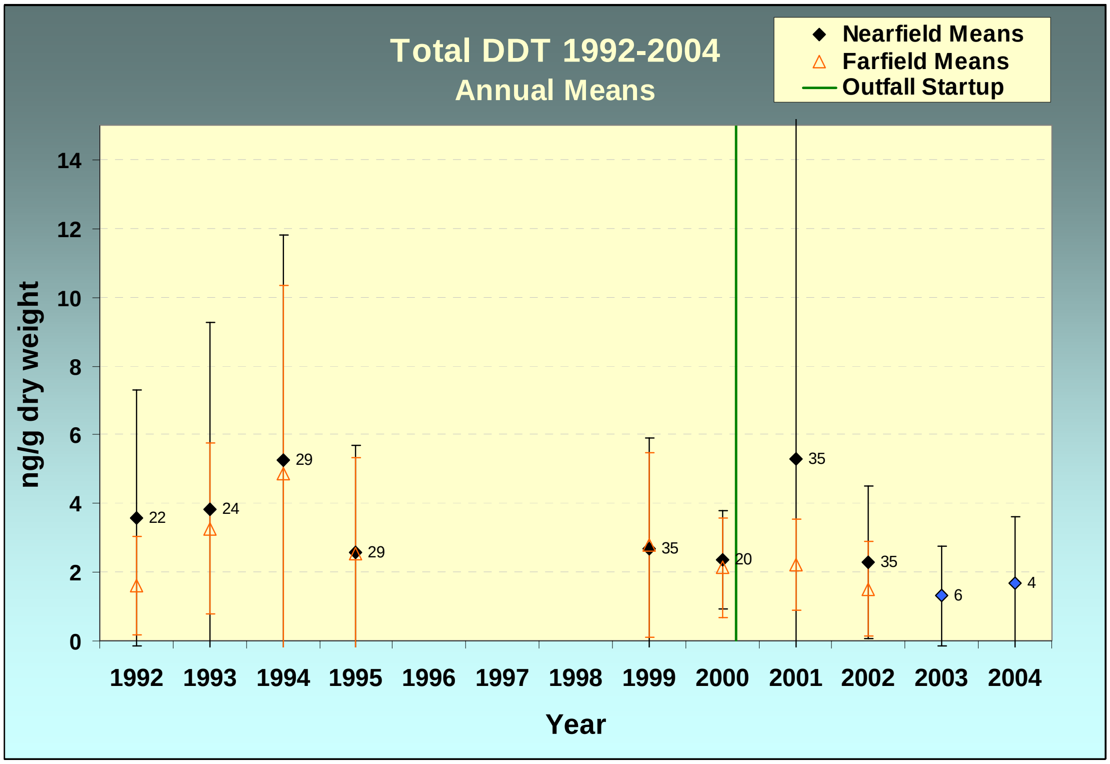


Figure 4-25. Temporal response of tDDT in Massachusetts Bay sediments. The number of samples in the Nearfield average and standard deviation is shown; note the reduction of Nearfield samples for 2003 and 2004, Farfield data was not collected in 2003 and 2004.

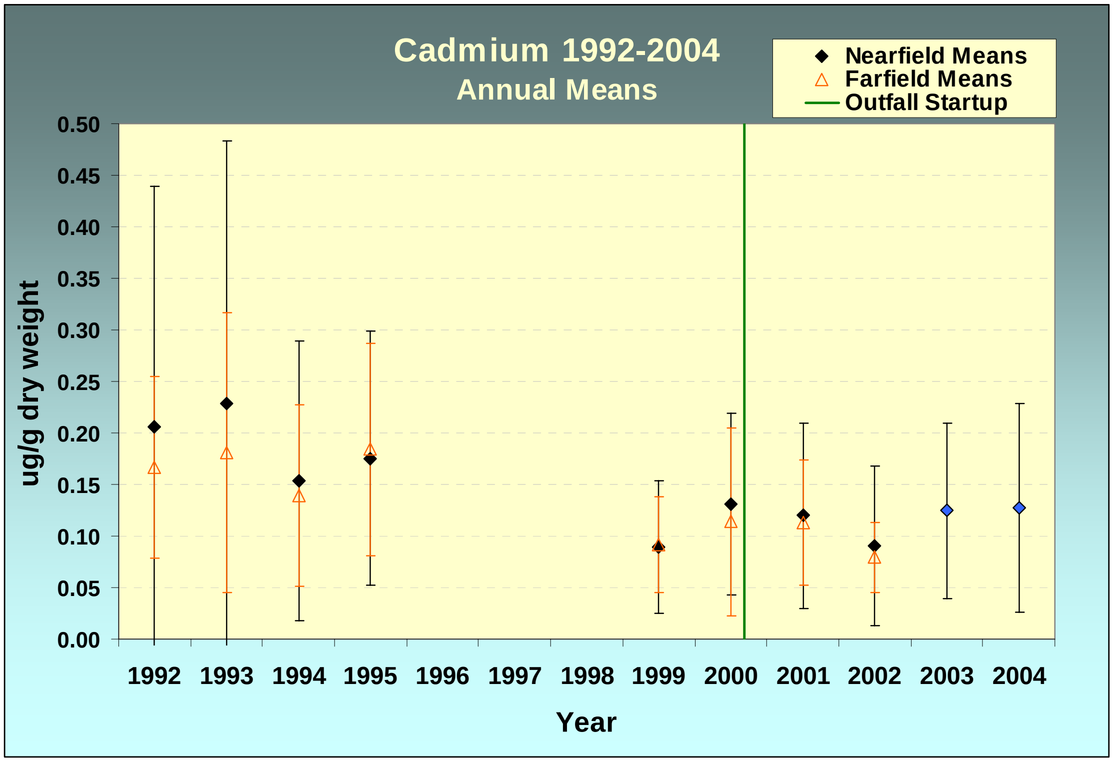


Figure 4-26. Temporal response of cadmium in Massachusetts Bay sediments.

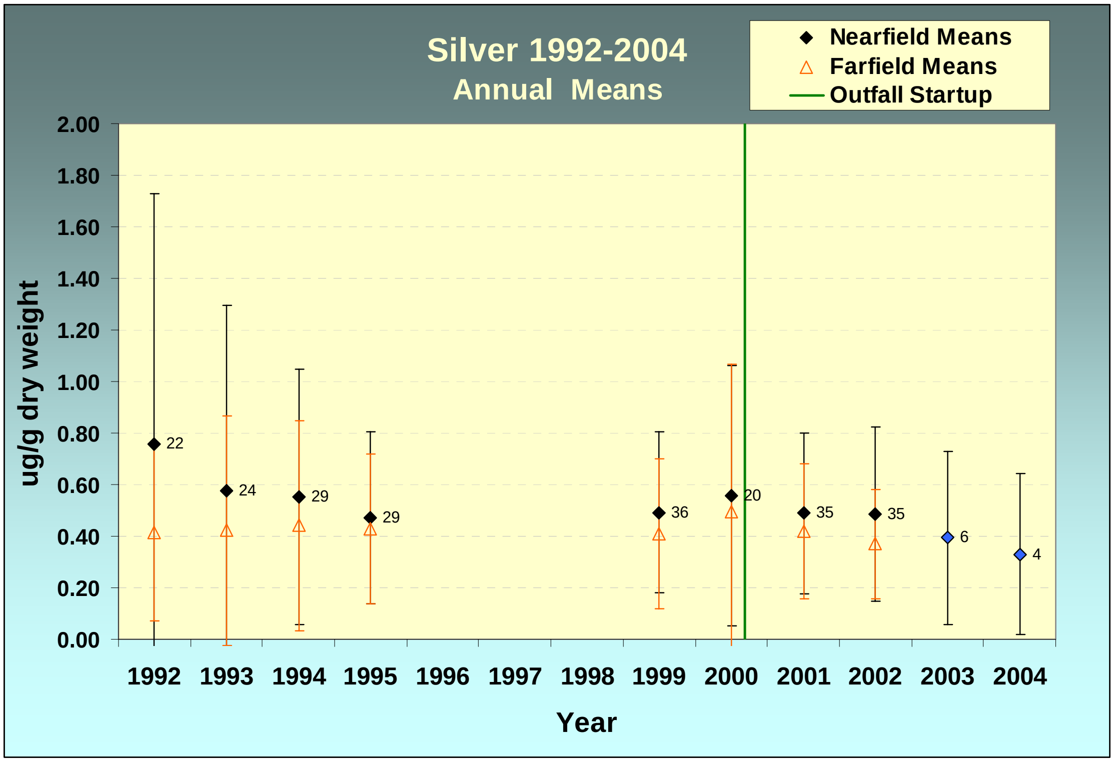


Figure 4-27. Temporal response of silver in Massachusetts Bay sediments.

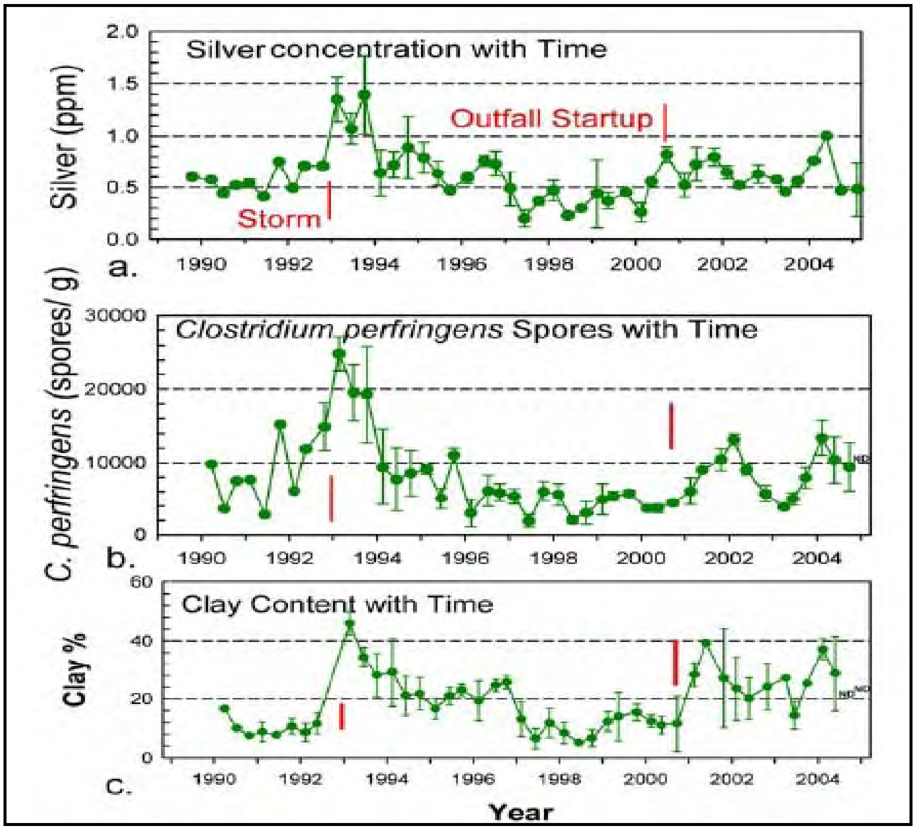


Figure 4-28. Silver, *C. perfringens*, and percent clay trends in sediments from USGS Station 3 in Massachusetts Bay (from Bothner and Butman 2005)

4.3 Sediment Quality Considerations

Complete sediment quality assessments are complex and can incorporate any of several measurement approaches including biological characteristics, toxicological data, or chemical data and combinations of these attributes. The only long-term information on sediment quality in Massachusetts Bay and Boston Harbor is the chemical and benthic infauna community data. The benthic infauna data have not revealed broad scale infaunal community impairment with the exception of a few stations such as T04 near Fox Point. Lacking toxicological information, and clear contaminant driven impacts to the benthic community, a surrogate approach using Sediment Quality Guidelines (SQG) (Long *et al.* 1995; http://response.restoration.noaa.gov/book_shelf/121_sedi_qual_guide.pdf) was chosen to evaluate whether changes in sediment quality have occurred in the system since the early 1990's.

For this analysis, yearly mean station contaminant levels were compared with a published marine ER-L (contaminant concentrations at which adverse biological effects are rarely observed) and ER-M (contaminant concentrations at which adverse biological effects are frequently observed) (Long *et al.* 1995) in a matrix of stations and chemicals. Matrices for the harbor and Massachusetts Bay were developed for selected years and those values higher than the ER-M and ER-L highlighted (see for example Table 4-6). The total number of values greater than the ER-M and ER-L were summed by station and by chemical for each year. Changes in sediment quality between years was evaluated by comparing the total number of ER-L and ER-M values between the years compared. Note that these comparisons do not consider analytical nor replicate sample variability since only one replicate was obtained at most stations in keeping with the monitoring program's focus on spatial changes. Thus, the comparisons simply indicate those chemicals that were found to be higher than the ER-L and ER-M values and should not be considered as statistically rigorous comparison.

4.3.1 Harbor

Table 4-6 and Table 4-7 are set up identically and convey the pattern of concentrations greater than the ER-L and ER-M in the Harbor in 1994 and 2002, respectively. In 1994 there were 211 concentrations greater than the ER-L and 52 greater than ER-M levels (total 263). By 2002 these had decreased to 190 and 25, respectively (Table 4-8) for a total of 215 concentrations greater than available Sediment Quality Guidelines, an 18 percent improvement. Whereas the majority of the concentrations greater than the ER-Ls occurred throughout the Dorchester Bay region in 1994, areas with concentrations higher than the ER-Ls were restricted to the Commercial Point region (Station DB14) by 2002. Mercury was the only chemical with concentrations greater than the ER-M at more than two stations in 2002. These stations are in the inner harbor (CO19) and Dorchester Bay (DB10, DB14, T04). Notably Stations DB03 and T01 improved. In 1994, numerous chemicals had concentrations above the ER-L and ER-M levels, while in 2002 fewer did. Consistent with the observed temporal trends, the number of stations exceeding the tDDT marine Sediment Quality Guideline decreased from 11 to 3. Clearly this analysis by chemical compound indicates Harbor wide improvements took place over the 1990's.

4.3.2 Bay

Table 4-9, Table 4-10, and Table 4-11 convey the pattern in chemicals exceeding ER-L and ER-M values in Massachusetts Bay in 1992, 1999 (one year pre-effluent diversion), and 2002 (two years post effluent diversion), respectively. A total of 26 stations from the Nearfield and Farfield are included in this comparison. Table 4-12 compares the number of chemical concentrations that were higher than the Sediment Quality Guidelines at each station by year and shows changes that occurred from 1992 to 1999, 1999 to 2002, and 1992 to 2002. Between 1992 and 1999 improvements in the sediment quality of Massachusetts Bay are evident. The total number of chemical concentrations higher than the ER-L and ER-M values decreased by 42 percent (209 >ER-L and 5 >ER-M in 1992 to 124 >ER-L and 0 >ER-M in 1999) (decreases of >85 ER-L and 5 >ER-M). Eight stations (FF14, FF11, NF02, NF05, NF08, NF09, NF16, and NF20) showed the greatest improvements against the SQG by 1999. Several stations closer to the outfall (FF12, NF13, NF15, NF18, NF19, NF10) were only slightly improved in 1999 relative to 1992.

In contrast to the improvements over the 1992 to 1999 period, changes from 1999 to 2002 were often in the opposite direction, but not at all stations or for all chemicals. Overall, the number of chemical concentrations above the SQGs increased sixteen percent (19 ER-L and 1 ER-M, respectively) (Table 4-12). The stations with the largest increase in chemicals above the ER-L values (4 to 12 chemicals) were NF02, NF05, NF08, NF16, and NF18. Stations NF09, NF12, FF13, FF12, and FF10 had one or two compounds added to the number chemicals above the ER-L. Decreases in the number of chemicals above the SQGs were observed at FF04, FF06, FF07, NF07, NF10, NF14, NF15, and NF20. No single chemical accounted for the changes relative the SQG from 1999 to 2002 (Figure 4-29). The changes in sediment quality in the short period following effluent diversion are limited in magnitude and are not spatially consistent with stations shown to have effluent contribution based on the *C. perfringens* data. Some of the concentration increases and decreases observed between 1999 and 2002 may be associated with temporal variability in sediment texture in this dynamic area. For example, Station NF02 showed by far the greatest increase in the number of contaminants above SQGs (12) between 1999 and 2002 and also major changes in the bulk sediment characteristics (i.e. percent files (silt + clay) increased from 5% to 61% and TOC increased from less than 0.2% to 1.9%). These changes would generally be expected to cause increases in contaminant levels by virtue of greater contaminant association with finer grained, organic rich sediments. The changes could also be associated with sampling and analytical uncertainties. However, since only one replicate was obtained at most stations in keeping with the monitoring program's focus on spatial changes, rigorous statistical treatment of the data was precluded.

Although quantitative analyses and comparisons to SQGs have not yet been conducted, raw data from sediment contaminant sampling in August 2005 suggest contaminants decreased from 2002 concentrations at many sites in the Nearfield, potentially due to coarsening of the sediment grain size characteristics and concomitant lowering of the amount of organic carbon in the sediments (pers. observation, D. Dahlen and K. Keay, February 2006). Nevertheless, the increases in *C. perfringens* and the changes observed in contaminant concentrations in this physically dynamic and temporally variable region underscore the appropriateness of periodically assessing the quality of the sediment.

Table 4-6. Contaminant levels in Boston Harbor in 1994 relative to Sediment Quality Guidelines. (See Figure 4-11 for station locations.)

	ER-L	ER-M	1994 C019	1994 DB01	1994 DB03	1994 DB04	1994 DB06	1994 DB10	1994 DB12	1994 DB14	1994 SWEX3	1994 T01	1994 T02	1994 T04	Total ER-L Exceedances	Total ER-M Exceedances
Total PCB	22.7	180	186.	88.1	45.7	62.2	7.21	373.	266.	348.	90.6	28.8	55.8	417.	6	5
Dieldrin	0.02	8	2.6	3.96	.474	6.17	.222	5.53	6.03	15.3	3.31	1.1	1.72	9.12	10	2
DDD[1]	2	20	23.6	15.3	5.39	18.9	.815	130.	29.1	108.	12.	6.2	7.77	46.1	3	5
DDE[1]	2.2	27	7.62	4.83	2.42	7.14	.29	11.7	12.8	18.3	5.29	2.04	3.53	17.1	10	0
DDT[1]	1	7	8.56	5.7	1.86	4.97	.269	9.68	8.67	37.2	6.36	2.64	2.82	8.6	6	5
cis-Chlordane	0.5	6	2.51	1.28	.553	6.2	.116	2.67	2.29	20.9	1.17	.761	1.12	3.73	9	2
Total PAH	4022	44792	19500	26200	10300	39700	495	20700	19300	127000	9880	7570	7560	22500	10	1
Acenaphthene	16	500	57.2	152.	130.	404.	1.33	72.6	137.	920.	27.6	33.3	20.7	79.	10	1
Acenaphthylene	44	640	216.	101.	42.4	95.6	3.27	147.	116.	366.	107.	49.4	71.6	172.	10	0
Anthracene	85.3	1100	356.	434.	256.	762.	6.31	272.	443.	2410.	153.	148.	123.	351.	10	1
Benz(a)anthracene	261	1600	925.	1260.	406.	1880.	22.4	912.	841.	7110.	439.	288.	339.	1080.	9	2
Benzo(a)pyrene	430	1600	895.	1250.	407.	1700.	26.4	1000.	844.	5510.	427.	232.	333.	992.	6	2
Chrysene	384	2800	1140.	1420.	452.	2060.	30.8	1160.	926.	7970.	505.	312.	393.	1290.	9	1
Dibenzo(a,h)anthracene	63.4	260	155.	234.	63.1	321.	4.26	196.	144.	965.	72.	37.5	56.4	175.	6	2
Fluoranthene	600	5100	2340.	3270.	1170.	4620.	64.	2210.	1850.	15600.	1060.	736.	917.	2940.	10	1
Fluorene	19	540	95.4	191.	149.	429.	2.77	108.	211.	1090.	48.5	61.4	35.9	112.	10	1
Naphthalene	160	2100	340.	166.	138.	368.	8.92	176.	205.	571.	142.	50.6	110.	172.	8	0
Phenanthrene	240	1500	816.	2010.	1190.	3920.	29.7	1060.	1660.	10400.	457.	467.	383.	1220.	7	4
Pyrene	665	2600	2080.	3640.	1360.	4950.	69.5	2630.	2530.	13000.	1020.	721.	853.	2530.	7	4
Cadmium	1.2	9.6	1.14	.844	.228	.82	.065	1.69	1.13	1.48	.423	.307	.485	2.12	3	0
Chromium	81	370	215.	157.	65.3	139.	35.	218.	209.	119.	194.	78.3	126.	254.	9	0
Copper	34	270	146.	134.	27.7	87.	12.3	198.	98.7	126.	95.7	26.7	59.3	158.	9	0
Lead	46.7	218	137.	152.	54.6	159.	28.4	182.	130.	347.	108.	32.8	63.1	199.	9	1
Mercury	0.15	0.71	.812	.741	1.35	.617	.075	1.18	.81	.771	.581	.26	.373	1.24	4	7
Nickel	20.9	51.6	37.3	34.7	15.3	28.5	9.	38.	34.	25.7	36.	20.5	23.3	37.3	9	0
Silver	1	3.7	4.76	3.48	.885	2.97	.359	5.05	3.76	2.18	4.03	.895	2.5	5.59	4	5
Zinc	150	410	218.	233.	69.7	168.	33.7	273.	172.	344.	156.	67.7	101.	266.	8	0
Total ER-L Exceedances			21	23	18	20	1	21	20	9	22	14	21	21	211	
Total ER-M Exceedances			5	3	1	6	0	6	6	18	1	0	0	6		52

Table 4-7. Contaminant levels in Boston Harbor in 2002 relative to Sediment Quality Guidelines.

	ER-L	ER-M	2002 C019	2002 DB01	2002 DB03	2002 DB04	2002 DB06	2002 DB10	2002 DB12	2002 DB14*	2002 SWEX3	2002 T01	2002 T02	2002 T04	Total ER-L Exceedances	Total ER-M Exceedances
Total PCB	22.7	180	93.1	66.7	25.	54.4	4.53	204.	100.	198.	53.8	13.6	39.5	132.	8	2
Dieldrin	0.02	8	a	a	a	a	a	a	a	a	a	a	a	a	NA	NA
DDD[1]	2	20	5.59	3.43	1.34	3.34	.306	35.5	5.66	28.9	3.08	.868	2.13	7.27	7	2
DDE[1]	2.2	27	3.05	2.41	.977	1.83	.151	6.	3.72	10.1	1.9	.552	1.39	4.32	6	0
DDT[1]	1	7	.715	.619	.174	.48	.439	6.35	.516	18.2	.883	.152	.396	1.87	2	1
cis-Chlordane	0.5	6	.961	.692	.17	.502	.043	2.74	.678	12.8	.576	.152	.552	1.7	8	1
Total PAH	4022	44792	11200	11900	5460	11200	628	15900	21800	93200	7190	3370	7150	18400	9	1
Acenaphthene	16	500	44.4	53.2	59.2	59.3	1.89	56.4	172.	895.	25.4	12.2	28.5	91.4	8	2
Acenaphthylene	44	640	140.	87.5	39.5	95.1	5.04	155.	186.	374.	89.	23.7	72.3	121.	9	0
Anthracene	85.3	1100	234.	217.	139.	226.	9.31	265.	477.	1870.	138.	67.9	125.	283.	9	1
Benz(a)anthracene	261	1600	508.	584.	241.	541.	30.5	714.	911.	4430.	330.	142.	338.	847.	8	1
Benzo(a)pyrene	430	1600	618.	669.	250.	599.	35.9	897.	904.	4430.	383.	155.	446.	1030.	7	1
Chrysene	384	2800	628.	696.	272.	618.	36.7	975.	958.	5560.	376.	157.	375.	1090.	6	1
Dibenzo(a,h)anthracene	63.4	260	110.	118.	38.9	109.	5.93	169.	152.	806.	64.1	25.	71.4	178.	8	1
Fluoranthene	600	5100	1050.	1380.	541.	1290.	65.6	1760.	1840.	10700.	658.	272.	635.	2020.	8	1
Fluorene	19	540	62.4	65.	68.9	63.	2.79	77.9	170.	911.	40.5	30.5	40.6	109.	10	1
Naphthalene	160	2100	210.	93.9	68.4	82.8	6.74	114.	179.	429.	93.2	31.2	90.7	118.	3	0
Phenanthrene	240	1500	513.	710.	491.	727.	28.9	777.	1610.	8130.	350.	190.	365.	1140.	8	2
Pyrene	665	2600	1070.	1220.	503.	1190.	58.	1590.	1900.	8160.	667.	257.	636.	1830.	7	1
Cadmium	1.2	9.6	.593	.486	.174	.393	.058	.845	.63	1.18	.183	.089	.257	.712	0	0
Chromium	81	370	208.	183.	66.6	145.	36.3	197.	143.	141.	168.	62.5	124.	171.	9	0
Copper	34	270	128.	126.	44.4	86.5	19.1	204.	77.5	190.	67.5	27.4	55.5	127.	10	0
Lead	46.7	218	130.	154.	69.8	102.	30.7	184.	134.	419.	88.8	37.7	63.2	145.	9	1
Mercury	0.15	0.71	.763	.692	.194	.498	.065	1.04	.615	.813	.583	.183	.315	.749	7	4
Nickel	20.9	51.6	39.3	31.6	24.9	31.	10.9	45.5	27.9	44.7	35.9	17.3	25.9	35.	10	0
Silver	1	3.7	3.19	2.72	.798	1.91	.333	2.92	1.89	1.97	1.87	.599	1.49	2.64	9	0
Zinc	150	410	221.	251.	86.9	164.	44.4	279.	141.	455.	142.	63.1	112.	216.	5	1
Total ER-L Exceedances			23	23	10	22	0	21	21	7	19	2	19	23	190	
Total ER-M Exceedances			1	0	0	0	0	3	2	18	0	0	0	1		25

*One PAH replicate was excluded due to anomomously high PAH concentrations

Table 4-8. Changes in ER-M and ER-L exceedances in Boston Harbor from 1994 to 2002.

	Total ER-L Exceedances		Total ER-M Exceedances		Change from 1994	
Station	**1994**	**2002**	**1994**	**2002**	**ER-L**	**ER-M**
C019	21	23	5	1	2	-4
DB01	23	23	3	0	0	-3
DB03	18	10	1	0	-8	-1
DB04	20	22	6	0	2	-6
DB06	1	0	0	0	-1	0
DB10	21	21	6	3	0	-3
DB12	20	21	6	2	1	-4
DB14	9	7	18	18	-2	0
SWEX3	22	19	1	0	-3	-1
T01	14	2	0	0	-12	0
T02	21	19	0	0	-2	0
T04	21	23	6	1	2	-5
Total	211	190	52	25	-21	-27

Table 4-9. Contaminant levels in Massachusetts Bay relative to Sediment Quality Guidelines 1992. (See Appendix A for a map of station locations.)

			1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992
	ER-L	ER-M	FF04	FF05	FF06	FF07	FF09	FF10	FF11	FF12	FF13	FF14	NF02	NF04	NF05	NF07	NF08	NF09	NF10	NF12	NF13	NF14	NF15	NF16	NF17	NF18	NF19	NF20
Total PCB	22.7	180	9.8	6.94	15.8	24.5	8.08	4.54	22.2	12.4	13.5	28.7	40.3	2.54	13.8	18.2	77.1	13.6	8.94	19.9	2.28	7.14	6.61	32.2	0	8.67	2.96	28.1
Dieldrin	0.02	8	0	0.162	0.434	0.343	0.463	0.238	1.63	0.39	0.251	1.16	0.916	0	0.446	0.32	2.61	0.544	0.435	0.788	0.0727	0.363	0.122	1.15	0	0.286	0.127	1.23
DDD	2	20		0.947	0.408	2.09	0.866	1.49	2.8	1.34	0.799	2.43	3.16		1.04	3.02	12.7	1.42	1.34	2.07	0.173	1.13	1.5	3.65		0.925	0.275	5.38
DDE	2.2	27		0.576	0.825	2.03	1.16	0.6	3.01	0.958	0.627	2.39	2.99	0.346	1.18	1.67	4.67	1.22	0.956	1.89	0.79	0.994	0.704	2.77		0.745	0.826	2.08
DDT	1	7		0.285	0.42			0.178	0.434	0.167		0.361						1.53								2.58		0.489
cis-Chlordane	0.5	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.74	0.0416	0	0	0	0	0	0	0.496
Total PAH	4022	44792	2810	1500	2750	3730	2040	1740	6820	2350	1100	4570	4190	428	6310	21500	20200	6750	4250	10600	394	4970	6290	12900	583	2960	332	16500
Acenaphthene	16	500	9.19	5.47	10.3	11.4	5.98	6.57	18.3	9.68	4.67	13.6	16.9	0.959	13	61.7	86.3	22	24.7	80.7	1.35	18.1	97.9	64.6	8.62	18.5	0.927	204
Acenaphthylene	44	640	19	10	17.5	46	12.8	14.8	57.1	14.8	11	34.2	27.5	2.49	59.1	396	229	68.1	28.1	77.8	5.95	44.2	22.1	111	3.35	21.2	4.71	65.6
Anthracene	85.3	1100	30.7	16.1	34.2	48.1	19.2	32.2	105	43.5	17.1	53.6	72.7	2.73	268	1030	410	209	86	302	8.13	53.3	231	324	17.9	83.3	8.5	632
Benz(a)anthracene	261	1600	129	70.7	130	171	111	98.3	347	118	44.5	224	193	28.8	363	1160	988	343	235	527	17.1	342	259	667	29.5	147	14.7	775
Benzo(a)pyrene	430	1600	140	73.2	136	181	87.3	87.7	337	126	53.5	237	230	16.3	349	1010	1010	344	210	521	20.7	238	252	673	20.9	146	16.3	723
Chrysene	384	2800	165	91.4	153	167	143	107	376	120	51.9	260	221	37.7	388	1000	911	320	235	543	17.8	336	260	658	29.7	149	16.2	781
Dibenzo(a,h)anthracene	63.4	260	17.9	10.2	17.7	27.9	18.3	14.4	47	17	7.55	35.2	35.3	5.02	50.1	145	145	50.4	34.9	71.4	2.94	43.9	15.4	96.3	3.68	22.1	2.11	95.2
Fluoranthene	600	5100	308	164	297	407	157	182	660	228	119	438	421	26.5	720	2270	1800	748	431	1170	43	578	805	1390	74.7	298	36.1	1830
Fluorene	19	540	17.5	10.9	18.2	26.4	12.1	11.9	44.4	15.2	7.07	27.5	26.9	1.91	40	265	196	69.5	36.4	110	2.8	26	110	105	12.5	32.2	2.26	328
Naphthalene	160	2100	29.9	23.4	42.3	57	55.9	19.3	50.7	25.1	14.9	77.2	52.7	8.8	45.7	198	236	103	62.5	147	7.3	61.5	63.2	119	3.96	51.2	6.98	272
Phenanthrene	240	1500	181	96.9	168	224	91.3	106	383	131	53.2	251	216	13.6	299	1520	1310	466	268	814	22.9	183	801	771	81.9	207	19.1	1930
Pyrene	665	2600	281	102	269	361	148	176	622	234	111	420	404	26.2	599	2050	1690	651	407	1080	41.3	459	686	1290	58.9	272	34.3	1590
Cadmium	1.2	9.6	0.136	0.119	0.128	0.218	0.0876	0.132	0.173	0.296	0.282	0.151	0.876	0.0395	0.119	0.084	0.808	0.102	0.102	0.181	0.0297	0.06	0.0747	0.105	0.035	0.0925	0.0526	0.358
Chromium	81	370	98.9	59.2	74.3	82.8	45.5	78.1	71.1	72.4	74.7	81.5	199	26.8	78.6	68.1	282	84.5	67.6	94.9	29.9	64.1	61.5	174	30.7	60.7	39.9	126
Copper	34	270	20.6	12.4	19	20.9	10.1	12.9	17.1	25	30.1	17.2	94.7	7.9	11.3	22.6	108	23.9	20.8	32	11.5	16.5	31.5	48.2	6.3	18.3	5.9	33
Lead	46.7	218	53.1	35.3	42.7	44.7	30.9	32.9	39.3	38.9	39.9	47.2	113	31	31	45.3	117	41	41.5	46.8	34.8	50.9	58.3	87.1	37.4	44.2	28	58
Mercury	0.15	0.71	0.179	0.0928	0.179	0.16	0.0606	0.0913	0.121	0.246	0.237	0.15	0.755	0.0337	0.135	0.485	1.36	0.19	0.195	0.432	0.053	0.128	0.245	0.645	0.0327	0.158	0.0605	0.431
Nickel	20.9	51.6	33.5	20.6	23.3	31.8	14.4	14.9	27.1	13.2	25.6	24.8	37.2	11	9.7	17.3	32.3	22.5	17.9	25.1	11	16.8	15.4	33.3	10.8	15.3	8.2	19.5
Silver	1	3.7	0.3	0.217	0.544	0.459	0.0986	0.346	0.188	0.768	1.11	0.214	3.74	0.0602	0.236	0.231	3.06	0.48	0.445	0.572	0.065	0.256	0.306	1.84	0.0334	0.294	0.136	0.481
Zinc	150	410	97.8	60	68.5	99.9	41.7	51.5	73.7	57.4	122	79.5	174	22.2	40.3	57.4	200	67.2	51.2	76.9	28.9	42.1	47.6	118	30.6	51.1	31.2	87.1
Total ER-L Exceedances			4	1	3	7	1	1	12	2	4	10	12	0	9	16	23	13	7	19	1	7	10	22	0	5	1	18
Total ER-M Exceedances			0	0	0	0	0	0	0	0	0	0	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1

Table 4-10. Contaminant levels in Massachusetts Bay relative to Sediment Quality Guidelines 1999.

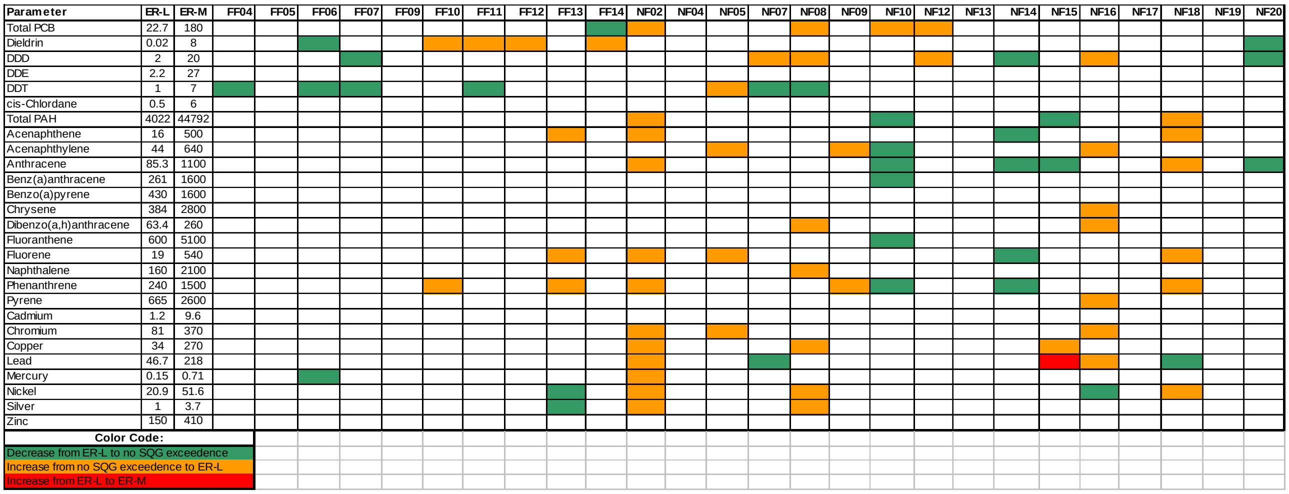
			1999	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**	**1999**
	ER-L	**ER-M**	**FF04**	**FF05**	**FF06**	**FF07**	**FF09**	**FF10**	**FF11**	**FF12**	**FF13**	**FF14**	**NF02**	**NF04**	**NF05**	**NF07**	**NF08**	**NF09**	**NF10**	**NF12**	**NF13**	**NF14**	**NF15**	**NF16**	**NF17**	**NF18**	**NF19**	**NF20**
Total PCB	22.7	180	6.92	3.57	7.38	10.1	2.56	2.62	7.46	8.05	22.5	29.1	2.95	1.37	6.62	24.4	18.7	9.42	7.64	16.5	0.872	3.59	5.44	13.1	0.721	4.09	3.94	9.97
Dieldrin	0.02	8	0.482	0.174	0.397	0.44	0.177	0	0	0	0.404	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.115
DDD	2	20	1.78	0.783	1.04	2.09	0.338	0.426	0.946	0.592	1.59	0.797	0.332		0.464	1	1.21	0.56	0.76	1.28		2.58	0.414	0.748		0.325	0.3	2.69
DDE	2.2	27	0.808	0.474	0.67	1.43	0.201		1.19	0.437	1.12	0.852	0.308	0.298	0.554	0.436	0.823		1.75	1.69		0.336	0.528	0.4		0.868	0.278	0.345
DDT	1	7	1.47	0.334	1.4	1.45	0.17	0.303	1.04	0.389	0.538	0.76	0.126	0.0959	0.429	1.06	4.29	0.878	0.524	2.29	0.065	0.505	0.535	0.407		0.208	0.214	
cis-Chlordane	0.5	6	0.126	0	0.0519	0.231	0	0.0281	0	0	0.243	0	0.0709	0.127	0.054	0	0.205	0.0538	0.084	0.0525	0	0	0	0.125	0	0.0408	0	0.0365
Total PAH	4022	44792	2190	696	1340	1780	652	3230	3300	2630	2480	2310	362	305	2360	17800	7400	4780	5530	14800	549	3290	4350	5960	159	1480	1450	3270
Acenaphthene	16	500	6.2	2.17	4.26	5.39	2.39	7.92	8.08	8.78	9.78	6.72	1.99	0.784	6.03	43.6	23.5	18	29.6	158	1.57	51.1	47.7	66.2	0.611	4.97	9.98	36.6
Acenaphthylene	44	640	22	6.66	11	14.5	6.38	22.1	32.4	16.6	18.4	22.5	2.34	3.53	26.3	220	64.5	39.9	48.3	70.3	3.51	9.73	13.2	29.4	1.18	14.6	8.12	15.9
Anthracene	85.3	1100	26.6	8.84	17	20.6	10.8	174	45.8	48.7	43.2	31.9	6.62	5.66	60.5	513	198	115	142	459	9.09	114	138	199	2.66	33.4	29.2	93.2
Benz(a)anthracene	261	1600	93.1	28.9	59.3	74.6	29.4	164	162	146	127	107	18.1	14.9	126	1100	425	279	314	803	23.5	162	213	321	7.67	80.9	70.7	178
Benzo(a)pyrene	430	1600	123	35.4	73.7	98.5	35.8	180	192	158	141	132	20.8	18.4	150	1150	429	291	331	800	25.2	140	216	312	8.9	92.5	79.8	170
Chrysene	384	2800	118	36.2	73	96.1	34.4	159	191	145	143	126	20.2	17.4	135	1060	420	267	305	779	24.3	158	208	311	8.85	81.3	77	176
Dibenzo(a,h)anthracene	63.4	260	22.1	6.83	13.6	17.1	6.28	22.8	29.4	24.2	20.2	22.1	3.42	2.84	23.2	133	52.7	45.9	46.1	110	3.96	16.4	31.4	40.1	1.08	14.1	11.8	22.8
Fluoranthene	600	5100	229	75.6	141	196	64.7	335	338	277	268	239	40.6	30.2	249	1730	837	492	611	1620	46.4	459	510	664	18.5	151	155	385
Fluorene	19	540	12.6	4.24	7.67	10.9	3.92	24.1	16.1	14.9	14.9	12.4	2.33	1.45	12.1	99.3	47.5	29.1	42.8	185	2.99	56.3	54.5	78.8	0.859	9	10.9	37.9
Naphthalene	160	2100	34.1	12.4	22.8	26.6	21.4	30.5	27.3	32.9	33.5	39.8	5.76	9.94	48.7	416	93.1	82.8	80.6	190	128	70.9	47.2	66.5	7.5	29.9	34	33.4
Phenanthrene	240	1500	123	41	76.2	104	36.2	239	180	139	141	127	22.7	13.2	113	640	427	239	354	1280	24.1	389	425	546	9.34	72.7	102	298
Pyrene	665	2600	210	67.6	129	174	61.2	387	326	279	258	225	38.3	30.2	238	1740	791	474	581	1520	43.3	376	458	617	17.8	147	154	354
Cadmium	1.2	9.6	0.0915	0.056	0.0366	0.148	0.0544	0.0713	0.138	0.0981	0.192	0.068	0.0064	0.0451	0.0967	0.104	0.221	0.105	0.0319	0.132	0.085			0.047	0.0347	0.0286	0.05	0.0363
Chromium	81	370	107	45.1	55.2	88.9	39.4	56.9	66	52.1	72.6	71.5	49.1	28.5	62.6	56	95.4	61	76	95.7	28.3	38.6	31.8	65.5	30.4	41.7	47.6	51.5
Copper	34	270	27.2	14.3	16.6	25.8	9.85	20.6	20.3	19.2	28.8	19.7	17.4	10.4	17	32.1	32.4	27.2	25.5	35.9	10.1	18.4	31.5	29.7	9.15	17	9.9	21.1
Lead	46.7	218	53.1	28.4	38.4	45.1	27.6	28.5	36.2	36.9	46.6	40.2	31.8	25.6	28	51.3	50.9	40.5	39.1	64.5	30	60	54.5	44.6	34.4	55.9	29.9	44.2
Mercury	0.15	0.71	0.212	0.09	0.166	0.201	0.0765	0.107	0.132	0.18	0.365	0.13	0.113	0.0402	0.099	0.261	0.311	0.207	0.213	0.445	0.061	0.17	0.138	0.254	0.0464	0.156	0.121	0.206
Nickel	20.9	51.6	31.3	13.9	18.4	31.7	14.3	17.7	23.2	17.1	23.2	23.3	19.4	8.4	14.3	16.9	19.1	19	15.2	27.1	7.9	10.8	9.4	21.5	6.6	7.3	12.2	19
Silver	1	3.7	0.344	0.219	0.395	0.492	0.21	0.269	0.256	0.478	1.34	0.242	0.341	0.199	0.228	0.298	0.918	0.392	0.416	0.622	0.153	0.304	0.254	0.692	0.193	0.328	0.278	0.643
Zinc	150	410	105	47.8	72.8	97.8	36.7	55.9	78.4	53.5	76	72	62.9	27.3	42.7	70.5	79.4	62.5	66.3	86.2	32.3	32.8	37.3	67.9	29	44.1	37.5	57.8
Total ER-L Exceedances			6	1	3	6	1	2	2	1	4	2	0	0	0	17	14	6	9	19	0	7	6	9	0	2	0	7
Total ER-M Exceedances			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 4-11. Contaminant levels in Massachusetts Bay relative to Sediment Quality Guidelines 2002.

			2002	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**	**2002**
Parameter	**ER-L**	**ER-M**	**FF04**	**FF05**	**FF06**	**FF07**	**FF09**	**FF10**	**FF11**	**FF12**	**FF13**	**FF14**	**NF02**	**NF04**	**NF05**	**NF07**	**NF08**	**NF09**	**NF10**	**NF12**	**NF13**	**NF14**	**NF15**	**NF16**	**NF17**	**NF18**	**NF19**	**NF20**
Total PCB	22.7	180	6.2	4.18	8.34	9.01	3.66	6.63	4.38	8.89	11.9	8.58	32.3	2.2	8.75	125	33.4	12.9	24.6	38.6	1.71	5.13	4.32	14.3	1.18	7.76	3.55	7.29
Dieldrin	0.02	8	0.495	0.294	ND	0.495	0.21	0.216	0.527	0.18	0.41	0.581	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DDD	2	20	1.02	0.551	1.01	0.981	0.324	0.809	0.847	0.849	0.751	0.956	1.83	0.222	1.13	2.75	3.97	1.27	1.19	3.57	0.174	0.476	0.474	2.16	0.0765	0.795	0.309	0.989
DDE	2.2	27	0.475	0.291	0.539	0.662	0.145	0.676	0.296	0.325	0.432	0.398	0.92	0.101	0.504	0.691	1.71	0.544	0.515	1.49	0.083	0.175	0.196	1.02	0.0377	0.386	0.15	0.439
DDT	1	7	ND	ND	0.183	ND	ND	ND	ND	0.323	ND	ND	ND	ND	1.27	ND	0.839	ND	ND	1.86	ND	ND	ND	ND	ND	0.236	ND	ND
cis-Chlordane	0.5	6	0.125	0.0601	0.0723	0.0971	0.056	0.103	0.0643	0.0721	0.135	0.044	0.175	0.026	0.0891	ND	0.323	0.046	0.0363	0.14	0.021	0.0273	0.05	0.108	0.019	0.0378	0.038	0.088
Total PAH	4022	44792	1920	944	1520	1780	788	3500	2460	3100	2680	2200	4690	607	4020	16600	9890	4910	3750	13700	433	1230	2500	10600	155	4090	987	3860
Acenaphthene	16	500	5.91	2.88	5.43	5.52	2.99	15.1	6.78	8.13	36.6	6.89	27	1.57	12.7	78.1	42.9	22.4	16.6	104	1.47	7.85	29.2	115	0.478	66.2	7.73	43.5
Acenaphthylene	44	640	21.8	10.3	15.4	17.4	9.54	36.7	29	40.7	14.1	25.8	37.8	8.66	54.2	260	116	63.5	40.4	118	4.91	9.31	13.7	58.3	1.83	24.6	8.33	22.5
Anthracene	85.3	1100	28	13.6	24.2	24.7	12.7	102	40	54.2	71.9	33.5	92.5	11.8	79.3	506	218	107	70.6	316	8.37	17.2	76.6	276	3.13	103	19.7	81.2
Benz(a)anthracene	261	1600	82.9	40.6	67.8	77.2	36.9	196	124	188	133	106	229	31.6	224	936	575	298	225	753	23.1	59.9	127	563	8.12	212	50.2	204
Benzo(a)pyrene	430	1600	106	52	83.2	99.5	39	154	131	156	116	113	235	32.8	98.1	729	388	185	94	493	24.8	18.6	119	358	8.96	118	57.9	109
Chrysene	384	2800	106	52.2	81.3	98.9	44.2	196	155	174	143	127	255	35.2	258	878	586	302	234	771	24.3	70.6	131	566	8.9	219	54.3	214
Dibenzo(a,h)anthracene	63.4	260	19.1	9.16	15.2	17.1	7.85	31.6	24.2	30.1	24.2	22.5	42.8	6.13	43.5	168	103	52	39.9	132	4.07	11.1	20	92.7	1.42	33	9.36	32.6
Fluoranthene	600	5100	200	103	157	198	79.9	419	252	331	309	224	490	59.9	450	2070	1110	507	409	1630	45.3	133	280	1320	16.6	497	112	471
Fluorene	19	540	11.5	5.57	9.28	11.1	4.85	30.9	13.4	14.7	42	12.5	37.6	2.93	26	171	79.2	36.5	25.9	135	2.55	11.7	34.2	136	0.804	68.1	8.1	49.9
Naphthalene	160	2100	26.2	13.7	23	23.1	24.6	39.1	18	29.2	32.3	32	83.4	21.1	95	445	198	131	76.3	270	11.7	25.5	32.7	129	2.98	74.5	14.9	62.2
Phenanthrene	240	1500	115	57.3	89.5	109	46.2	287	146	136	278	128	302	25.8	222	996	630	278	223	1060	23.4	94.4	245	1070	8.15	474	73.2	383
Pyrene	665	2600	183	91.4	145	175	74.7	422	239	356	270	210	452	58.4	401	1830	1060	491	387	1470	43.8	121	253	1160	15.6	431	101	421
Cadmium	1.2	9.6	0.0798	0.0579	0.0628	0.131	0.044	0.074	0.111	0.107	0.108	0.075	0.146	0.018	0.0786	0.0765	0.257	0.078	0.0804	0.129	0.022	0.013	0.04	0.085	0.0094	0.045	0.058	0.049
Chromium	81	370	109	70.7	76.7	98	52.7	79.8	80.5	60.6	72.8	80	102	32.7	86.9	74.1	127	73.7	76.3	143	46	54.4	45.7	92.3	34.8	68.1	55	61.4
Copper	34	270	23.7	13.8	17.2	23.6	10.5	14.6	18.4	17.3	26.1	16.3	36.4	9.4	16.8	26.1	36.6	25.4	23.6	42.6	16	32	42.3	32.5	6.25	26	10.8	27
Lead	46.7	218	48.4	28.4	34.7	43.6	30.2	35.3	37.8	34.7	39.9	39.5	48.8	27.2	37.4	42.5	57.2	38.5	40	70	n/a	91.5	235	54.7	25.2	30.3	30.6	n/a
Mercury	0.15	0.71	0.166	0.0889	0.145	0.169	0.06	0.118	0.122	0.182	0.244	0.132	0.308	0.046	0.12	0.268	0.26	0.163	0.18	0.498	0.062	0.225	0.144	0.322	0.0535	0.154	0.093	0.185
Nickel	20.9	51.6	30.2	17.5	20.6	27	12.6	14.3	23.5	15.9	18.7	21.9	27.5	5.5	16	18.7	22.9	15	16.9	28.1	11.6	16	11.7	20.2	2.35	21.7	15	19.6
Silver	1	3.7	0.361	0.246	0.419	0.528	0.172	0.268	0.278	0.489	0.77	0.28	1.04	0.125	0.269	0.299	1.06	0.36	0.41	0.8	0.139	0.262	0.225	0.598	0.113	0.277	0.243	0.413
Zinc	150	410	107	60.1	66.9	100	46.1	58.4	82.7	53.2	70.6	77.1	87.5	29.5	56.6	63.7	87.6	59.3	60.1	106	35.2	50.2	51.4	83	34.1	50.4	45.4	69.3
Total ER-L Exceedances			5	1	0	4	1	4	2	2	5	2	12	0	4	16	20	8	4	21	0	2	4	15	0	7	0	4
Total ER-M Exceedances			0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0

Table 4-12. Changes in ER-M and ER-L exceedances in Massachusetts Bay from 1992 to 2002.

	Total ER-L Exceedances			Total ER-M Exceedances			Change 1992 to 1999		Change 1999 to 2002		Change 1992 to 2002	
Station	**1992**	**1999**	**2002**	**1992**	**1999**	**2002**	**ER-L**	**ER-M**	**ER-L**	**ER-M**	**ER-L**	**ER-M**
FF04	4	6	5	0	0	0	2	0	-1	0	1	0
FF05	1	1	1	0	0	0	0	0	0	0	0	0
FF06	3	3	0	0	0	0	0	0	-3	0	-3	0
FF07	8	6	4	0	0	0	-2	0	-2	0	-4	0
FF09	1	1	1	0	0	0	0	0	0	0	0	0
FF10	1	2	4	0	0	0	1	0	2	0	3	0
FF11	12	2	2	0	0	0	-10	0	0	0	-10	0
FF12	2	1	2	0	0	0	-1	0	1	0	0	0
FF13	4	4	5	0	0	0	0	0	1	0	1	0
FF14	11	2	2	0	0	0	-9	0	0	0	-9	0
NF02	12	0	12	2	0	0	-12	-2	12	0	0	-2
NF04	0	0	0	0	0	0	0	0	0	0	0	0
NF05	9	0	4	0	0	0	-9	0	4	0	-5	0
NF07	15	17	16	1	0	0	2	-1	-1	0	1	-1
NF08	23	14	20	1	0	0	-9	-1	6	0	-3	-1
NF09	13	6	8	0	0	0	-7	0	2	0	-5	0
NF10	7	9	4	0	0	0	2	0	-5	0	-3	0
NF12	19	19	21	0	0	0	0	0	2	0	2	0
NF13	1	0	0	0	0	0	-1	0	0	0	-1	0
NF14	7	7	2	0	0	0	0	0	-5	0	-5	0
NF15	10	6	4	0	0	1	-4	0	-2	1	-6	1
NF16	22	9	15	0	0	0	-13	0	6	0	-7	0
NF17	0	0	0	0	0	0	0	0	0	0	0	0
NF18	5	2	7	0	0	0	-3	0	5	0	2	0
NF19	1	0	0	0	0	0	-1	0	0	0	-1	0
NF20	18	7	4	1	0	0	-11	-1	-3	0	-14	-1
Total	**209**	**124**	**143**	**5**	**0**	**1**	**-85**	**-5**	**19**	**1**	**-66**	**-4**
Percent change in number of exceedances							**-42%**		**16%**		**-33%**	



Parameter	ER-L	ER-M	FF04	FF05	FF06	FF07	FF09	FF10	FF11	FF12	FF13	FF14	NF02	NF04	NF05	NF07	NF08	NF09	NF10	NF12	NF13	NF14	NF15	NF16	NF17	NF18	NF19	NF20
Total PCB	22.7	180										🟩	🟧				🟧		🟧	🟧								
Dieldrin	0.02	8			🟩			🟧	🟧	🟧		🟧																🟩
DDD	2	20				🟩										🟧	🟧			🟧		🟩		🟧				🟩
DDE	2.2	27																										
DDT	1	7	🟩		🟩	🟩			🟩						🟧	🟩	🟩											
cis-Chlordane	0.5	6																										
Total PAH	4022	44792											🟧						🟩				🟩			🟧		
Acenaphthene	16	500									🟧		🟧									🟩				🟧		
Acenaphthylene	44	640													🟧			🟧	🟩					🟧				
Anthracene	85.3	1100											🟧						🟩			🟩	🟩			🟧		🟩
Benz(a)anthracene	261	1600																	🟩									
Benzo(a)pyrene	430	1600																										
Chrysene	384	2800																						🟧				
Dibenzo(a,h)anthracene	63.4	260															🟧							🟧				
Fluoranthene	600	5100																	🟩									
Fluorene	19	540									🟧		🟧		🟧							🟩				🟧		
Naphthalene	160	2100															🟧											
Phenanthrene	240	1500						🟧			🟧		🟧					🟧	🟩			🟩				🟧		
Pyrene	665	2600																						🟧				
Cadmium	1.2	9.6																										
Chromium	81	370											🟧		🟧									🟧				
Copper	34	270											🟧				🟧						🟧					
Lead	46.7	218											🟧			🟩							🟥	🟧		🟩		
Mercury	0.15	0.71			🟩								🟧															
Nickel	20.9	51.6									🟩		🟧				🟧							🟩		🟧		
Silver	1	3.7									🟩		🟧				🟧											
Zinc	150	410																										

Color Code:
🟩 Decrease from ER-L to no SQG exceedence
🟧 Increase from no SQG exceedence to ER-L
🟥 Increase from ER-L to ER-M

Figure 4-29. Difference plot showing direction of change of chemical concentration change between 1999 and 2002 in Massachusetts Bay relative to ER-L and ER-M Sediment Quality Guidelines.

5 BIOACCUMULATION PERSPECTIVES

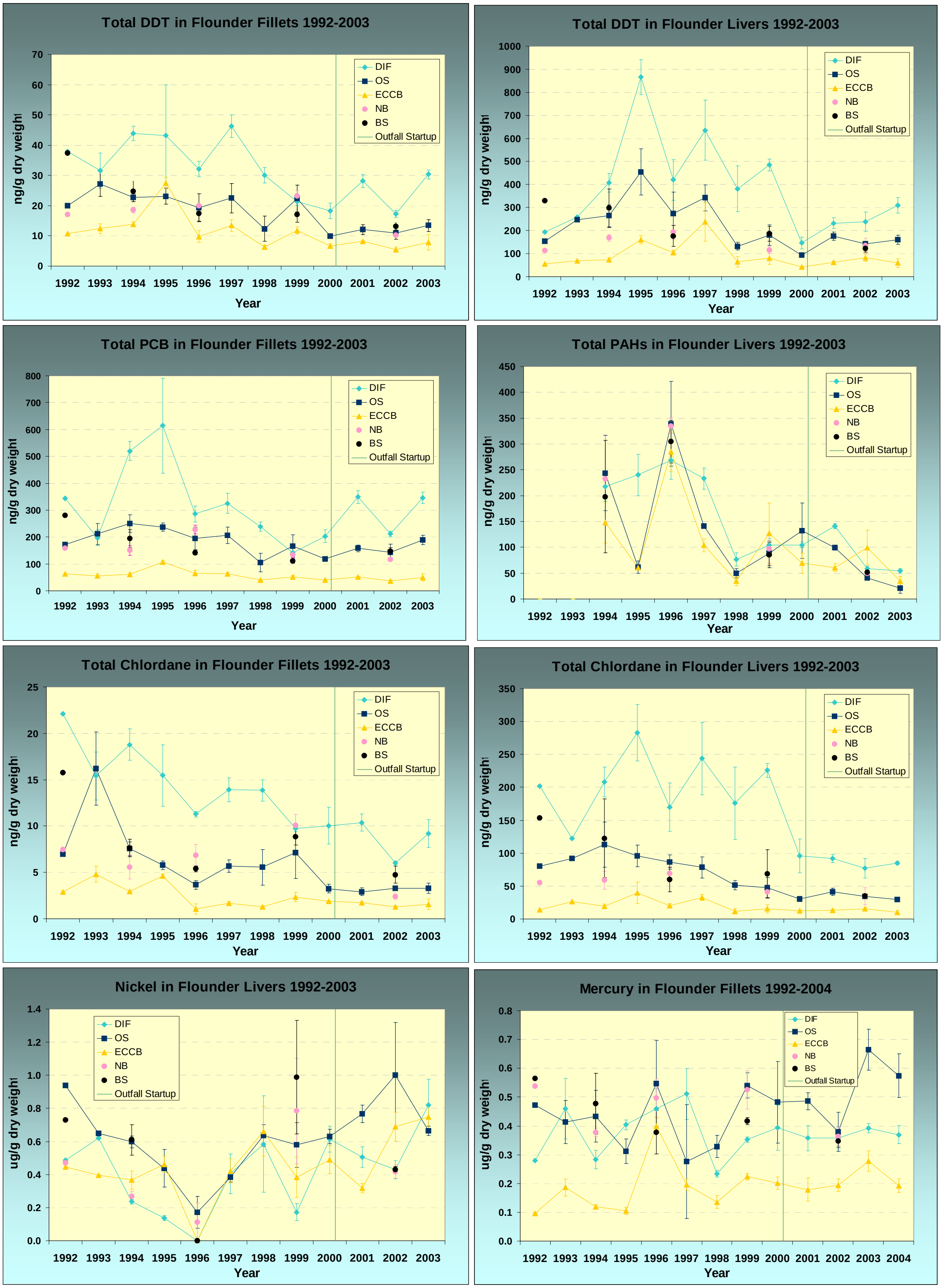
The MWRA's Harbor and Outfall Monitoring (HOM) Program (MWRA 1997) includes long-term biomonitoring for fish and shellfish. The goal of the biomonitoring is to provide data to assess potential environmental impacts of effluent discharge into Massachusetts Bay. These data are used to ensure that discharge from the new outfall does not result in adverse impacts to fish and shellfish by measuring and comparing contaminant levels in tissue with established thresholds (MWRA 2001a). This chapter includes discussion of contaminant levels and changes in lobster and flounder tissue, flounder health as measured by histopathology of livers, and bioaccumulation predictions based on caged mussels near the outfall, as well as comparison to contaminant data in tissue of similar species from other regions.

5.1 Trends in Contaminants in Indicator Organisms (Flounder and Lobster)

As part of the fish and shellfish monitoring program, the body burdens of contaminants have been determined for both edible tissue (i.e., fillet, meat) and liver tissue in winter flounder and lobster hepatopancreas since 1992. This section summarizes select contaminant levels in flounder and lobster tissue since the monitoring program began and considers the results as they relate to trends in sediment quality. The health of winter flounder is also discussed in relation to tissue contaminant levels.

Flounder-spatial patterns The overall spatial distribution of contaminant levels in flounder fillet and liver is consistent with the regional distribution of sediment contaminants. That is, there are higher levels of contaminants in Boston Harbor than in offshore Massachusetts Bay and Cape Cod Bay (Section 4.2) Organic contaminant concentrations (tPCB, tDDT, pesticides) in flounder fillet and liver have historically been highest in fish collected within Boston Harbor at Deer Island Flats (DIF) and lowest in winter flounder from eastern Cape Cod Bay (ECCB) (Figure 5-1). Metal body burdens are generally similar in samples from DIF and the outfall site (OS) and lowest in those from ECCB. Contaminant concentrations at Nantasket Beach (NB) and Broad Sound (BS) are generally similar to those found at OS.

Temporal patterns Fillet and liver concentrations of total chlordanes, tDDT, and dieldrin have tended to decrease gradually throughout the region since the early to mid-90's (Figure 5-1; dieldrin not shown). Total PAHs, which are measured only in livers, decreased more dramatically between 1996 and 1998. Total PCBs have shown no discernible trend, with elevated concentrations observed in 1994 and 1995 in fillets and concentrations in livers in 1995 comparable to those of other years (Figure 5-1). In general, metals concentrations were more variable by station than the levels of organic contaminants were and did not show any consistent temporal trends. One exception is nickel, which increased in flounder livers from DIF, OS, and ECCB after 1996, after having shown a steady decrease between 1992 and 1996. In addition, mercury has been elevated in flounder fillet at OS since 2003, and concentrations at DIF and ECCB have been stable since 1999. Slightly elevated lead, copper, and silver appear to be present at OS since 1999.



Source: Lefkovitz *et al*. 2004

Figure 5-1. Contaminant concentrations in flounder fillet and liver.

Most wastewater began receiving secondary treatment at the Deer Island facility beginning in 1998 with the inter-island tunnel transfer from the Nut Island treatment plant. In September 2000, the new Massachusetts Bay outfall was opened, ending treated wastewater discharge to Boston Harbor. Temporal trends in flounder tissue contaminant data may be an indirect indicator of the environmental effect of these changes and improvements in the wastewater treatment system. Concentrations of select contaminants (tPAH, tDDT, mercury, and copper) during the three years after effluent discharge diversion to Massachusetts Bay (2001 – 2003) were similar to or lower than levels during the three years prior to discharge diversion (1998 – 2000) (Table 5-1). The exception was tPCB, which was higher, in some cases substantially higher, in flounder fillet and liver during the three years after discharge diversion (Table 5-1). Two possible contributing factors to the increase in tPCB during the post-diversion period (2001 – 2003) were an increase in concentrations of PCB congener 180 due to analytical interferences and possibly wetter/snowier weather during the 2000 – 2002 period, which may have delivered precipitation and runoff laden with high levels of organic contaminants to the region (Lefkovitz *et al.* 2004). The overall tPCB trends do not change dramatically by excluding PCB congener 180 from the calculation of tPCB. These data indicate that for contaminants other than tPCB, there have been no substantial changes in contaminant concentrations in flounder from the three sites within the first three years of outfall startup.

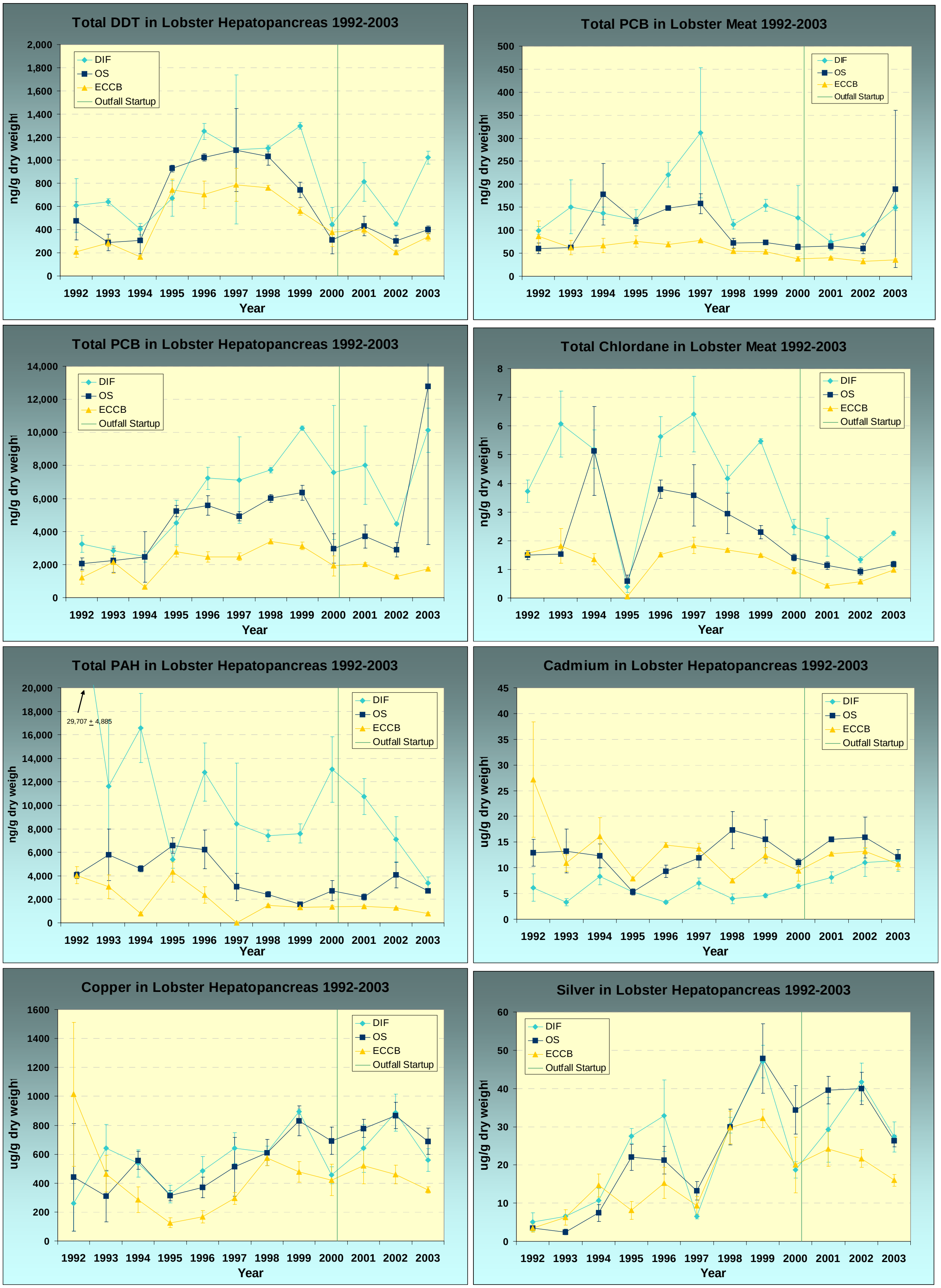
Table 5-1. Comparison of contaminants in flounder tissue during pre- and post-diversion periods. Mean and standard error of annual measurements are shown.

Location	**DIF**	**DIF**	**OS**	**OS**	**ECCB**	**ECCB**
Year	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 - 2003**
n	**9**	**9**	**9**	**9**	**9**	**9**
Flounder Fillet						
tPCB	194 ± 49	302 ± 78	130 ± 32	163 ± 24	44 ± 7	46 ± 8
tDDT	23 ± 6	25 ± 7	15 ± 7	12 ± 1	8 ± 3	7 ± 2
Mercury	0.3 ± 0.08	0.4 ± 0.02	0.4 ± 0.1	0.5 ± 0.1	0.2 ± 0.05	0.2 ± 0.05
Flounder Liver						
tPAH	95 ± 16	84 ± 49	90 ± 41	54 ± 41	77 ± 47	65 ± 33
tPCB	2259 ± 627	3711 ± 707	1222 ± 71	2419 ± 203	353 ± 99	437 ± 73
tDDT	337 ± 174	260 ± 43	136 ± 44	159 ± 16	63 ± 19	68 ± 13
Mercury	0.3 ± 0.1	0.4 ± 0.07	0.6 ± 0.1	0.5 ± 0.1	0.3 ± 0.03	0.2 ± 0.08
Cu	65 ± 46	52 ± 8	134 ± 45	106 ± 28	103 ± 34	64 ± 19

Units for organic contaminants are ng/g dry weight.
Units for metals are µg/g dry weight.

Lobster-spatial patterns Similar to the spatial tendencies observed in the winter flounder contaminant data, organic contaminant concentrations in lobster meat and hepatopancreas are generally highest in lobsters collected at DIF and lowest in lobsters from ECCB (Figure 5-2). Metal body burdens are generally similar in samples from DIF and OS and lowest from ECCB, except for nickel, where they are usually highest at ECCB.

Temporal patterns Like the temporal trends for flounder, total chlordanes, tPAH, and dieldrin (not shown) in both lobster meat and hepatopancreas have steadily decreased at most sites since the early to mid-1990's (Figure 5-2). Total DDT and tPCB concentrations in lobster meat have decreased steadily at all three stations since 1997, except for a small increase in both compounds at DIF and for only PCBs at OS in 2003 (Figure 5-2). Hepatopancreas concentrations of tDDT and tPCB increased during the mid to late 1990's at all three stations before falling back to pre-1995 levels. The exceptions were the relatively high tPCB concentrations at DIF since 1999 and at OS in 2003. The 2003 increase in tPCB was due to one lobster that had extremely high PCB concentrations that did not fit the typical congener pattern observed throughout the project. It is believed that the lobster may not have come from the site's general population (Lefkovitz *et al* (2004).



Total DDT in Lobster Hepatopancreas 1992-2003

Total PCB in Lobster Meat 1992-2003

Total PCB in Lobster Hepatopancreas 1992-2003

Total Chlordane in Lobster Meat 1992-2003

Total PAH in Lobster Hepatopancreas 1992-2003

Cadmium in Lobster Hepatopancreas 1992-2003

Copper in Lobster Hepatopancreas 1992-2003

Silver in Lobster Hepatopancreas 1992-2003

Source: Lefkovitz *et al* 2004

Figure 5-2. Contaminant concentrations in lobster meat and hepatopancreas.

Temporal trends in metals concentrations are less consistent than for the organic contaminants and, for some metals, tend to show increasing concentrations in lobster hepatopancreas. Cadmium concentrations in hepatopancreas from DIF have been increasing steadily since 1998, becoming more similar to levels measured at OS and ECCB (Figure 5-2). Levels of copper have been increasing in lobster hepatopancreas from DIF and OS since the early 1990's. Silver concentrations increased in hepatopancreas at all three stations from 1993 to 1999 and have remained elevated since then.

To look at the effect of moving the location of the effluent discharge, it is reasonable to compare the three years pre- and post-diversion. During this time most effluent received secondary treatment. While tPCB, tDDT, and tPAH for meat and hepatopancreas at DIF and ECCB were numerically lower after diversion, OS showed a different pattern (Table 5-2). Although tPAH and tPCB were numerically higher at the outfall site after diversion, they were not statistically different than the pre-diversion values. The PCB increase was caused by one lobster collected in 2003 whose tissues had extremely high PCB concentrations. Total DDTs were statistically lower at OS after diversion. None of the representative metals (i.e., mercury and copper) at any of the stations showed a significant change between the pre- and post-diversion periods.

Table 5-2. Comparison of contaminants in lobster tissue during pre- and post-diversion periods. Mean and standard error of annual measurements are shown

Location	**DIF**	**DIF**	**OS**	**OS**	**ECCB**	**ECCB**
Year	**1998 - 2000**	**2001 – 2003**	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 – 2003**
N	**9**	**9**	**9**	**9**	**9**	**9**
Lobster Meat						
tPCB	132 ± 21	104 ± 39	70 ± 5	119 ± 98	49 ± 9	36 ± 4
tDDT	11 ± 5	10 ± 3	7 ± 2	6 ± 1	8 ± 3	6 ± 1
Mercury	0.8 ± 0.1	0.9 ± 0.1	1.0 ± 0.06	0.9 ± 0.1	0.7 ± 0.06	0.6 ± 0.07
Lobster Hepatopancreas						
tPAH	9353 ± 3203	8916 ± 2570	2239 ± 605	3135 ± 1328	1384 ± 86	1351 ± 84
tPCB	8518 ± 1505	7539 ± 2865	5107 ± 1863	6458 ± 5490	2820 ± 792	1676 ± 384
tDDT	949 ± 447	762 ± 291	697 ± 363	378 ± 66	566 ± 191	314 ± 101
Mercury	0.3 ± 0.02	0.3 ± 0.07	0.5 ± 0.08	0.3 ± 0.03	0.3 ± 0.05	0.2 ± 0.02
Copper	654 ± 223	695 ± 170	711 ± 111	778 ± 89	491 ± 76	445 ± 85

Units for organic contaminants are ng/g dry weight.
Units for metals are µg/g dry weight.

The declining concentrations of organic contaminants (tPAH, tDDT, tPCB, total chlordane) in winter flounder and lobster are consistent with those seen in sediments in the outer Harbor since 1994 (Table 4-2). In contrast, the noted decreases in metals concentrations (i.e., mercury, cadmium, and silver) in outer Harbor sediments have not been observed in flounder and lobster tissue. In general, either no temporal trends were evident or there were increasing trends in the levels of metals in flounder and lobster tissue. These increases in metals concentrations in flounder and lobster tissue may be due to subtle changes in metal bioavailability through sediment processes or increased availability of metals remobilized from the sediments and accumulated in plankton and other food resources that bioaccumulate contaminants from the water rather than sediments. This is consistent with the expectations of contaminant releases from sediment driven by the improved redox levels and lower organic content of the sediments.

Both the tissue chemistry and sediment data show less variability within and among stations in recent years, with concentrations tending to converge toward a common value similar to levels measured at ECCB, though contaminant concentrations among stations still reflect the spatial trend of higher concentrations in organisms from Boston Harbor and lower concentrations in those from offshore locations (OS and ECCB). This trend in the data may be an indication that the Massachusetts Bay system is stabilizing after the improvements to the wastewater treatment system, movement of the effluent outfall offshore, the banning of PCBs and pesticides, and stronger regulations in the Clean Water Act for PAHs .

Concentrations of contaminants in flounder and lobster collected from Boston Harbor and Massachusetts and Cape Cod Bays are generally similar to or lower than in organisms from other regions in the northeast (i.e., Long Island Sound [Corps 2002] and Rhode Island Sound [EPA 2004]) analyzed using similar method to the MWRA program, with a few notable exceptions (Table 5-3). For example, tPCB in flounder from DIF were slightly higher (~36%) than in flounder from Long Island Sound (LIS) and nearly 4 times those from Rhode Island Sound (RIS). Total DDTs showed a similar pattern. Mercury concentrations were two to four times higher in flounder fillet from DIF, OS, and ECCB, and four to six times higher in flounder liver from DIF and OS than in those from the other regions. Copper concentrations in flounder liver from OS were approximately two times higher than from LIS and RIS.

Lobster concentrations of tPCB (meat and hepatopancreas) and tPAH (hepatopancreas only) were higher at DIF and OS than from the other regions (Table 5-3), with tPCB concentrations being a factor of three to four times higher, and tPAH approximately 34 times higher than in RIS and up to a factor of 5 higher than LIS. Total DDT (tDDT) concentrations were also higher in lobster from DIF (1.5 to 3.5 times) than in those from LIS or RIS.

Table 5-3. Comparison of contaminants in flounder and lobster tissue from other areas.

Flounder Fillet					
Location	**LIS[1]**	**RIS[2]**	**DIF[3]**	**OS[3]**	**ECCB[3]**
Year	**2000**	**2001 & 2002**	**2001 - 2003**	**2001 - 2003**	**2001 - 2003**
n	**7**	**7**	**9**	**9**	**9**
tPCB	38 ± 11	14 ± 4	52 ± 13	27 ± 3	8 ± 1
tDDT	5.8 ± 1.6	1.9 ± 0.5	4.3 ± 1.1	2.0 ± 0.1	1.3 ± 0.2
Mercury	0.02 ± 0.005	0.03 ± 0.006	0.06 ± 0.004	0.08 ± 0.02	0.04 ± 0.008
Flounder Liver					
n	**7**	**7**	**9**	**9**	**9**
tPAH	34 ± 6	35 ± 23	20 ± 10	14 ± 7	16 ± 10
tPCB	706 ± 485	360 ± 117	853 ± 131	558 ± 18	103 ± 28
tDDT	106 ± 60	50 ± 4	60 ± 9	37 ± 3	16 ± 5
Mercury	0.02 ± 0.006	0.03 ± 0.004	0.08 ± 0.01	0.12 ± 0.02	0.01 ± 0.02
Copper	12 ± 2	15 ± 1	12 ± 3	24 ± 5	15 ± 4
Lobster Meat					
n	**15**	**8**	**9**	**9**	**9**
tPCB	8 ± 4	6 ± 1	15 ± 7	14 ± 9	5 ± 1
tDDT	1 ± 0.4	0.7 ± 0.2	1.4 ± 0.5	0.8 ± 0.2	0.8 ± 0.1
Mercury	0.07 ± 0.02	0.1 ± 0.02	0.1 ± 0.03	0.1 ± 0.02	0.08 ± 0.02
Lobster Hepatopancreas					
n	**15**	**8**	**9**	**9**	**9**
tPAH	353 ± 106	63 ± 16	2142 ± 1191	940 ± 252	330 ± 96
tPCB	826 ± 112	515 ± 146	2266 ± 949	1953 ± 1650	479 ± 114
tDDT	123 ± 18	67 ± 16	229 ± 96	118 ± 28	89 ± 29
Mercury	0.07 ± 0.02	0.1 ± 0.04	0.1 ± 0.02	0.1 ± 0.004	0.06 ± 0.005
Copper	756 ± 169	454 ± 115	204 ± 38	242 ± 20	125 ± 23

Units for organic contaminants are ng/g wet weight.
Units for metals are μg/g wet weight.
n = number of replicates.
[1] Data from Corps 2002.
[2] Data from EPA 2004.
[3] Corresponding dry weight data reported in Lefkovitz *et al.* 2004.

It is assumed that flounder and lobster sampled are from the location from which they are collected and that they have reached a steady state with that environment. Because they are migratory organisms, flounder and lobster may be integrating a larger area of the Massachusetts Bay system than that represented by the sampling location. Despite their migratory nature, flounder and lobster are useful in monitoring temporal and spatial trends in environmental contaminant levels and complement the data obtained through the collection and analysis of sediment samples by indicating not only which contaminants are present but also which ones are being taken up and bioaccumulated in organisms in the area.

5.2 Flounder Condition in Boston Harbor and Massachusetts Bay

Since 1991, livers from winter flounder collected from Boston Harbor, Massachusetts Bay, and Cape Cod Bay have been analyzed for the presence and extent of various lesions, including three types of hydropic vacuolation (centrotubular, tubular, and focal), macrophage aggregation, biliary duct proliferation, and neoplasia. Overall there has been a steady system-wide reduction in contaminant-associated pathology (i.e., neoplasia and hydropic vacuolation) in winter flounder in the past decade (Lefkovitz *et al*. 2004). Data collected in recent years lack the high lesion prevalence characteristic of flounder in the mid-to-late 1980s. Hydropic vacuolation, because of its relationship to environmental contaminants, has been one of the principal lesions monitored in winter flounder throughout the program. Centrotubular hydropic vacuolation (CHV) is the least severe and most common form of the lesions observed in the collections. The general trend of CHV prevalence at DIF is downward from 1991 to 2000, remaining lower in 2002 – 2004 than in the peak years of 1991 – 1994 (Figure 5-3). The prevalence of CHV at Broad Sound since 2000 has remained much lower than the prevalence observed during the peak years of 1991 – 1993. The prevalence at Nantasket Beach decreased in 2000 and has remained low since then (Figure 5-3). CHV at the Outfall Site fell marginally in 2001 and has remained below the baseline mean, except for in 2002. Hydropic vacuolation at OS showed statistically significant decreases in 2001-2003 when compared to predischarge levels (1998 – 2000). At the reference site in Eastern Cape Cod Bay, CHV prevalence has been variably low throughout the study.

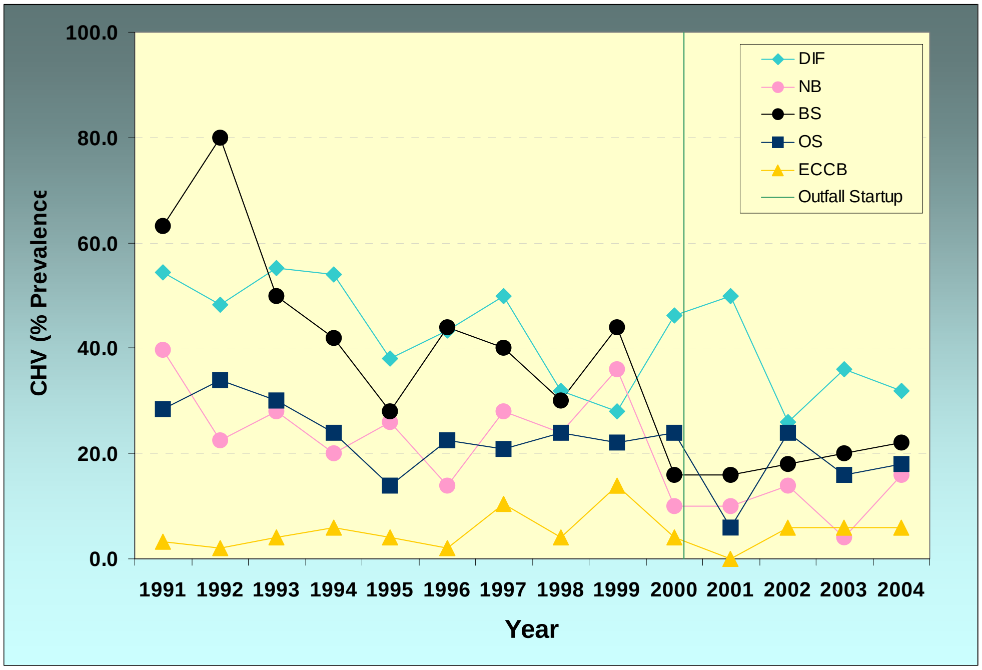


Figure 5-3. Prevalence of centrotubular hydropic vacuolation in winter flounder livers.

During the 2003 fish and shellfish study, a marked prevalence of ulcers was observed on the blind surface of a number of flounder, especially in those collected from the Boston Harbor-western Massachusetts Bay region. Researchers at the National Marine Fisheries Service (NMFS) and the Massachusetts Division of Marine Fisheries (MADMF) also observed similar ulcers beginning in 2002 and 2003 (Moore 2003). These ulcers were observed only rarely prior to 2001. Additional winter flounder studies were conducted in 2004 and 2005 to increase the number of sampling stations and surveys for which winter flounder are examined for external lesions. An in-depth microbiological study of the ulcer lesions to attempt to correlate specific organisms with the lesions was also conducted.

Results from the three surveys conducted in 2004 and from four 2005 surveys show that the prevalence of ulcers appears to be highest in the spring, with the severity and incidence decreasing from April to June (Table 5-4). Ulcers were either absent or healing in the fall NMFS surveys in 2002 and 2003, suggesting a seasonal aspect to the syndrome (Moore *et al.* 2004). The microbiological studies of the ulcers in 2004 and 2005 suggest that bacteria are not the primary agents in this syndrome (Moore *et al.* 2005). Fungal elements or viral particles were not observed. Prior insult to the dermis of the fish likely allowed the opportunistic and normal (indigenous) flora bacteria isolated from the ulcers to infect tissues. Seasonal and inter-annual factors which co-vary could hypothetically be associated with the ulcers. These include changes in the fish during spawning, seasonal precipitation, sediment resuspension and transport, inter-annual climate variations, undetected changes in effluent chemistry, and seasonal pathogen blooms and predation. Continued evaluation of the prevalence and severity of the lesion should continue in cooperation with state and federal fisheries agencies and scientists. Further evaluation of seasonal or interannual changes in Massachusetts Bay sediment quality that might be related to the syndrome is also recommended.

Table 5-4. Prevalence of external ulcers on the blind surface of winter flounder sampled during the MWRA program.

	Deer Island			**Broad Sound**			**Outfall**			**FF09**			**Nantasket Beach**			**Cape Cod Bay**		
	U	H	*n*	U	H	*n*	U	H	*n*	U	H	*n*	U	H	*n*	U	H	*n*
April 2003	20	-	15	16	-	50	24	-	50	NS	NS	NS	6	-	50	0	-	50
April – May 2004	22	0	50	12	0	50	36	0	50	42	0	50	30	0	50	0	0	50
June 2004	0	2	50	0	6	48	14	6	50	NS	NS	NS	6	0	16	NS	NS	NS
September 2004	-	-	0	0	0	1	NS	NS	NS	0	8	50	NS	NS	NS	NS	NS	NS
January 2005	-	-	0	-	-	0	0	0	4	0	0	50	NS	NS	NS	NS	NS	NS
March 2005	-	-	0	NS	NS	NS	-	-	0	10	3	29	NS	NS	NS	NS	NS	NS
April 2005	0	0	50	NS	NS	NS	14	0	50	16	0	50	14	2	50	0	0	50
June 2005	NS	NS	NS	NS	NS	NS	4	6	50	-	-	0	0	4	50	NS	NS	NS
Total	8	1	165	9	2	149	18	2	254	14	2	229	12	1	216	0	0	150

Source: Moore *et al*. 2005, Gagnon and Lescarbeau 2005.
U = Percent of winter flounder with ulcerations.
H = Percent of winter flounder with healed ulcers.
n = Number of winter flounder sampled
NS = Not sampled.

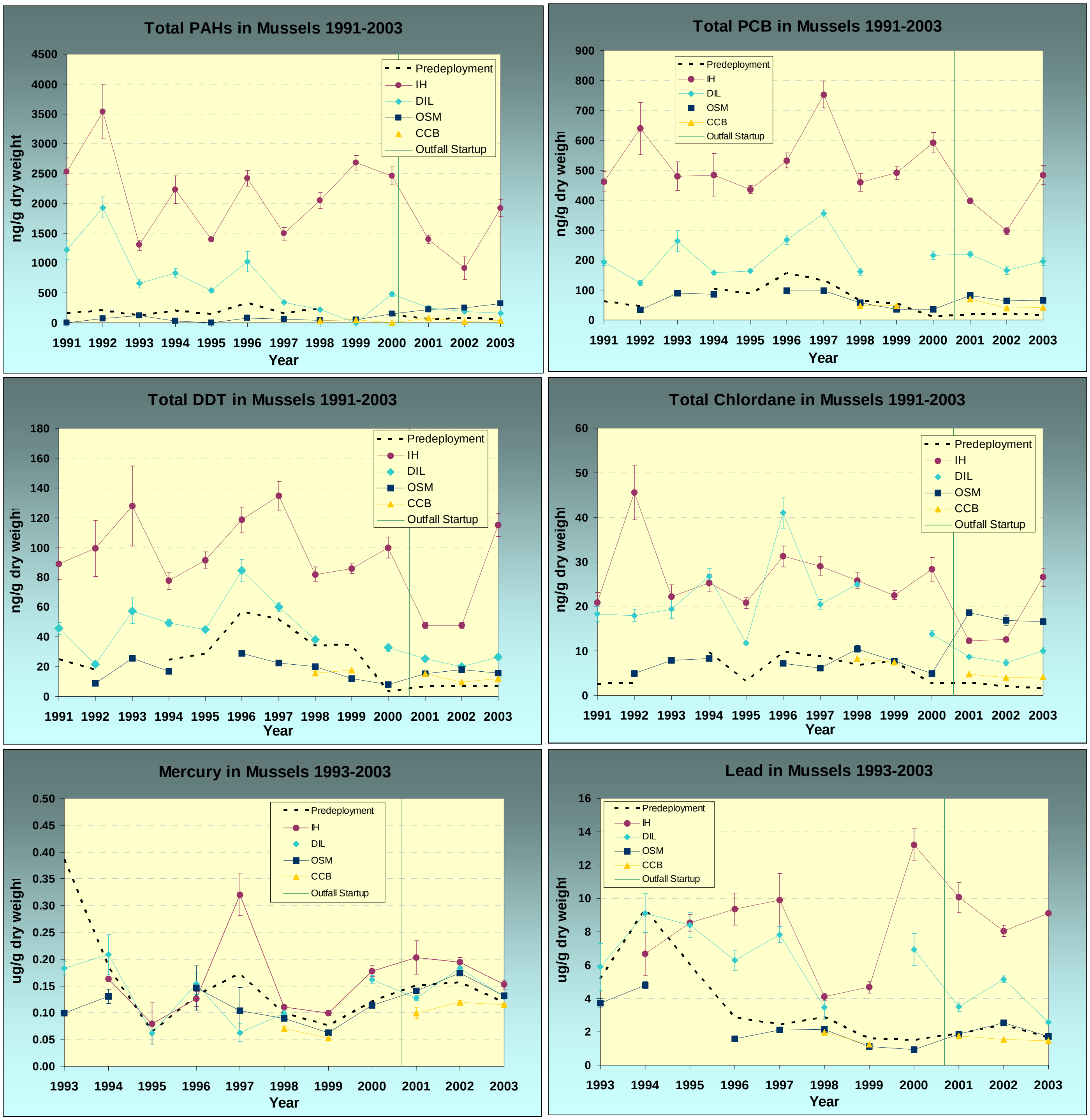
5.3 Bioaccumulation in Shellfish

One of the indicator species used in the MWRA fish and shellfish monitoring program is the blue mussel *(Mytilus edulis*). Arrays of mussels are deployed in and recovered from Boston Harbor and the Bays to determine the short-term accumulation of anthropogenic contaminants in mussel tissue and to evaluate NPDES permit conditions for compounds that bioaccumulate. Since 1991, mussels collected from Sandwich, MA, Gloucester, MA, Rockport, MA, or Stover's Point in Maine have been deployed for up to 60 days in cages suspended near Deer Island Light (DIL), in Boston's inner harbor (IH), the Outfall Site (OS), and since 1998 in Cape Cod Bay (CCB). Prior to the outfall diversion in 2000, the Outfall mussels were deployed near the B-Buoy, a navigation aid to Boston Harbor, about 1 km south of the MWRA diffuser in Massachusetts Bay. After diversion, the Outfall Site station was re-located to ~100 m south of the diffuser. In 2002 and 2003, caged mussels were also deployed at the B-Buoy (LNB) to provide information on the bioaccumulation potential outside of the diffuser's initial mixing zone.

Pre-deployment contaminant levels have been consistently low, especially since the late 1990's, although variation occurs in several chemicals primarily related to the changing source location of the mussels. In general, the highest caged mussel contaminant levels were measured in the mussels deployed in the inner harbor. Since 1998 the lowest concentrations measured were typically in mussels deployed at Cape Cod Bay (Figure 5-4). The mussels deployed in Cape Cod Bay typically exhibited small amounts of contaminant depuration and bioaccumulation relative to the pre-deployment levels depending on the chemical and mussel source location.

Some important trends are also apparent in the caged mussel data set particularly after the effluent diversion in 2000. Total PAH concentrations in mussels deployed at Deer Island Light (DIL) have declined steadily since the early 1990s; tDDT and total chlordane have declined from peak values in 1996. Significantly, tPAH, tPCB, tDDT, total chlordane, and lead in the mussels deployed in the Inner Harbor (IH) experienced a large decrease in concentration from 2000 to 2001 (Figure 5-4) after effluent diversion to Massachusetts Bay. Concentrations continued to decrease or were stable in 2002, before increasing again in 2003. This pattern may be partially explained by the drought the region experienced in 2001-2002, which may have decreased contaminant loading to the harbor. At OS, tPAH concentration was elevated above baseline levels from 2000 to 2003.

Moreover, concentrations of select organic contaminants (tPAH, tPCB, tDDT, total chlordane) were generally lower in mussels deployed in the Inner Harbor (IH) and at Deer Island Light (DIL) during the post-diversion period (2001 – 2003) than during the three years prior to diversion of effluent to Massachusetts Bay (1998-2000) (Table 5-5). Post-diversion concentrations of mercury and lead were generally higher at IH and DIL than pre-diversion concentrations. Concentrations of tPAH, tDDT, tPCB, total chlordane, dieldrin, mercury, and lead were significantly higher in mussels deployed at the outfall site during the post-diversion period (2001 – 2003) than during the pre-diversion period (1998 – 2000). Concentrations of most contaminants in mussels deployed in Cape Cod Bay were similar during the pre- and post-diversion periods, except for mercury, which almost doubled during the post-diversion period.



Source: Lefkovitz *et al.* 2004

Figure 5-4. Contaminant concentrations in mussels.

Table 5-5. Comparison of contaminants in mussel tissue during pre- and post-diversion periods. Mean and standard error of annual measurements are shown

Location	IH	IH	DIL	DIL	OS	OS	CCB	CCB
Year	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 - 2003**	**1998 - 2000**	**2001 - 2003**
N	**15**	**15**	**10**	**15**	**24**	**24**	**16**	**16**
tPAH	2396 ± 322	1411 ± 501	351 ± 189	200 ± 43	78 ± 54	266 ± 58	46 ± 8	49 ± 34
tPCB	515 ± 69	393 ± 93	188 ± 38	194 ± 27	44 ± 12	74 ± 14	48 ± 1	51 ± 17
tDDT	89 ± 10	70 ± 39	35 ± 4	24 ± 3	13 ± 5	16 ± 2	17 ± 1	12 ± 3
tChlordane	26 ± 3	17 ± 8	19 ± 8	9 ± 1	8 ± 3	17 ± 1	8 ± 1	4 ± 0.4
Mercury	0.13 ± 0.04	0.18 ± 0.03	0.13 ± 0.04	0.15 ± 0.03	0.09 ± 0.02	0.15 ± 0.02	0.06 ± 0.01	0.11 ± 0.01
Lead	7.3 ± 5.1	9.1 ± 1.0	5.2 ± 2.4	3.7 ± 1.3	1.4 ± 0.6	2.0 ± 0.4	1.6 ± 0.5	1.6 ± 0.2

Units for organic contaminants are ng/g dry weight.
Units for metals are µg/g dry weight.
tDDT is the sum of 6 congeners. Total chlordane is the sum of heptachlor, heptachlor epoxide, cis-chlordane, and trans-nonachlor.

Regional mussel contaminant data are available through the Gulfwatch program (www.gulfofmaine.org). Gulfwatch is an international monitoring program organized and administered by the Gulf of Maine Council on the Marine Environment (GOMC) that tracks spatial and temporal trends of contaminants in populations of blue mussels around the Gulf of Maine (GOMC, 2003). Samples are collected each fall from 56 sites on a rotating basis and analyzed for trace metals, PCBs, PAHs, and pesticides. Sampling sites within Massachusetts include stations in the Inner Harbor, outer Boston Harbor (near Long Island) and Sandwich, which is one of five benchmark sites sampled annually. Some contaminant concentrations for mussels measured during the Gulfwatch program are comparable to those measured in mussels deployed as part of the MWRA monitoring program, while for other contaminants, concentrations between the programs are quite different (e.g., within a factor of 1.8 for organic contaminants, seven for mercury, and four for lead (Table 5-6)). Similar to MWRA findings, the Gulfwatch data show that the body burden of contaminants in mussels is highest in the Inner Harbor, decreasing with distance from the harbor, and that caged mussels deployed in the environment are able to equilibrate with the surrounding water column and provide tissue contaminant data that are reasonably comparable to that obtained from indigenous mussel populations.

Table 5-6. Comparison of contaminants in mussel tissue from other areas.

Location	Boston Inner Harbor		Outer Harbor		Cape Cod		Maine
Program	**GW**	**MWRA**	**GW**	**MWRA**	**GW**	**MWRA**	**MWRA**
Station	**MAIH**	**IH**	**MALI**	**DIL**	**MASA**	**CCB**	**SP**
Year	**1998**	**1998 - 2000**	**1999**	**1998 - 2000**	**1998 - 2000**	**1998 - 2000**	**2002 - 2003**
n	**4**	**15**	**5**	**10**	**12**	**16**	**10**
tPAH	3333 ± 223[a]	2396 ± 322	394 ± 51[a]	351 ± 189	44 ± 26[a]	46 ± 8	69 ± 7
tPCB	740 ± 39[b]	515 ± 69	166 ± 11[b]	188 ± 38	41 ± 12[b]	48 ± 1	18 ± 4
tDDT	106 ± 14	89 ± 10	22 ± 2	35 ± 4	30 ± 7	17 ± 1	7 ± 0.06
Mercury	0.55 ± 0.02	0.13 ± 0.04	0.4 ± 0.1	0.13 ± 0.04	0.42 ± 0.07[c]	0.06 ± 0.01	0.14 ± 0.03
Lead	32.3 ± 3.3	7.3 ± 5.1	5.9 ± 0.5	5.2 ± 2.4	2.8 ± 0.6[c]	1.6 ± 0.5	2.0 ± 0.5

Source of Gulfwatch data: http://www.gulfofmaine.org/gulfwatch/results.asp
GW = Gulfwatch
Units for organic contaminants are ng/g dry weight.
Units for metals are µg/g dry weight.
[a] tPAH value is Total 24 PAHs.
[b] GulfWatch tPCB includes additional congeners (5, 15, 90, 95, 132, 190, 208).
tDDT is the sum of 6 congeners.

In 2001, the year after flow to the Massachusetts Bay outfall was established, the mussels deployed at the Outfall Site exceeded thresholds set for tPAH (NOAA 24 PAHs) and total chlordane (Hunt *et a*l. 2002a). Total PAH and chlordane thresholds were also exceeded in 2002, and PAH thresholds were exceeded in 2003. These exceedances were unexpected, since it was thought that the thresholds had been set at a level above any expected change from baseline. As a result, an investigative study was conducted to understand why the levels were greater than expected and evaluate possible factors affecting measured contaminant levels in caged mussels (Hunt *et al*. 2002a). Theoretical bioaccumulation equations (Pruell *et al.* 1986; Bergen *et al.* 1993; Neff and Burns 1996) were used to estimate the expected mussel concentrations based upon measured effluent concentrations and dilution. Calculations were performed using individual compounds and then the calculated values were summed as defined for the threshold for 24 NOAA PAHs and total chlordane. Calculations were also performed for two PCB congeners, PCB 138 and PCB 153. It was assumed that the uptake of contaminants by mussels was from the dissolved phase only, based on work by Geyer *et al.* (1982) and Pruell *et al.* (1986). Recent data and information on the contaminants were used, including MWRA effluent concentrations, unpublished organic compound phase partitioning data in effluents from treatment plants similar to MWRA's, and K_{ow} values. The measured offshore effluent dilution and low offshore background concentrations were also factored into the calculations performed. The background concentration was assumed to be that of Cape Cod Bay.

Results of the investigative study (Hunt *et al.* 2002) found that the tPAH and chlordane concentrations measured in the mussels deployed in the vicinity of the outfall in 2001 are consistent (within a factor of two) with predictions based on recent theory of bioaccumulation in mussels using measured concentrations in the effluent, assumed partitioning between dissolved and particulate phases, and the likely water column concentrations the mussels were exposed to at the deployment locations. Several factors were identified as being critical to the prediction of levels of contaminants in caged mussels:

- Duration and frequency of exposure to the diluted effluent plume,
- Ambient water contaminant concentrations,
- Effluent contaminant concentrations,
- Measurement errors and estimates of K_{ow}.

Even though thresholds were exceeded, there was no indication of any environmental impact from the exceedances. Water quality criteria for PAHs and chlordanes were met in the effluent before dilution, and the mussels deployed at different MWRA monitoring stations contained concentrations of PAHs and chlordane well below the applicable FDA limits.

5.4 Comparison to Mussel Watch Data Tends

Systematically collected long-term data on the level of chemicals in natural populations of bivalves are available from NOAA's National Status and Trends (NS&T) Program Mussel Watch Project. The data are available at http://ccma.nos.noaa.gov/cit/data/. This program has collected indigenous bivalves from 292 sites distributed throughout the coastal and estuarine regions of the United States to monitor for spatial distributions and temporal trends of contaminants since 1986 (O'Connor and Lauenstein 2006). These include seven sites in the Boston Harbor and Massachusetts Bay region (Table 5-7). O'Connor and Lauenstein (2006) updated their earlier national and regional trend evaluation with data generated through 2003 and report that chemicals "*with concentrations on a decreasing trend in 1993 remain on that trend*". Furthermore, they indicate "*concentrations of two chemicals, lindane (gamma isomer of hexachlorocyclohexane) and high molecular weight PAHs, not on a decrease through 1993 are now showing such a trend*", that "*no chemical concentrations are increasing on a national scale*", and that "*cadmium remains the only metal showing a national trend*". Moreover, they find the data obtained since 1996 "*reveal some trends in concentrations of metals within geographic groups of sites*".

O'Connor and Lauenstein (2006) define a trend as "*a statistically significant correlation between contaminant concentration and year*" based on Spearman rank correlations which are free of assumptions about concentrations at a site being normally distributed with a common variance among sites. Table 5-7 shows whether an increase or decrease was significant at the $p < 0.05$ level (D, I, respectively), or at the $0.1 > p > 0.05$ level (d, i). Many contaminants in the Massachusetts Bay system show a significant downward trend (Table 5-7). However, arsenic, nickel and selenium exhibit significant upward trends at some sites. The most significant upward trends (at the 95% level) are for arsenic in Nahant, Dorchester, and Hingham Bays, and for selenium in Hingham Bay and Brewster Island.

Table 5-7. Contaminant trends in the Massachusetts Bay/Boston Harbor region from the national Mussel Watch Project as reported in O'Connor and Lauenstein (2006).

Site	General Location	Specific Location	Years	Lindane	tClordane	tDDT	tDieldrin	tPCB	tButyltin	LMW PAH	HMW PAH	tPAH	As	Cd	Cu	Hg	Ni	Pb	Se	Zn
MBNB	Massachusetts Bay	Nahant Bay	8		D	D							I							
BHDI	Boston Harbor	Deer Island	13	d	D	d	d		D	D		d			d	D		d		d
BHDB	Boston Harbor	Dorchester Bay	12	D	D		D						i		D		i	D		D
BHHB	Boston Harbor	Hingham Bay	13		D				D				I						i	
BHBI	Boston Harbor	Brewster Island	14		D	D	d		D										I	
MBNR	Massachusetts Bay	North River	7	D	D	D	D	D										d		
DBCI	Duxbury Bay	Clarks Island	11		D	D	D	D							D					

Several of the Mussel Watch sites exhibit downward trends for three or more contaminants (Table 5-7). The Deer Island site had the largest number of chemicals with downward trends (11). The other sites had between two and six chemicals with significant downward trends. The Nahant site had the fewest number of downward trends (2) plus one chemical (arsenic) with a significant upward trend. Two chemicals did not show any trending at any site (high molecular weight PAH and cadmium). Among the sites, only Deer Island shows a trend in tPAH (downward). In contrast, total chlordane trends downward at all seven sites, while tDieldrin and tDDT trend downward at five sites, although only four of these sites trend downward for both chemicals. The only sites with significant tPCB concentration trends were North River in Massachusetts Bay and Clarks Island in Duxbury Bay. Both of these sites are south of Boston Harbor. Overall, the Mussel Watch data point to improved environmental quality in the harbor and Bay over the past 20 years with respect to chemical contamination.

Comparison of trends reported in the Mussel Watch data with the apparent trends in the MWRA data is informative even though the monitoring designs differ. For example, Mussel Watch data are derived from indigenous populations of mussels collected in the spring, while the MWRA data are derived from short term (60-day) summer deployments of mussels collected from a "clean location" and assumed to equilibrate with the water quality over the 60 days. The caged mussel data (see above discussion) from the vicinity of Deer Island clearly suggest a decrease in tPAH and lead data since the early 1990's, and tDDT and total chlordane since 1996. These apparent trends are consistent with the statistically significant trends in Mussel Watch data measured in the indigenous mussel population sampled near Deer Island over a slightly longer period of record (13 years of Mussel Watch Data versus 10 years of MWRA data). These trends coincide with downward trends in contaminant loading from MWRA (Section 3) and in the surface sediment as considered in Section 4.2.

To determine the significance level of the apparent trends in the MWRA caged mussel results (see for example Figure 5-4), the MWRA data from 1994 through 2003 were subjected to the Spearman's Rank test used by O'Connor and Lauenstein (2006). The analyses found statistically significant downward trends (95% significance level) between many chemical concentrations and year (Table 5-8) at the Deer Island and Inner Harbor locations. The Deer Island site had the greatest number of downward trends (8 of 10 chemicals). At the Inner Harbor Site, 4 of 10 chemicals had significant decreasing trends and one had a significantly increasing trend. The trend in tDDT at the Inner Harbor site was significant at the 90% level and no trends were evident for tPCBs and mercury at Deer Island. Trends in lindane, lead, and the three PAH chemical classes were not significant at >90% level for the Inner Harbor.

Table 5-8. Significance of trends in ten years (1994 to 2003) of MWRA caged mussel bioaccumulation data using Spearman Rank Correlation.

MWRA Site	Years	Lindane	tChlordane	tDDT	Dieldrin	tPCB	LMW PAH	HMW PAH	tPAH	Hg	Pb
Deer Island Light	9	D	D	D	D		D	D	D		D
Inner Harbor	10		D	d	D	D				i	
Outfall Site	9	I	I	D		D	I	I	I	I	
LNB Site	8		I	D	D	D	i	I	I		D

The trends in the chemical data from the caged mussels deployed near Deer Island are generally similar in direction to those recorded by the indigenous populations sampled from this area by the Mussel Watch program, and often at a higher significance level. Notable differences in the trend data among the Harbor sites include an increasing trend in the MWRA mercury data at the Inner Harbor site (versus decreasing or no trend in the Mussel Watch data) and a decreasing trend in the MWRA Deer Island HMW PAH data (versus no trend in the Mussel Watch data).

Although there are statistically significant upward trends (95% level) in mercury, the three PAH measures, total chlordane and lindane at the MWRA outfall site, the mercury trend is due to background, and the concentration levels of PAH, chlordane and lindane remain low. The mussels deployed at the B-Buoy (LNB) approximately 1 km south of the diffuser showed similar trends to those at the outfall site with the exception of lindane, lead, mercury, and dieldrin, which did not show significant trends at one or the other site. The upward trends at the outfall site are consistent with those expected based on the experimental design, which placed the caged mussels at OS directly in the effluent plume, an area that previously displayed low bioaccumulation levels and presumed to experience slightly higher contaminant levels as a result of the discharge. However, comparison of the post-deployment mussel data to pre-deployment data indicates the outfall may not be fully responsible for the trends in several of the contaminants. For example, the temporal data from OS show that increasing trends in mercury is likely related to the initial status of the mussels used in the study (Figure 5-5). As noted in the 2003 Annual Fish and Shellfish report (Lefkovitz *et al*. 2004), mercury at OS and LNB closely mirror the upward trends in pre-deployment mussels after 1999. Note the post-diversion data from the LNB location also mirrors the pre-deployment mussel concentrations but were slightly lower than at the OS location. As a result, the mercury at this station does not show a statistically significant trend. Note also that the difference between the before- and after-deployment data for mercury and lead at OS decreased or reversed ranking after diversion (e.g., pre-diversion data consistently showed contaminant depuration, whereas post-diversion data do not). In contrast, the data from the LNB site which is 1,000 m from the OS site showed similar differences to those observed prior to diversion. This is consistent with greater dilution of the effluent at the LNB location. In contrast to these sites, the mercury in the mussels deployed in Cape Cod Bay appeared to decrease relative to the pre-deployment levels (Figure 5-4). Taken together these data suggest the conditions relative to mercury at the outfall site are similar to those where the mussels were collected.

The results for tDDT, tChlordane (Figure 5-5), and tPCB and tPAH (not shown) were similar to lead and mercury but the magnitude of the pre- versus post-diversion changes were greater. Note the statistical analysis suggested there is no trend for lead at OS and a decreasing trend at LNB, consistent with the variability in data and influence of the pre-deployment lead concentration in the mussels. In comparison, while the decreasing trends for tDDT and tPCB at OS and LNB were significant, there are clear inflection points in these parameters in 2000, with concentrations decreasing before diversion and increasing after diversion. Noteworthy in the organic chemical data is the large concentration increases since 2000 that do not mirror the pre-deployment concentrations. The data for PAH and tChlordane (Figure 5-4) suggest the statistical trends better reflect outfall related effects since the pre-deployment concentrations of these chemicals were lower relative to the post-deployment levels and more uniform, creating confidence that the statistical analysis reflects true trends in the bioaccumulation rather than changes in the level of contaminants in the pre-deployment mussels, as suggested by the lead and mercury data.

These analyses also suggest the use of caged mussels for monitoring long-term trends in bioaccumulation require selection of the mussels that have low contaminant levels and that sufficient time is allowed for bioaccumulation and depuration processes to reach equilibrium to ensure the caged mussels reflect the true conditions at the site being monitored.

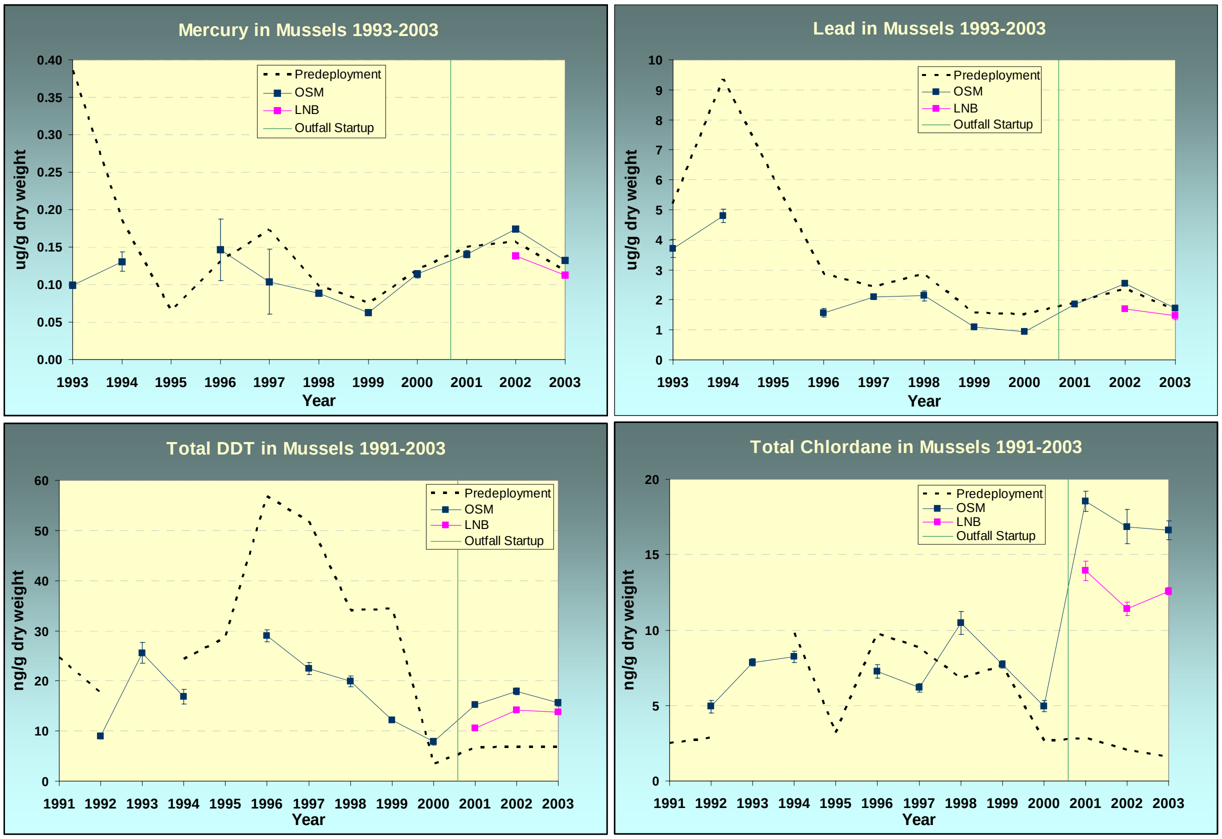


Figure 5-5. Comparison of contaminant trends in caged mussel from the outfall site with pre-deployment contaminant levels.

5.5 Summary

The MWRA bioaccumulation data offers a sound foundation for predicting the short-term environmental response near the outfall based on effluent quality. The low concentrations of contaminants in the effluent are not expected to produce an environmental response beyond that which has been measured in the first three years following diversion. In the future, it will be important to have well documented effluent chemistry data to understand the potential for short-term impact. This information can be coupled with sediment chemistry data, which provides an indication of long-term changes from effluent discharge. Monitoring bioaccumulation of contaminants in caged mussels is an intermediate approach, which should be conducted if the effluent composition changes or if there is reason to think that effluent characteristics have changed (e.g., contaminant levels, organic carbon content). Monitoring for bioaccumulation in Massachusetts Bay can be addressed by mussel data from other sites monitored by the Mussel Watch Program.

6 EXPECTATIONS FOR THE FUTURE

MWRA's monitoring program and studies by USGS (Bothner and Butman 2005) have documented that the diversion of MWRA's sewage effluent into offshore Massachusetts Bay did not cause acute impacts. Moreover, the water and sediment quality of Boston Harbor is improving. Nevertheless, concerns remain about the long-term fate and impacts of effluent-related contaminants in the Bay. These concerns include whether there is a potential for long-term increase of contaminants in the vicinity of the discharge and the potential for bioaccumulation in living resources which may cause ecological and human health risks. This section discusses these concerns.

6.1 Changes to the Bay's Sediments

The transfer of the MWRA effluent discharge into offshore Massachusetts Bay was expected to cause minor local impact to the sediments of Massachusetts Bay (EPA 1988), and that a measurable response in the sediments could take years to develop (Coates 1995). These expectations have been confirmed through four years of post-diversion monitoring which show the discharge has not resulted in an acute adverse impact in the water column, sediment, or key indicator organisms. Moreover, measured MWRA loadings to the Bay are far less than hypothesized in the outfall planning phases and lower than anticipated based on pilot treatment plant studies of the mid-1990's.

Continued effective operation and maintenance of DITP, and continued decline in levels of regulated watershed and airshed contaminants will keep future contaminant loadings at or lower than today's levels. Within Boston Harbor, contaminant loads introduced via CSOs will continue to decline as facility improvements are completed. Because CSOs are a relatively minor source of toxic contaminants compared to runoff, future significant improvements will depend upon improving the quality of stormwater.

Lower contaminant loading rates over the past two decades are clearly manifested in improvements to sediment quality in Boston Harbor. These improvements are expected to continue as the contaminant inputs stabilize or decline further and the sediments go through natural attenuation, driven by processes including sediment accumulation, contaminant burial, and natural degradation. As expected, transfer of the effluent into Massachusetts Bay has slightly increased levels of sewage tracers such as *C. perfringens* near the outfall but not in other regions of the bays. Dilution and transport of the effluent is as expected (Signell in Bothner and Butman 2005) and should continue. Because the effluent is cleaner than expected, the accumulation of contaminants in sediments will be even slower than predicted by Coates (1995). The monitoring data in the Bays to date confirm that changes to sediment quality will generally be slow, although the small increase in the number of chemicals that are higher than ER-L and ER-M sediment quality guidelines stresses the need for continued vigilance and understanding of the sediment dynamics of the region. For compounds with an assigned Sediment Quality Guideline, continued monitoring may affirm if the changes observed from 1999 to 2002 are attributable to the effluent or to other sources or to sediment dynamics.

Bothner and Butman (2005) report recent improvements in the understanding of sediment transport in the system. These new findings enable the development of hypotheses about the ultimate deposition sites of contaminants that do not escape the bays through water transport. The USGS long-term oceanographic current measurements, sediment trap, and sediment transport studies show that storms with large surface waves are key, causing sediment resuspension and transport in Massachusetts Bay (Butman, Warner, and Bothner in Bothner and Butman 2005). USGS reports that tidal currents, wind-driven currents, or currents associated with the spring runoff are typically not strong enough alone to resuspend sediments, and thus do not enable transport. Also, an oscillatory current, associated with surface waves, of about 10 cm/s is sufficient to resuspend fine-grained bottom sediments (silt and clay), but this sediment resuspension threshold is rarely exceeded in water deeper than 50 m. In Massachusetts Bay, the largest waves are typically associated with winds from the northeast because of the unobstructed fetch from the Gulf of Maine. Thus, storms with northeast winds dominate sediment transport. These are more likely to occur in winter than summer.

Bothner and Butman found that sediment resuspension and transport resulting from wind conditions is the primary mechanism that ultimately moves particulate material, including that from Boston Harbor and from the outfall, into Stellwagen Basin. Generally the transport pathways are southeastward along the Massachusetts coast with some penetration into the north central portion of Cape Cod Bay. They also report that some material can escape Massachusetts Bay into the Gulf of Maine. The wind direction influences the amount of material exported from the system and where the export occurs. MWRA has several sediment monitoring stations in the depositional sediments of Stellwagen Basin and Cape Cod Bay, which could detect major changes (which are not expected) in contaminants in those areas. Detection of subtle changes would require a more expansive spatial design. Detection of subtle changes in sediment quality would require a more expansive spatial sampling design to ensure that accurate attribution across all sources can be made.

Future changes in the bioaccumulation response in the indicator organisms analyzed under the MWRA monitoring program are expected to be minimal. Data presented in Section 5 clearly point to improved conditions in Boston Harbor compared to those experienced 10 or more years ago and limited response to date in the organisms collected in Massachusetts Bay. Within-station variability is decreasing and annual average concentrations appear to be decreasing. Even so, the variability is such that detection of subtle shifts in bioaccumulation will be difficult. However, given the direction of change in the sediments, exceedance of public health action levels in the fish and shellfish monitored is unlikely. Improved histopathology in the flounder point to lower stress on this fishery, although the unusual occurrence of lesions in 2002 to 2005 gave rise to concerns regarding the role of the outfall relative to this phenomenon. Continued monitoring of the presence of these lesions is warranted. Unfortunately, in general the scientific understanding of the causes of skin lesions in fish is very incomplete. State and federal ocean resource managers may want to pursue more studies that can help understand how flounder may be contracting these lesions.

Observed changes in mercury and silver levels in the flounder and lobster collected in Massachusetts Bay are of note, but are difficult to understand in the context of the outfall given the mobility and migration patterns of these two species. Increases in metals levels may be caused by increased metal bioavailability (perhaps from biogeochemical processes and harbor cleanup), increased production of methyl mercury compounds in sediments, and flux to the overlying water (See Section 2), or, animals could be migrating into the area from locations that have different contaminant levels. Also, this program's assumption that the target organism's habitation at the collection sites is sufficiently long to account for the measured bioaccumulation may not be true. MWRA's program cannot distinguish whether measured contaminants reflect equilibration with the local environment where the animals are collected or are from exposure during migration, or some combination of these factors. Further research may be needed to ensure that the future monitoring program accurately represents the interactions among the outfall-influenced sediments, and bioaccumulation in the chosen indicator organisms.

Current understanding of the system and contaminant transport and fate suggests that the MWRA outfall has a small, localized, effect on build-up of contaminants in the nearby sediments and that any modest increases related to the discharge will take many years to be detected. Future research and monitoring should take into consideration the biogeochemical cycles of these chemicals to gain a better understanding of the role of the outfall and its effects relative to bioaccumulation in this system.

6.2 Emerging Chemicals Of Concern

Over the past decade, concerns about the environmental effects of several classes of chemicals have emerged from the scientific and regulatory communities. The following discussion highlights two types of chemicals of emerging concern: endocrine disruptor compounds (EDCs), and brominated flame retardants (BFRs). This section provides a brief overview of EDCs and BFRs, the impacts that concern investigators, and the effectiveness of sewage treatment processes to remove them from the waste stream. Much research is in progress regarding the environmental and ecological effects of these compounds, which will form the basis for any future regulation of treatment or discharge of these chemicals. Historically, few analytical techniques have existed for detecting low concentrations of these compounds in the environment. This lack of technology has limited the understanding of the environmental occurrence, fate, and potential effects of these emerging chemical contaminants.

An EDC is defined as "an exogenous agent that interferes with the production, release, transport, metabolism, binding, action, or elimination of natural hormones in the body responsible for the maintenance of homeostasis and the regulation of developmental processes" (Kavlock 1996). EDCs include natural and synthetic hormones (e.g., estrogens, androgens, plant hormones), pharmaceuticals, and industrial chemicals and their byproducts (e.g., pesticides, phthalates, surfactants, bisphenol A (BPA), alkylphenols, and nonylphenol ethoxylates (NPnEO)). Adverse effects, such as abnormal development and function of sex organs, development of cancer, and birth defects are produced when these compounds act directly or indirectly on the endocrine system or target organs of the reproductive, immune, or neurological systems. In 1996, EPA's Office of Research and Development (ORD) identified endocrine disruption as one of its top six research priorities and developed a risk-based research approach to address some of these uncertainties (http://www.epa.gov/endocrine/).

BFRs have been widely used over the past two decades as flame retardants in textiles, plastics, furniture, and electronic equipment. More than 75 different BFRs are in use today, with tetrabromobisphenol A (TBBP A), hexabromocyclododecane (HBCD), and three technical mixtures of polybrominated diphenyl ethers (PBDEs) (Penta-, Octa- and Deca-BDEs) making up the majority of BFR production at this time (Birnbaum and Staskal 2004). Polybrominated biphenyls (PBBs), another class of BFRs, were banned in the US in 1976 because of animal feed poisonings in Michigan. BFR residues are ubiquitous in the environment and are found in locations far from their production or use. They are environmentally persistent and known to accumulate in animals at higher trophic levels. Concentrations of some BFRs are rapidly increasing in both the environment and in humans. Recent data on PBDEs in US residents included the highest individual values (9960 and 4060 ng/g of lipid) and mean values (399 ng/g) ever reported (Johnson-Restrepo *et al*. 2005). Toxicity data for these compounds is limited, but available animal studies demonstrate that potential adverse effects include liver toxicity, endocrine disruption, behavioral changes, and impaired learning and memory (Birnbaum and Staskal 2004). The European Union banned the manufacturing and use of Penta- and Octa-BDEs in 2004, and production in the US was discontinued in 2005. However, there is no plan to phase out Deca-BDEs, which represent approximately 80% of the total PBDE production worldwide (Birnbaum and Staskal 2004; Betts 2005). Currently in the United States there are no established safety standards on the manufacture, use, or disposal of BFRs.

Wastewater treatment plants and sewers have been identified as major sources of EDCs (including sex hormones and NPnEO) to receiving water bodies, which act as the principal sinks of these compounds (Esperanza *et al*. 2004). The effect of wastewater treatment processes on EDCs is an area of active investigation. Some EDCs are removed during treatment, while others may be generated or increased in activity. Estrone, estradiol, and ethynilestradiol in municipal influent were measured by Baronti *et al.* (2000) at concentrations of up to 132 ng/L, 25 ng/L, and 13 ng/L, respectively. Microbial degradation in sewers and wastewater treatment plants may generate or activate estrogenic byproducts from non-estrogenic parent compounds commonly found in wastewater influent (Esperanza *et al*. 2004; Baronti *et al.* 2000). For example, anaerobic biodegradation of widely-used nonionic surfactants (NPnEO) during wastewater treatment forms the EDCs nonylphenol and nonylphenol ethoxylates (Esperanza *et al.* 2004). Esperanza *et al.* (2004) measured hormone and NPnEO concentrations that were higher in primary effluent than in the influent, and Leusch *et al.* (2005) also found primary effluent to be slightly more estrogenic than the influent in one assay.

Removal efficiency of EDCs by wastewater treatment varies greatly by compound, facility, and treatment process (Metcalf and Eddy 2005), and can range from negligible to greater than 99% (Ternes 1998). Researchers found that the concentrations of organic compounds in the effluents and receiving streams vary in response to the size of the receiving water body, technology and operation of the treatment plant, and the chemical characteristics of the sewage influent (Phillips *et al.* 2004). EDCs are removed during sewage treatment through biodegradation and adsorption on sludges. Andersen *et al.* (2003) demonstrated that during activated sludge treatment, most estrogens are either eliminated or bound to sludge, which acts as a sink for many EDCs (Metcalf and Eddy 2005). Esperanza *et al.* (2004) found that the removal of NPnEOs, estradiol, estrone, and ethinylestradiol from the liquid phase in the aeration tanks of two pilot scale plants exceeded 96%, 94%, 52%, and 50%, respectively and that both estrogens and surfactants partitioned to the solid phase to varying degrees. Activated sludge treatment at six major sewage treatment plants in the area of Rome, Italy removed estriol (95%), estradiol (87%), ethynilestradiol (85%) and estrone (61%) from the influent (Baronti *et al.* 2000). Median concentrations of these estrogens in treated effluent from several domestic activated sludge sewage treatment plants in various countries ranged from 3-9 ng/L (estriol), <1 – 6 ng/L (estradiol), and <0.2 – 9 ng/L (ethynilestradiol), (Baronti *et al.* 2000). In another study, secondary activated sludge treatment (followed by nitrification/ denitrification) removed >95% of the estrogenic activity, with tertiary treatment removing greater than 95-98% of all estrogenic activity (Leusch *et al.* 2005). Some researchers have found strong evidence that biological treatment can be optimized or engineered for effective removal (Metcalf and Eddy 2005).

Many EDCs enter receiving waters via the discharge of raw or treated wastewater. Baronti *et al.* (2000) detected estrone (0.33 ng/L), estradiol (0.11 ng/L), estriol (1.5 ng/L) and ethinylestradiol (0.04 ng/L) in the Tiber River downstream of mechanical sewage treatment plant and raw sewage discharges. EDCs have also been detected at low levels in Boston Harbor and Massachusetts Bay. Bottom sediment, plankton, and clam samples collected in Boston Harbor and Stellwagen Bank contained bisphenol A at concentrations of 1 – 30 ng/g (Stuart *et al.* 2005). Caffeine, a potential tracer for water soluble, biodegradable organic contaminants, such as EDCs, has been found to be ubiquitous in sewage and coastal waters of Massachusetts Bay, with the highest concentrations detected in 1998 and 1999 at the Deer Island outfall at the mouth of Boston Harbor (Siegener and Chen 2002).

MWRA has recently funded (with the Sea Grant college program) research to measure estrogenic activity in treated effluent and in receiving waters in Boston Harbor and Massachusetts Bay (Siegener and Chen 2002) and is supportive of ongoing research by EPA and others (for example, the Water Environment Research Foundation) on EDCs.

6.3 Summary

The MWRA has successfully and effectively implemented major wastewater facility improvements that have dramatically reduced the loading of contaminants under their control to coastal Massachusetts. The reductions over the past decade have demonstrably improved the quality of sediment in Boston Harbor while exerting minimal impact to the sediments of Massachusetts Bay. Continued changes and improvements can be expected harbor wide as the natural biogeochemcial processes continue to modify and bury contaminants, making them less accessible for bioaccumulation by organisms. The improvement to sediment quality of Boston Harbor is evident in recovery of the health of major living resources (e.g. winter flounder health) and general reductions in contaminant levels in fish and shellfish resources in the system.

Unlike twenty years ago when Boston's wastewater facilities were a major source and conduit of contaminants to Boston Harbor and Massachusetts Bay, the MWRA of the twenty-first century will contribute a far smaller percentage of total contaminant loadings to the harbor/Bay system. The current high effectiveness of the treatment process at the Deer Island Sewage Treatment Plant and continuing facility improvements lessen the ability of the MWRA to further reduce loads into the future. Moreover, expectations of minimal future environmental degradation from the discharge reduce the need for MWRA to be the focus of future major reductions in contaminant sources to Massachusetts Bay.

Maintaining this current status does, however, require the MWRA to continue its vigilance in controlling industrial, commercial, and residential contaminant inputs to its collection system and to ensure its treatment plant operations continue to provide the most effective contaminant removal possible. Through effective management of its operations and applications of its regulatory authority, MWRA can continue its regional leadership in contaminant source reduction and provide a national example for effective sewage treatment and plant management. Regulation and reduction in future contaminant loadings to coastal Massachusetts may be better focused on controlling loadings from distant and nonpoint sources. Continued MWRA monitoring for changes near the outfall in Massachusetts Bay are warranted based on potential sediment quality degradation at some locations near the outfall. Additional understanding of the role of the outfall on mercury methylation in Massachusetts Bay sediments and the potential for bioaccumulation is needed. Such understanding will significantly help to understand the apparent increases in mercury in flounder sampled from the vicinity of the outfall.

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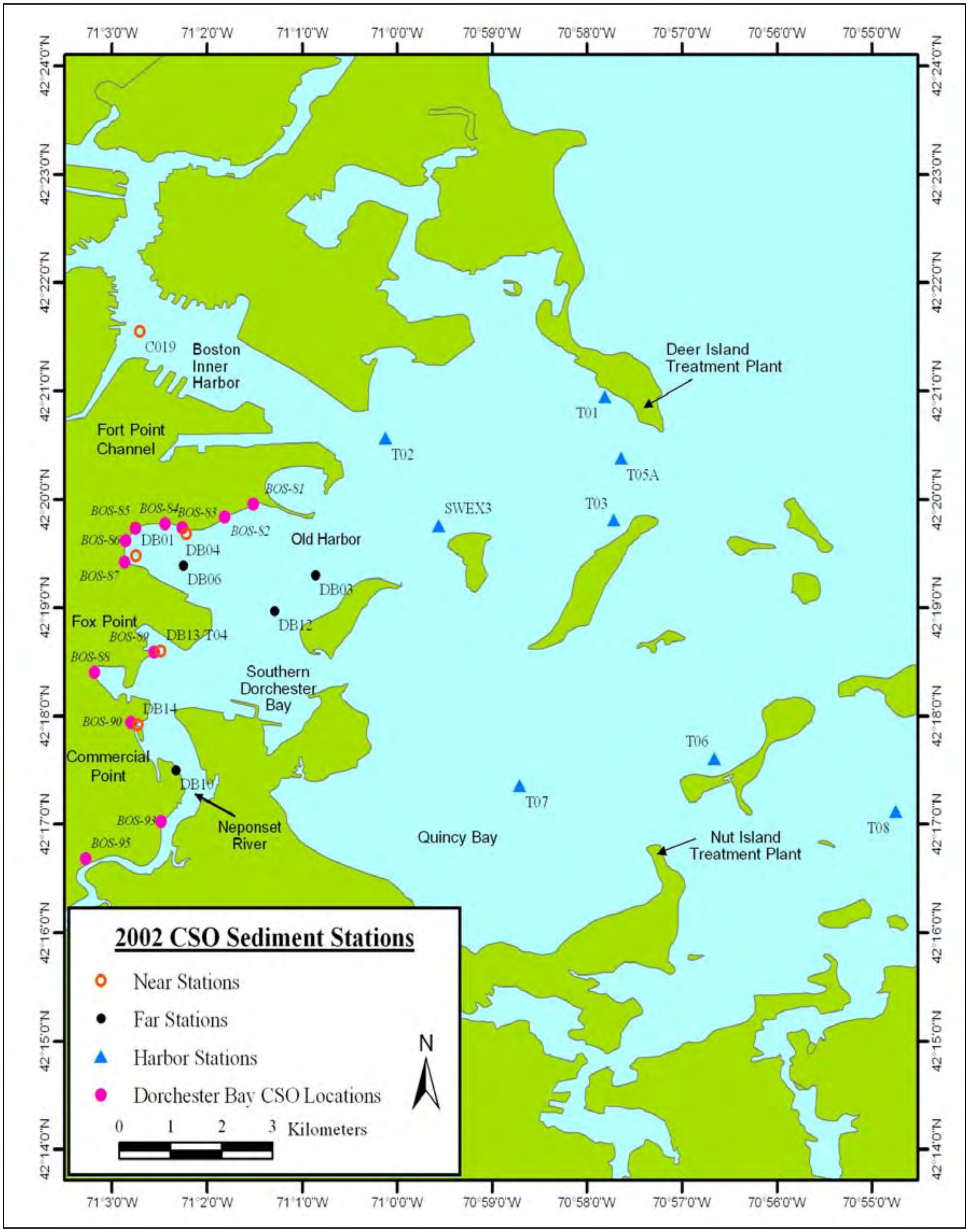
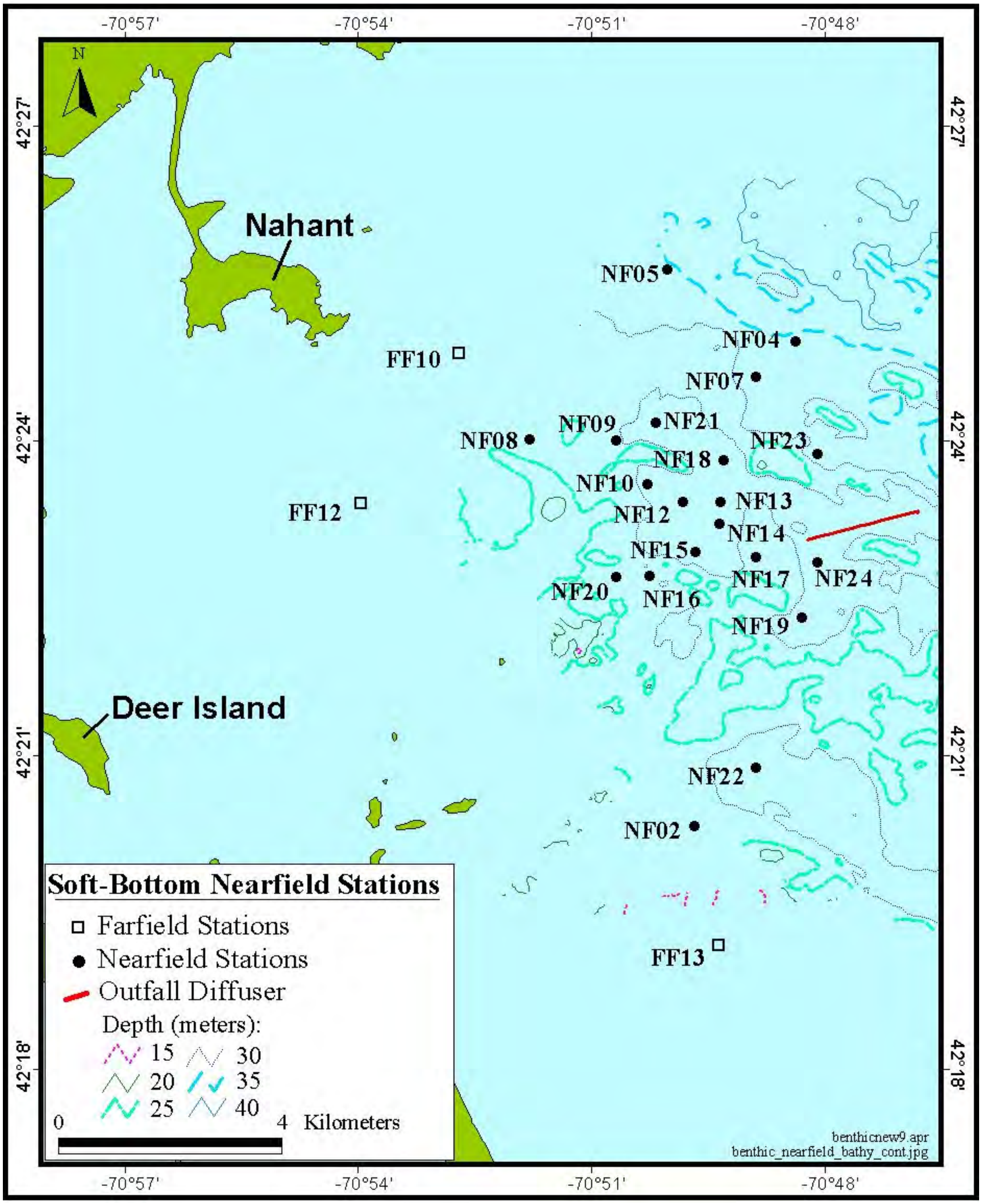
APPENDIX A: STATION MAPS

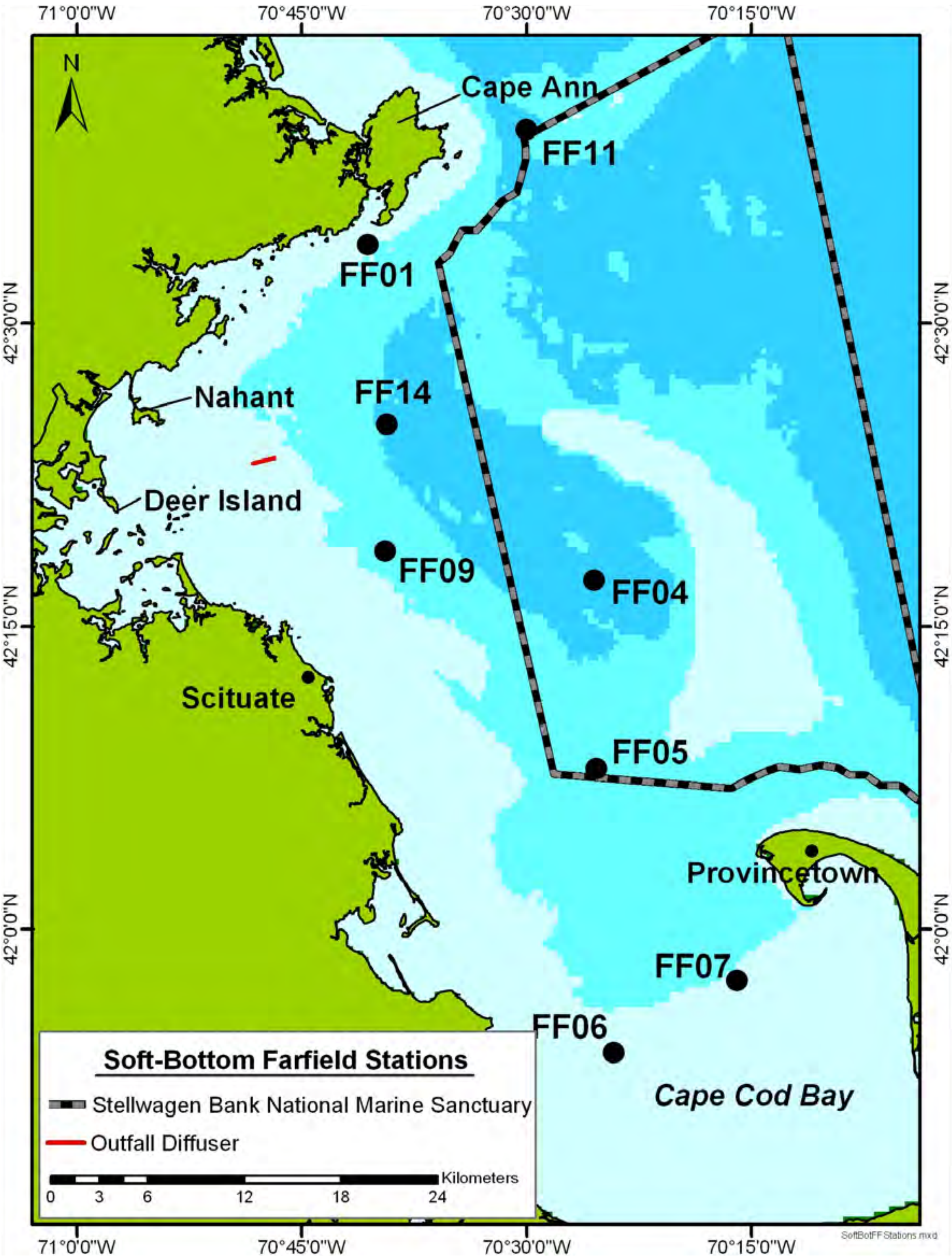
Boston Harbor sediment stations sampled by MWRA



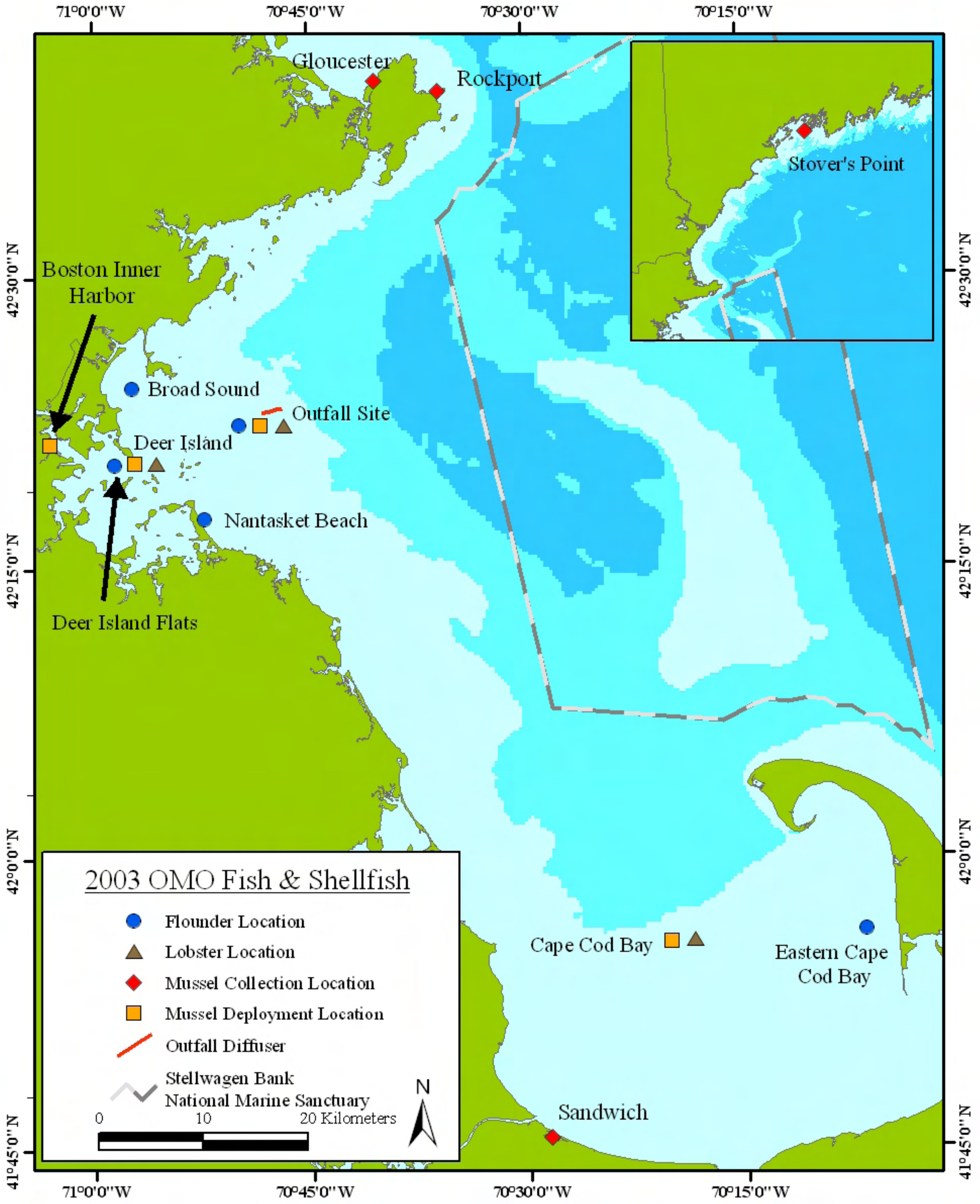
Massachusetts Bay Nearfield sediment stations sampled by MWRA



Massachusetts Bay Farfield sediment stations sampled by MWRA

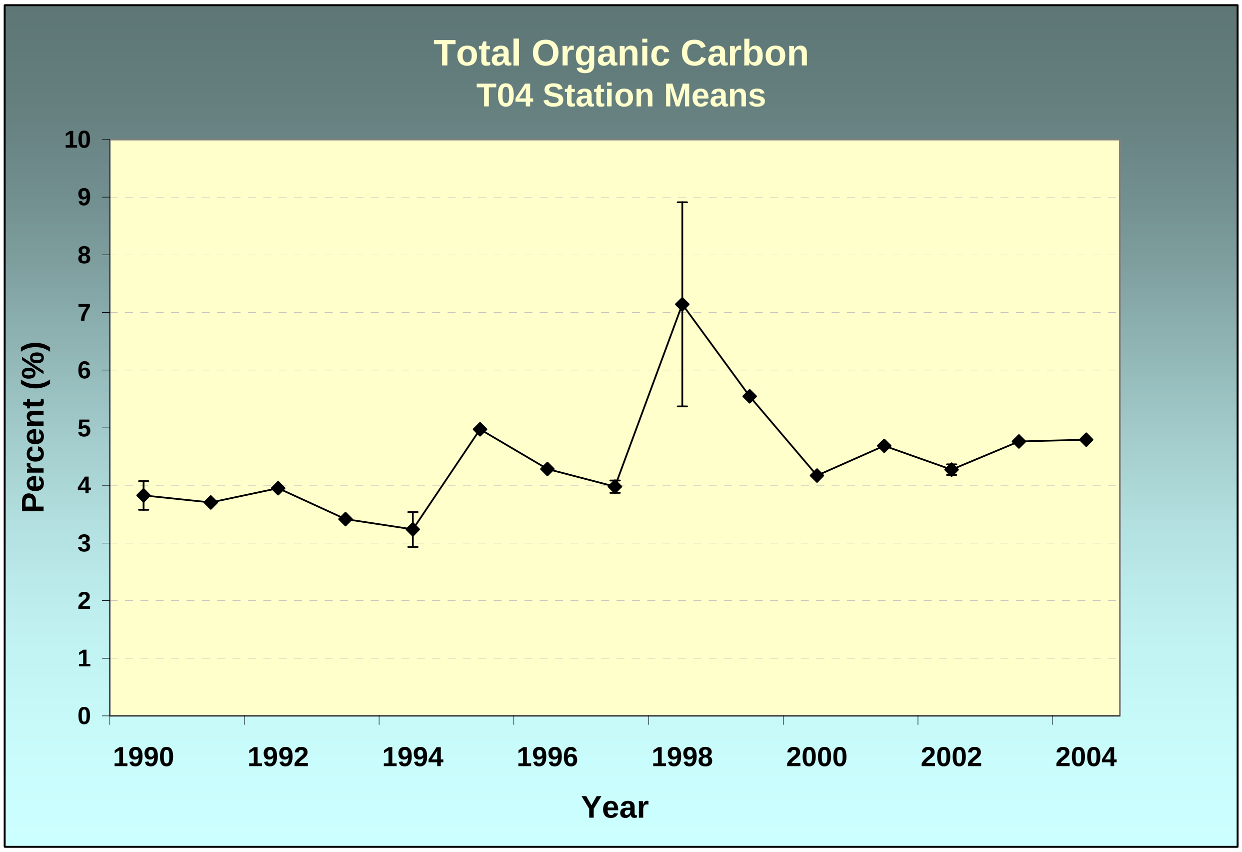


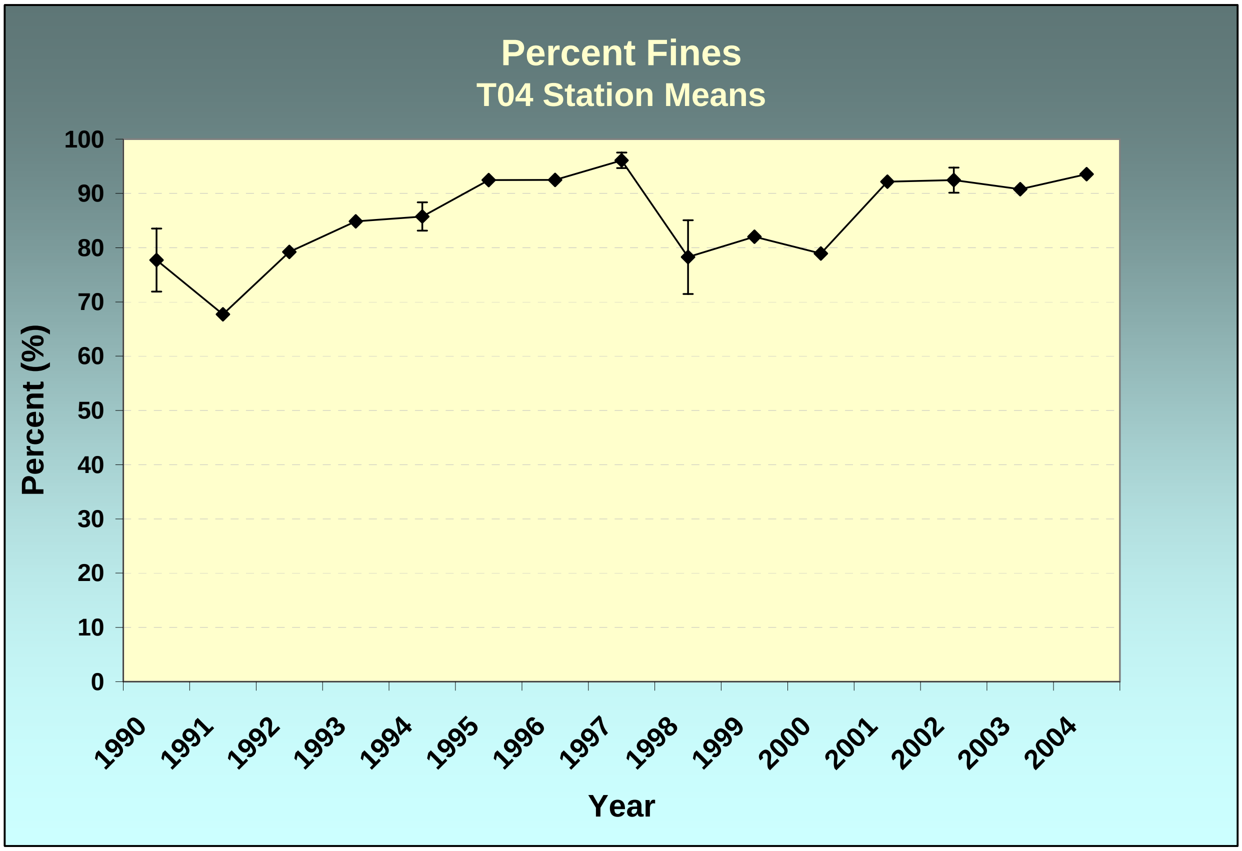
Fish and shellfish stations occupied by MWRA.

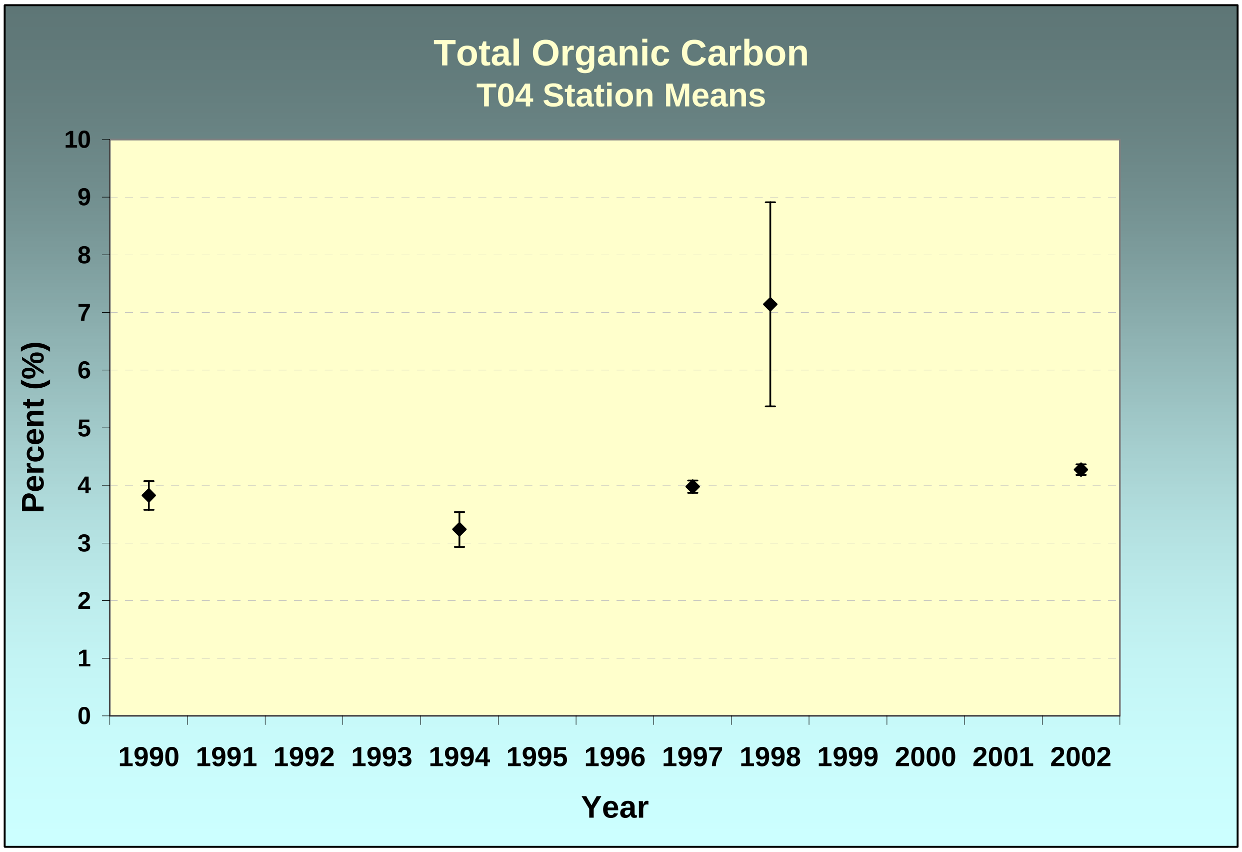


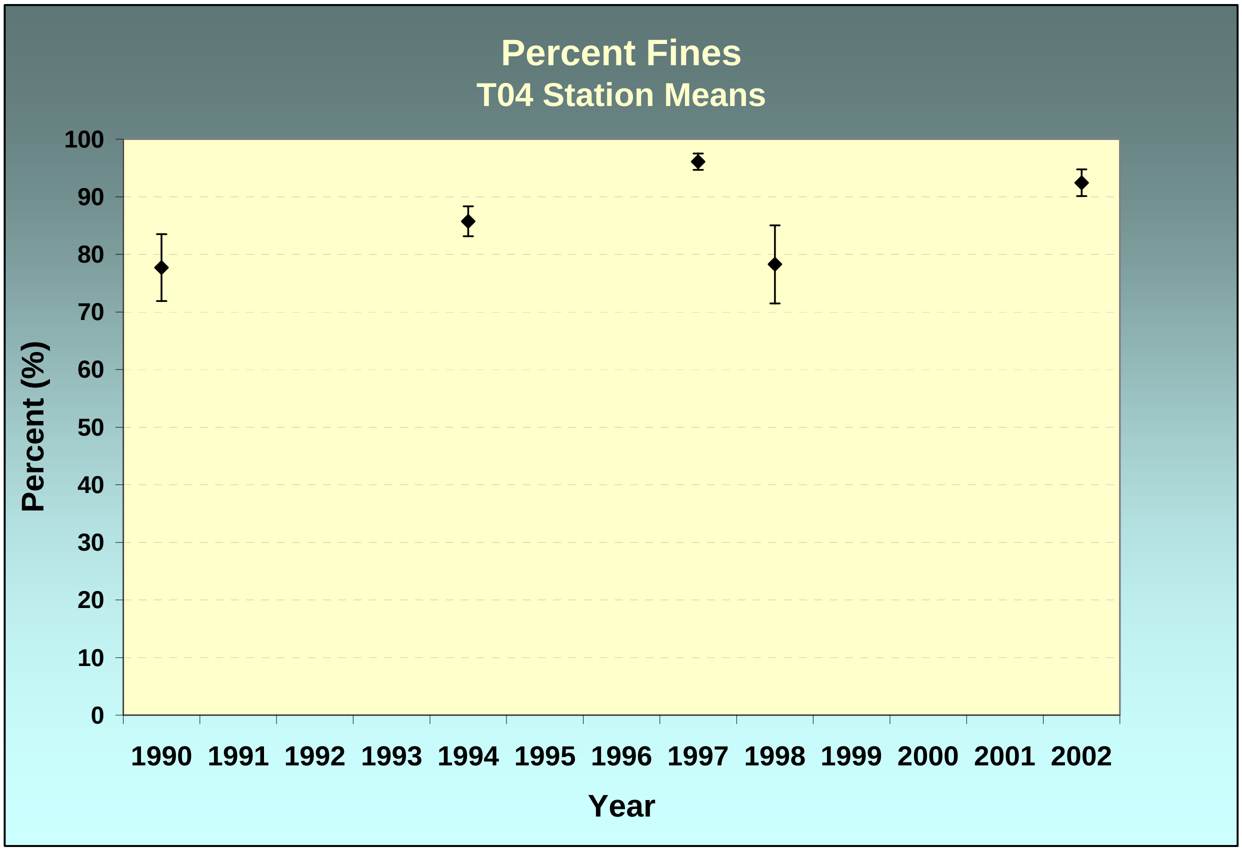
APPENDIX B: TEMPORAL TRENDS OF CONTAMINANTS IN SURFACE SEDIMENTS OF BOSTON HARBOR

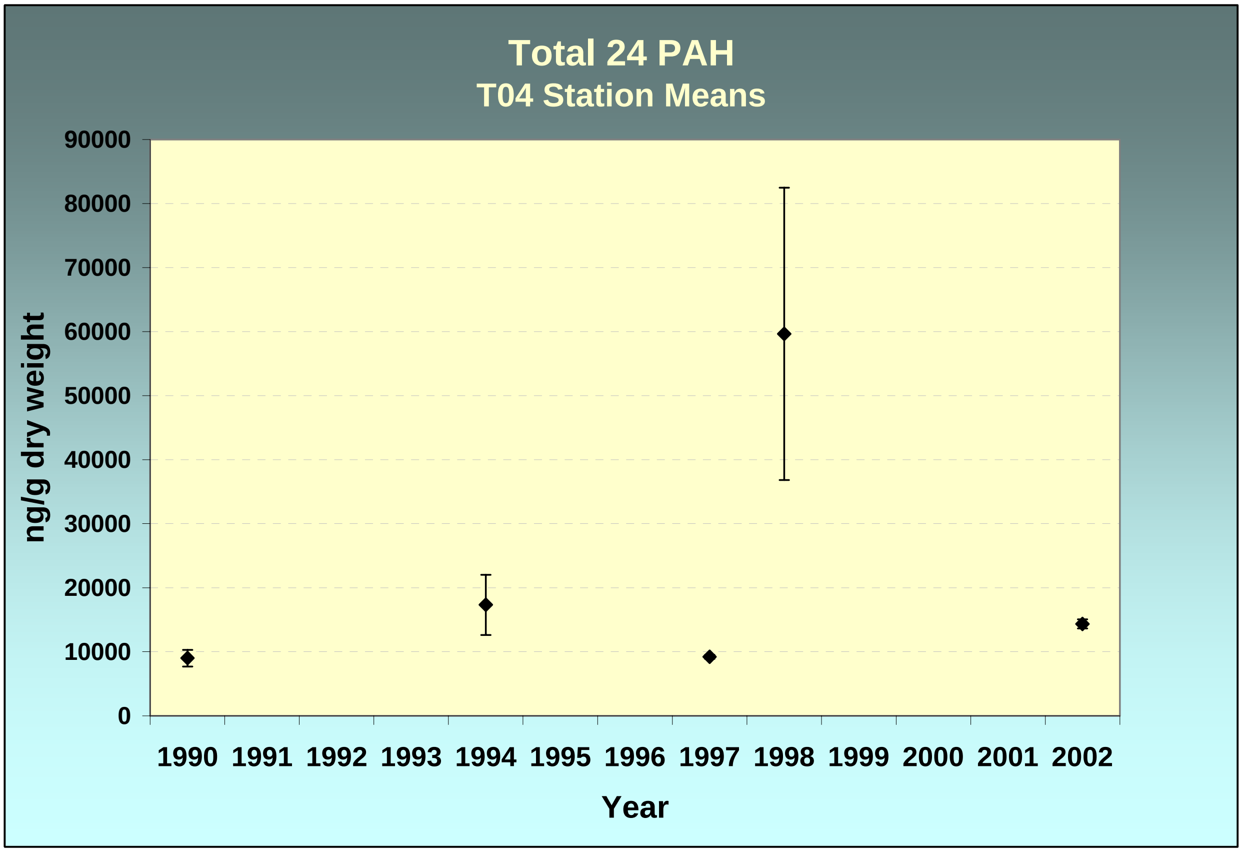
T04

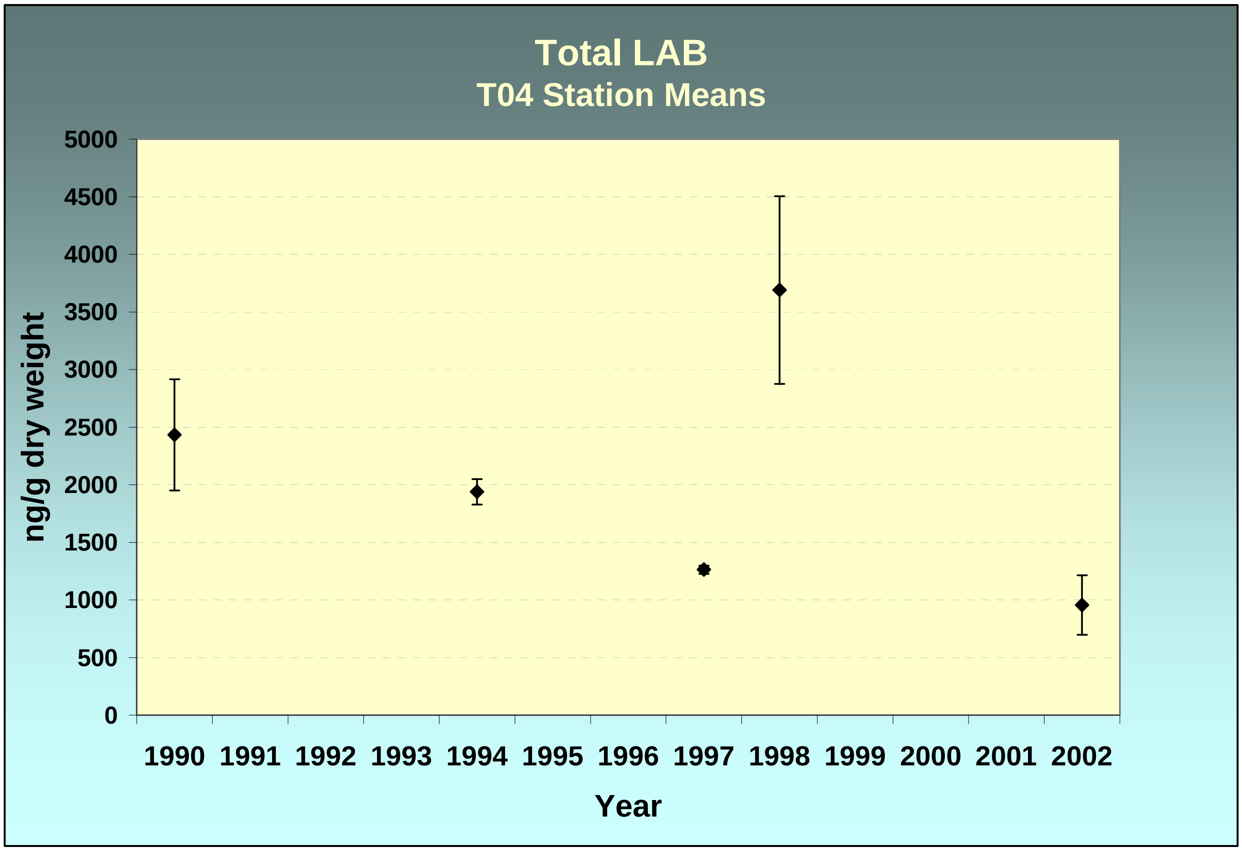

Total Organic Carbon
T04 Station Means
Percent (%)
0
1
2
3
4
5
6
7
8
9
10
1990
1992
1994
1996
1998
2000
2002
2004
Year

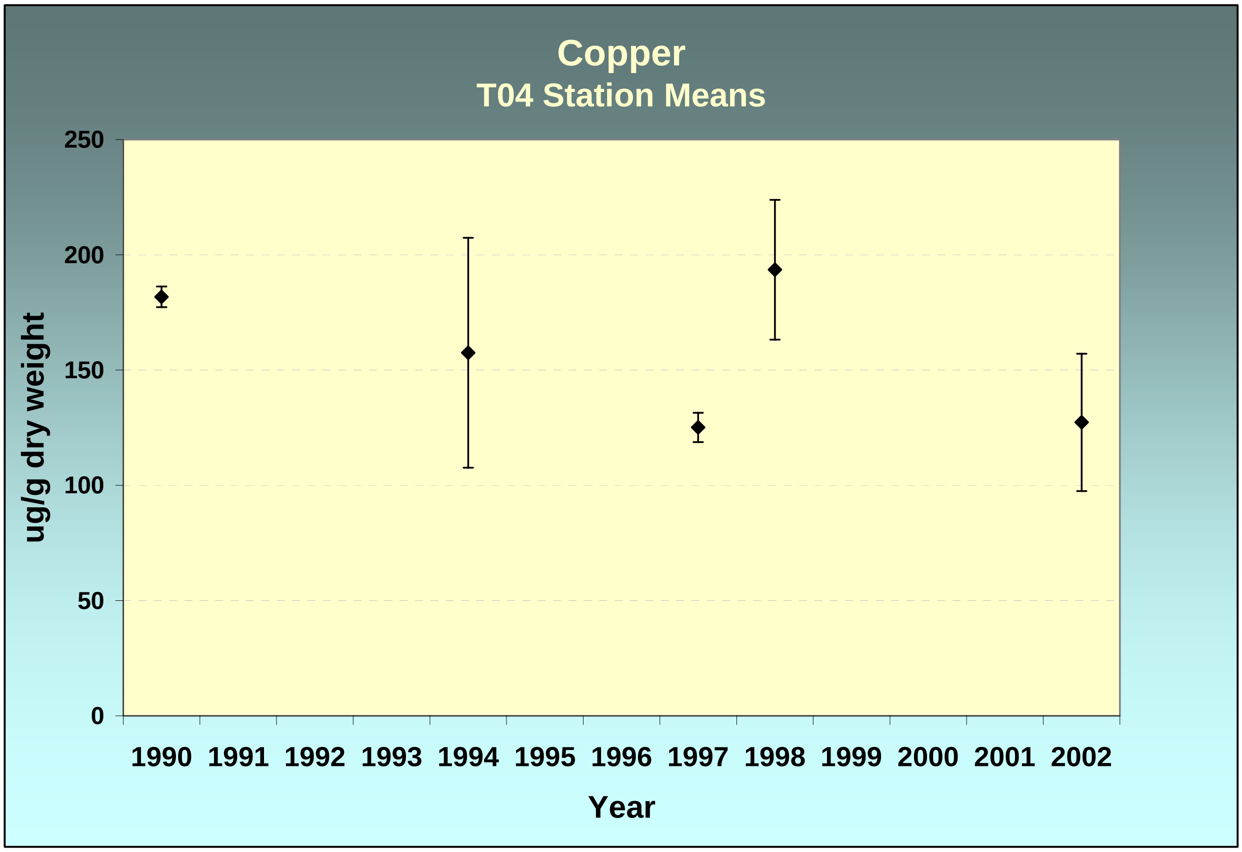

Percent Fines
T04 Station Means
Percent (%)
0
10
20
30
40
50
60
70
80
90
100
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

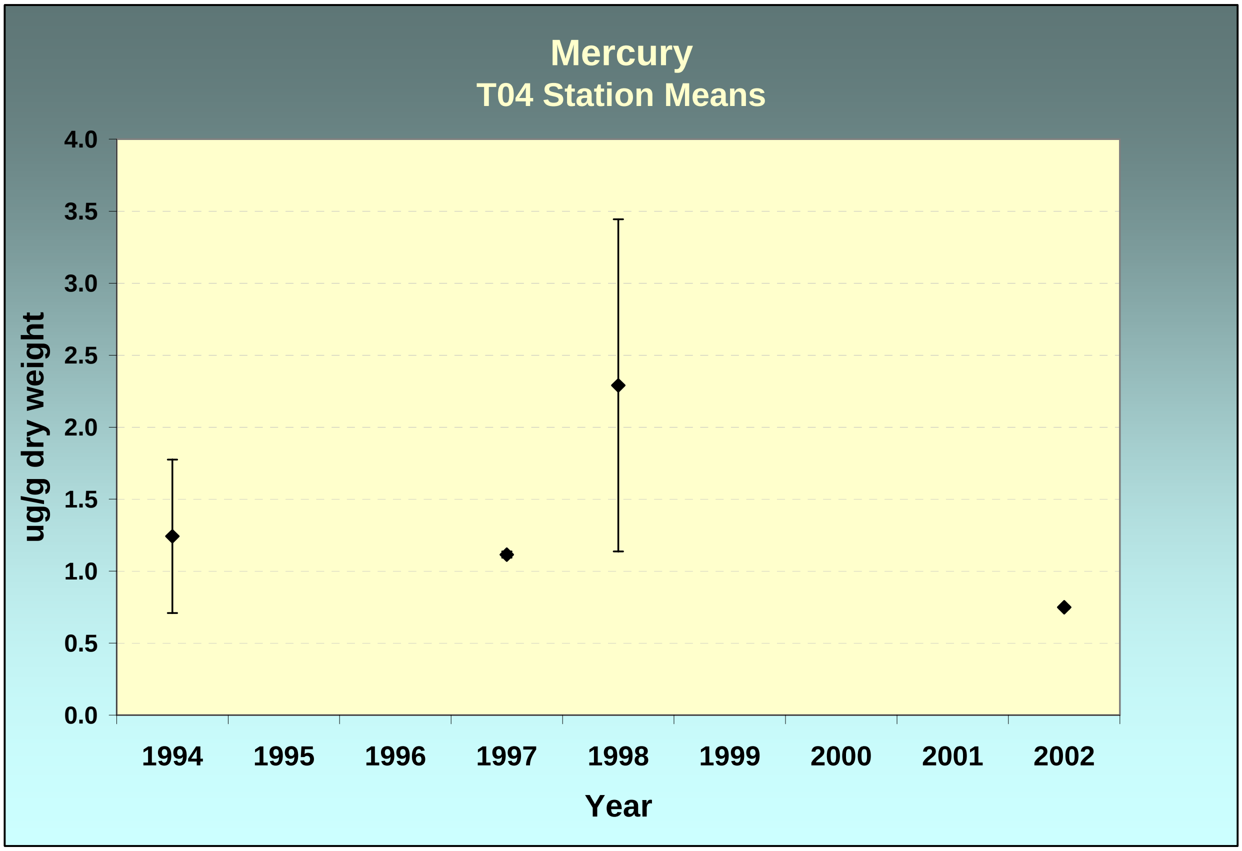

Total Organic Carbon
T04 Station Means
Percent (%)
10
9
8
7
6
5
4
3
2
1
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

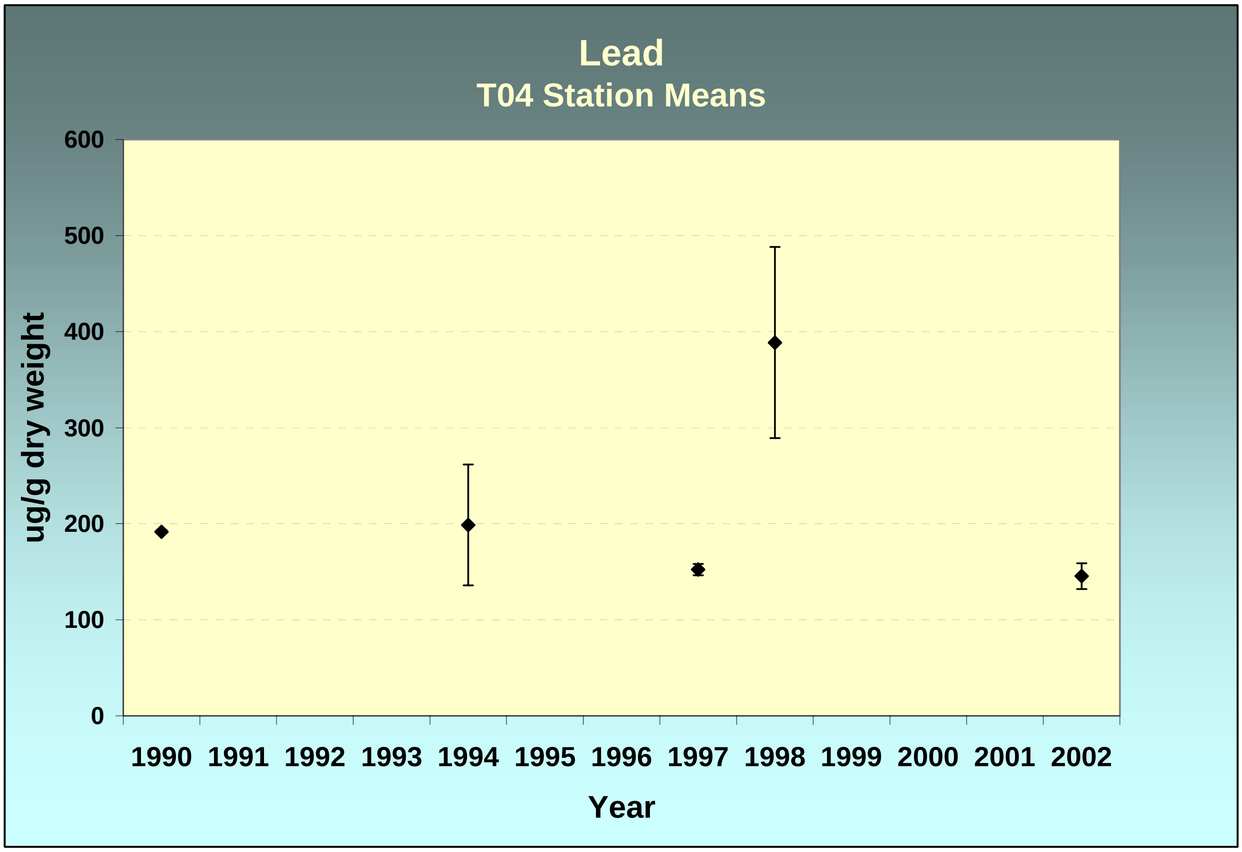

Percent Fines
T04 Station Means
Percent (%)
100
90
80
70
60
50
40
30
20
10
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

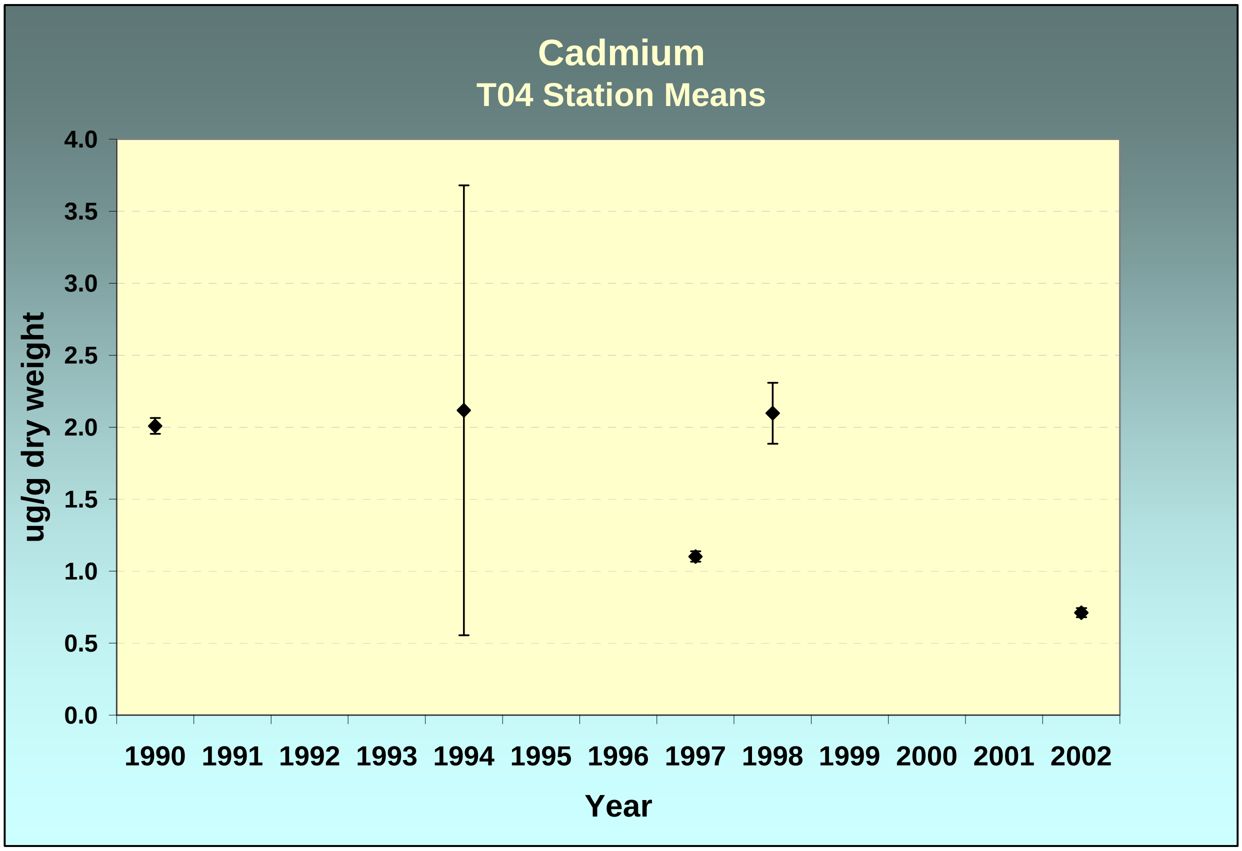

Total 24 PAH
T04 Station Means
ng/g dry weight
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

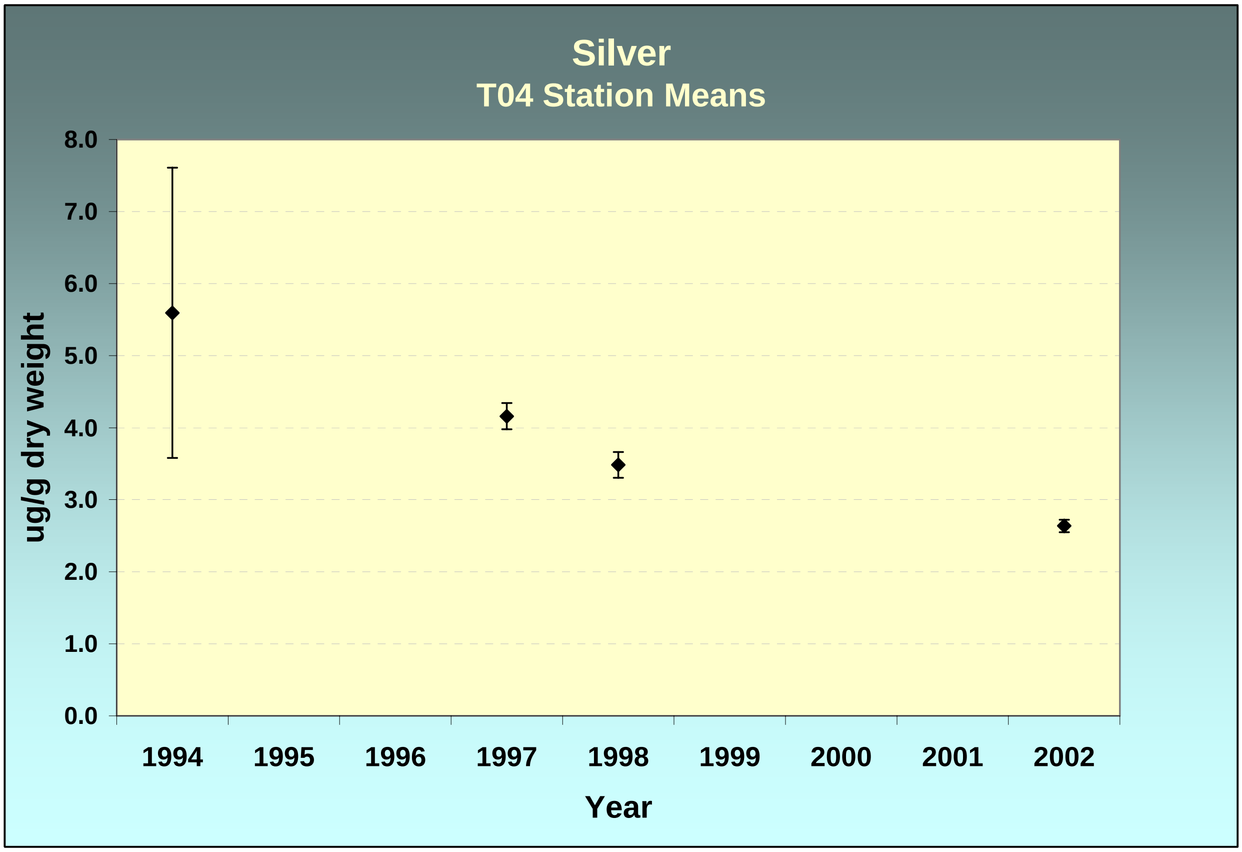

Total LAB
T04 Station Means
ng/g dry weight
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year


Copper
T04 Station Means
ug/g dry weight
250
200
150
100
50
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

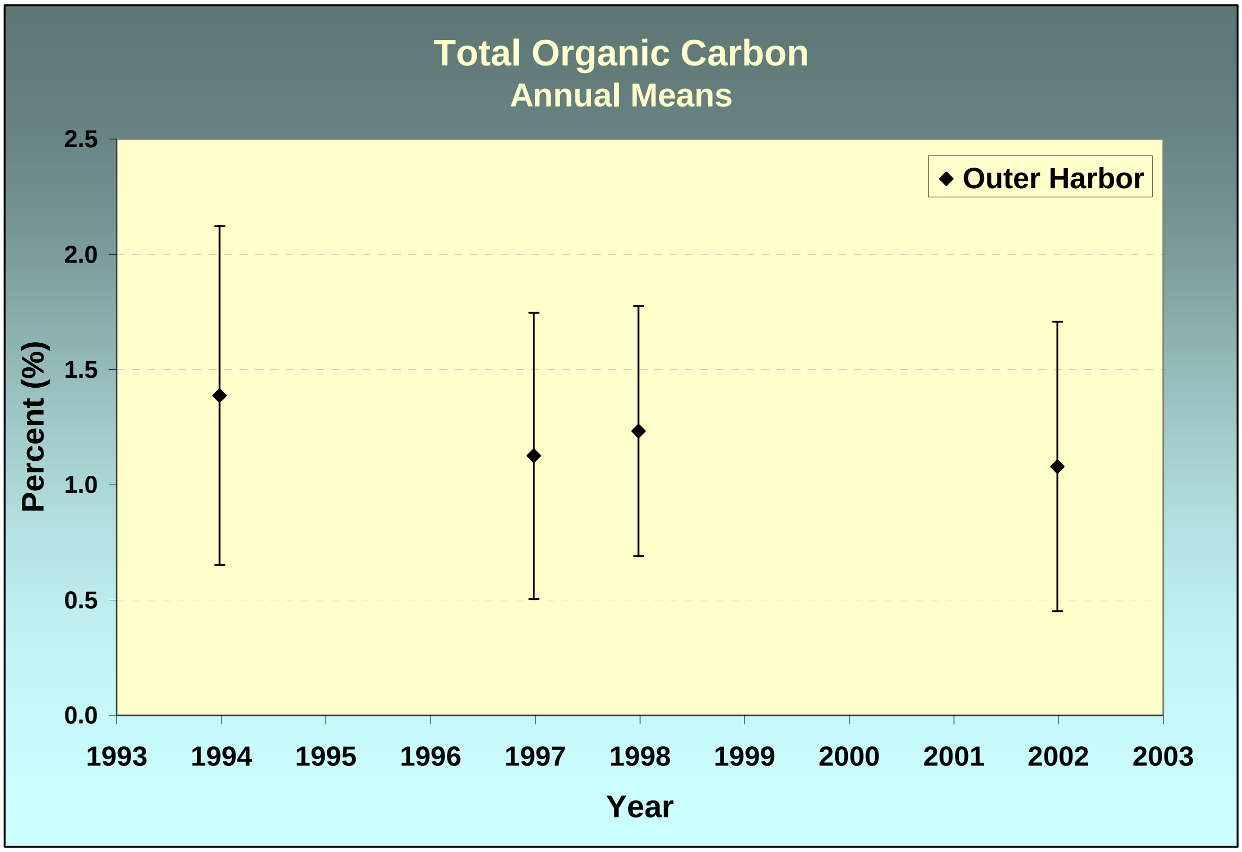

Mercury
T04 Station Means
ug/g dry weight
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

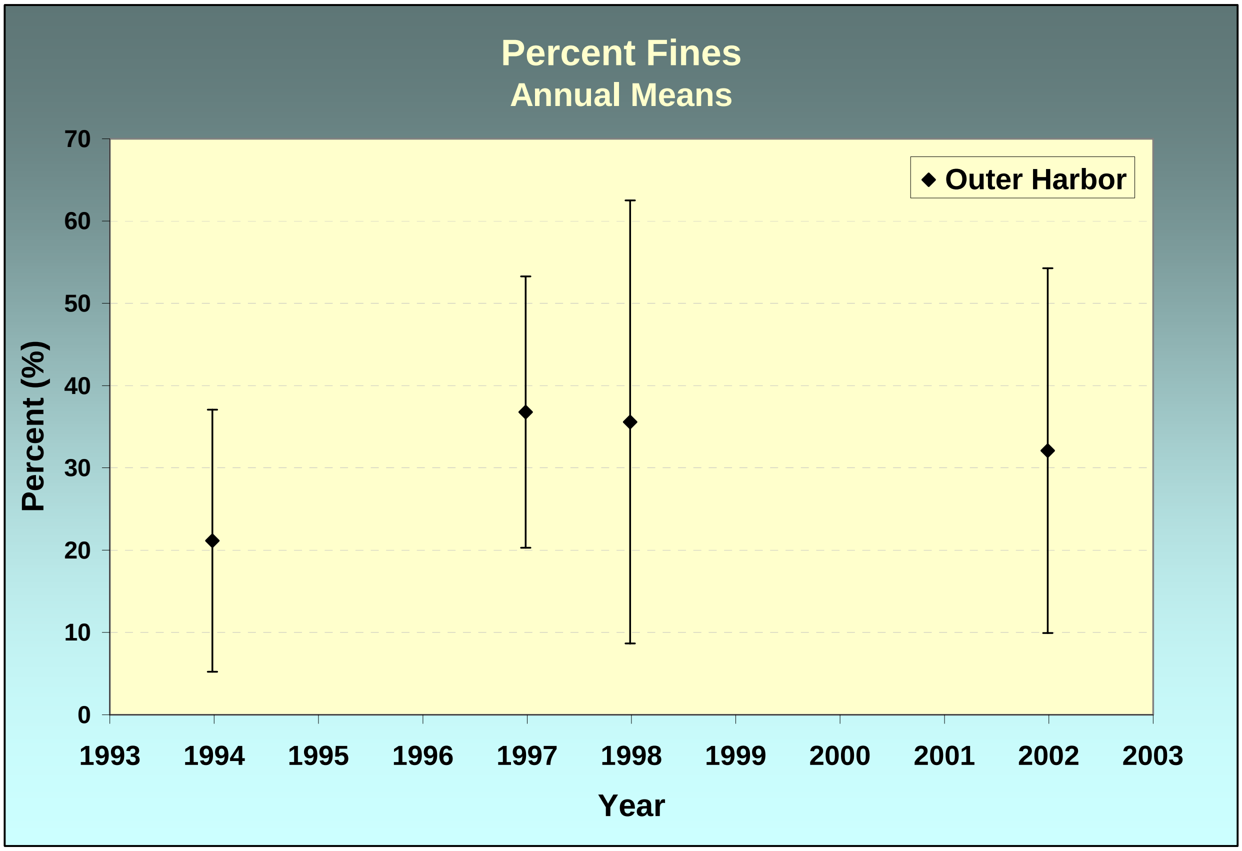

Lead
T04 Station Means
600
500
400
300
200
100
0
ug/g dry weight
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

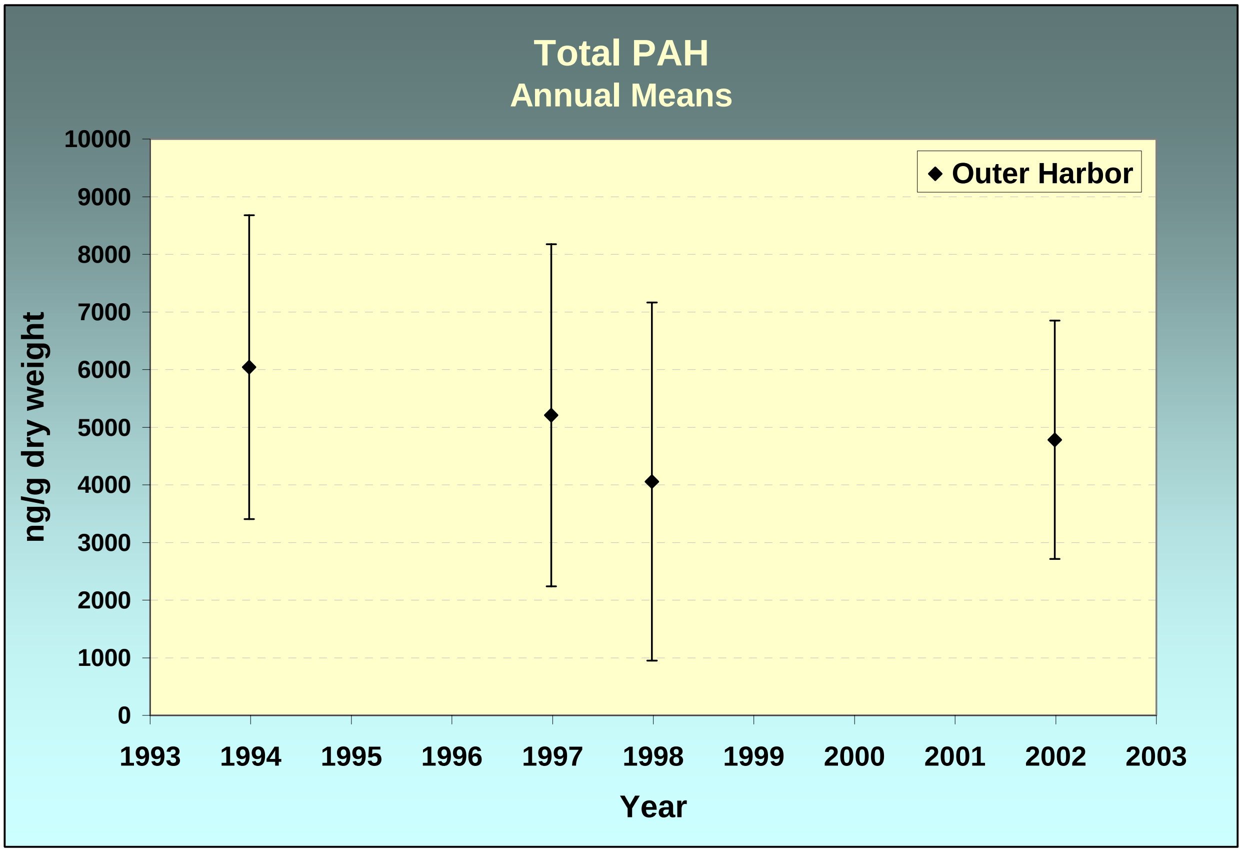

Cadmium
T04 Station Means
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ug/g dry weight
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

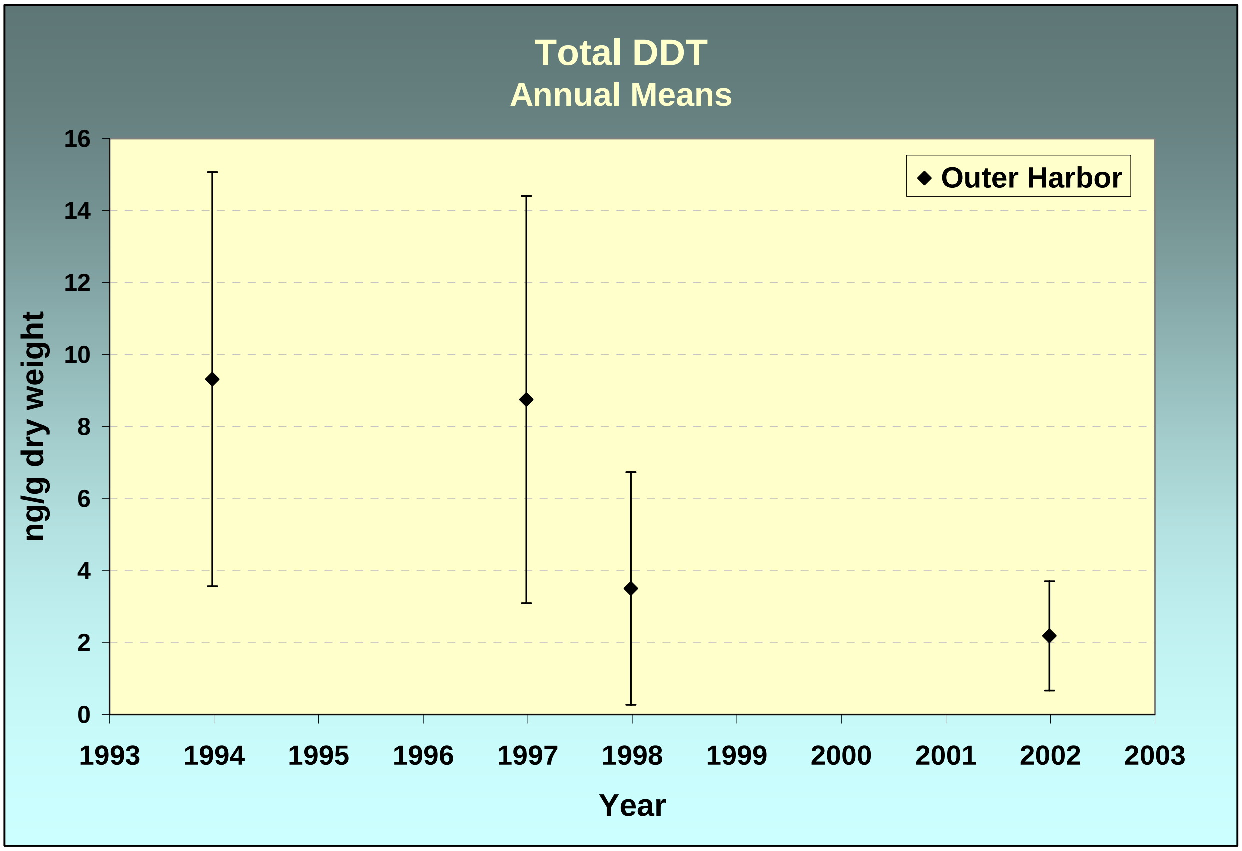

Silver
T04 Station Means
ug/g dry weight
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
Year

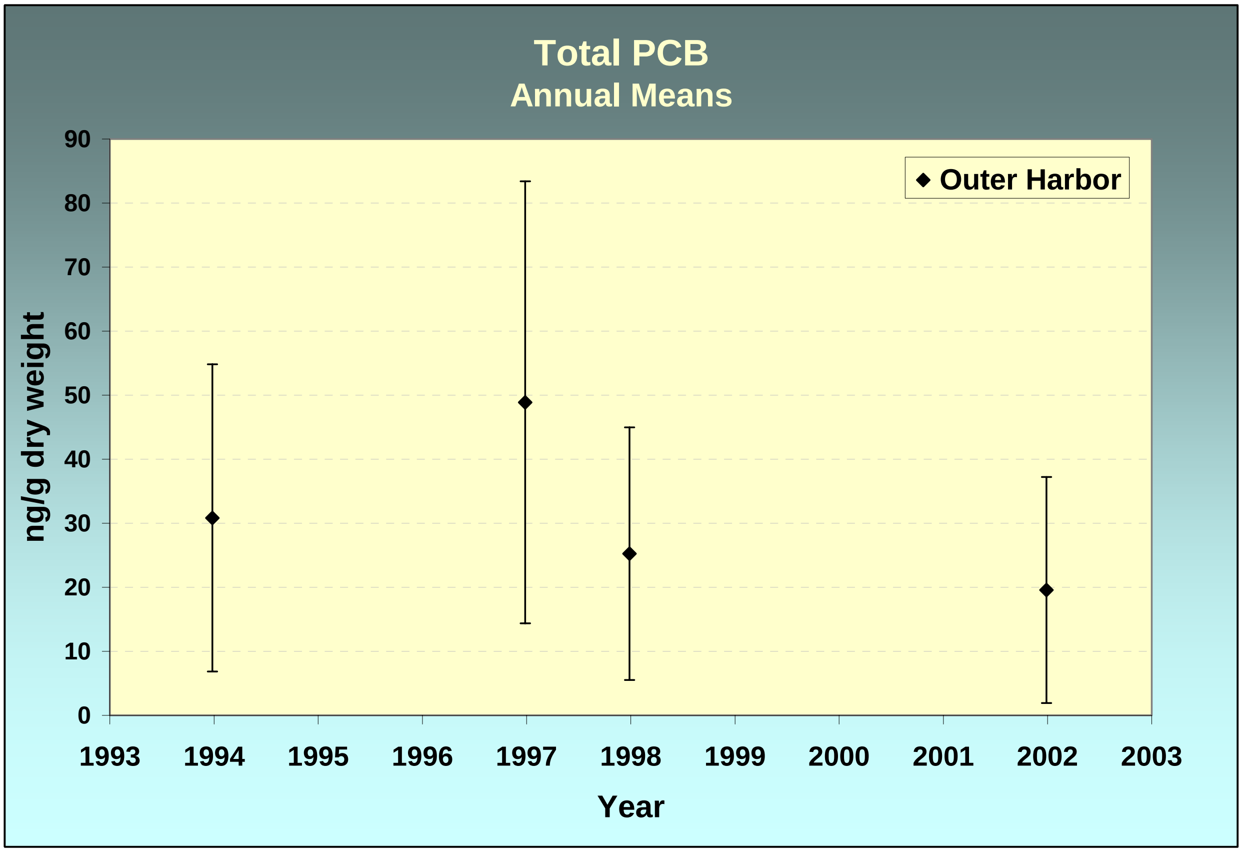
Outer Harbor

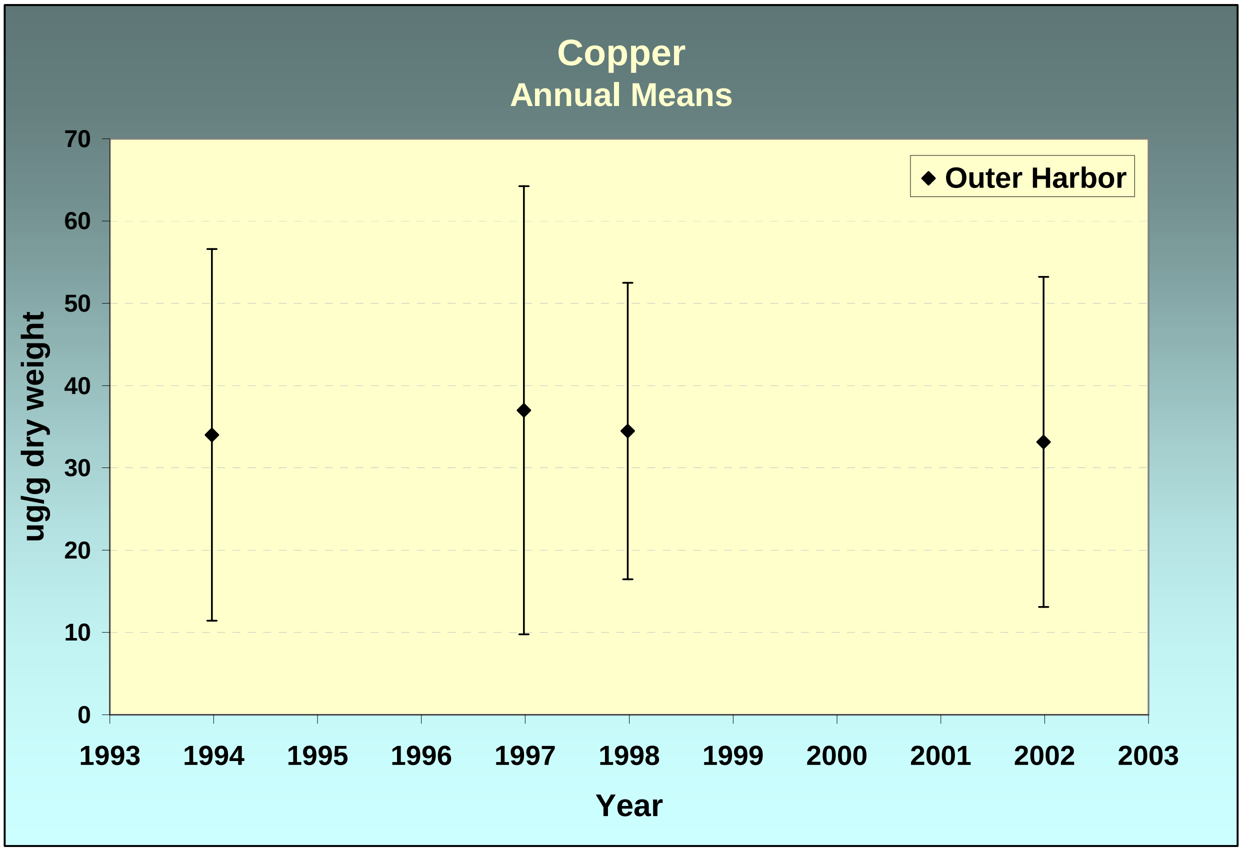

Total Organic Carbon
Annual Means
Percent (%)
2.5
2.0
1.5
1.0
0.5
0.0
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

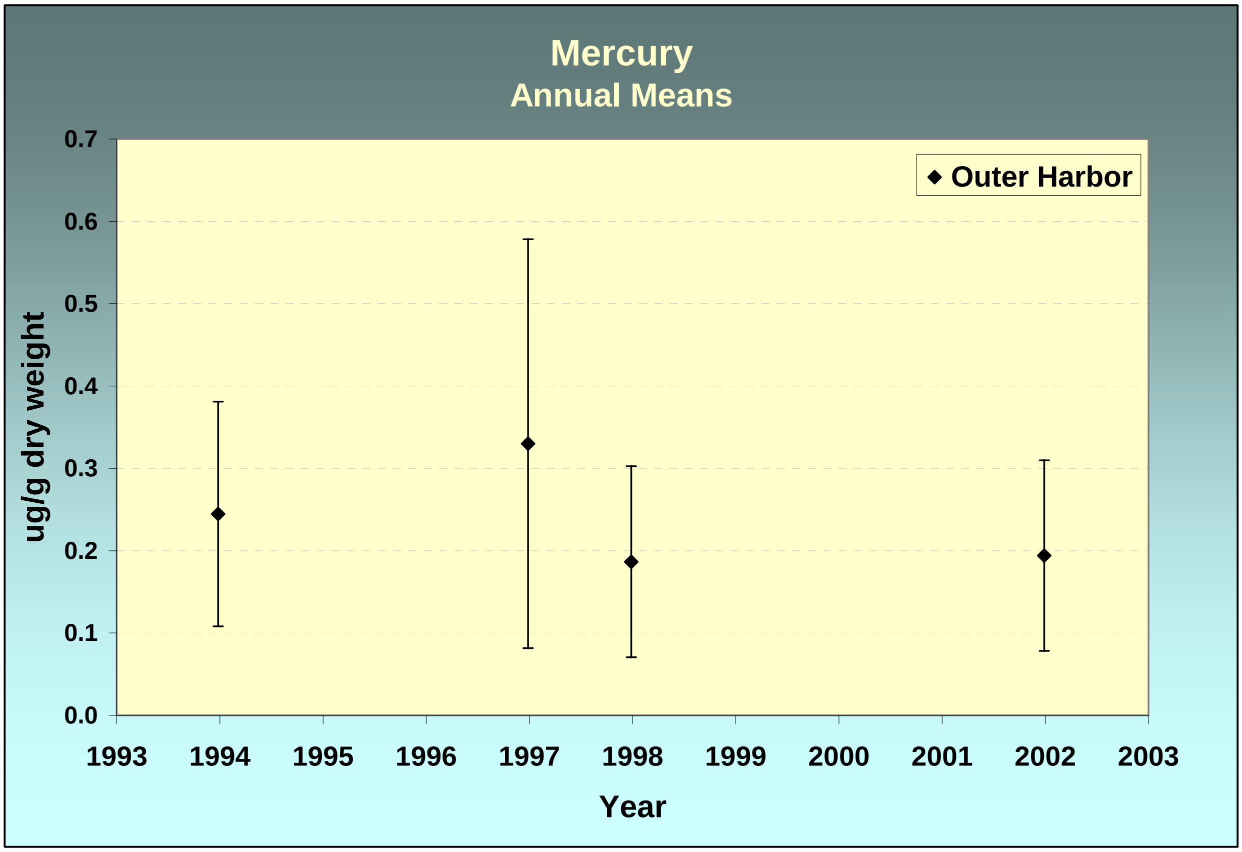

Percent Fines
Annual Means
Percent (%)
70
60
50
40
30
20
10
0
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

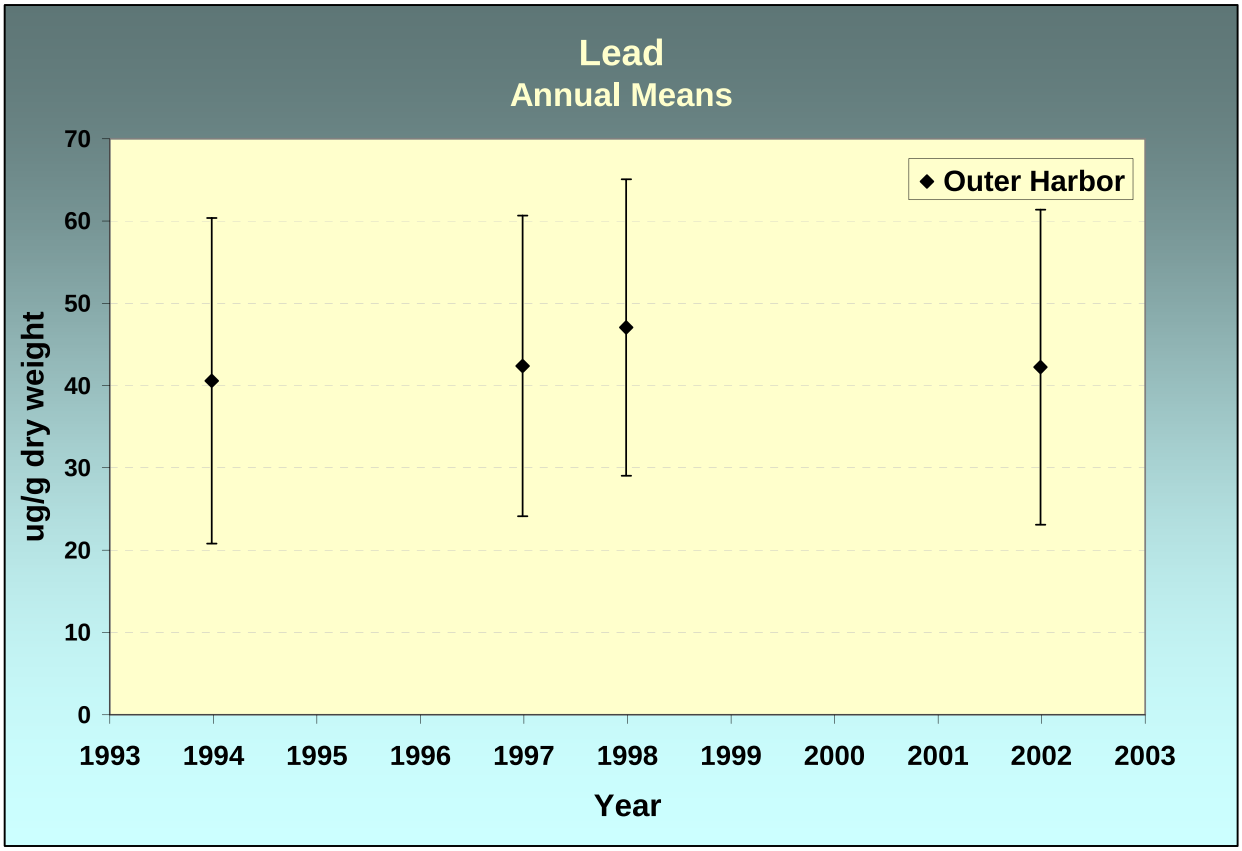

Total PAH
Annual Means
ng/g dry weight
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

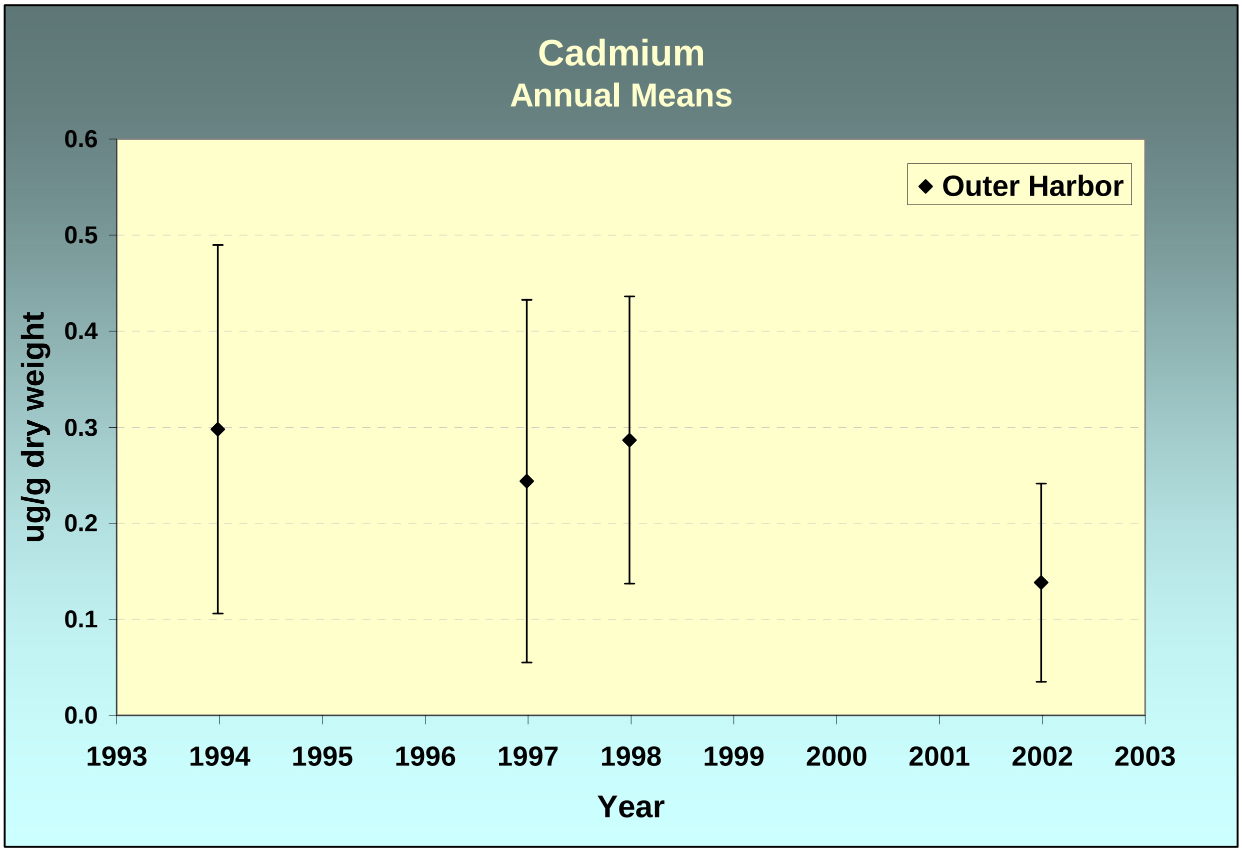

Total DDT
Annual Means
ng/g dry weight
16
14
12
10
8
6
4
2
0
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

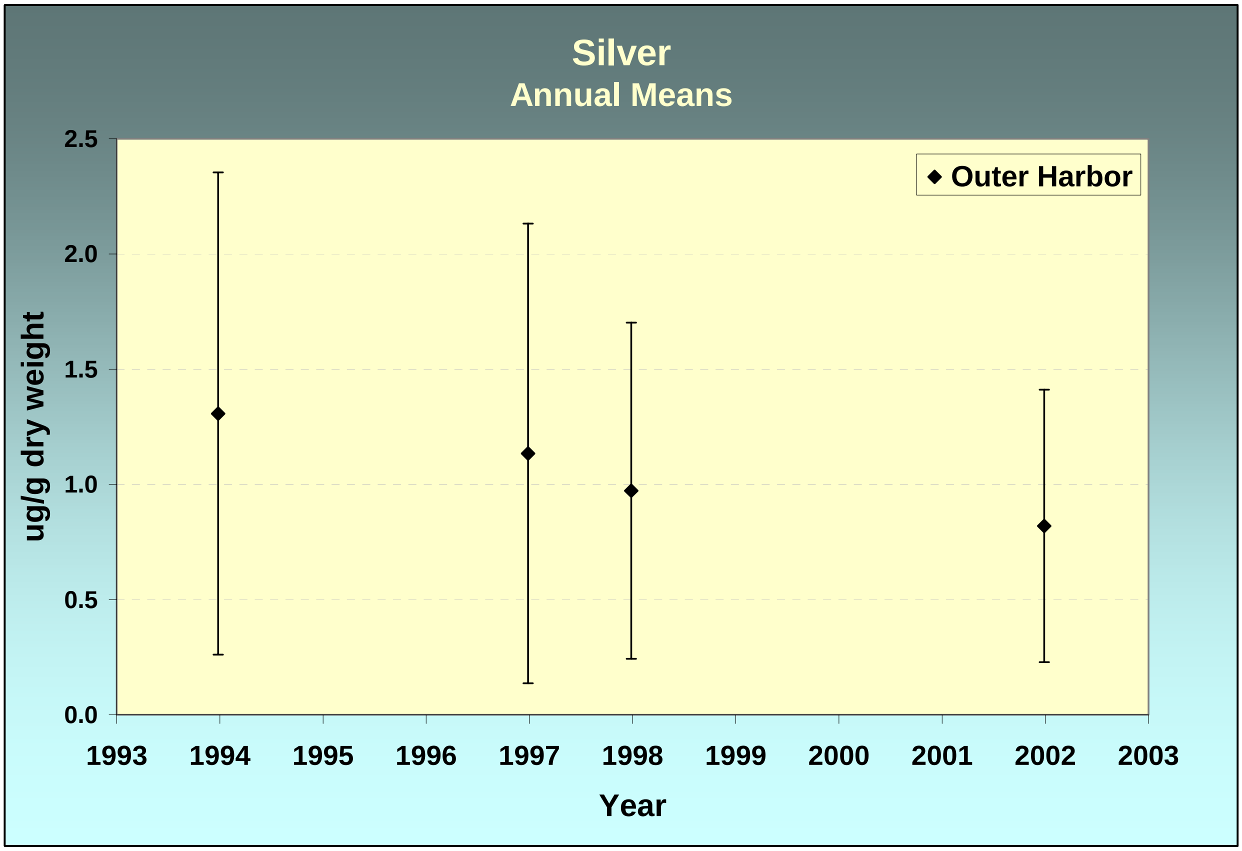

Total PCB
Annual Means
Outer Harbor
ng/g dry weight
0
10
20
30
40
50
60
70
80
90
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year


Copper
Annual Means
Outer Harbor
ug/g dry weight
0
10
20
30
40
50
60
70
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

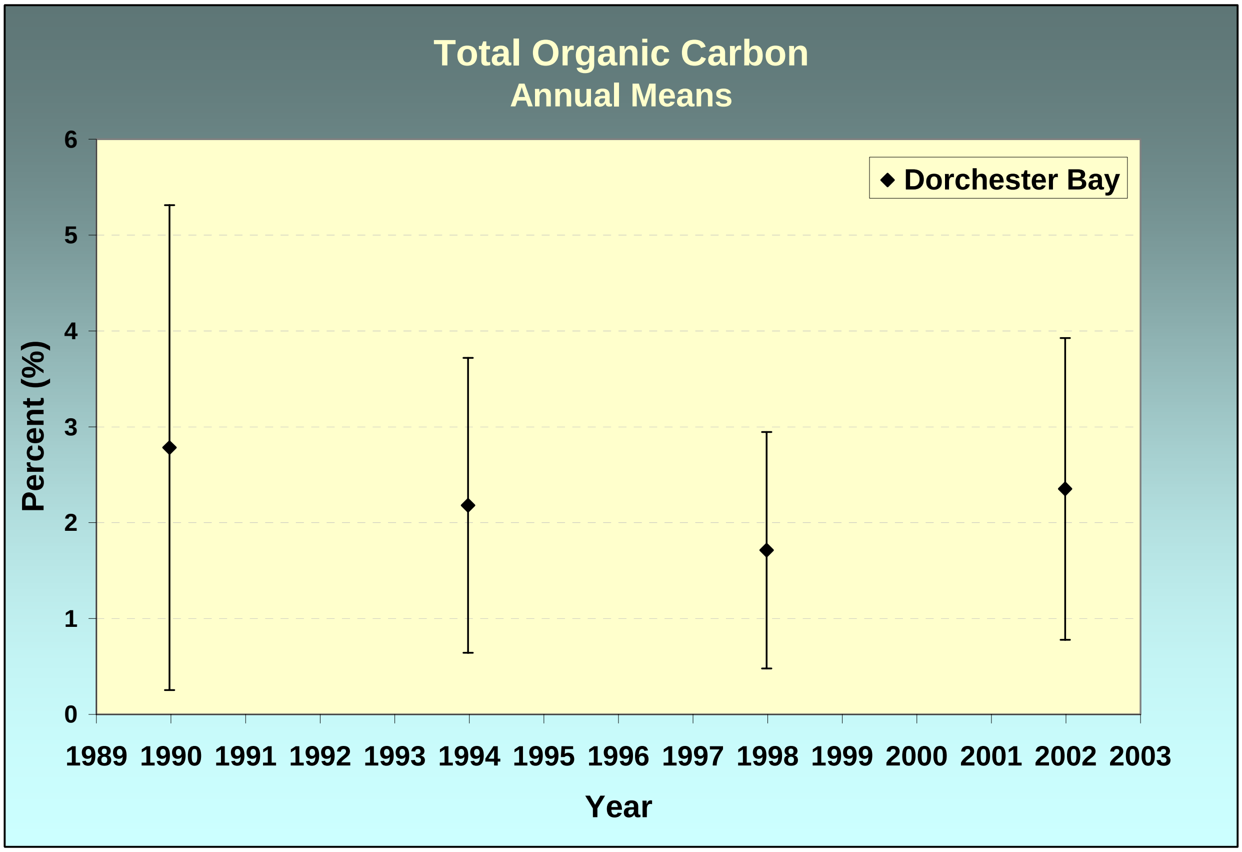

Mercury
Annual Means
ug/g dry weight
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

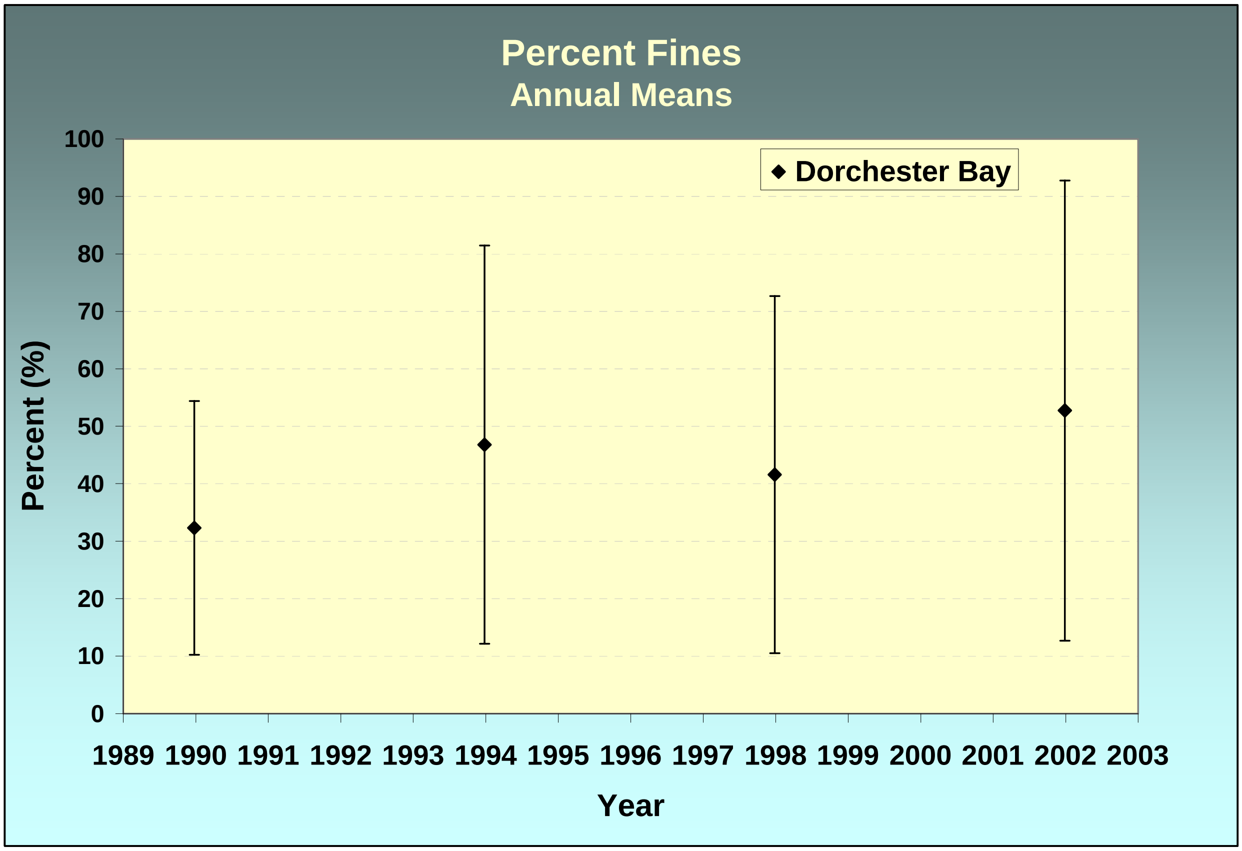

Lead
Annual Means
ug/g dry weight
0
10
20
30
40
50
60
70
◆ Outer Harbor
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

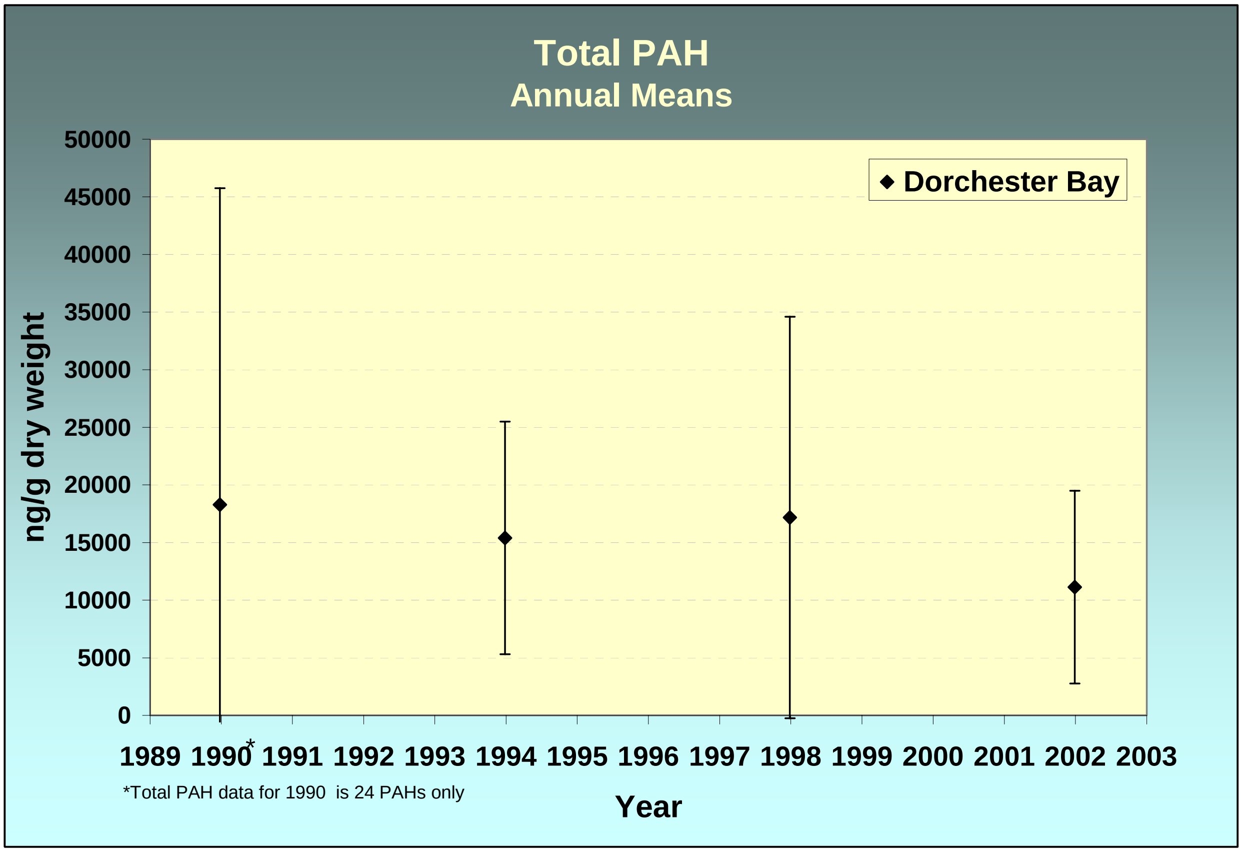

Cadmium
Annual Means
◆ Outer Harbor
ug/g dry weight
0.0
0.1
0.2
0.3
0.4
0.5
0.6
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

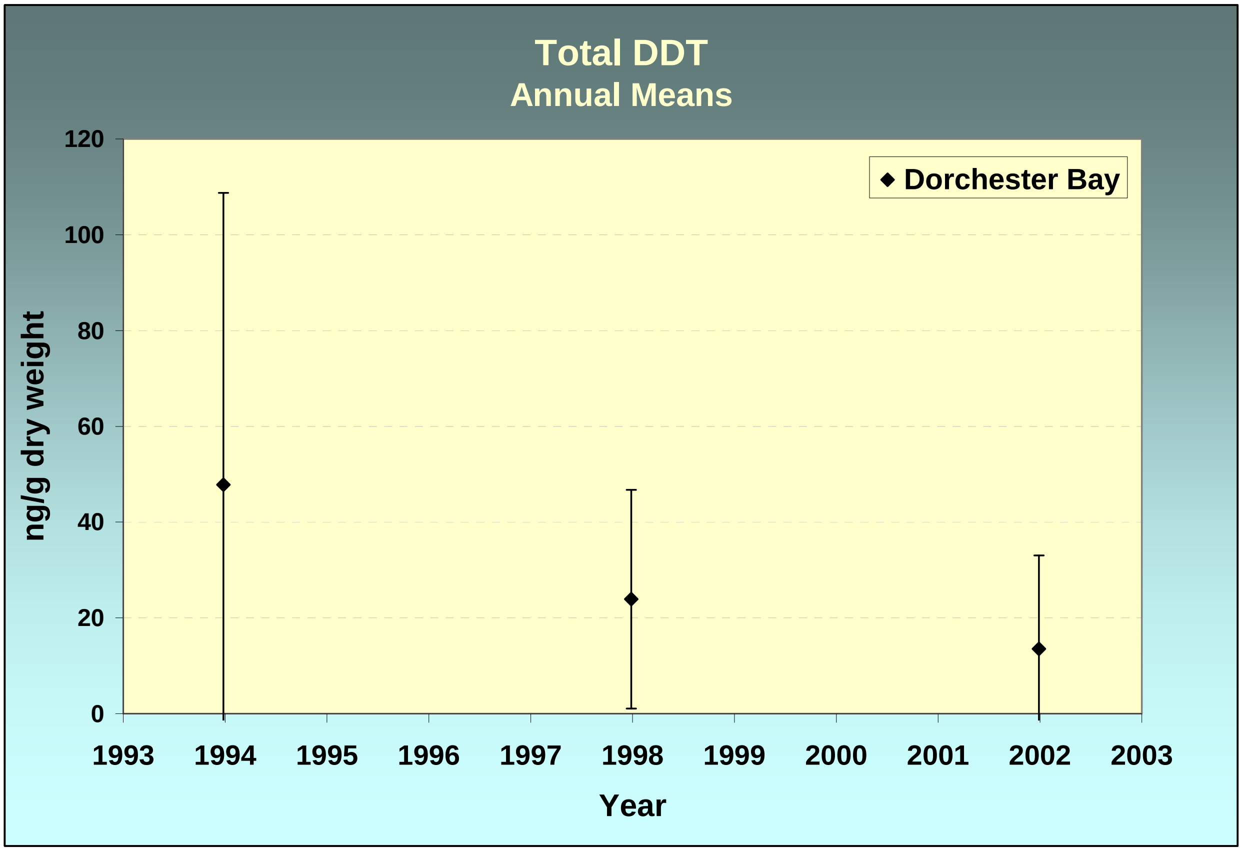

Silver
Annual Means
◆ Outer Harbor
ug/g dry weight
0.0
0.5
1.0
1.5
2.0
2.5
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

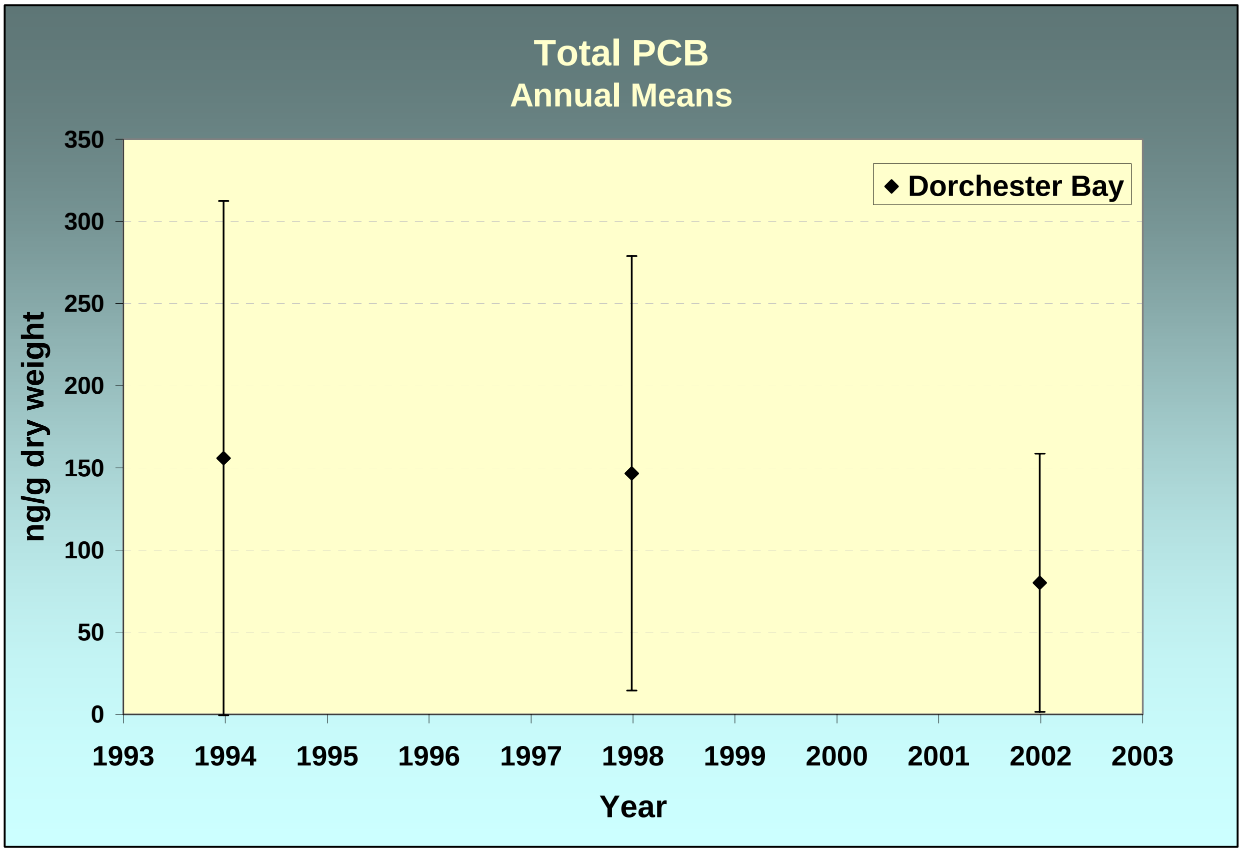
Dorchester Bay

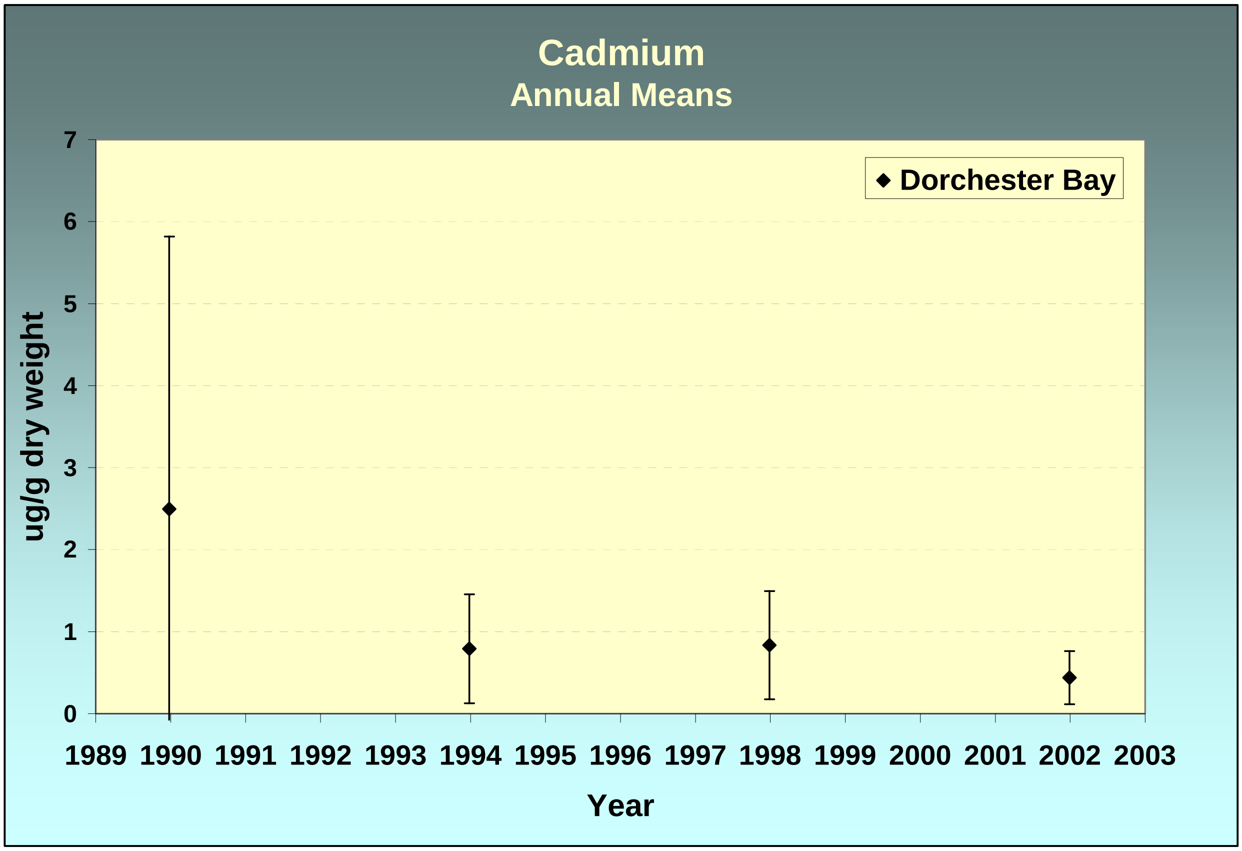

Total Organic Carbon
Annual Means
◆ Dorchester Bay
Percent (%)
0
1
2
3
4
5
6
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

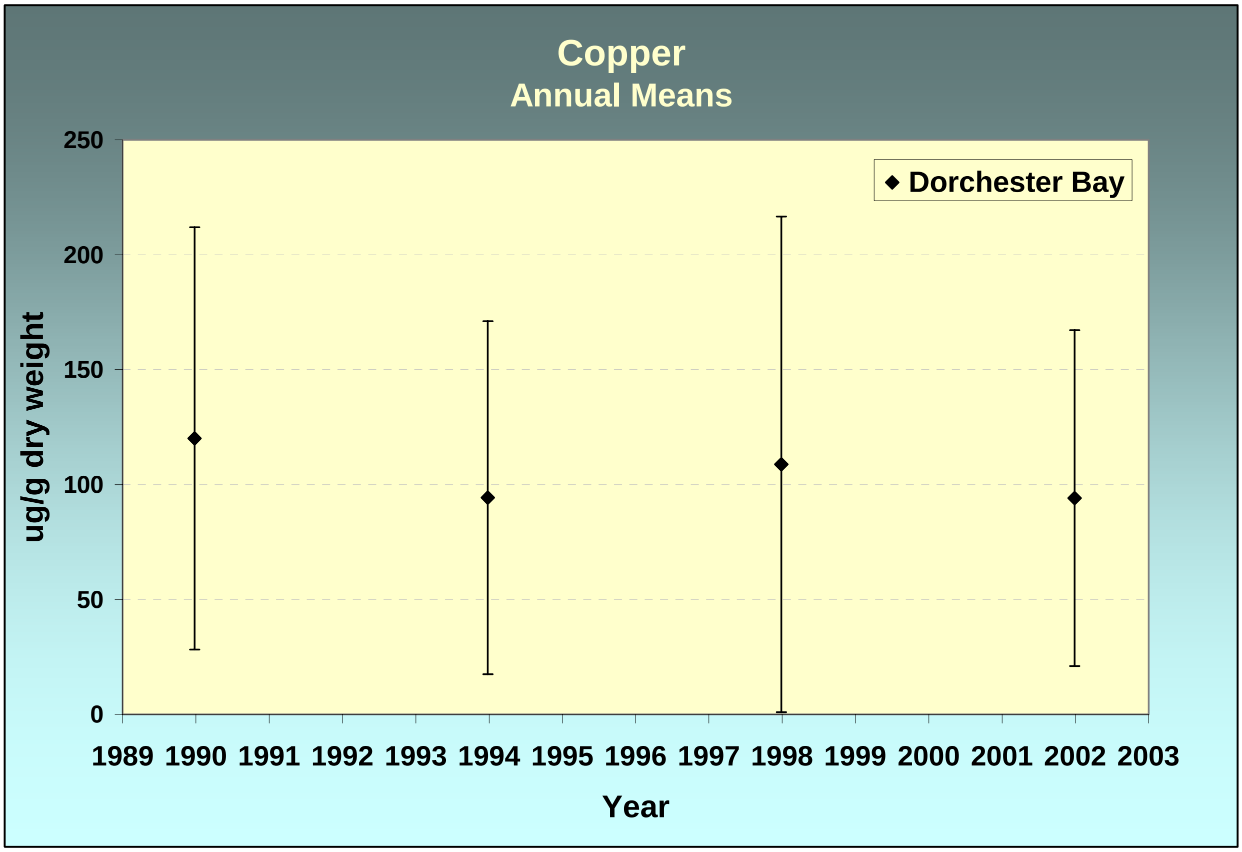

Percent Fines
Annual Means
◆ Dorchester Bay
Percent (%)
0
10
20
30
40
50
60
70
80
90
100
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

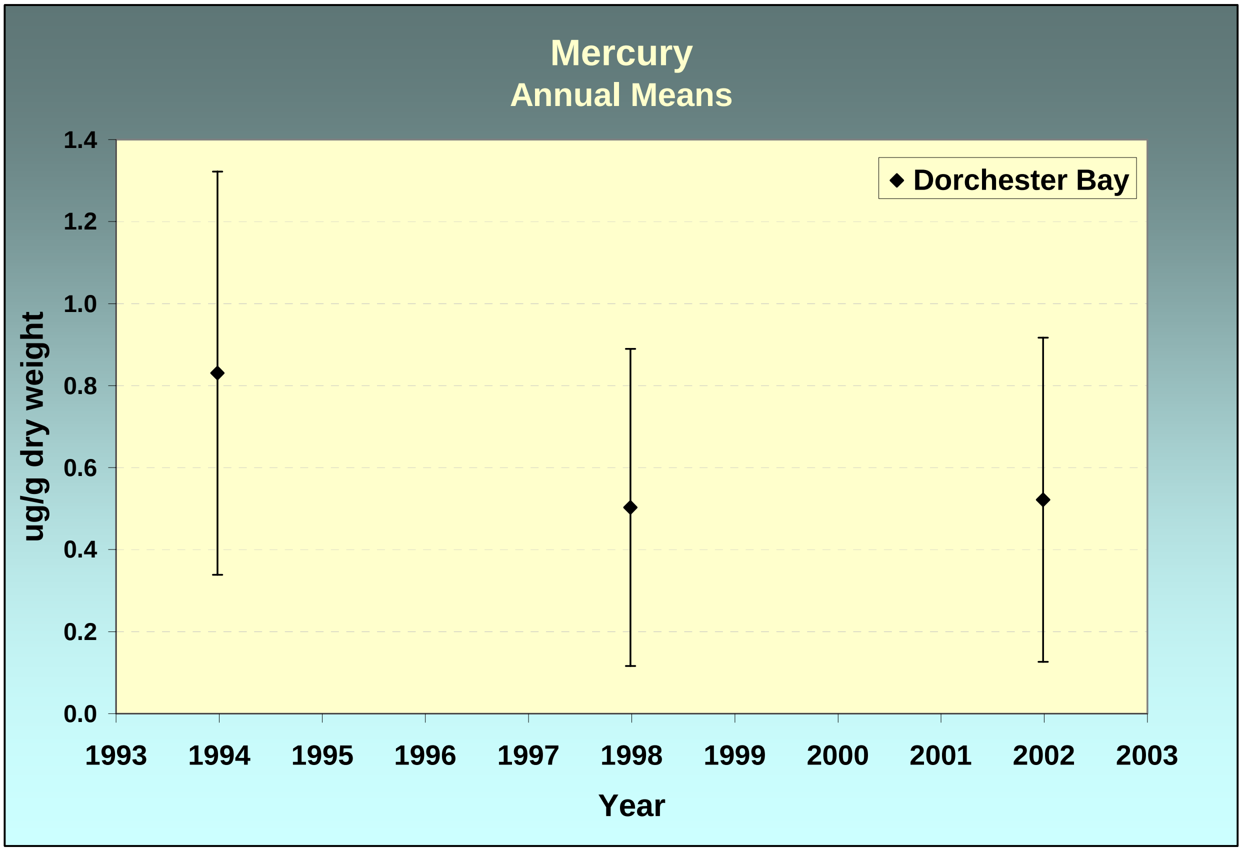

Total PAH
Annual Means
ng/g dry weight
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
◆ Dorchester Bay
1989 1990* 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003
*Total PAH data for 1990 is 24 PAHs only
Year

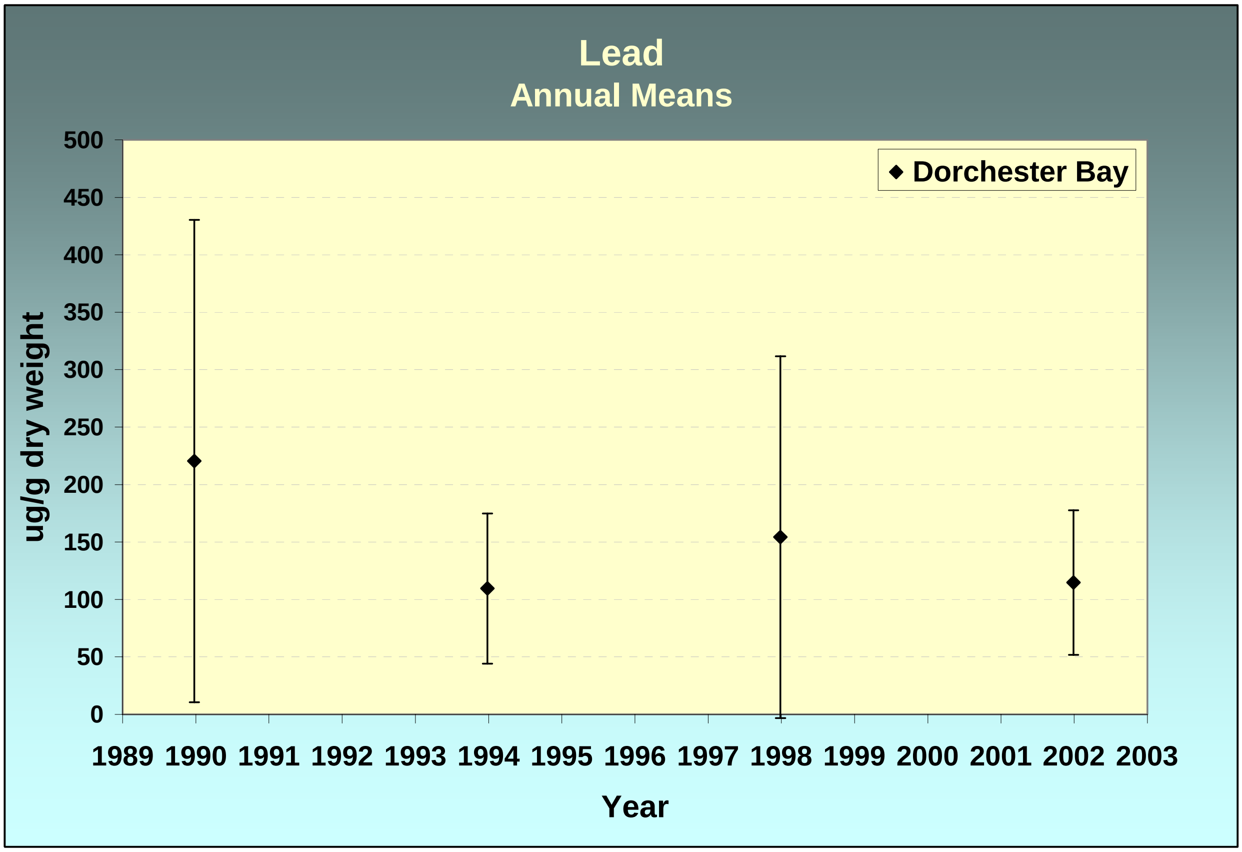

Total DDT
Annual Means
ng/g dry weight
120
100
80
60
40
20
0
◆ Dorchester Bay
1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003
Year

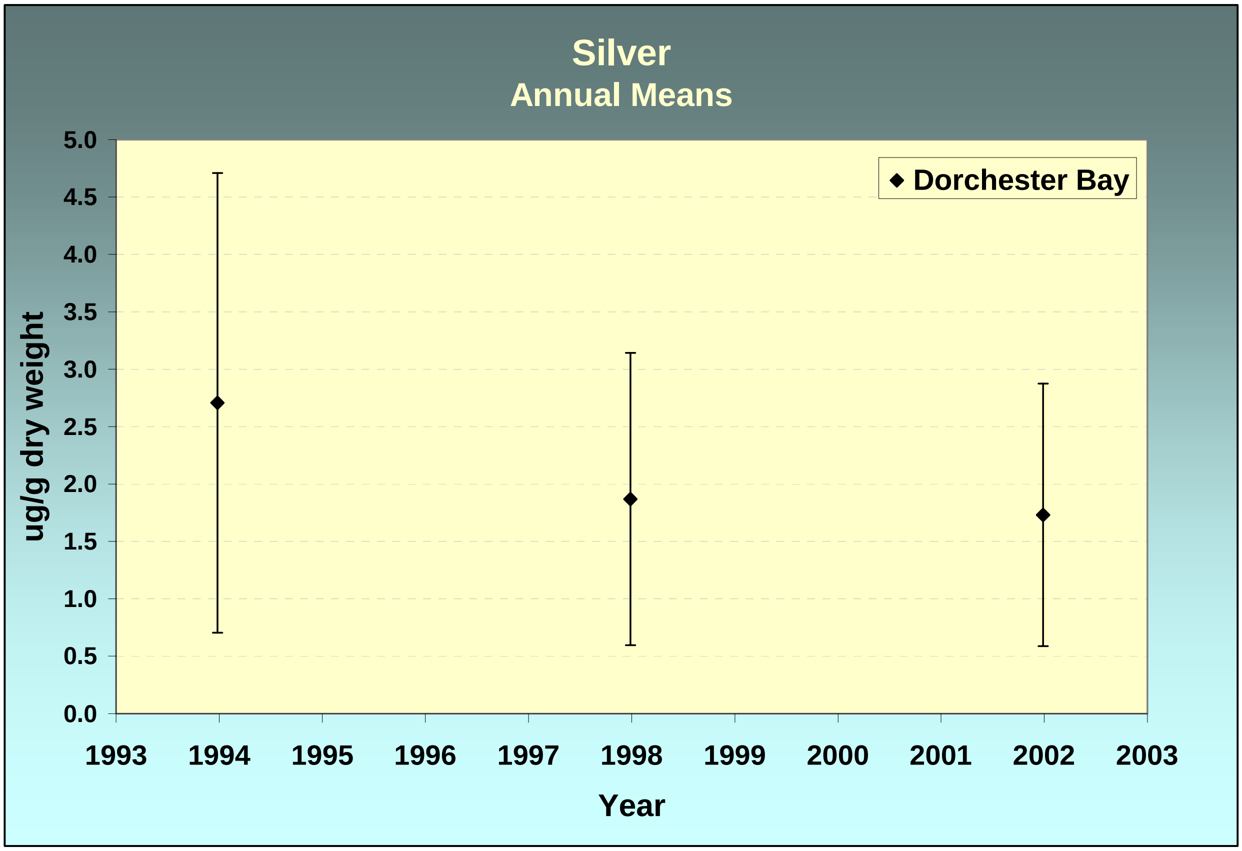

Total PCB
Annual Means
◆ Dorchester Bay
ng/g dry weight
0
50
100
150
200
250
300
350
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year


Cadmium
Annual Means
◆ Dorchester Bay
ug/g dry weight
0
1
2
3
4
5
6
7
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

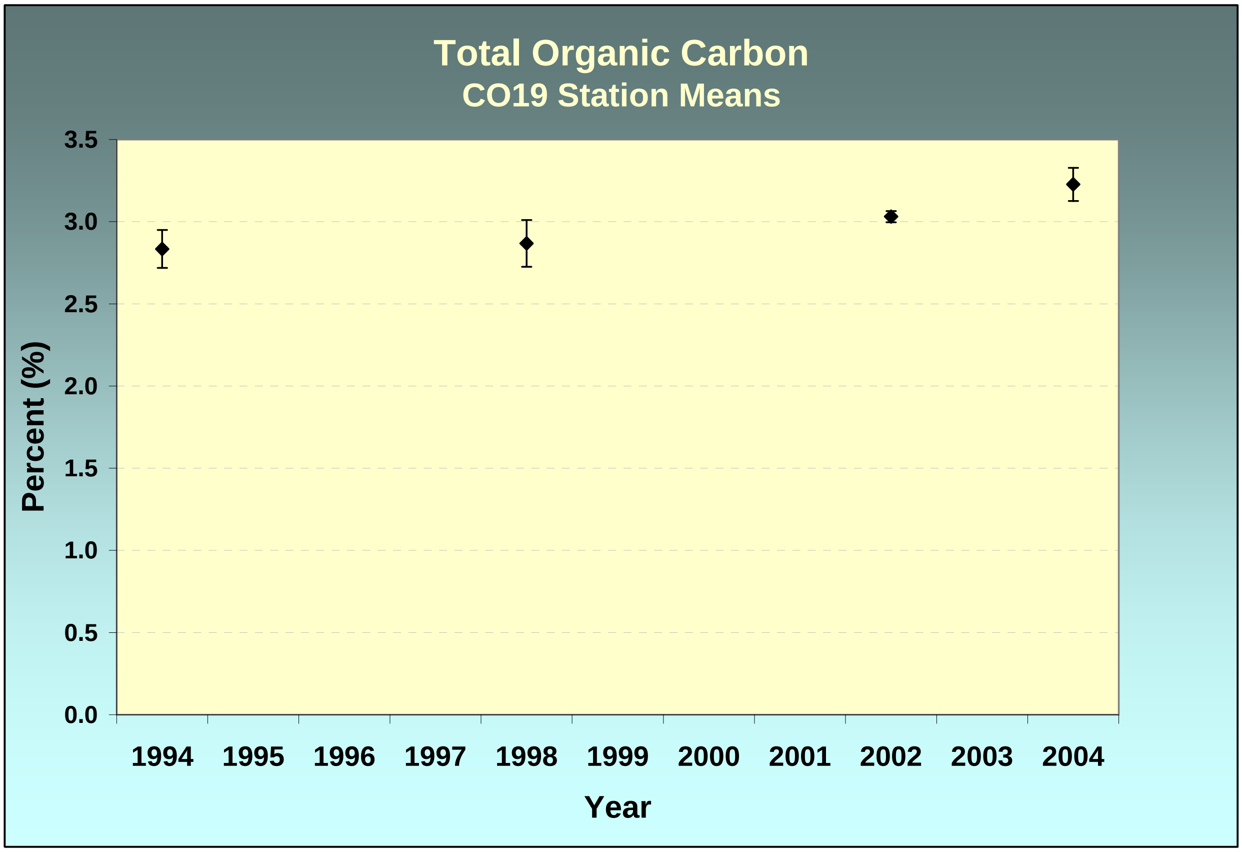

Copper
Annual Means
ug/g dry weight
250
200
150
100
50
0
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year
◆ Dorchester Bay

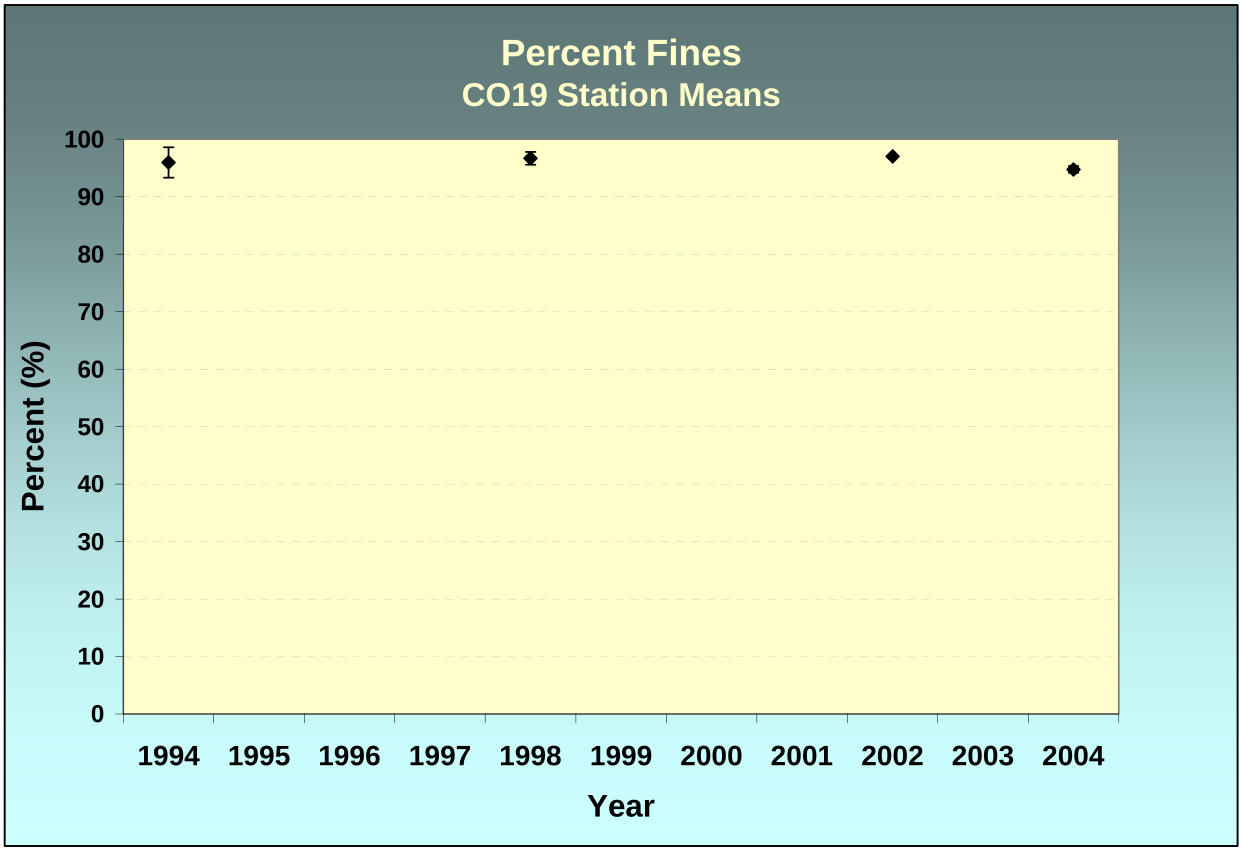

Mercury
Annual Means
ug/g dry weight
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year
◆ Dorchester Bay

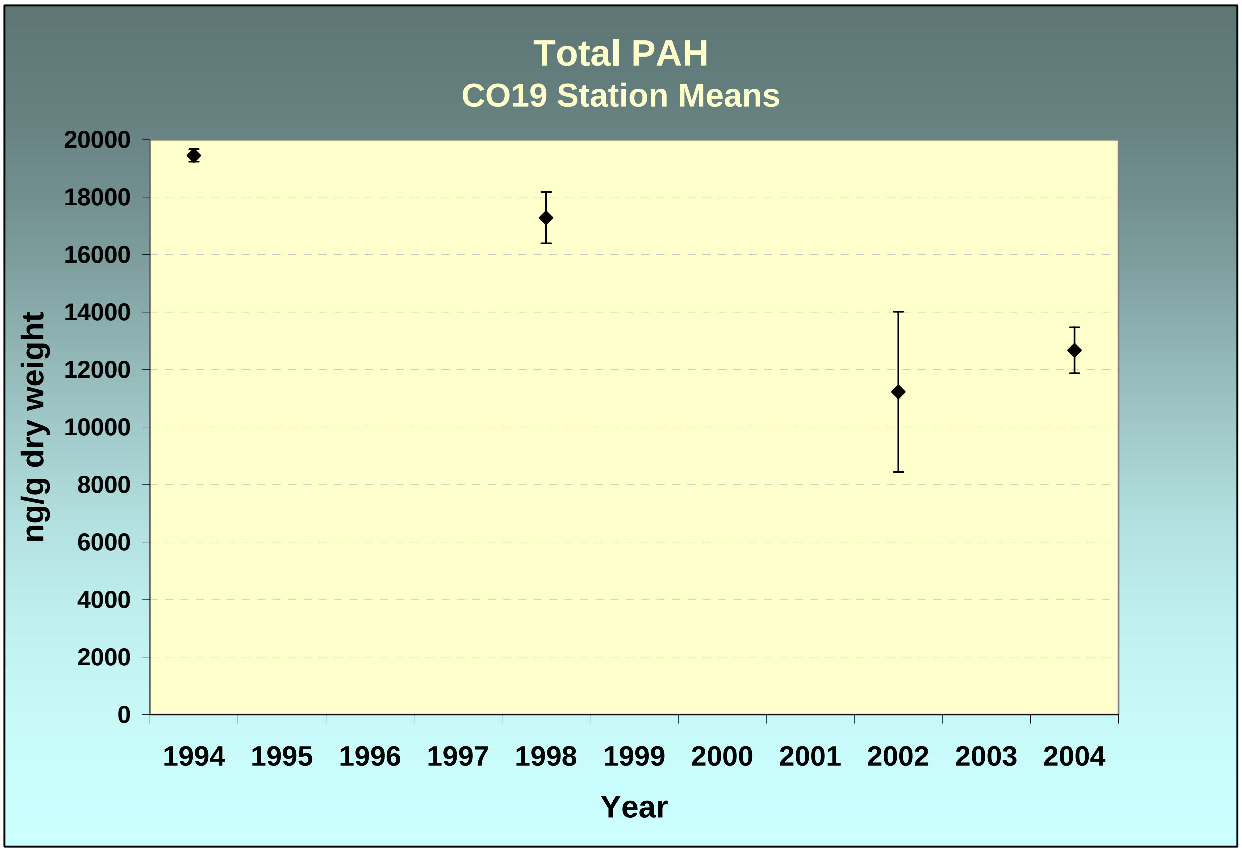

Lead
Annual Means
◆ Dorchester Bay
ug/g dry weight
0
50
100
150
200
250
300
350
400
450
500
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

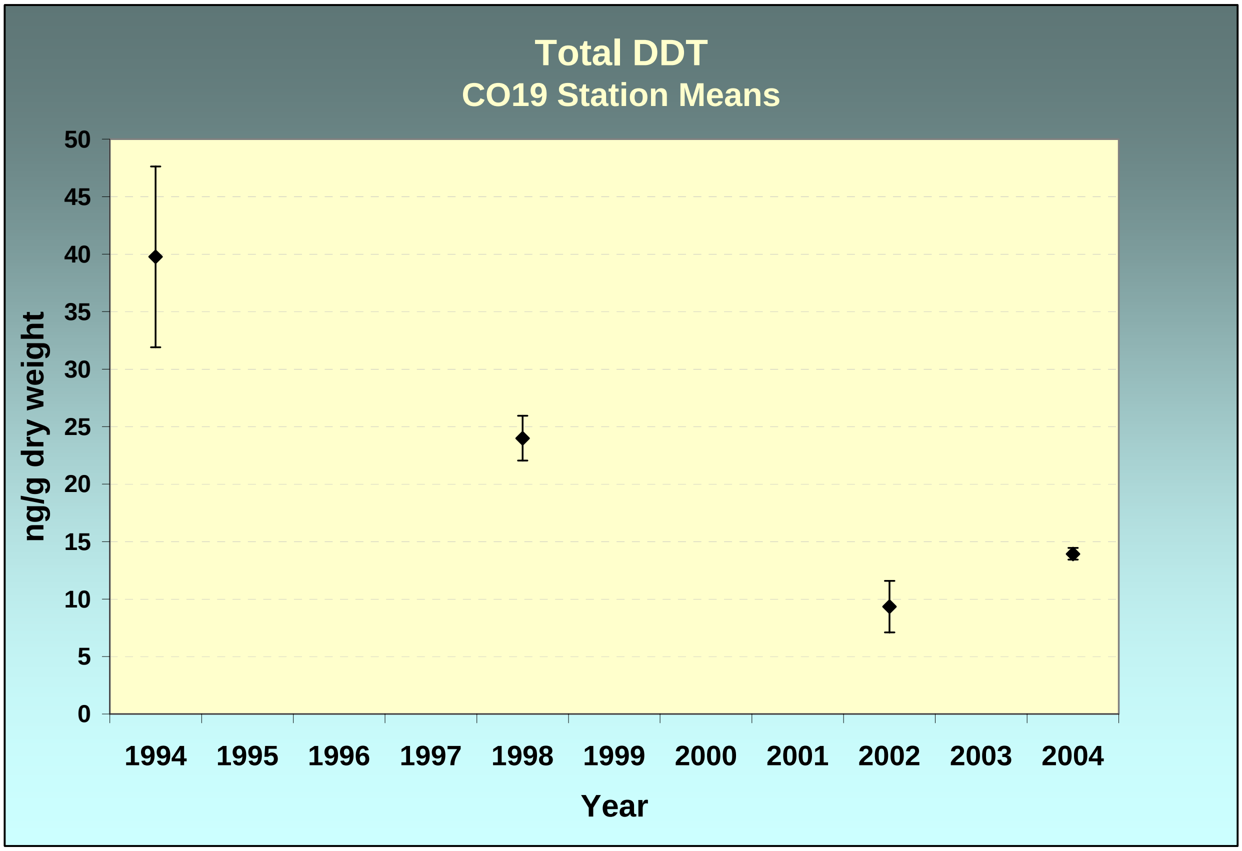

Silver
Annual Means
◆ Dorchester Bay
ug/g dry weight
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
Year

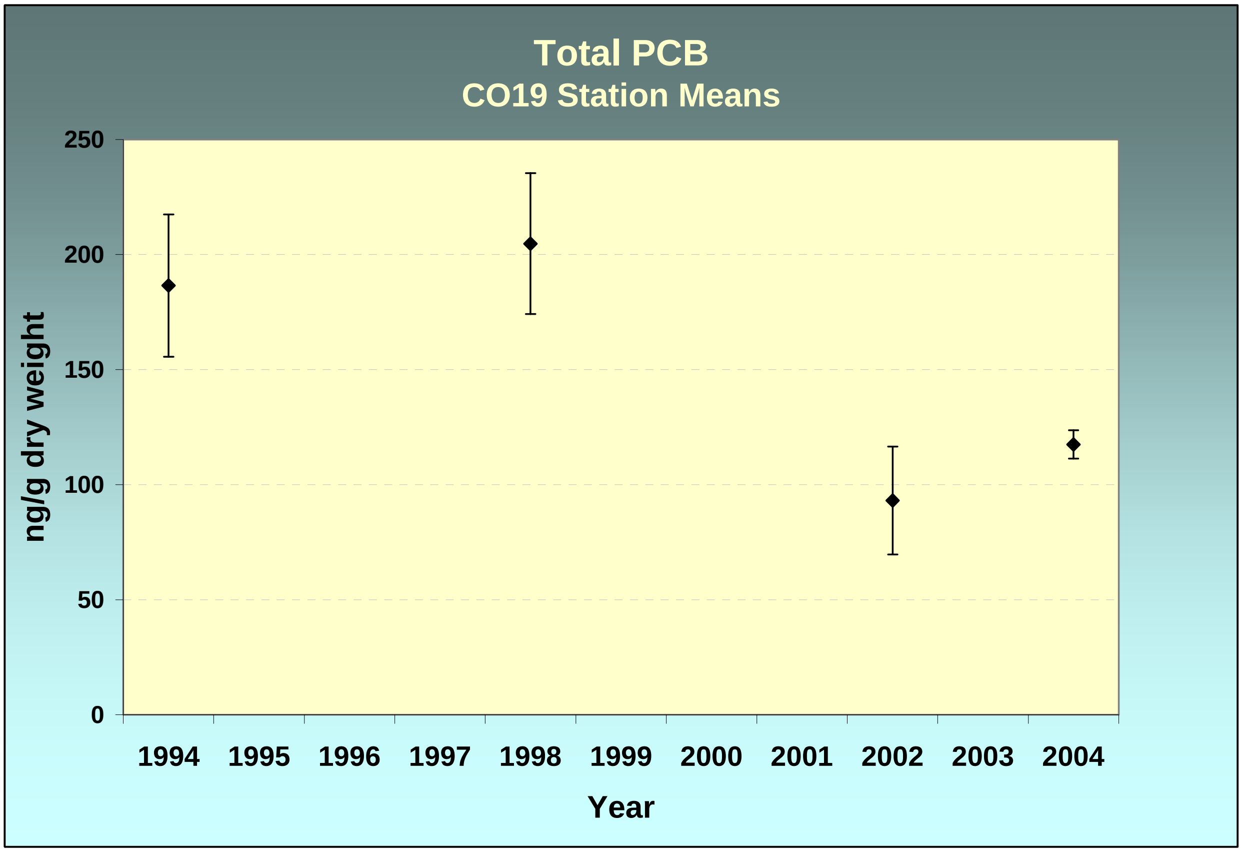
Inner Harbor (CO19)

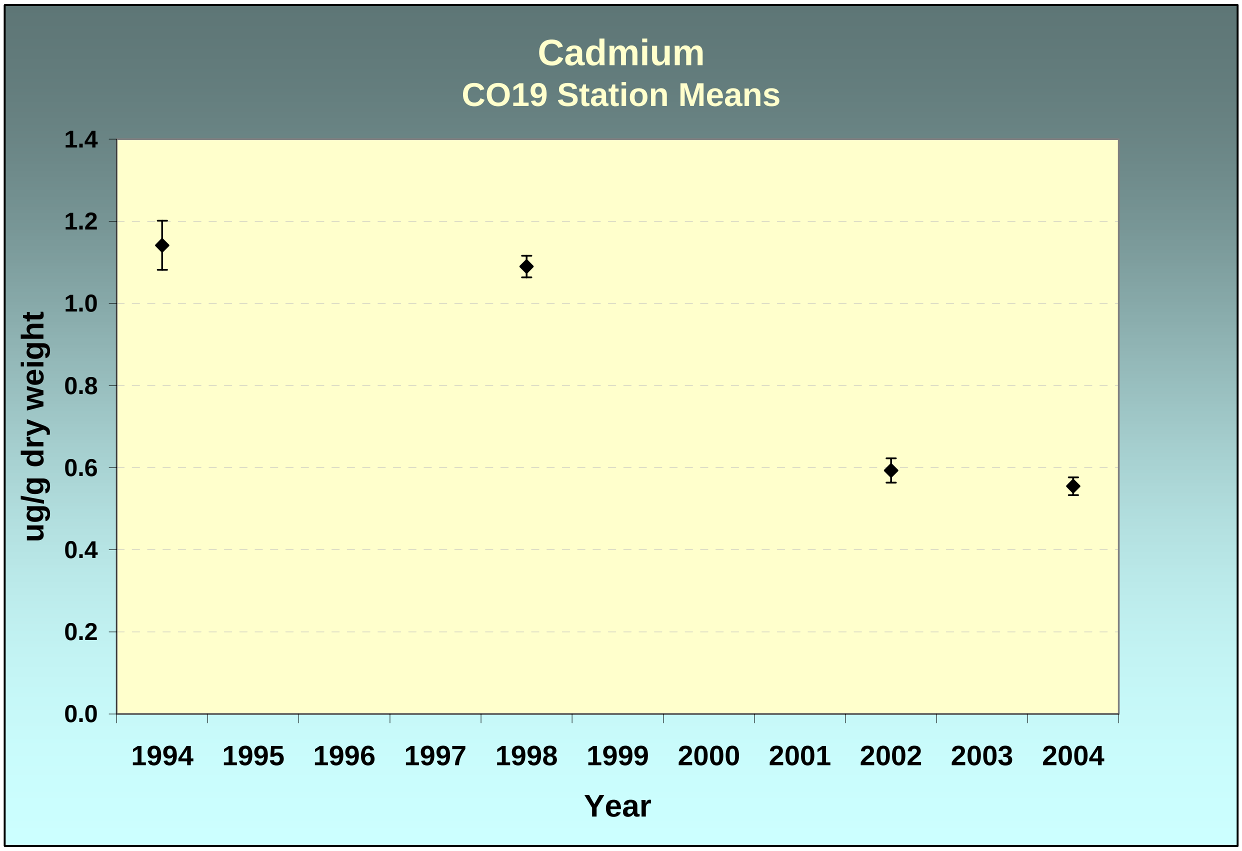

Total Organic Carbon
CO19 Station Means
Percent (%)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

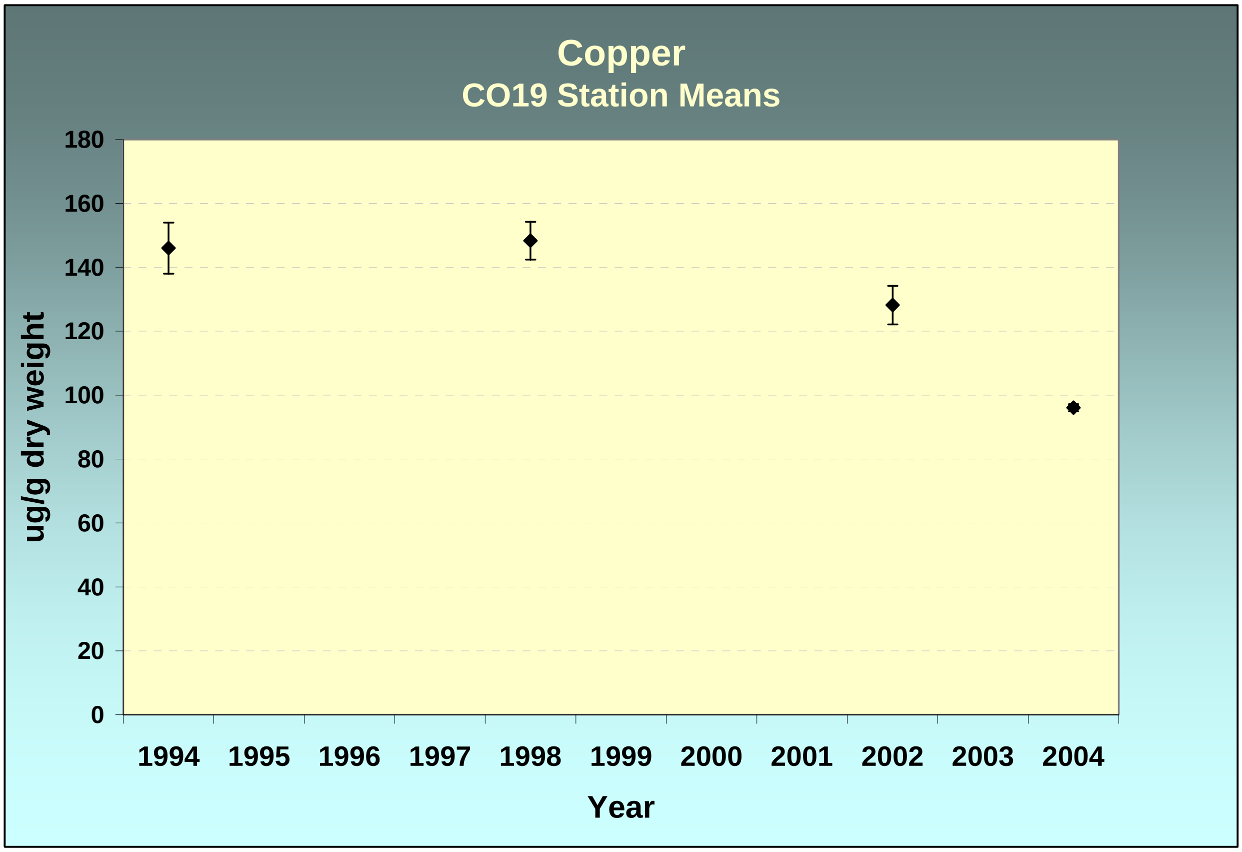

Percent Fines
CO19 Station Means
Percent (%)
100
90
80
70
60
50
40
30
20
10
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

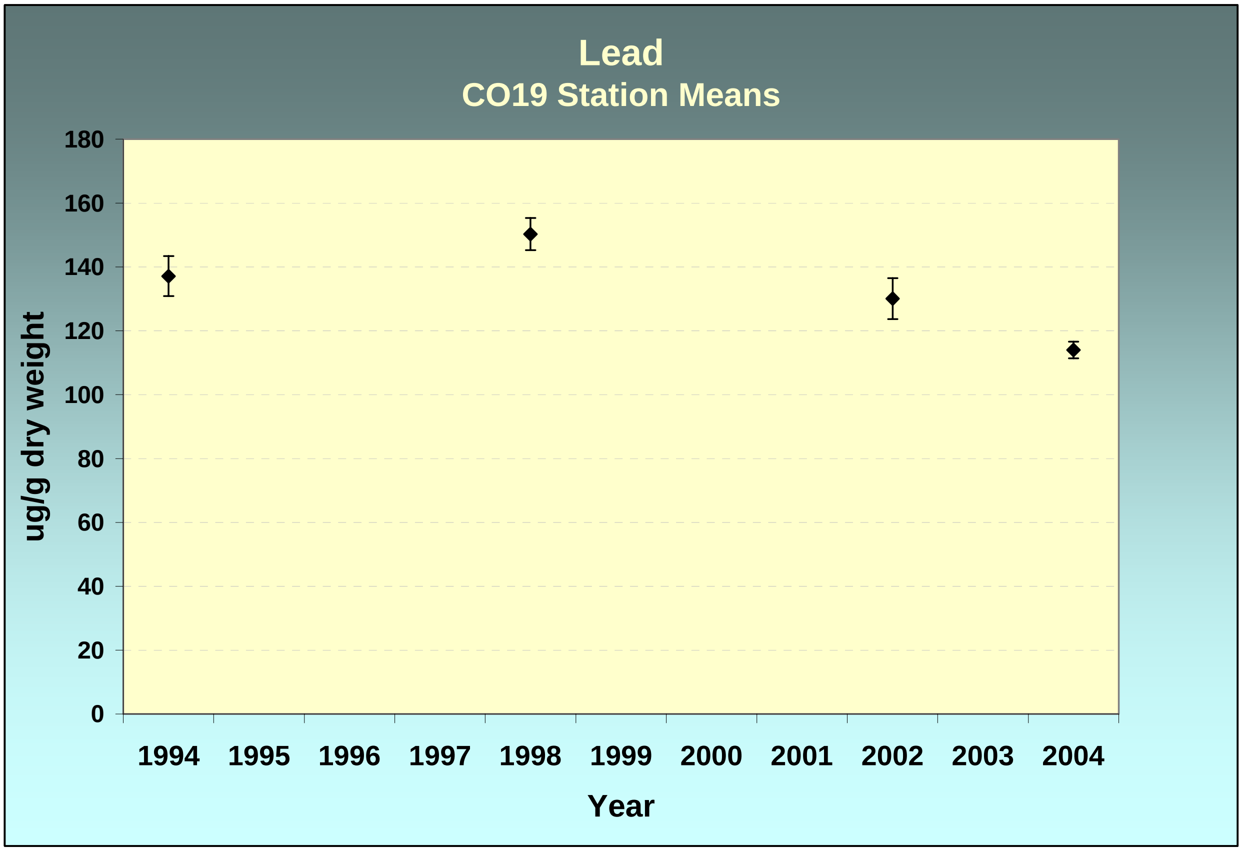

Total PAH
CO19 Station Means
ng/g dry weight
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

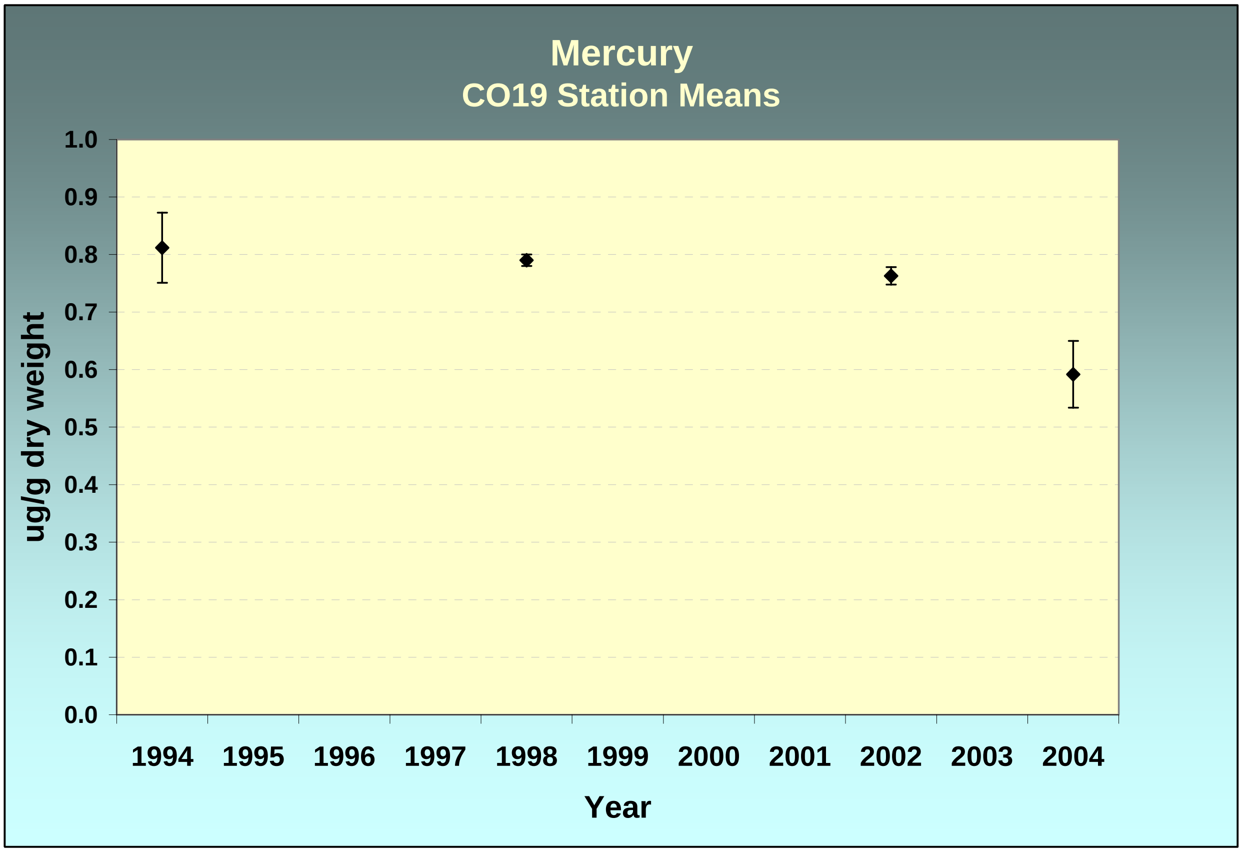

Total DDT
CO19 Station Means
ng/g dry weight
50
45
40
35
30
25
20
15
10
5
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

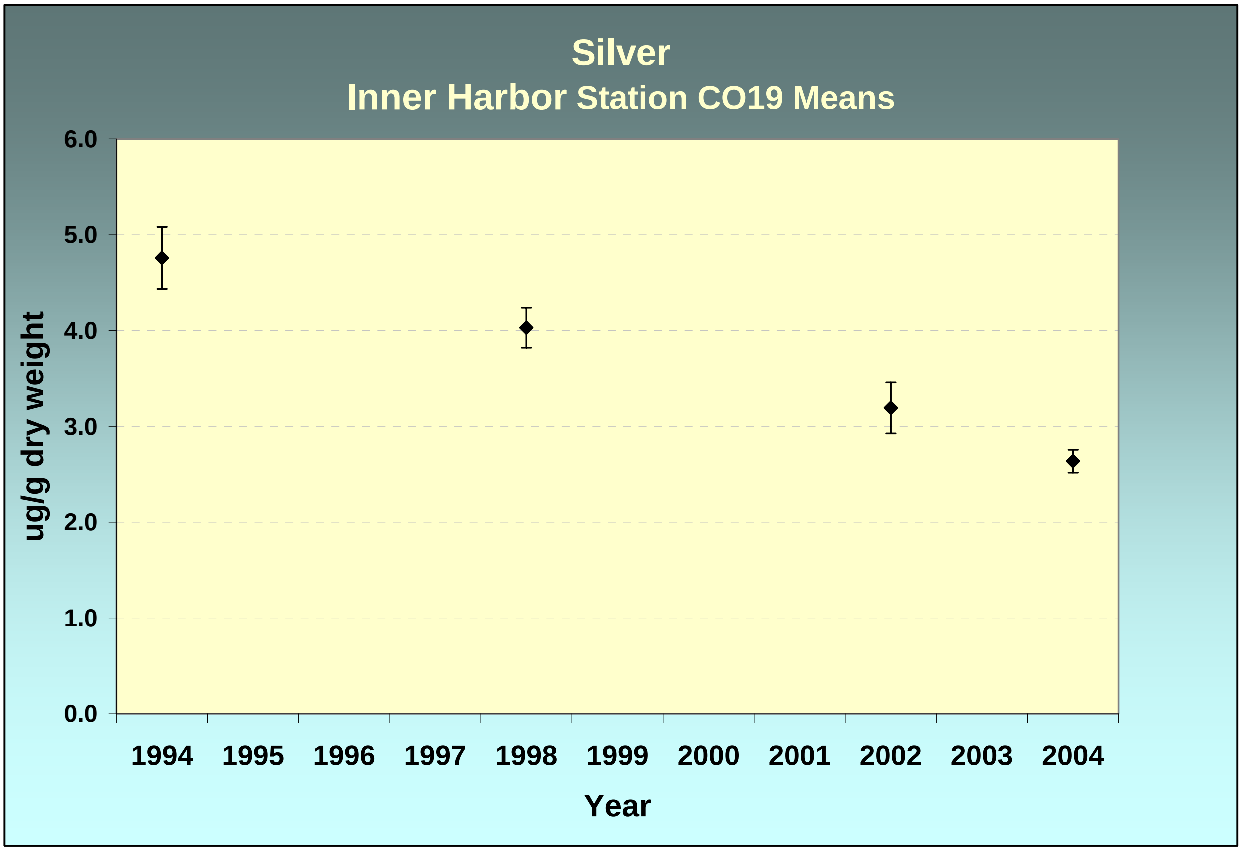

Total PCB
CO19 Station Means
ng/g dry weight
250
200
150
100
50
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year


Cadmium
CO19 Station Means
ug/g dry weight
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

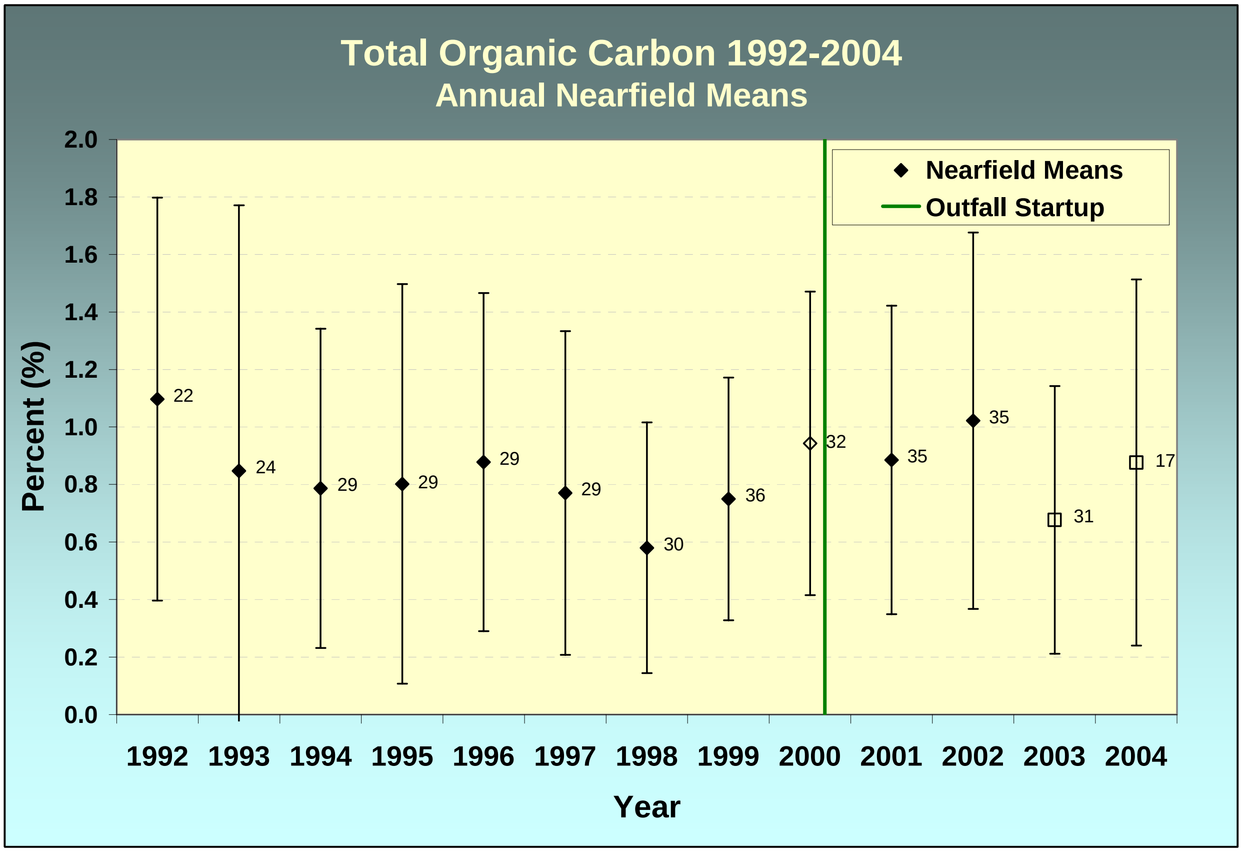

Copper
CO19 Station Means
ug/g dry weight
180
160
140
120
100
80
60
40
20
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

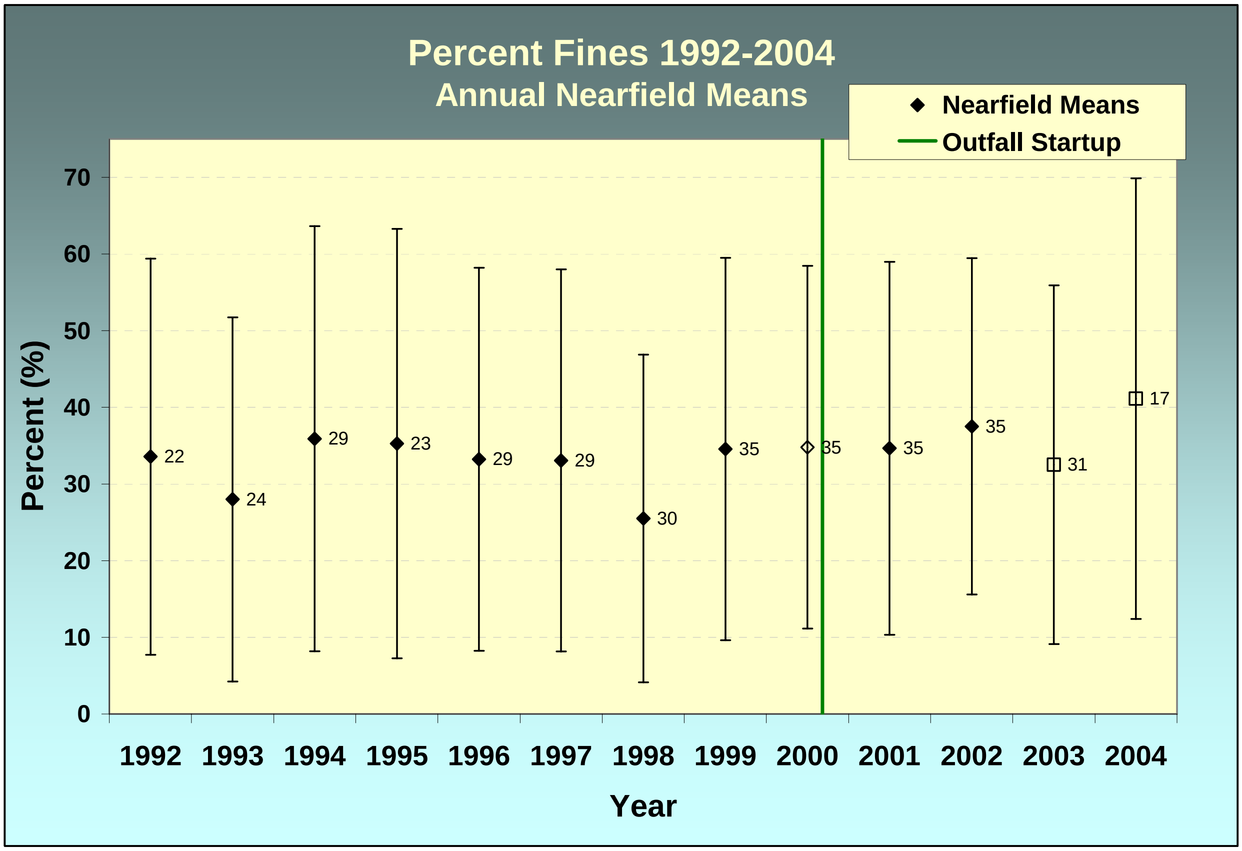

Lead
CO19 Station Means
ug/g dry weight
180
160
140
120
100
80
60
40
20
0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

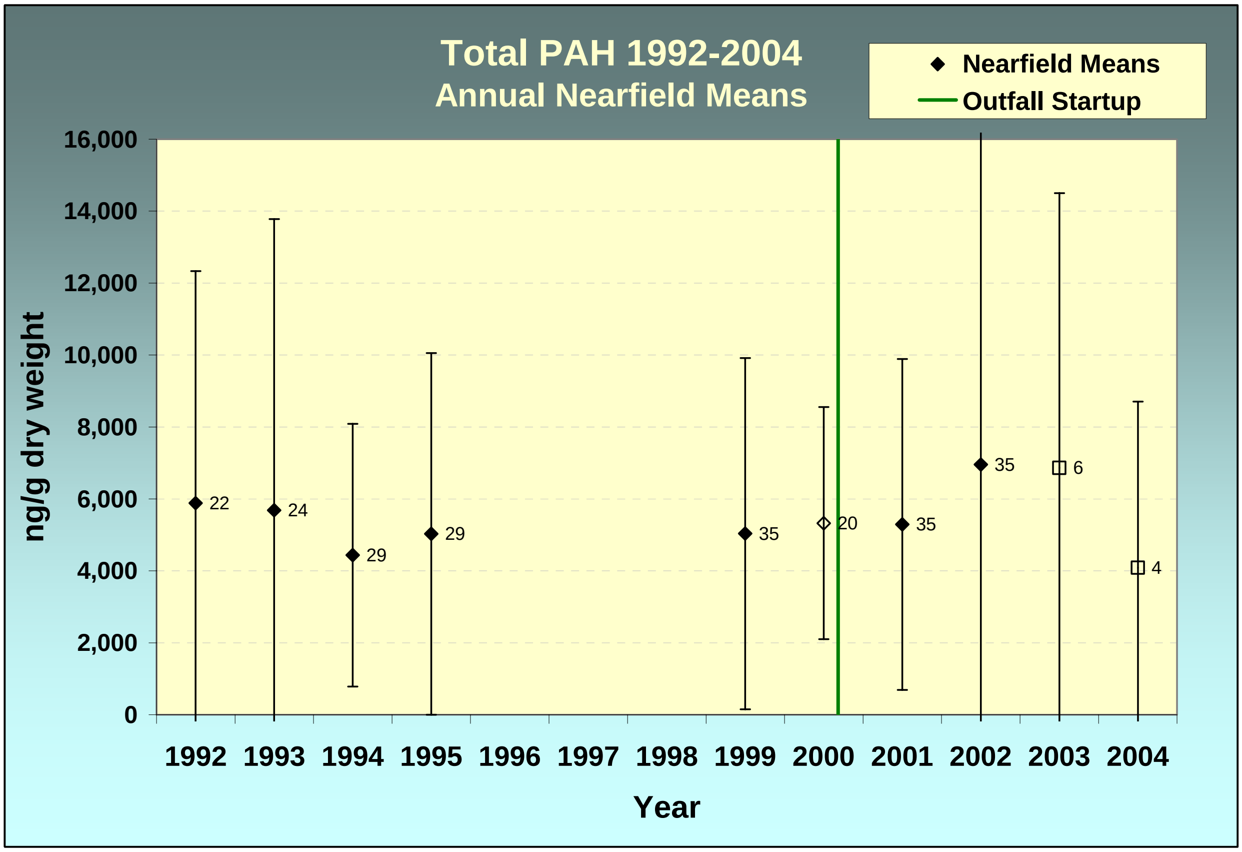

Mercury
CO19 Station Means
ug/g dry weight
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

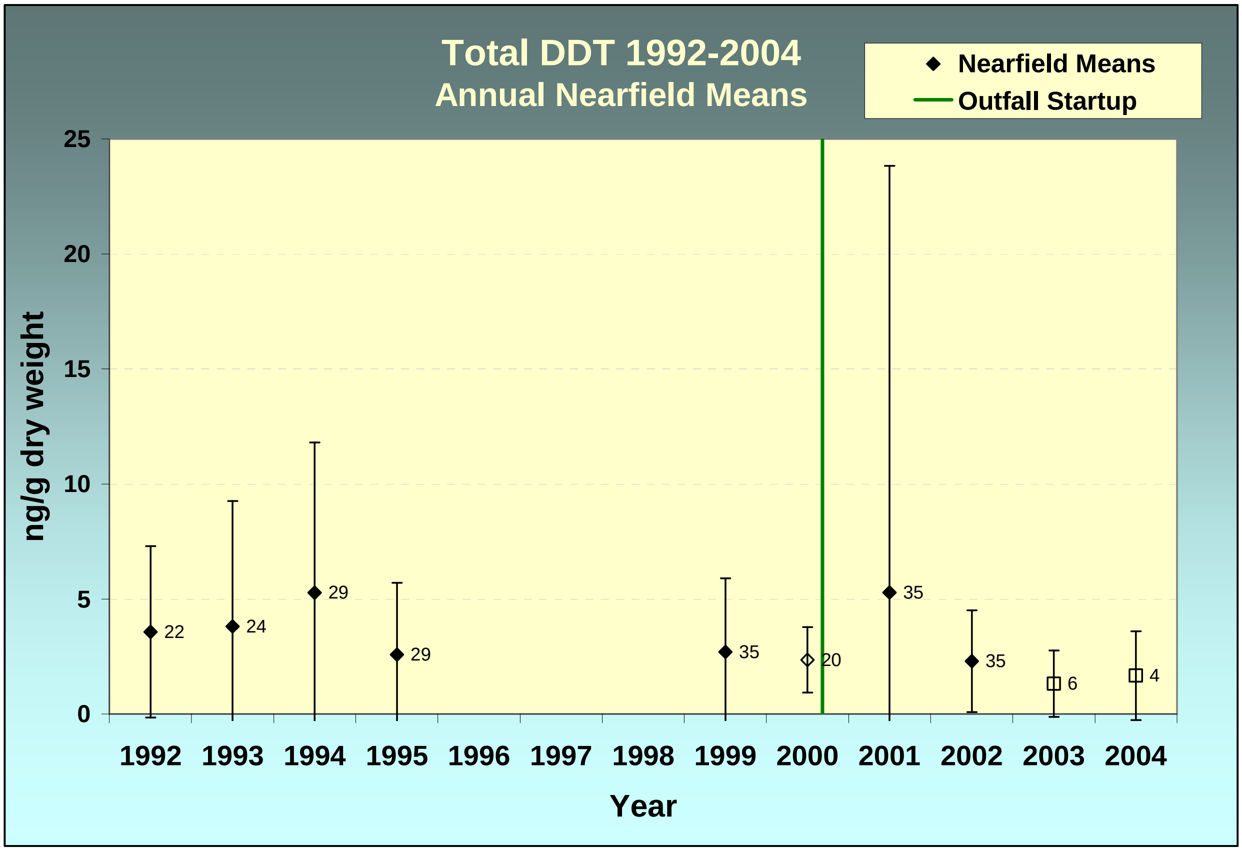

Silver
Inner Harbor Station CO19 Means
ug/g dry weight
6.0
5.0
4.0
3.0
2.0
1.0
0.0
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

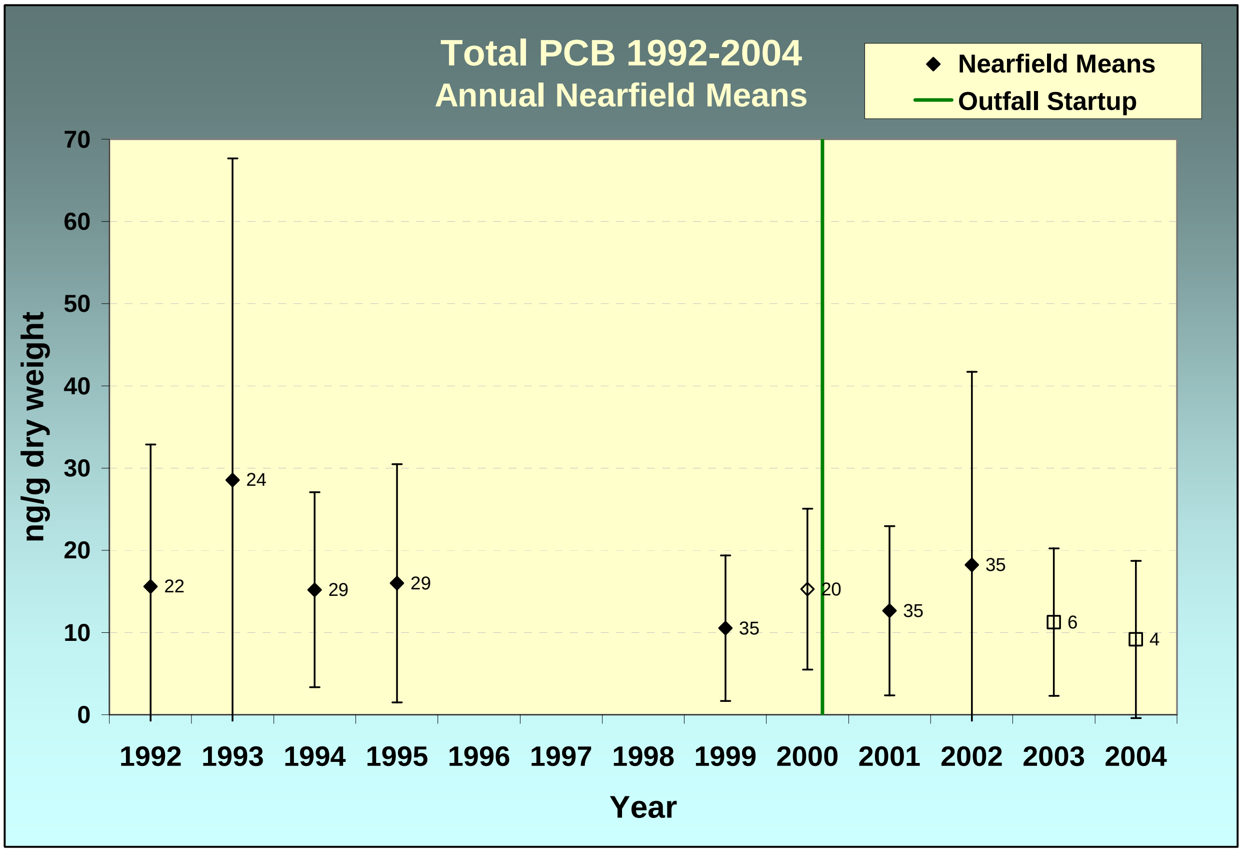
Nearfield

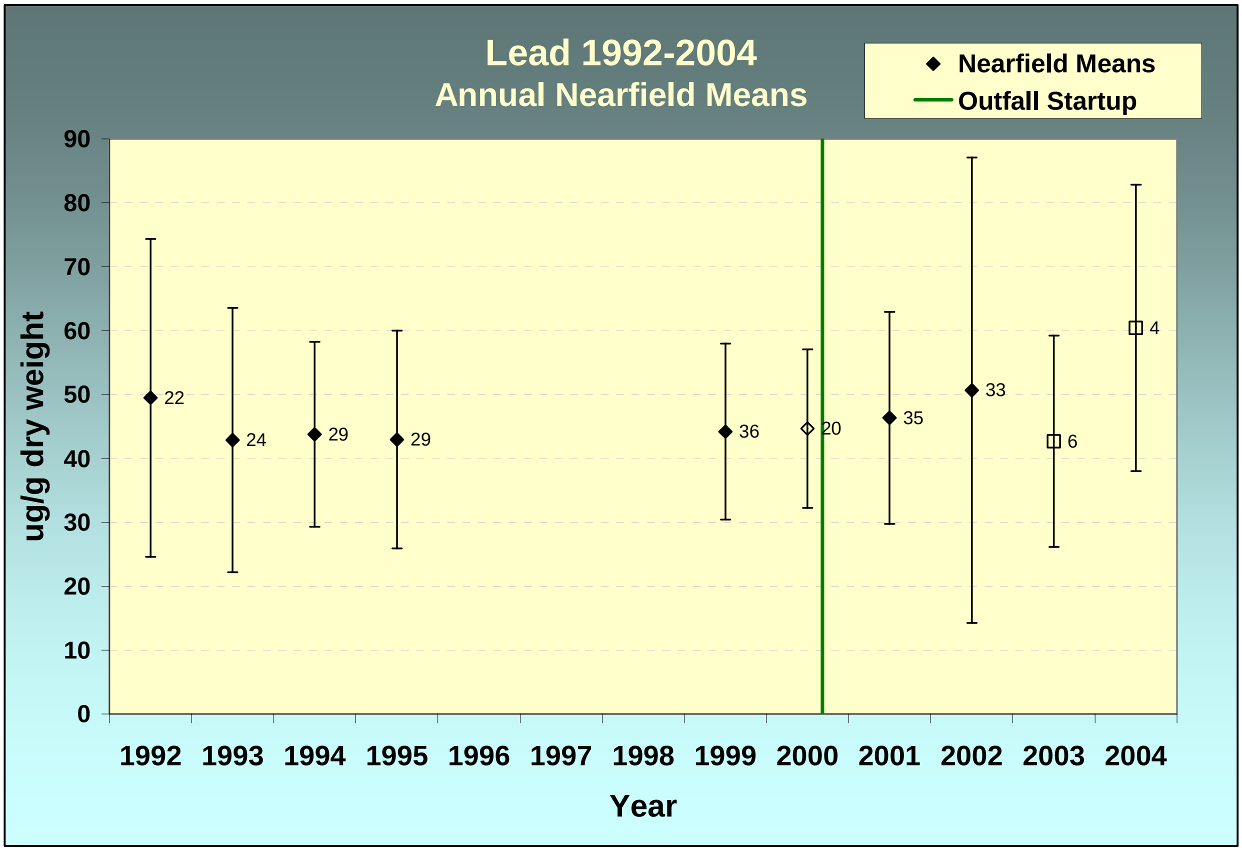

Total Organic Carbon 1992-2004
Annual Nearfield Means
Nearfield Means
Outfall Startup
Percent (%)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
22
24
29
29
29
29
30
36
32
35
35
31
17
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

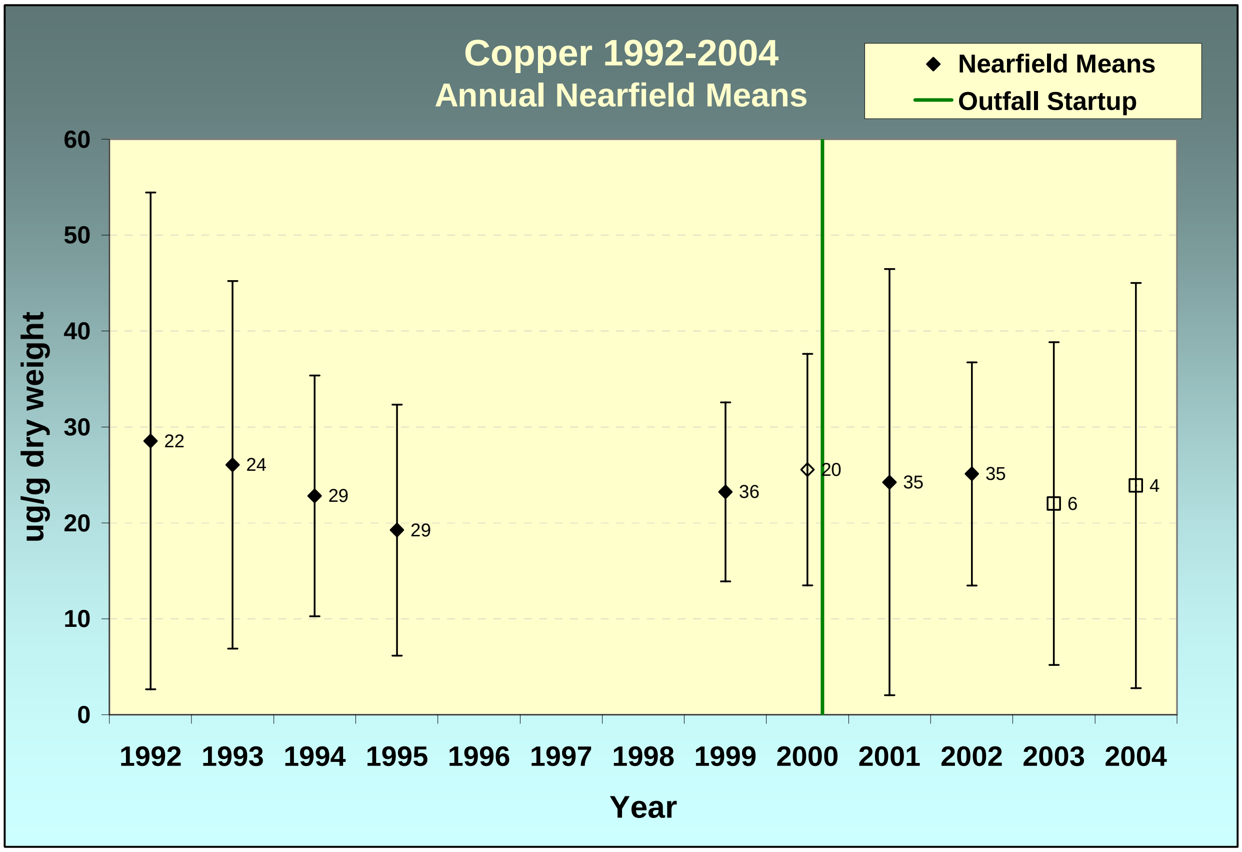

Percent Fines 1992-2004
Annual Nearfield Means
Nearfield Means
Outfall Startup
Percent (%)
70
60
50
40
30
20
10
0
22
24
29
23
29
29
30
35
35
35
35
31
17
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

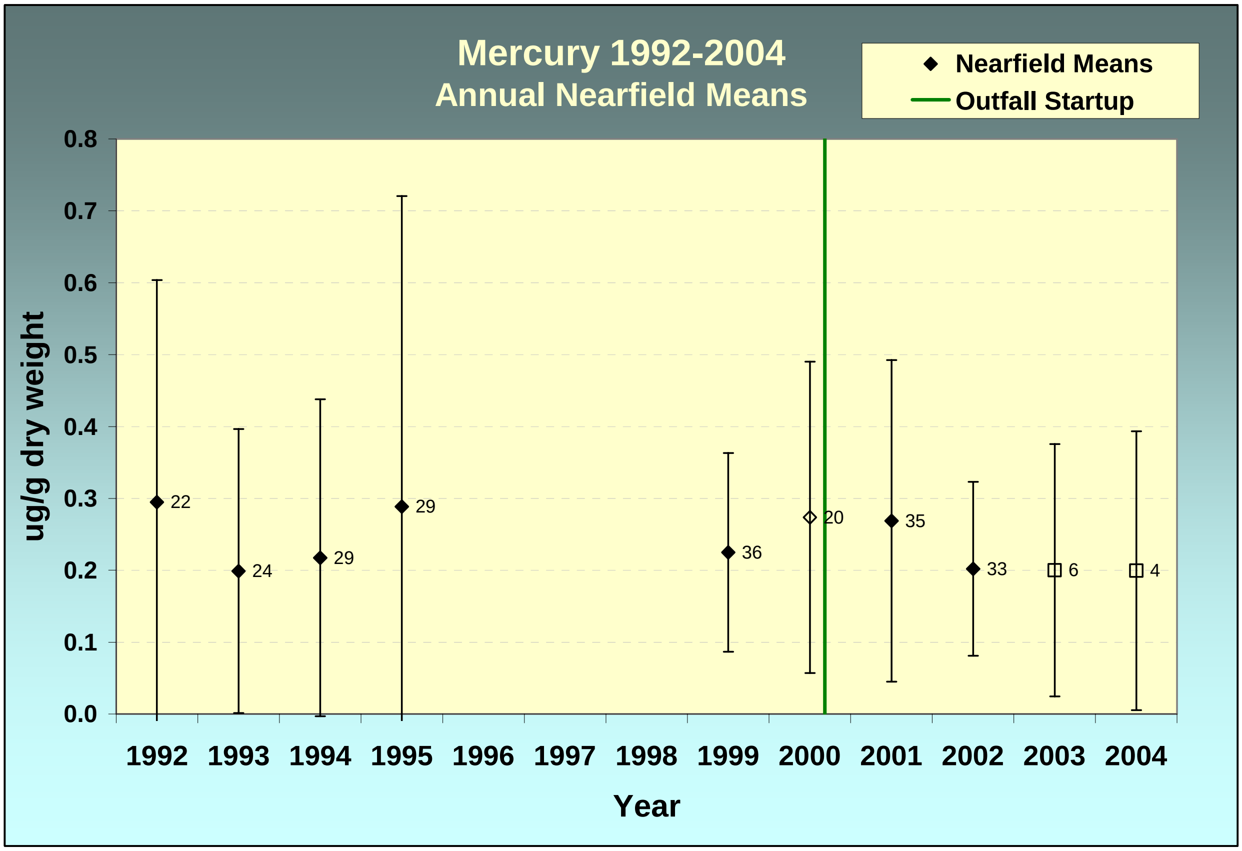

Total PAH 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ng/g dry weight
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
22
24
29
29
35
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

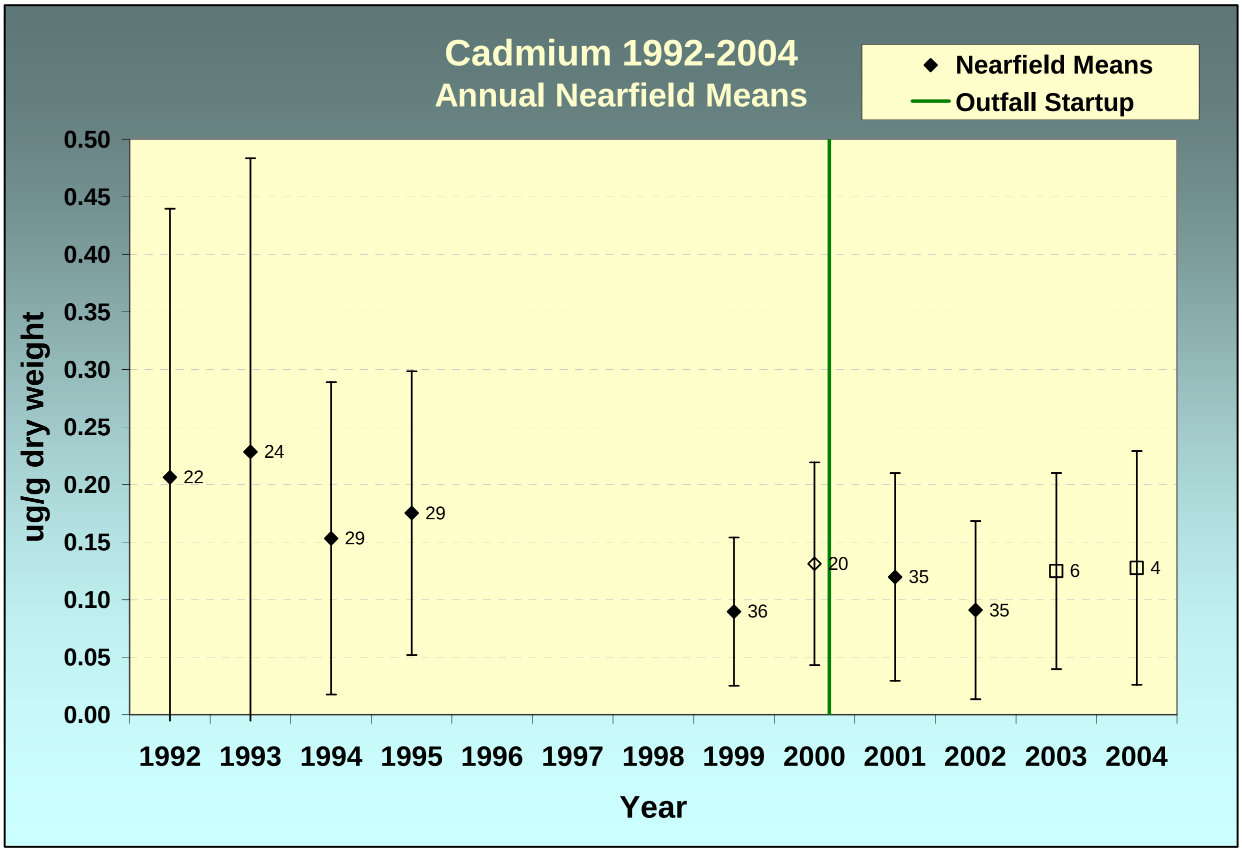

Total DDT 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ng/g dry weight
25
20
15
10
5
0
22
24
29
29
35
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

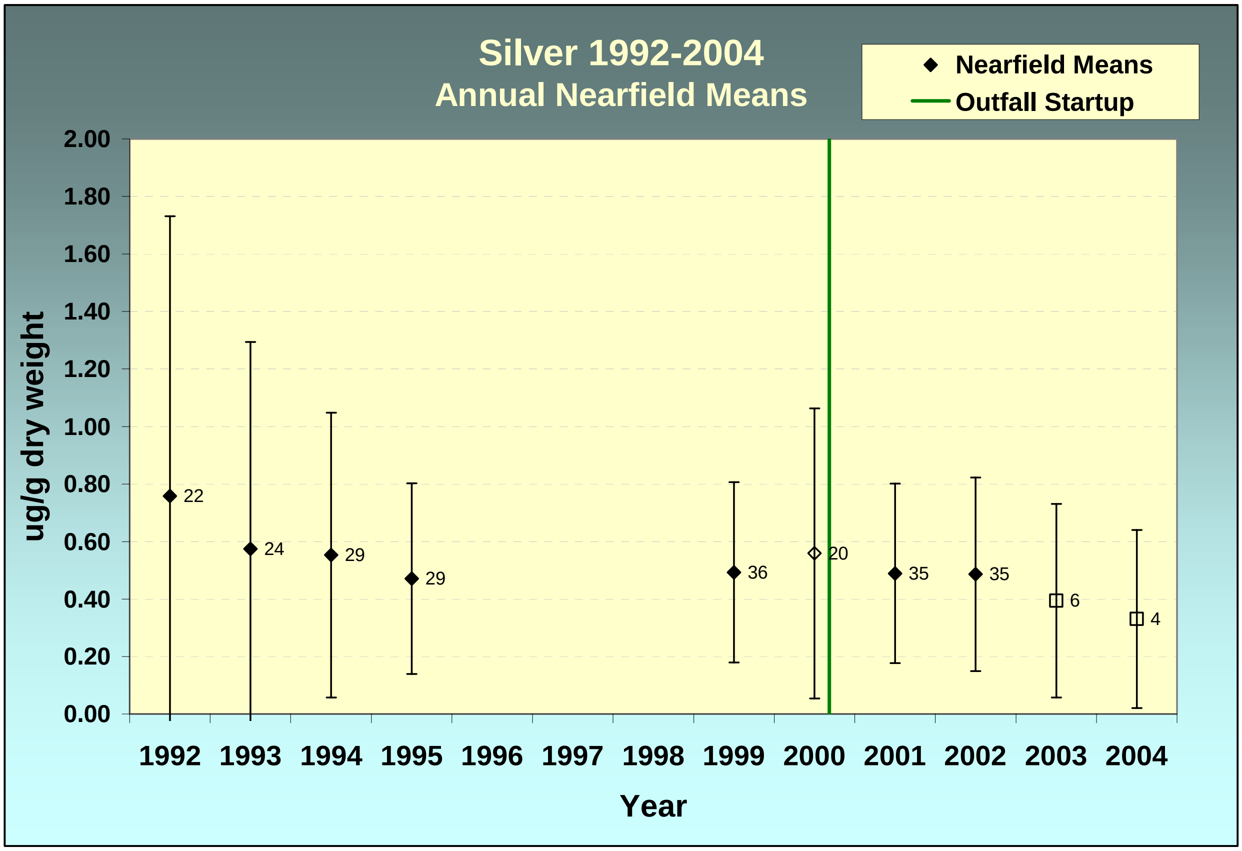

Total PCB 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ng/g dry weight
70
60
50
40
30
20
10
0
22
24
29
29
35
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year


Lead 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ug/g dry weight
90
80
70
60
50
40
30
20
10
0
22
24
29
29
36
20
35
33
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

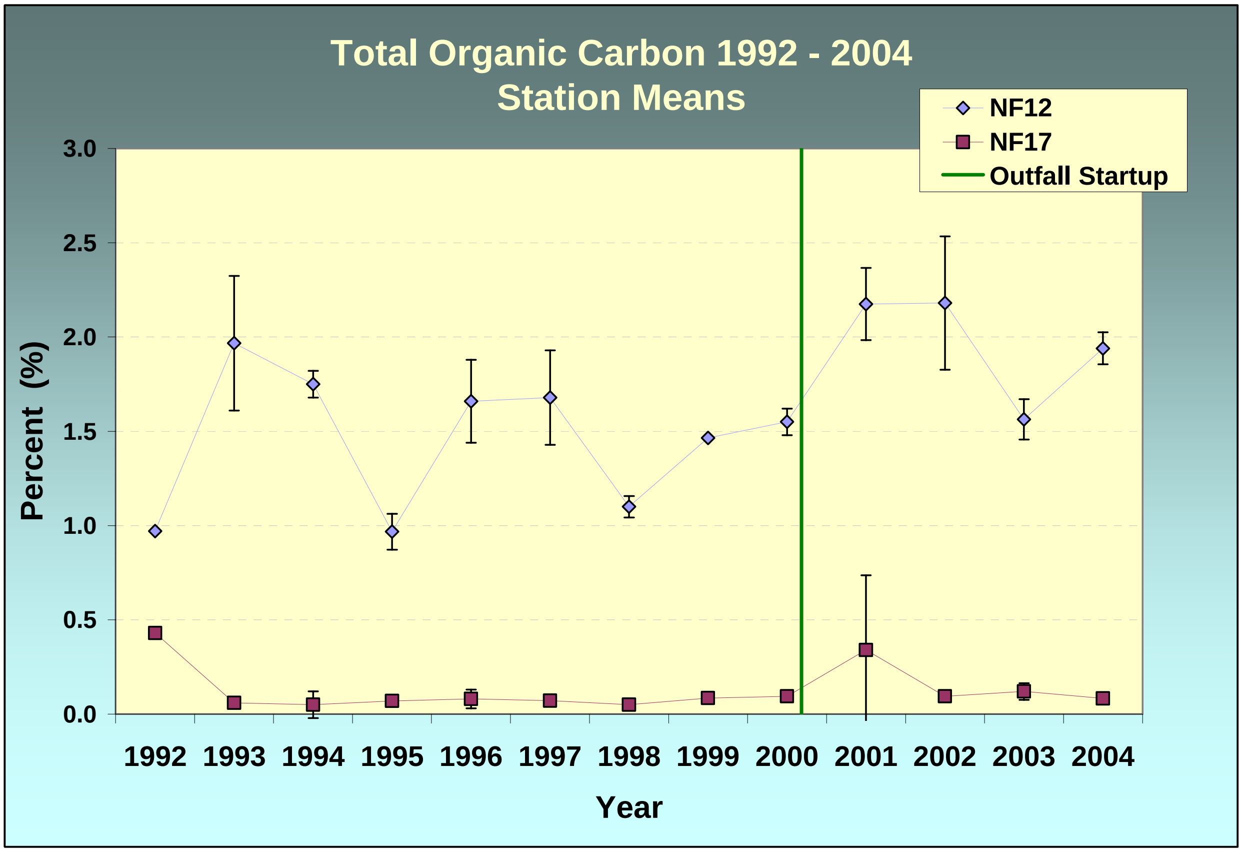

Copper 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ug/g dry weight
0
10
20
30
40
50
60
22
24
29
29
36
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

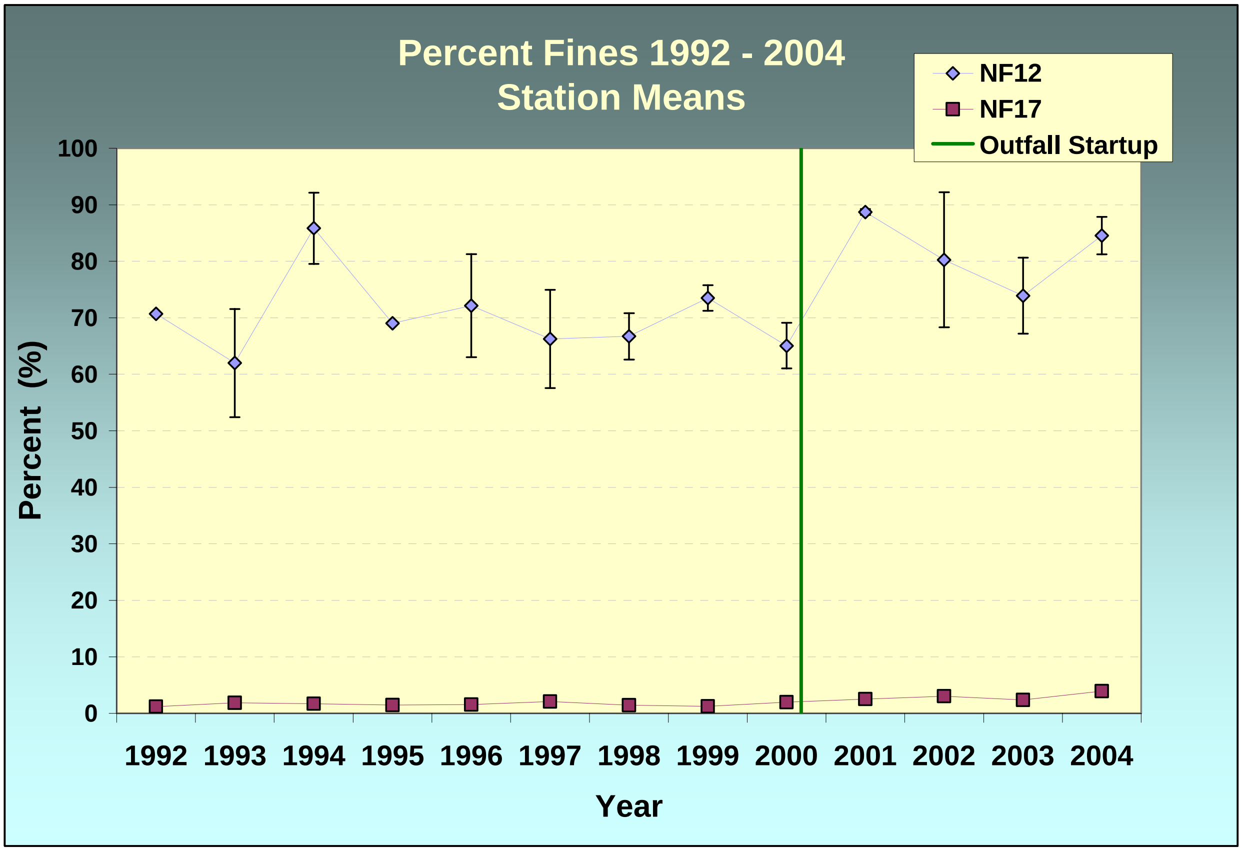

Mercury 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ug/g dry weight
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
22
24
29
29
36
20
35
33
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

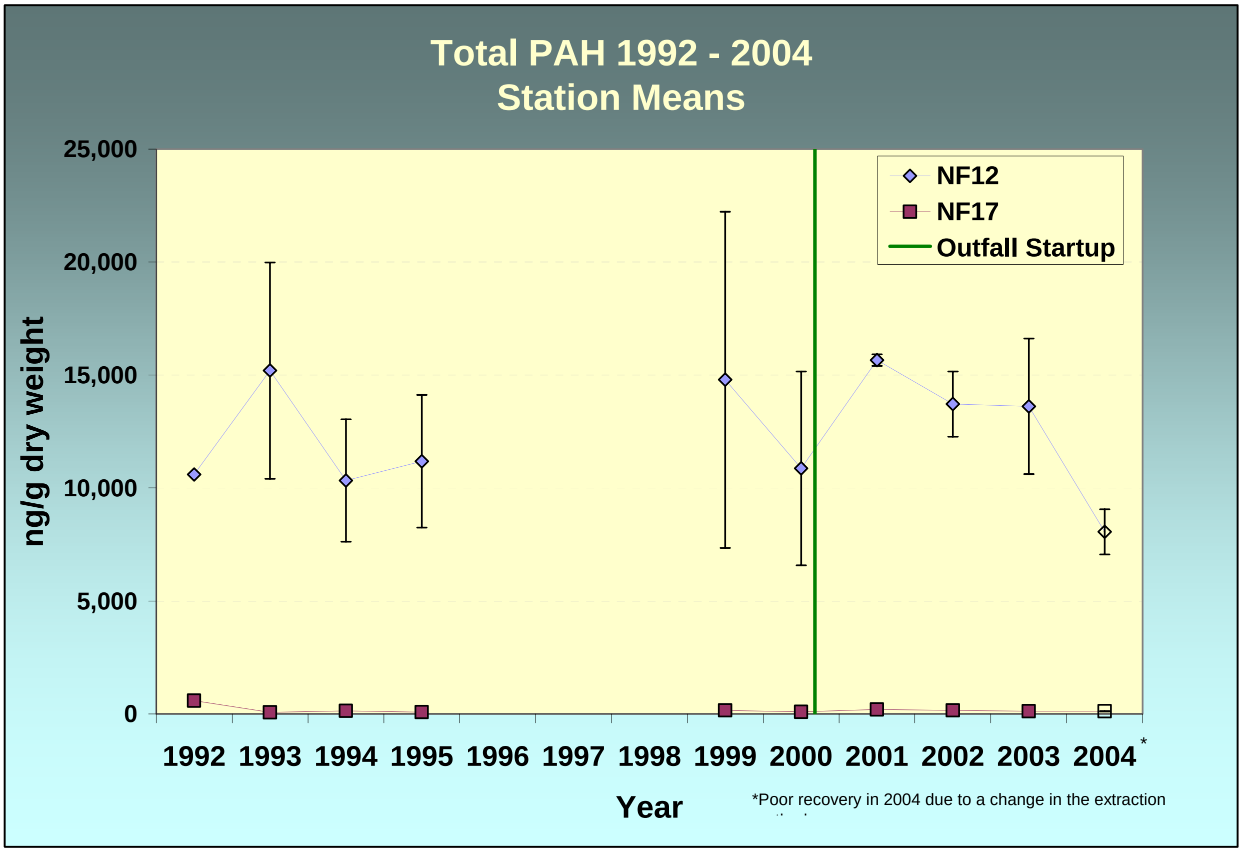

Cadmium 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ug/g dry weight
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
22
24
29
29
36
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

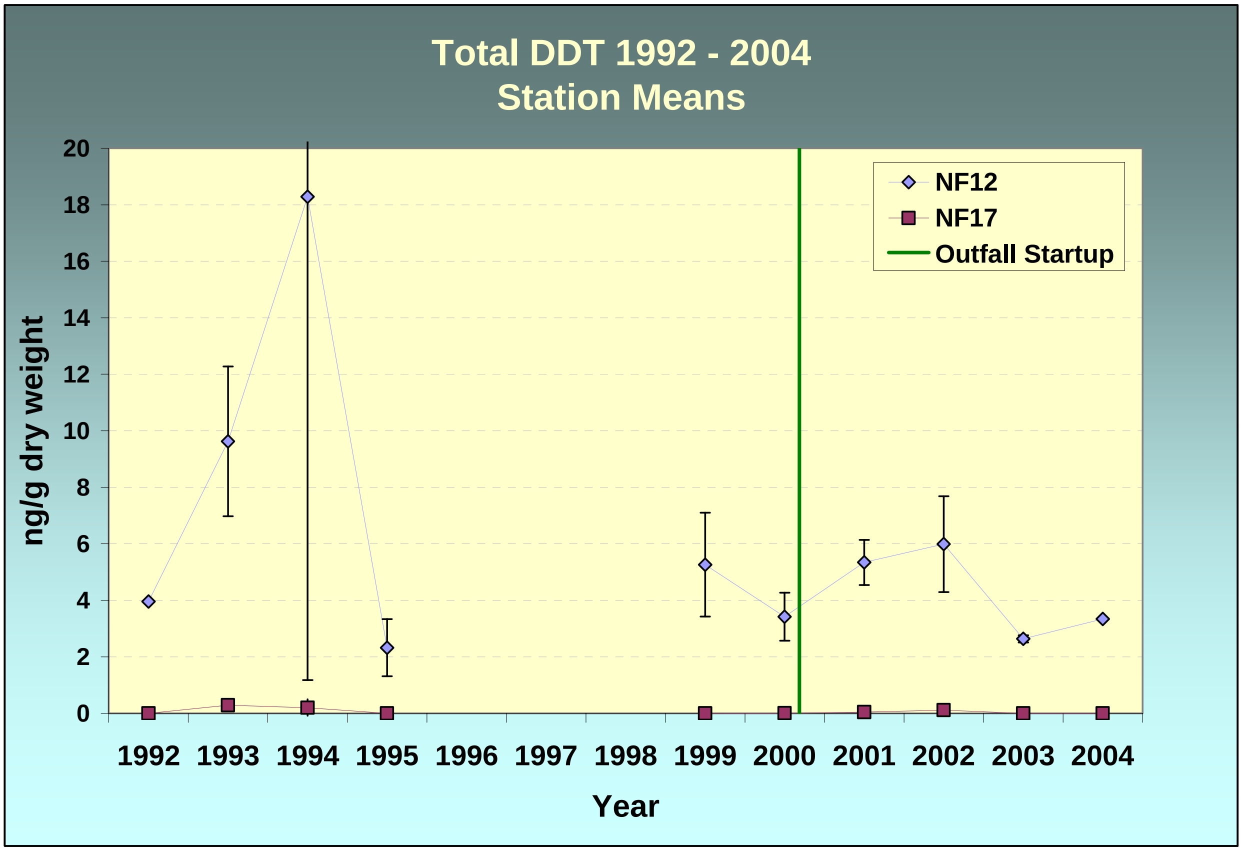

Silver 1992-2004
Annual Nearfield Means
◆ Nearfield Means
Outfall Startup
ug/g dry weight
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
22
24
29
29
36
20
35
35
6
4
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

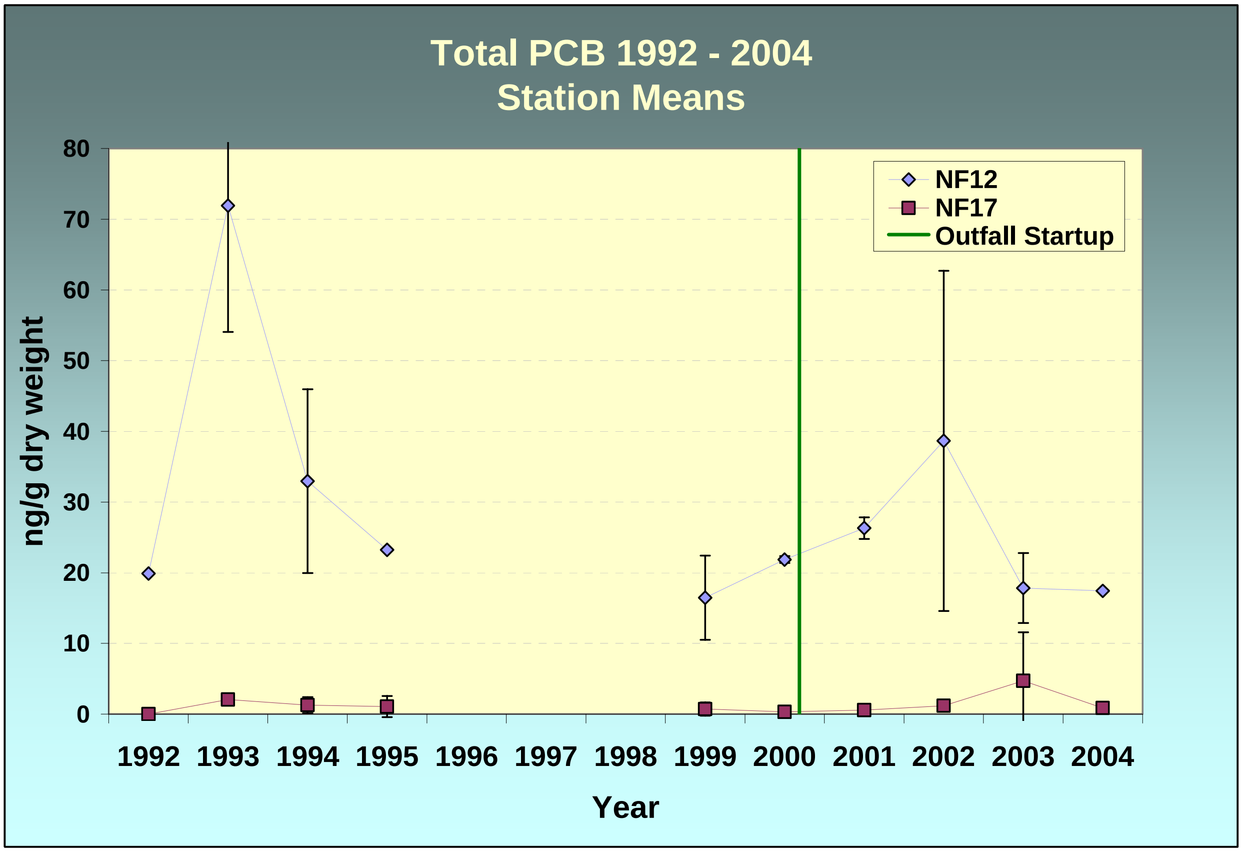
Nearfield Stations NF12 and NF17

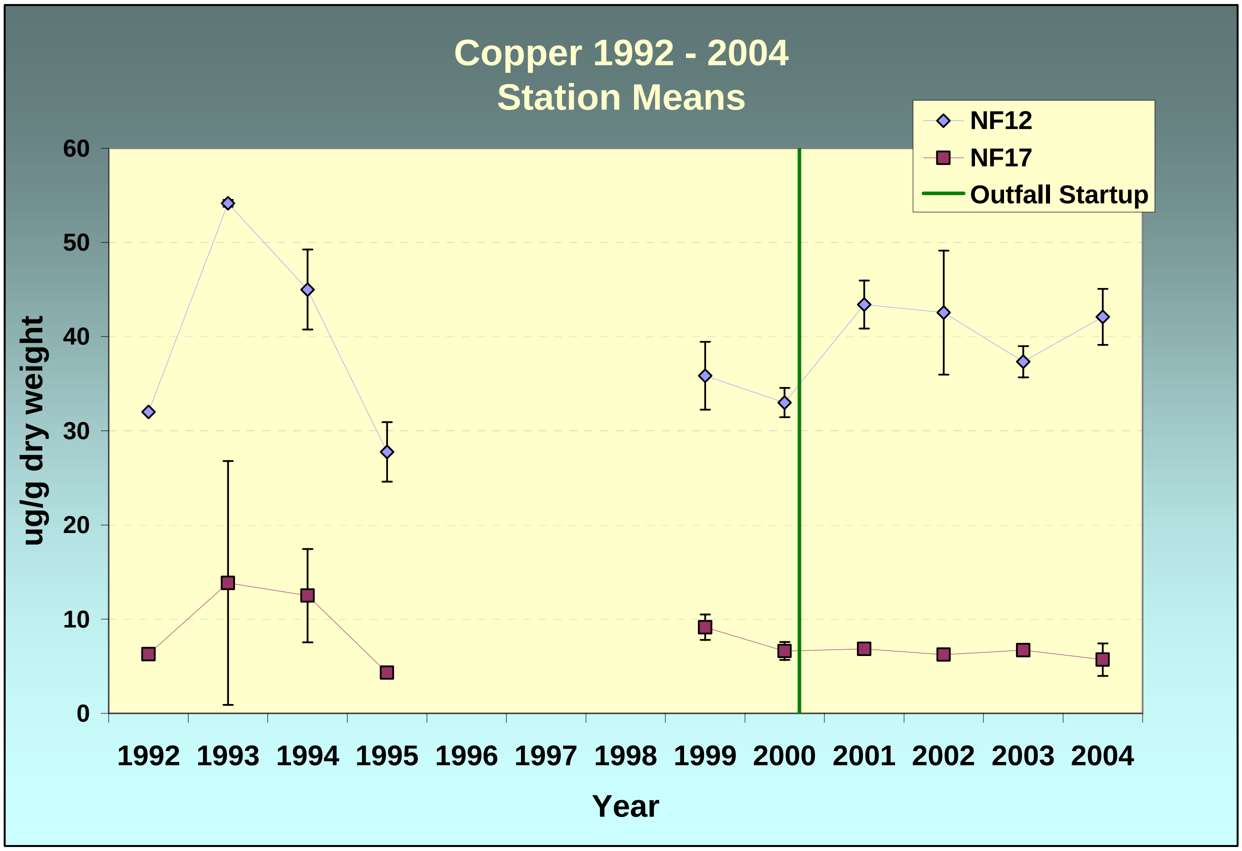

Total Organic Carbon 1992 - 2004
Station Means
NF12
NF17
Outfall Startup
Percent (%)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

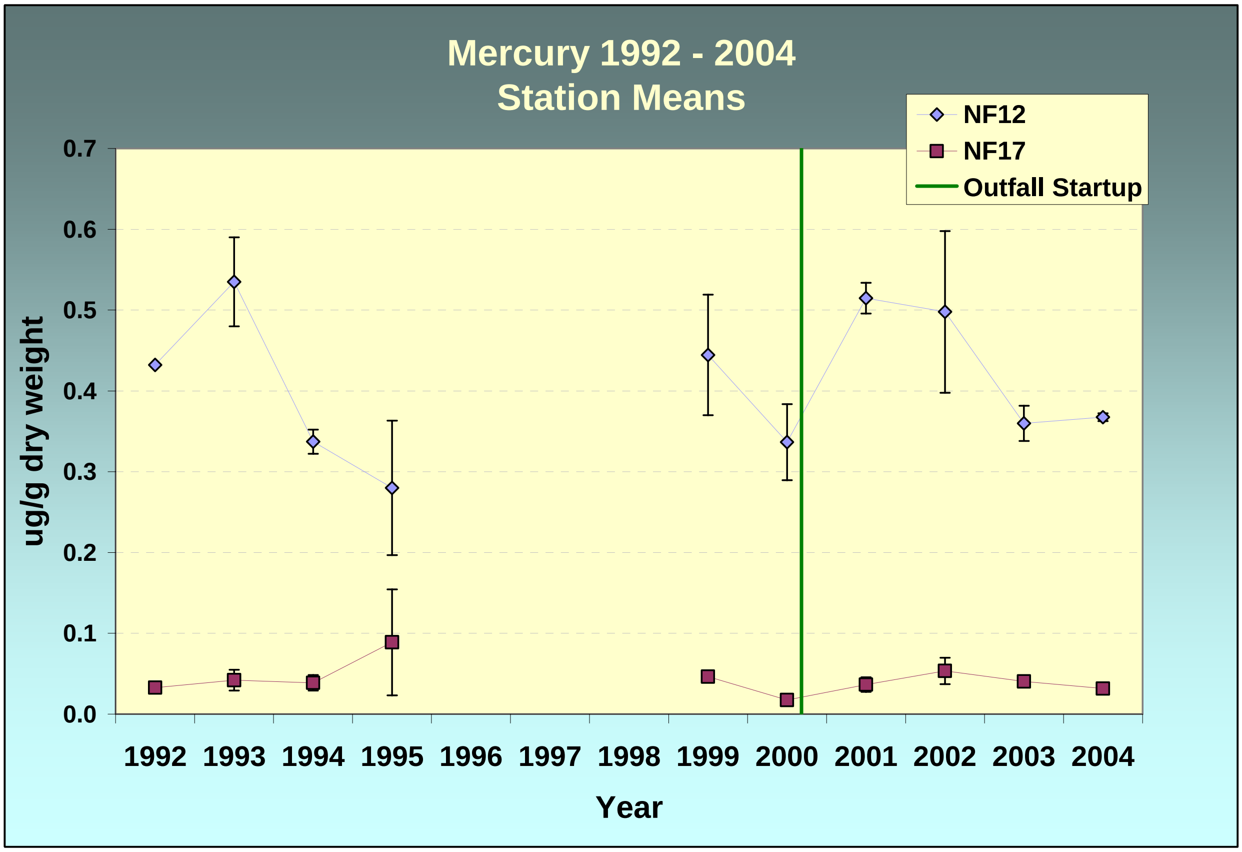

Percent Fines 1992 - 2004
Station Means
NF12
NF17
Outfall Startup
Percent (%)
100
90
80
70
60
50
40
30
20
10
0
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

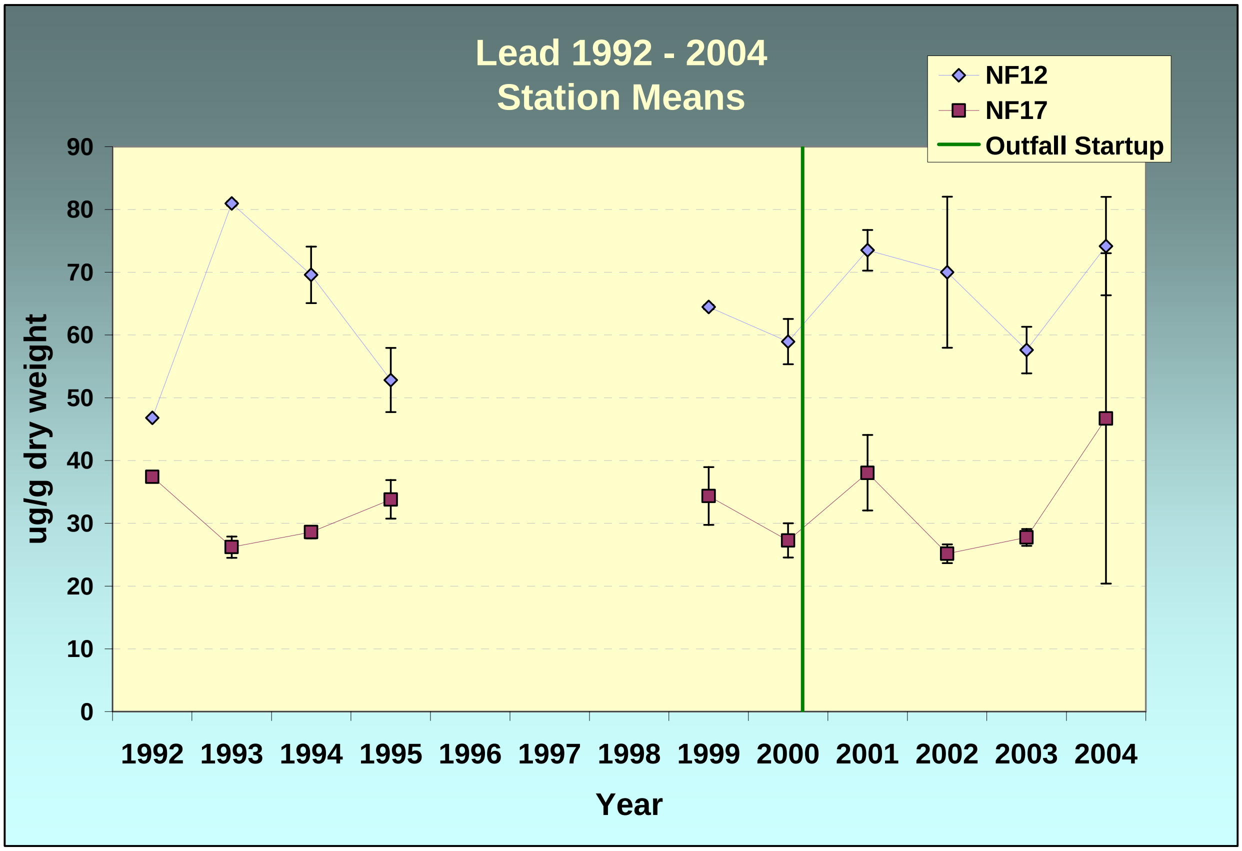

Total PAH 1992 - 2004
Station Means
ng/g dry weight
25,000
20,000
15,000
10,000
5,000
0
NF12
NF17
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004*
Year
*Poor recovery in 2004 due to a change in the extraction

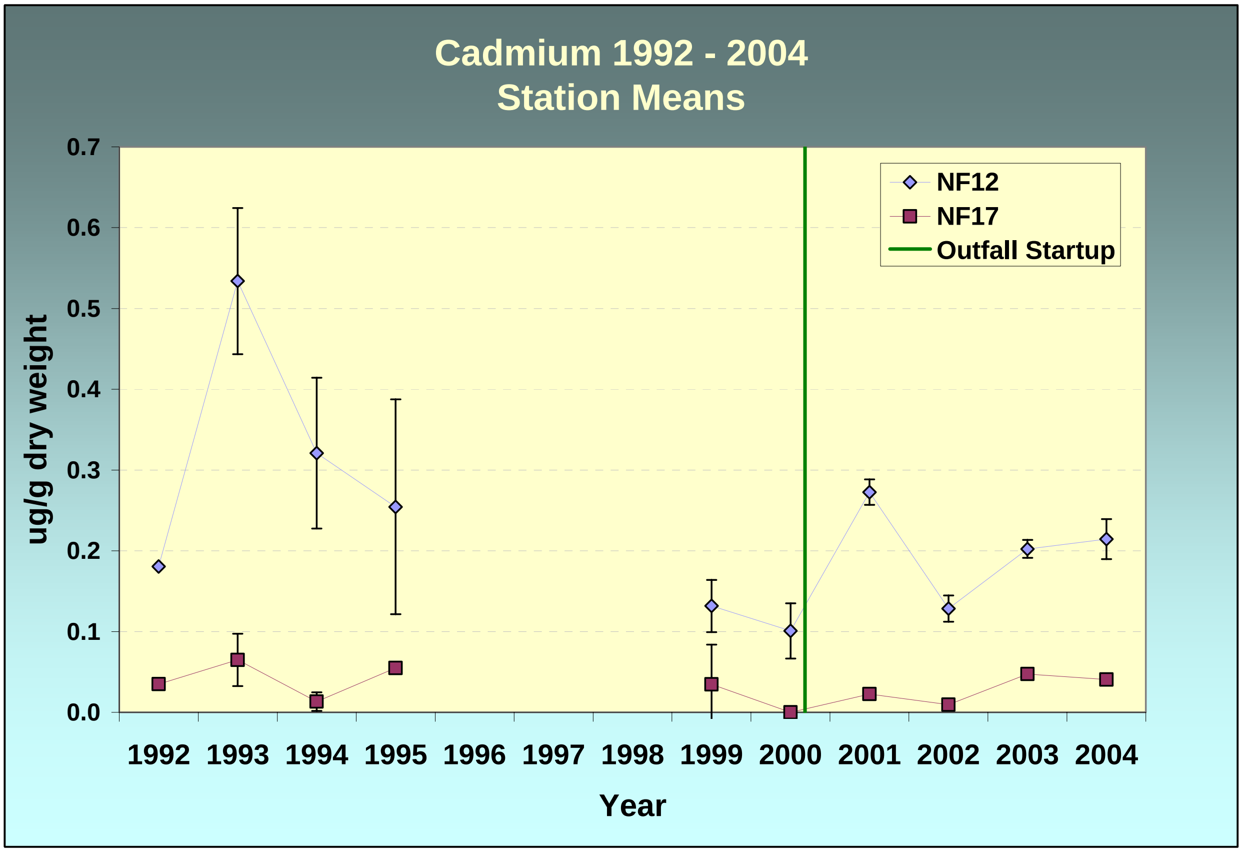

Total DDT 1992 - 2004
Station Means
ng/g dry weight
20
18
16
14
12
10
8
6
4
2
0
NF12
NF17
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

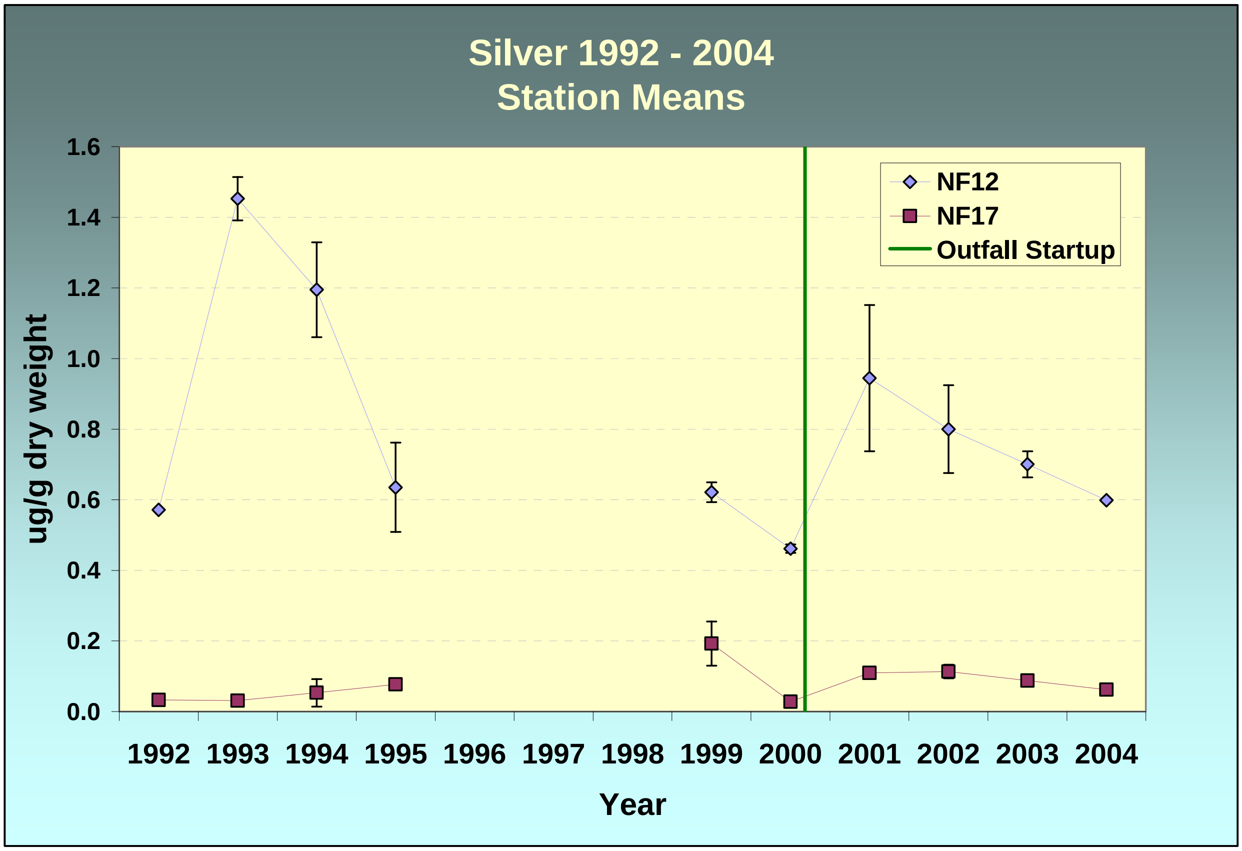

Total PCB 1992 - 2004
Station Means
ng/g dry weight
80
70
60
50
40
30
20
10
0
NF12
NF17
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year


Copper 1992 - 2004
Station Means
ug/g dry weight
60
50
40
30
20
10
0
NF12
NF17
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

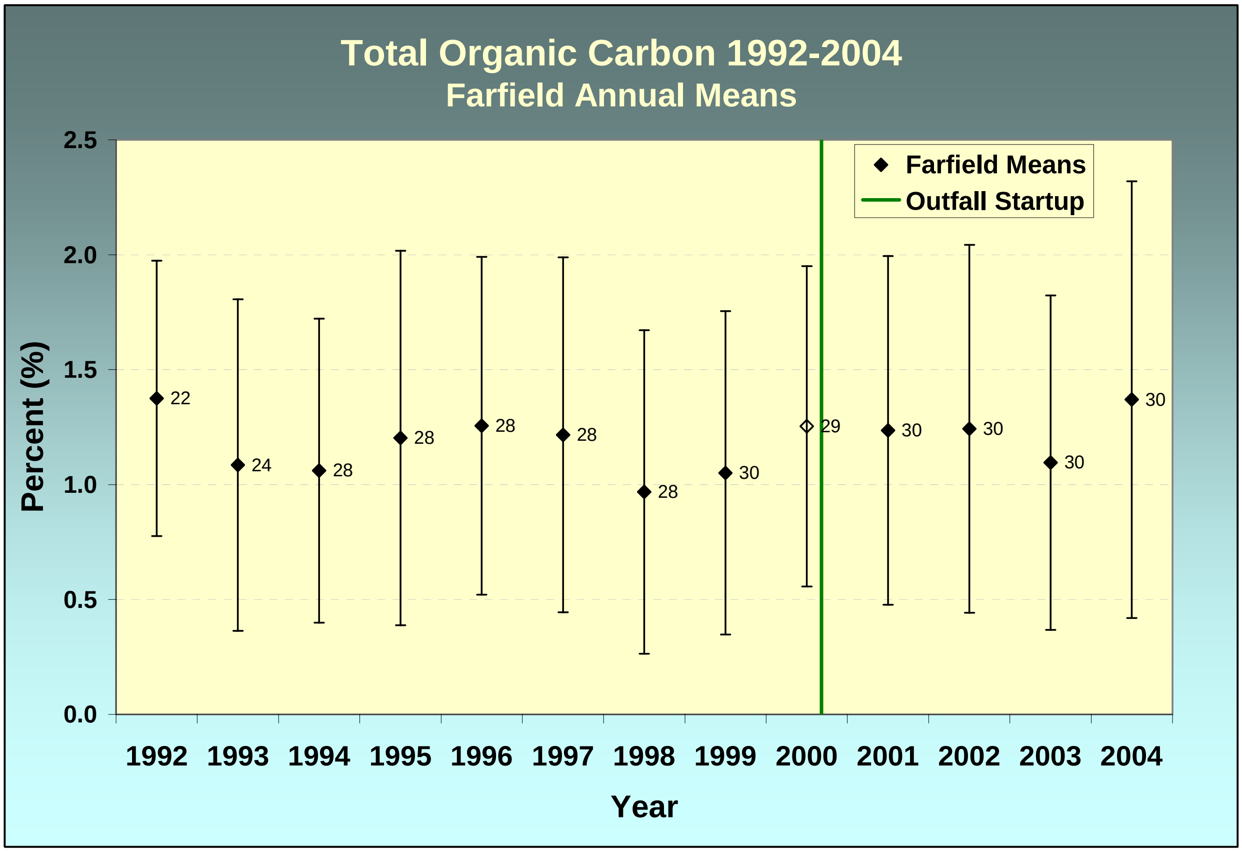

Mercury 1992 - 2004
Station Means
NF12
NF17
Outfall Startup
ug/g dry weight
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

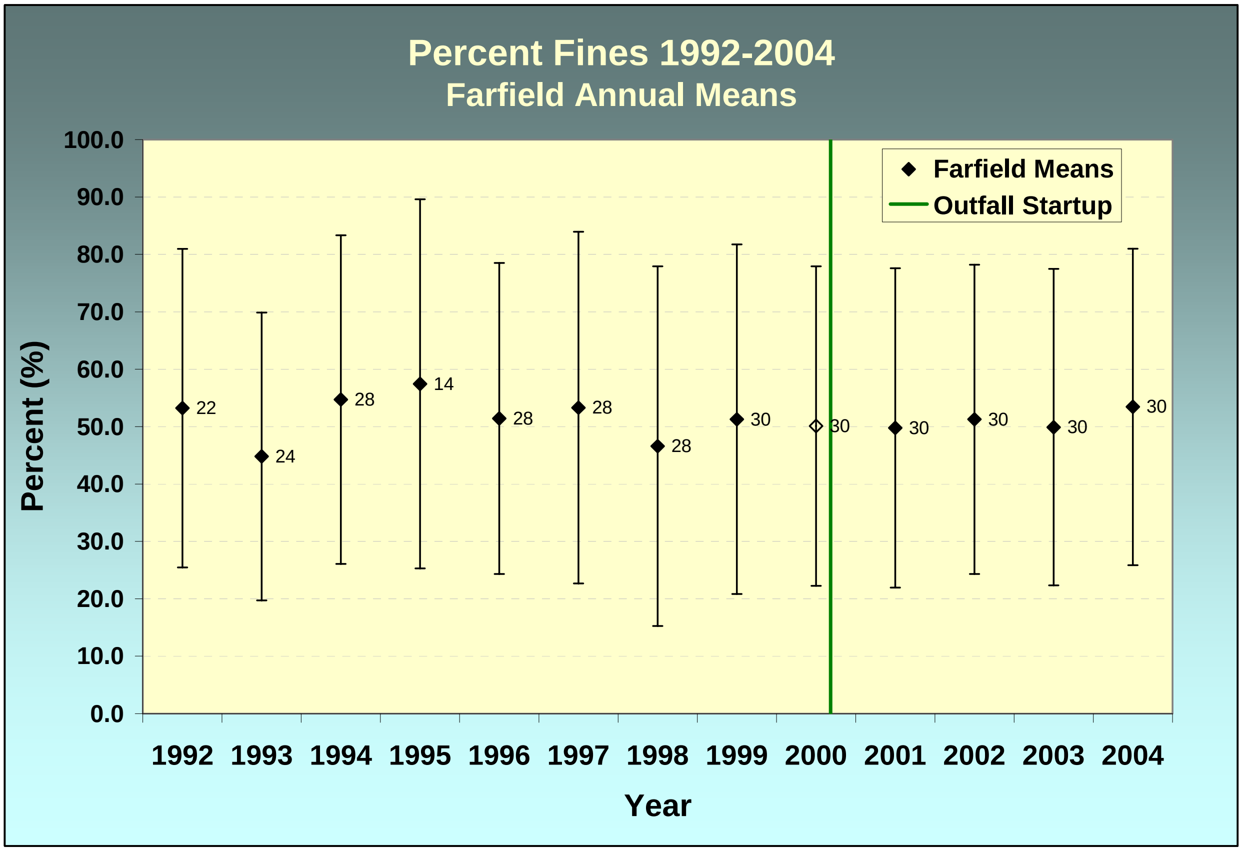

Lead 1992 - 2004
Station Means
NF12
NF17
Outfall Startup
ug/g dry weight
0
10
20
30
40
50
60
70
80
90
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

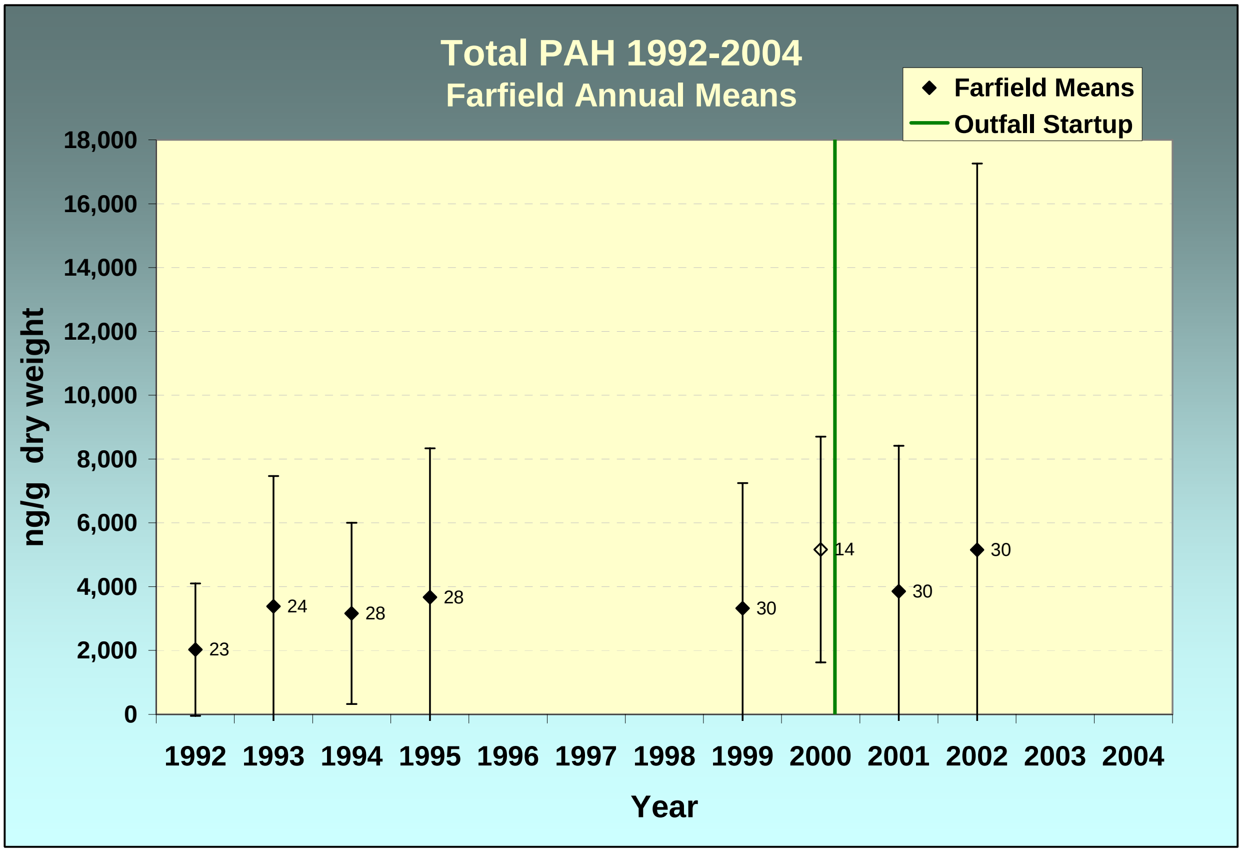

Cadmium 1992 - 2004
Station Means
ug/g dry weight
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year
NF12
NF17
Outfall Startup

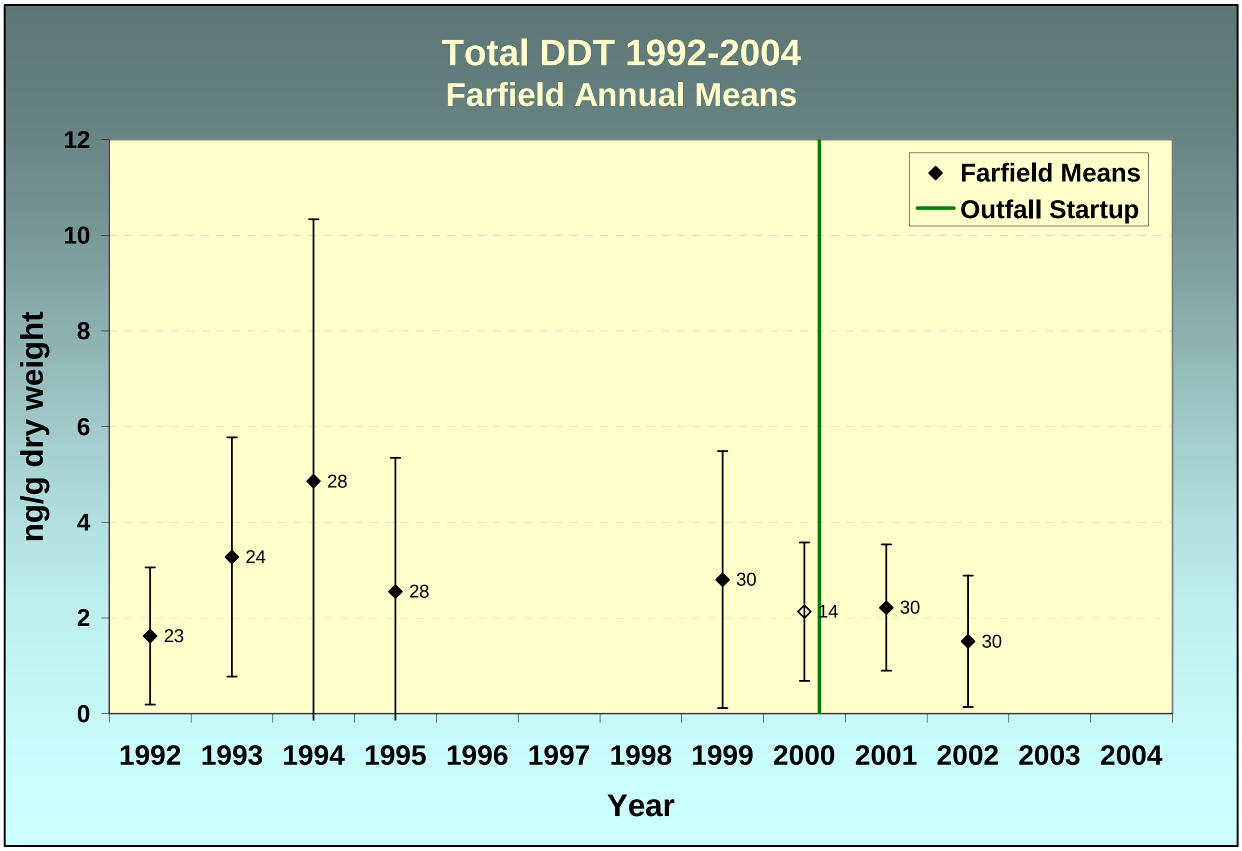

Silver 1992 - 2004
Station Means
ug/g dry weight
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year
NF12
NF17
Outfall Startup

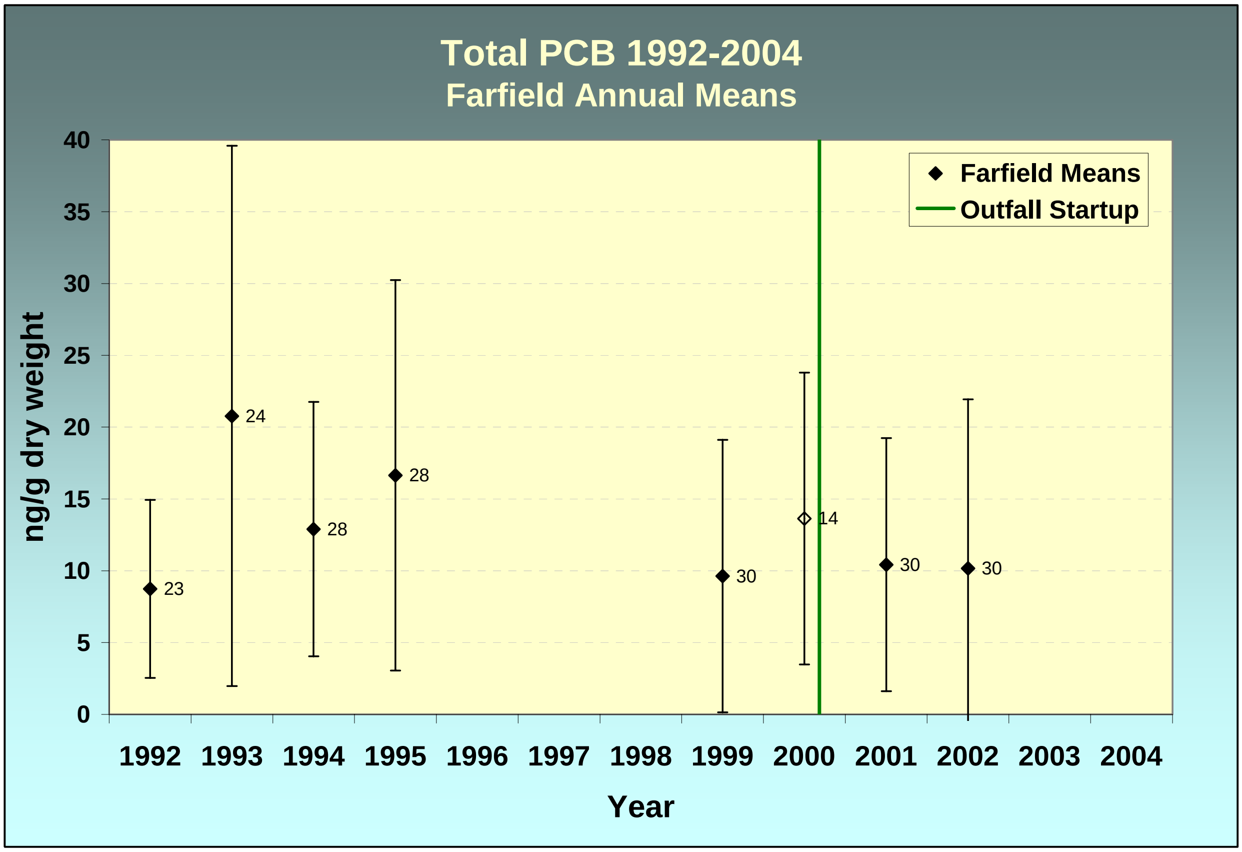
Farfield

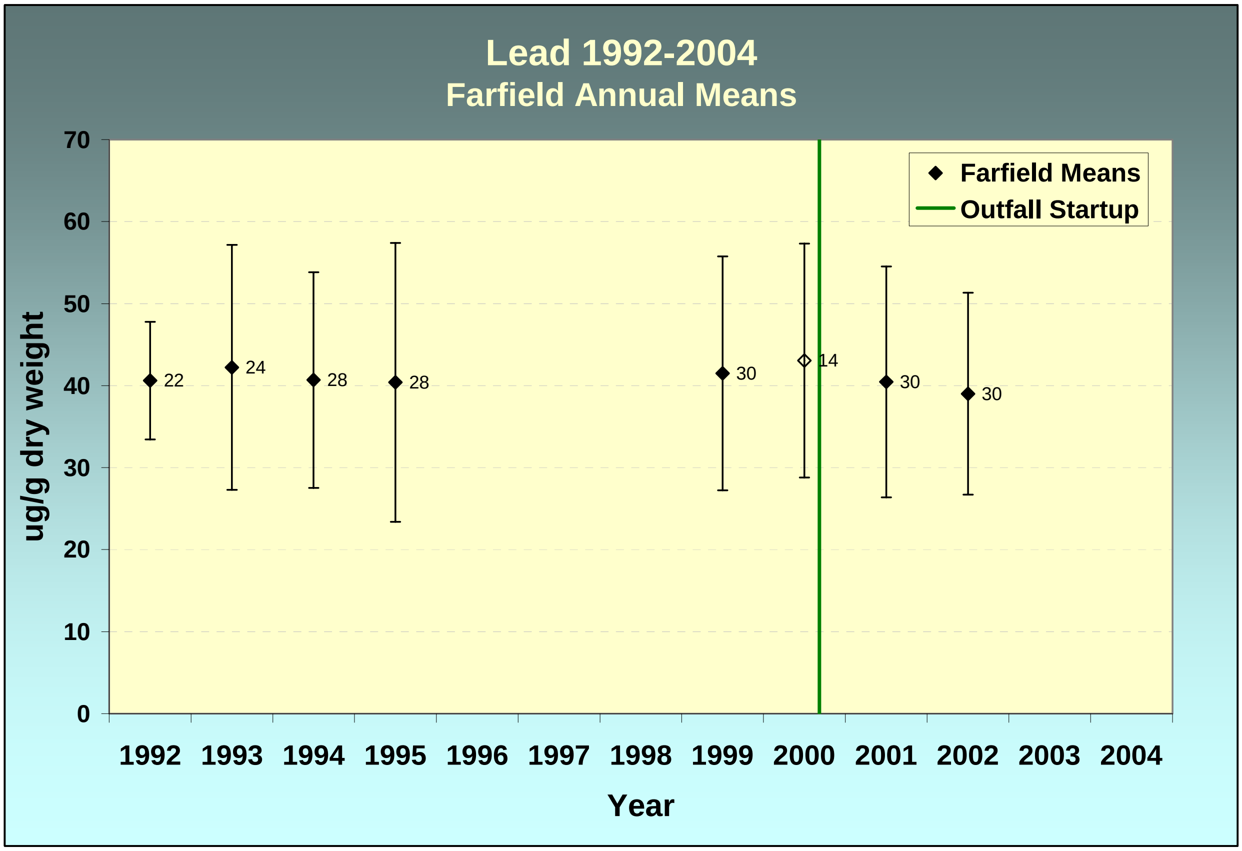

Total Organic Carbon 1992-2004
Farfield Annual Means
Farfield Means
Outfall Startup
Percent (%)
2.5
2.0
1.5
1.0
0.5
0.0
22
24
28
28
28
28
28
30
29
30
30
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

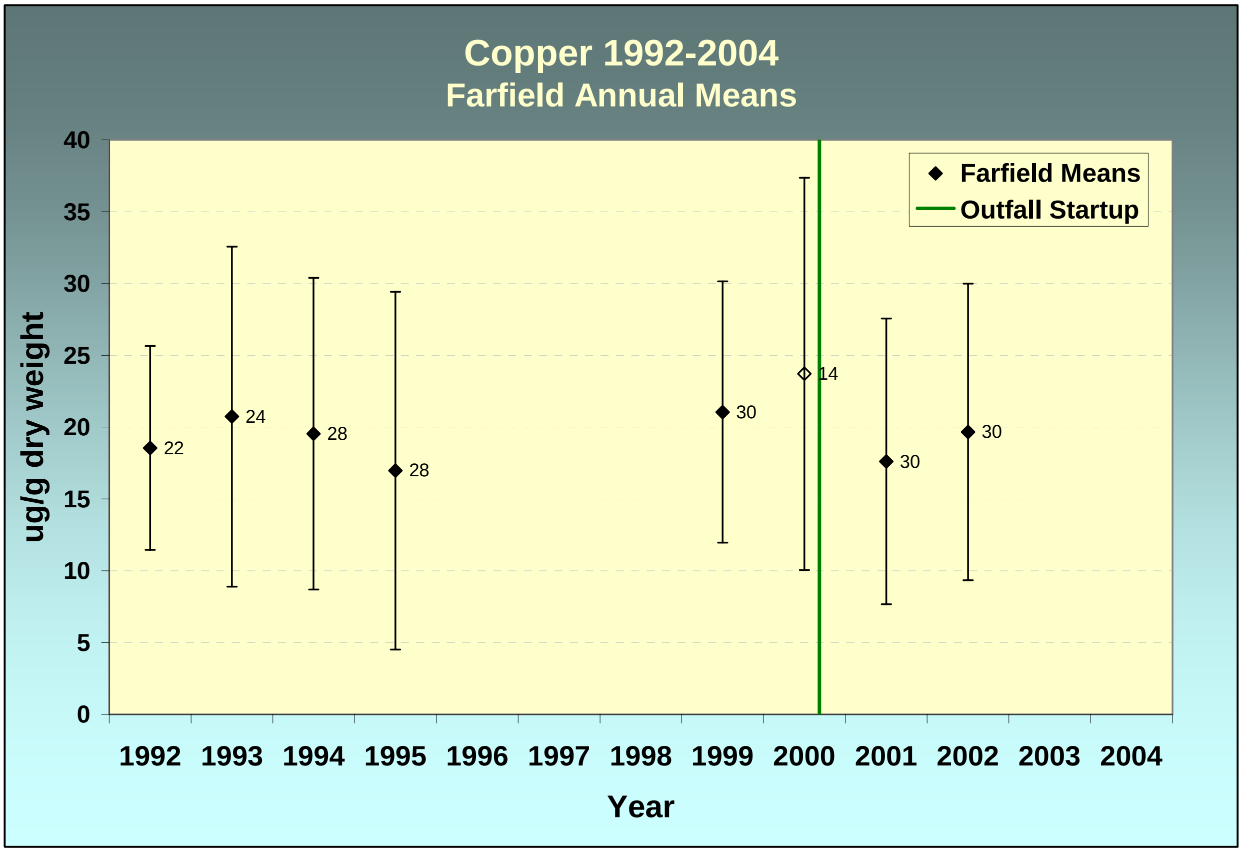

Percent Fines 1992-2004
Farfield Annual Means
Farfield Means
Outfall Startup
Percent (%)
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
22
24
28
14
28
28
28
30
30
30
30
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

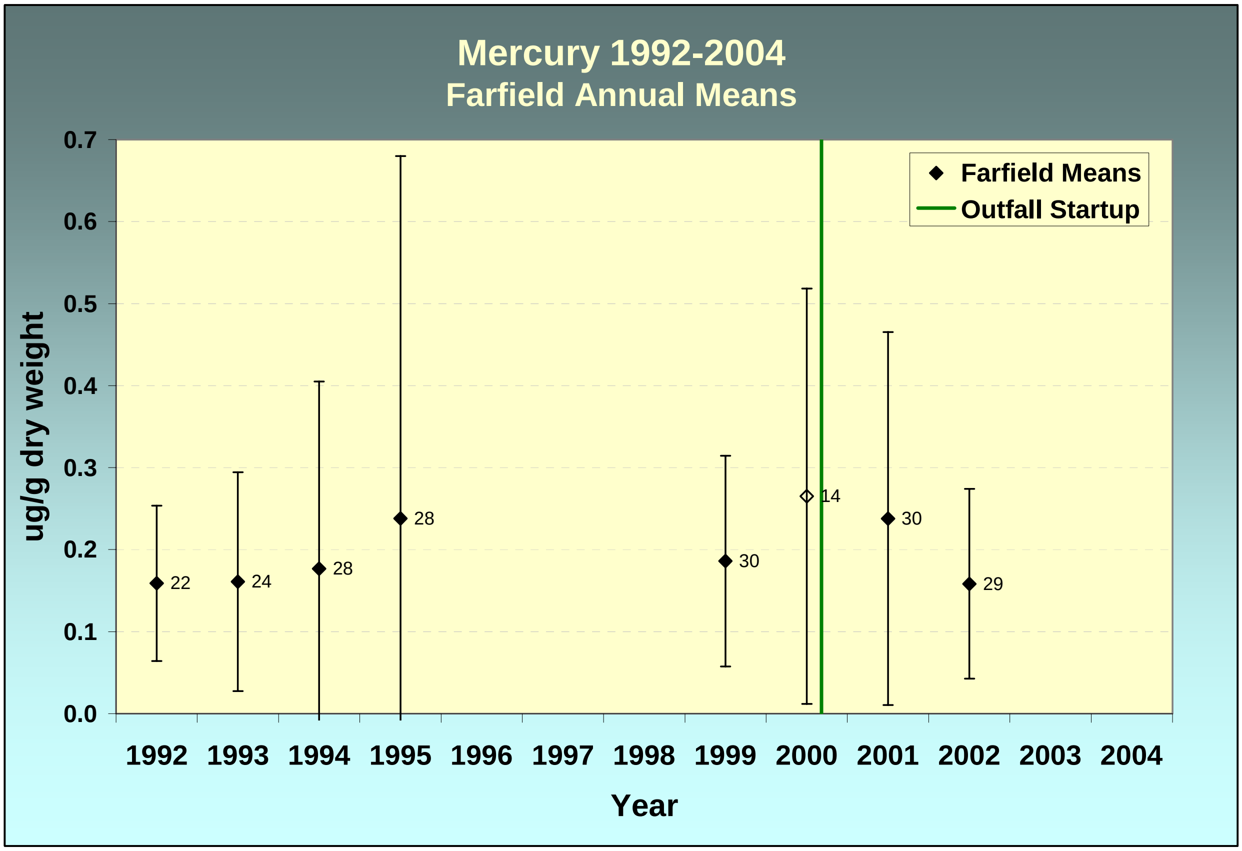

Total PAH 1992-2004
Farfield Annual Means
◆ Farfield Means
Outfall Startup
ng/g dry weight
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
23
24
28
28
30
14
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

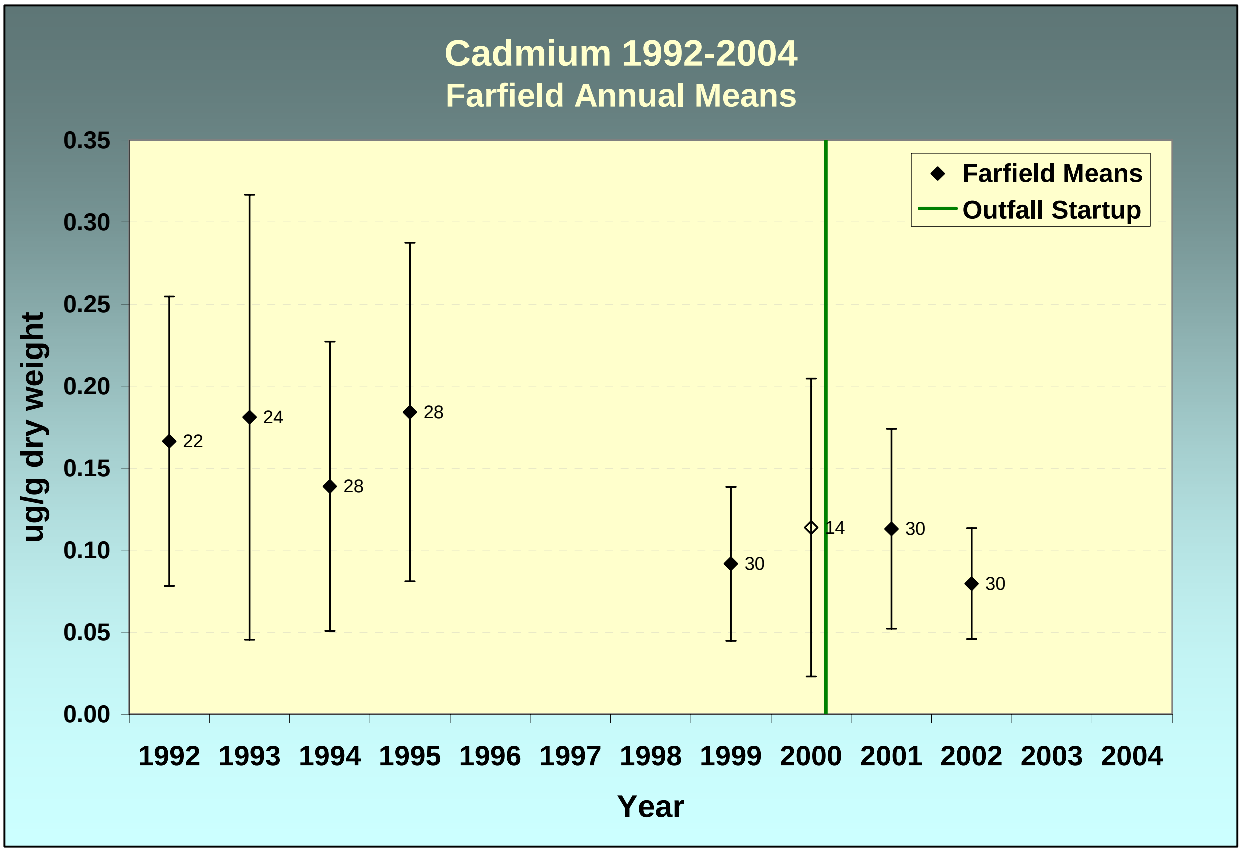

Total DDT 1992-2004
Farfield Annual Means
◆ Farfield Means
Outfall Startup
ng/g dry weight
12
10
8
6
4
2
0
23
24
28
28
30
14
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year

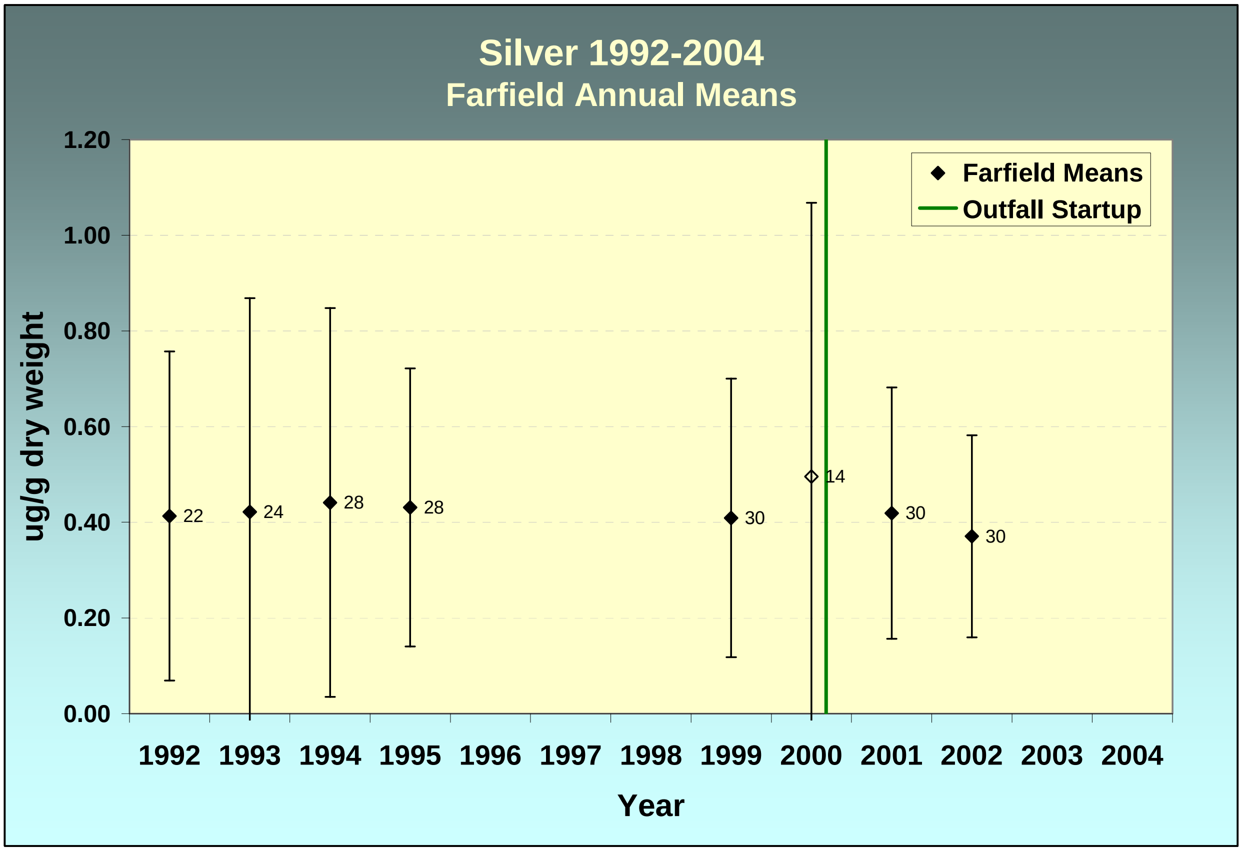

Total PCB 1992-2004
Farfield Annual Means
ng/g dry weight
0
5
10
15
20
25
30
35
40
23
24
28
28
30
14
30
30
Farfield Means
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year


Lead 1992-2004
Farfield Annual Means
ug/g dry weight
0
10
20
30
40
50
60
70
22
24
28
28
30
14
30
30
Farfield Means
Outfall Startup
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year


Copper 1992-2004
Farfield Annual Means
ug/g dry weight
Year
Farfield Means
Outfall Startup
0
5
10
15
20
25
30
35
40
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
22
24
28
28
30
14
30
30


Mercury 1992-2004
Farfield Annual Means
ug/g dry weight
Year
Farfield Means
Outfall Startup
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
22
24
28
28
30
14
30
29


Cadmium 1992-2004
Farfield Annual Means
ug/g dry weight
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
22
24
28
28
30
14
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year
◆ Farfield Means
Outfall Startup


Silver 1992-2004
Farfield Annual Means
ug/g dry weight
1.20
1.00
0.80
0.60
0.40
0.20
0.00
22
24
28
28
30
14
30
30
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
Year
◆ Farfield Means
Outfall Startup

APPENDIX C: STATIONS SAMPLED IN BOSTON HARBOR/MASSACHUSETTS BAY BY MWRA SINCE 1990

This table includes the parameters measured by year by station under the MWRA Harbor and Outfall Monitoring program

Station	Analyte	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
C019	toc					X				X				X		X
DB01	toc	x				X				X				X		
DB03	toc	x				X				X				X		
DB04	toc	x				X				X				X		
DB06	toc	x				X				X				X		
DB10	toc	x				X				X				X		
DB11	toc	x				X										
DB12	toc	x				X				X				X		
DB14	toc	x				X				X				X		
SWEX3	toc					X				X				X		
T01	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T02	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T03	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T04	toc	x	X	X	X	X	X	X	X	X	X	X	X	X	X	X
T05	toc		X	X												
T05A	toc		X		X	X	X	X	X	X	X	X	X	X	X	X
T06	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T07	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T08	toc		X	X	X	X	X	X	X	X	X	X	X	X	X	X
C019	pyro_pahs					X				X				X		X
DB01	pyro_pahs					X				X				X		
DB03	pyro_pahs					X				X				X		
DB04	pyro_pahs					X				X				X		
DB06	pyro_pahs					X				X				X		
DB10	pyro_pahs					X				X				X		
DB11	pyro_pahs					X										
DB12	pyro_pahs					X				X				X		
DB14	pyro_pahs					X				X				X		
SWEX3	pyro_pahs					X				X				X		
T01	pyro_pahs					X			X	X				X		
T02	pyro_pahs					X			X	X				X		
T03	pyro_pahs								X					X		
T04	pyro_pahs					X			X	X				X		
T05A	pyro_pahs								X					X		
T06	pyro_pahs								X					X		
T07	pyro_pahs								X	X				X		
T08	pyro_pahs					X			X	X				X		
C019	petro_pahs					X				X				X		X
DB01	petro_pahs					X				X				X		
DB03	petro_pahs					X				X				X		
DB04	petro_pahs					X				X				X		
DB06	petro_pahs					X				X				X		
DB10	petro_pahs					X				X				X		
DB11	petro_pahs					X										
DB12	petro_pahs					X				X				X		
DB14	petro_pahs					X				X				X		
SWEX3	petro_pahs					X				X				X		
T01	petro_pahs					X			X	X				X		
T02	petro_pahs					X			X	X				X		
T03	petro_pahs								X					X		
T04	petro_pahs					X			X	X				X		
T05A	petro_pahs								X					X		
T06	petro_pahs								X					X		
T07	petro_pahs								X	X				X		
T08	petro_pahs					X			X	X				X		

Station	Analyte	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
C019	pcbs					X				X				X		X
DB01	pcbs					X				X				X		
DB03	pcbs					X				X				X		
DB04	pcbs					X				X				X		
DB06	pcbs					X				X				X		
DB10	pcbs					X				X				X		
DB11	pcbs					X										
DB12	pcbs					X				X				X		
DB14	pcbs					X				X				X		
SWEX3	pcbs					X				X				X		
T01	pcbs					X			X	X				X		
T02	pcbs					X			X	X				X		
T03	pcbs								X					X		
T04	pcbs					X			X	X				X		
T05A	pcbs								X					X		
T06	pcbs								X					X		
T07	pcbs								X	X				X		
T08	pcbs					X			X	X				X		
C019	pahs					X				X				X		X
DB01	pahs					X				X				X		
DB03	pahs					X				X				X		
DB04	pahs					X				X				X		
DB06	pahs					X				X				X		
DB10	pahs					X				X				X		
DB11	pahs					X										
DB12	pahs					X				X				X		
DB14	pahs					X				X				X		
SWEX3	pahs					X				X				X		
T01	pahs					X			X	X				X		
T02	pahs					X			X	X				X		
T03	pahs								X					X		
T04	pahs					X			X	X				X		
T05A	pahs								X					X		
T06	pahs								X					X		
T07	pahs								X	X				X		
T08	pahs					X			X	X				X		
C019	metals					X				X				X		X
DB01	metals	x				X				X				X		
DB03	metals	x				X				X				X		
DB04	metals	x				X				X				X		
DB06	metals	x				X				X				X		
DB10	metals	x				X				X				X		
DB11	metals					X										
DB12	metals	x				X				X				X		
DB14	metals	x				X				X				X		
SWEX3	metals					X				X				X		
T01	metals					X			X	X				X		
T02	metals					X			X	X				X		
T03	metals								X					X		
T04	metals	x				X			X	X				X		
T05A	metals								X					X		
T06	metals								X					X		
T07	metals								X	X				X		
T08	metals					X			X	X				X		

Station	Analyte	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
C019	labs					X				X				X		
DB01	labs	x				X				X				X		
DB03	labs					X				X				X		
DB04	labs	x				X				X				X		
DB06	labs					X				X				X		
DB10	labs					X				X				X		
DB11	labs					X										
DB12	labs	x				X				X				X		
DB14	labs	x				X				X				X		
SWEX3	labs					X				X				X		
T01	labs					X			X	X				X		
T02	labs					X			X	X				X		
T03	labs								X					X		
T04	labs	x				X			X	X				X		
T05A	labs								X					X		
T06	labs								X					X		
T07	labs								X	X				X		
T08	labs					X			X	X				X		
C019	fines					X				X				X		X
DB01	fines	x				X				X				X		
DB03	fines	x				X				X				X		
DB04	fines	x				X				X				X		
DB06	fines	x				X				X				X		
DB10	fines	x				X				X				X		
DB11	fines	x				X										
DB12	fines	x				X				X				X		
DB14	fines	x				X				X				X		
SWEX3	fines					X				X				X		
T01	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T02	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T03	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T04	fines	x	X	X	X	X	X	X	X	X	X	X	X	X	X	X
T05	fines		X	X												
T05A	fines		X		X	X	X	X	X	X	X	X	X	X	X	X
T06	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T07	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T08	fines		X	X	X	X	X	X	X	X	X	X	X	X	X	X
C019	ddt					X				X				X		X
DB01	ddt					X				X				X		
DB03	ddt					X				X				X		
DB04	ddt					X				X				X		
DB06	ddt					X				X				X		
DB10	ddt					X				X				X		
DB11	ddt					X										
DB12	ddt					X				X				X		
DB14	ddt					X				X				X		
SWEX3	ddt					X				X				X		
T01	ddt					X			X	X				X		
T02	ddt					X			X	X				X		
T03	ddt								X					X		
T04	ddt					X			X	X				X		
T05A	ddt								X					X		
T06	ddt								X					X		
T07	ddt								X	X				X		
T08	ddt					X			X	X				X		

Station	Analyte	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
C019	coprostanol					X				X				X		
DB01	coprostanol	x				X				X				X		
DB03	coprostanol					X				X				X		
DB04	coprostanol	x				X				X				X		
DB06	coprostanol					X				X				X		
DB10	coprostanol					X				X				X		
DB11	coprostanol					X										
DB12	coprostanol	x				X				X				X		
DB14	coprostanol	x				X				X				X		
SWEX3	coprostanol					X				X				X		
T01	coprostanol					X				X				X		
T02	coprostanol					X				X				X		
T03	coprostanol													X		
T04	coprostanol	x				X				X				X		
T05A	coprostanol													X		
T06	coprostanol													X		
T07	coprostanol									X				X		
T08	coprostanol					X				X				X		
C019	clostridium					X				X				X		X
DB01	clostridium	x				X				X				X		
DB03	clostridium	x				X				X				X		
DB04	clostridium	x				X				X				X		
DB06	clostridium	x				X				X				X		
DB10	clostridium	x				X				X				X		
DB11	clostridium	x				X										
DB12	clostridium	x				X				X				X		
DB14	clostridium	x				X				X				X		
SWEX3	clostridium					X				X				X		
T01	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T02	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T03	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T04	clostridium	x	X	X	X	X	X	X	X	X	X	X	X	X	X	X
T05	clostridium		X	X												
T05A	clostridium		X		X	X	X	X	X	X	X	X	X	X	X	X
T06	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T07	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
T08	clostridium		X	X	X	X	X	X	X	X	X	X	X	X	X	X
C019	24_pahs					X				X				X		X
DB01	24_pahs	x				X				X				X		
DB03	24_pahs	x				X				X				X		
DB04	24_pahs	x				X				X				X		
DB06	24_pahs	x				X				X				X		
DB10	24_pahs	x				X				X				X		
DB11	24_pahs					X										
DB12	24_pahs	x				X				X				X		
DB14	24_pahs	x				X				X				X		
SWEX3	24_pahs					X				X				X		
T01	24_pahs					X			X	X				X		
T02	24_pahs					X			X	X				X		
T03	24_pahs								X					X		
T04	24_pahs	x				X			X	X				X		
T05A	24_pahs								X					X		
T06	24_pahs								X					X		
T07	24_pahs								X	X				X		
T08	24_pahs					X			X	X				X		

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