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Assessment of sediment contamination in Casco Bay, Maine, USA

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Sediment studies indicate decadal decreases for many chemical contaminants in Casco Bay.

Abstract

The current status of contaminant concentrations in Casco Bay, decadal trends of these contaminants and changes in their geographical distribution are assessed using sediment samples collected approximately 10 years apart. In general, regulated contaminants appeared to be decreasing in concentration. Total PAH and dioxins/furans concentrations did not significantly change over this period. Total organochlorine pesticides, 4,4-DDE, 4,4-DDD, total DDT, PCB, tributyltin and total butyltin decreased in concentration. Trace element concentrations in sediments decreased at the majority of the sampling sites for chromium, nickel, and selenium while arsenic, cadmium, copper, lead, mercury, silver, and zinc remained relatively constant. None of the contaminants measured has increased by more than a factor of 2. Selected sites located in the Inner Bay, where concentrations are higher and new inputs were more likely, showed increased concentrations of contaminants. Most contaminants were not found at concentrations expected to adversely affect sediment biota based on ERL/ERM guidelines.

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Keywords: Estuarine sediment; Organochlorine; PAH; Trace element; Organotin

1. Introduction and background

Casco Bay is located on the coast of Maine in Cumberland County. The major city on the bay is Portland which serves as a major docking facility and Maine's principal fishing port (Larsen et al., 1983a). The embayment is over 45 km long and averages 12.9 km in width. Its numerous islands are topographic highs between glacial scoured valleys. The rivers provide an average daily inflow to the bay of 60 m³/s of freshwater. The highest monthly average flow rates (NOAA, 1985) are in April (137 m³/s) and the lowest in September (23 m³/s). Cumberland County, with an area of 3000 km², accounts for most of the drainage basin for the Casco Bay estuary. The average tidal range for the bay is approximately 2.7 m (NOAA, 1985). Casco Bay can be sub-divided into five

geographic areas, Inner Bay, Outer Bay, West Bay, East Bay, and Cape Small (Fig. 1), and three depositional regions, inner, middle, and outer regions (Belknap et al., 1987). The outer region is characterized by virtually no sediment cover on bathymetric highs and without major sediment accumulation in bathymetric lows. This region is strongly influenced by wave action resulting in low sediment accumulation rates. This wave action is the dominant factor affecting the coastlines of the outer islands. The middle region has a thicker glacier marine till (the Presumpscot formation) and Holocene mud. The inner region is characterized by sedimentary accumulation with thick Holocene mud, drowned stratified sands, and only a slightly reworked Pleistocene section (Belknap et al., 1987). Wood et al. (1989) reported sedimentation rates ranging from 0.0 to 5.8 mm yr⁻¹ for tidal marshes in Casco Bay.

The Casco Bay estuary covers 518 km² with a watershed of 2550 km². Located within the watershed are 41 towns with 12 major lake and river systems that discharge freshwater to the

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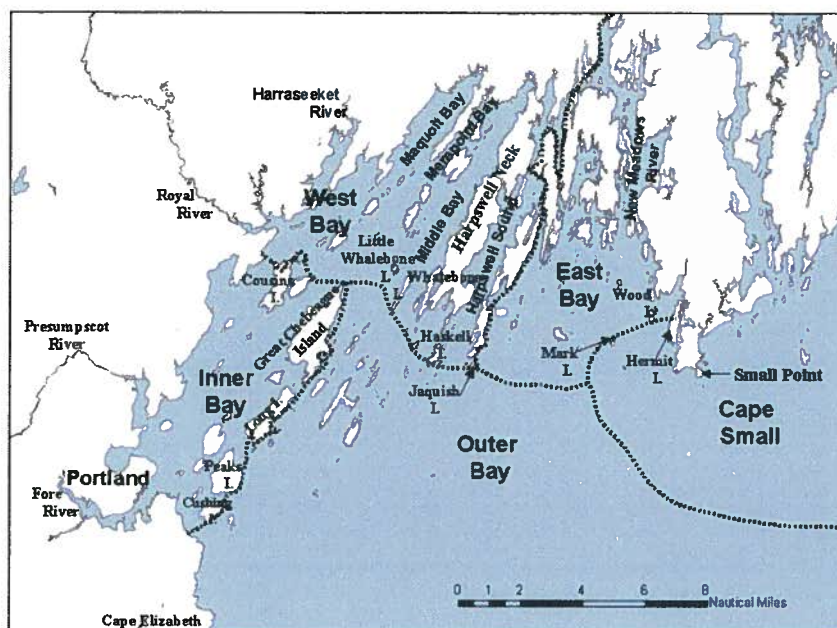


Fig. 1. Geographical subdivisions of Casco Bay.

bay including the Presumpscot, Stroudwater, Royal, and Fore Rivers (Casco Bay Partnership, 2005). The Kennebec/Androscoggin River, which discharges just north of Casco Bay, is a source of water and contaminants to the bay under certain wind and current regimes. Land use will affect the input and composition of contaminants reaching Casco Bay. Land use patterns have changed between 1982 and 1997 with the Portland metropolitan area increasing by 17% and farmland and forestland conversion to urban uses increasing by 108% (Casco Bay Partnership, 2005). The area has experienced rapid growth since 1960, the population has increased by 210,000 (USEPA, 2007) as rural areas are transformed into suburban bedroom communities. The most densely populated portions of the Casco Bay watershed receive higher anthropogenic inputs compared to other regions of Casco Bay; these areas include Portland, the banks of the Fore and Presumpscot Rivers, and Back Cove. An assessment of sediment contamination for trace elements, hydrocarbons including polynuclear aromatic hydrocarbons (PAH), chlorinated pesticides and polychlorinated biphenyls (PCB) was undertaken in 1991 (Kennicutt et al., 1992, 1994). Surface sediment samples (top 2 cm) were collected from 65 sites in Casco Bay. The sites were selected based on depth, circulation, sediment type and historical data. In 1994, 28 of the original Casco Bay sampling sites were re-sampled to assess the contamination of surface sediments for butyltin, dioxin/furan and planar PCB and five additional sampling sites were added. Two of the new sites were analyzed for dioxin/furan and planar PCB while the other three sites were analyzed for butyltins (Wade et al., 1995a,b). Recently, another assessment of sediment contamination in Casco Bay was initiated with the collection and analysis of sediments from many of the original stations during the summers of 2000 and 2001 and at 18 new randomly selected sites.

The objective of this study was to develop a sediment contamination assessment by comparing the data from the 1990s to the data collected a decade later and updating the conclusions from previous work (Kennicutt et al., 1992, 1994; Wade et al., 1995a,b) and to determine any temporal trends for the contaminant fields. All the contaminant data are put in perspective by using effects range low (ERL) and effects range medium (ERM) criteria and comparing concentrations to sediment quality guidelines to determine the potential of these contaminants to cause adverse effects to biota (Long and Morgan, 1990; Long et al., 1995, 1998; Field et al., 1999). Sediment toxicity data (based on *Ampelisca* toxicity test significance) collected at 30 sites in Casco Bay as part of EPA National Coastal Assessment indicated no significant toxicity based on the *Ampelisca* toxicity test (USEPA, June 2007).

2. Methods

Surficial sediment samples (top 2 cm) were collected for all samplings. The sampling sites were selected to provide representative coverage of the entire bay. The Geochemical and Environmental Research Group (GERG) at Texas A&M University collected and analyzed the 1991 and 1994 sediment samples. Samples for PAH and organochlorine analysis were extracted by Soxhlet with methylene chloride, extracts were dried using sodium sulfate, concentrated to approximately 1 ml using the Kuderna-Danish technique, treated with copper granules and purified using open column silica/alumina chromatography. Aromatic hydrocarbons were quantified by gas chromatography with a mass selective detector (GC-MSD). Pesticides and PCB were quantified by gas chromatography with an electron capture detector (GC-ECD) (Kennicutt et al., 1992, 1994; Wade et al., 1995a,b, 1997). For dioxin and furan analysis, sediments were extracted using the Dean–Stark technique with toluene followed by an acid/silica slurry and column extract purification. The quantitative determination of tetra- through octa-polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the sample extracts used isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The concentration of butyltins including tetrabutyltin,

tributyltin, dibutyltin, and monobutyltin was determined as described by Wade et al. (1990) for sediments. Sediments for trace metal analysis were digested in a mixture of nitric, perchloric and hydrofluoric acid. A saturated boric acid solution was added to complete the dissolution. Concentrations of iron, manganese, and zinc were determined by flame AAS. Silver, arsenic, cadmium, copper, nickel, lead, and selenium were determined by graphite furnace AAS (Kennicutt et al., 1994).

The 2000/2001 sediment samples were collected by the Casco Bay Estuary program and analyzed for trace elements, chlorinated pesticides, PAH and PCB by ICF International (formerly Arthur D. Little) and analyzed for butyltins, planar PCB and dioxin/furan by RPC Chemical and Biotechnical Services using EPA analytical methods. Sediment samples were extracted for organic analyses following EPA Method 3550A using 1:1 methylene chloride:acetone. Extracts were dried using sodium sulfate, concentrated to approximately 1 ml using the Kuderna-Danish technique, treated with copper granules and purified using open column alumina chromatography. Aromatic hydrocarbons were quantified by gas chromatography with a mass selective detector (GC-MSD). Pesticides and PCB were quantified by gas chromatography with an electron capture detector (GC-ECD). Dioxins and furans were extracted and analyzed following EPA method 1613B using HRGC/HRMS.

Samples for trace metal analysis at ICF were digested in open vessels using nitric acid/hydrofluoric acid with the resulting solutions analyzed for trace elements by inductively coupled plasma/mass spectrometry and for matrix elements by inductively coupled plasma/atomic emission spectrometry. For selenium aliquots of the digested solution were further digested using hydrochloric acid, aqueous urea was added and samples were analyzed using hydride generation inductively coupled plasma/mass spectrometry. Mercury was separately digested using sulfuric acid, potassium persulfate, and nitric acid and analyzed using cold vapor atomic absorption.

In general the analytical methods used by GERG, ICF and RPC provide comparable results based on the quality control information on procedural blank, duplicate, matrix spike and standard reference material analytical results reported by each laboratory. There were some slight differences in what compounds were reported for PAH and PCB between the two sampling periods; consequently phenanthrene, benzo(e)pyrene, perylene and alkylated PAH were excluded from our assessment. The same PCB congeners were not reported for both sample sets; consequently, 18 PCB congeners (PCB 8, 18, 28, 44, 52, 101, 105, 110, 118, 128, 138, 153, 170, 180, 187, 195, 206, and 209) are summed and multiplied by 2 to estimate total PCB present (O'Connor, 1998). The dioxin/furan data for 2,3,7,8-tetrachlorodibenzofuran (TCDF) were not easily compared since the 2000/2001 2,3,7,8-TCDF data represent the maximum possible concentration due to the potential for co-elution while the earlier data included second column confirmations to eliminate possible interferences.

A total of 59 of the original 65 sites collected in 1991 had collection locations close enough to be considered reoccupation of these sites. A total of 29 of the original 31 sites collected in 1994 had collection locations close enough to be considered reoccupation of these sites for dioxins, planar PCB and butyltins. A simple technique to help visualize large data sets for temporal trends is to plot the data as frequency distributions for each sampling period. Data with a normal distribution on a log scale tend to have an "S" shaped curve. Where there are small temporal concentration differences, the data plots would be expected to have very similar distributions; if one sampling period had significantly different concentrations, the curves would be separated from one another. Each analyte or the sum of selected analytes was plotted and these plots were evaluated to detect the temporal trend for each contaminant(s). Spatial trends are visualized by using graduated symbols that represent different concentration ranges on the geographic information system (GIS) map of Casco Bay (Wade and Sweet, 2005).

3. Results and discussion

Concentrations of selected analytes from the sampling periods and their relationship to sediment quality guidelines (SQG) are provided in Table 1 (Long and Morgan, 1990; Long et al., 1995, 1998; Field et al., 1999). The geographic

distribution of contaminants is initially controlled by the area where they enter the bay and secondarily by oceanographic conditions that redistribute sediments (Gustafsson et al., 1998). Sediments from the Inner Bay region closest to Portland, ME contain the highest levels of trace metals, PCB, dichlorodiphenyl-trichloroethanes (DDT), and chlordane. For contaminants other than PAH (and these are only present at a few locations) and PCB at one location, the levels of contamination in Casco Bay would not be considered high on a national basis (Macauley et al., 1994; Long et al., 1995). Temporal variability was difficult to precisely assess due to sediment inhomogeneity, the patchy distribution of contaminants, and variations in the contaminants measured. However, in general, the contaminant concentrations measured in these studies were within the ranges reported in previous studies of bay systems in the United States (Macauley et al., 1994; USEPA, 1997).

The highest 25% of organic contaminants in the 1991 study were found at 11 Inner Bay, 2 Outer Bay, 3 East Bay, and 1 Cape Small site (see Fig. 2a). Eight of the 10 most highly contaminated stations were located in the Inner Bay region including the six stations with the highest concentrations. The lowest levels of organic contaminants were in the Cape Small and West Bay regions. High levels of organic contaminants tended to co-occur at a single location. Locations with the 25% highest levels of inorganic contamination were at 12 Inner Bay, 3 East Bay, and 1 Outer Bay location (see Fig. 2b). Nine of the 10 locations with the highest concentrations were in the Inner Bay region including the eight highest stations. The lowest metal concentrations occurred in the Cape Small region. Eleven stations were ranked in the highest 25% for both inorganic and organic contaminants. Nine of these 11 were located in the Inner Bay.

In the 1991 study, contaminants related to human activities were detectable throughout Casco Bay but in most cases occur at low concentrations. A variety of processes release contaminants to Casco Bay and these chemicals have accumulated in bay sediments. The focus of contamination in the Inner Bay region was directly associated with population centers and industrialization. Localized contaminations by various chemicals were generally far below levels suspected of evoking a toxic biological response.

Several sets of historical data are particularly germane to the present study. Larsen et al. (1983a,b,c, 1984) measured trace metals, PAH and PCB in sediments from Casco Bay collected in 1980. A further study of sediment contaminants in Casco Bay was conducted as part of two multi-year studies by NOAA's Benthic Surveillance Program and the National Status and Trends Program. Sediments were collected between 1984 and 1988 at a few sites with selected sites occupied more than once. A more extensive suite of individual analytes were measured in the 1991 study compared to the 1980 study. However, the same general suite of contaminants was selected for analysis. Finally, two sediment transects were sampled by the Maine Department of Environmental Protection in 1989 and analyzed for trace metals, PCB, and PAH (Doggett, DEP, personal communication). A summary of these studies was presented by Kennicutt et al. (1992). The limited nature of the

Table 1
Summary data from Casco Bay regions for both sampling periods with ERL and ERM guideline values (from Long et al., 1995)

| Chemical | Guidelines | | Inner Bay 1991 (n = 25) | | | | | Inner Bay 2000/2001 (n = 32) | | | | |
|------------------------------------|-------------------------|----------------------------|-------------------------|---------|---------|-----------|--------|------------------------------|---------|---------|-----------|--------|
| | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median |
| Trace elements (ppm) | | | | | | | | | | | | |
| Arsenic | 8.2 | 70 | 1.6 | 16.0 | 10.3 | 4.5 | 10.9 | 1.0 | 16.0 | 10.4 | 3.9 | 10.0 |
| Cadmium | 1.2 | 9.6 | 0.2 | 0.9 | 0.4 | 0.2 | 0.4 | 0.0 | 0.7 | 0.4 | 0.2 | 0.4 |
| Chromium | 81 | 370 | 31.0 | 91.0 | 67.6 | 24.8 | 79.0 | 20.0 | 96.0 | 65.9 | 22.3 | 73.5 |
| Copper | 34 | 270 | 7.9 | 48.4 | 23.1 | 11.4 | 22.3 | 4.0 | 44.0 | 21.9 | 9.7 | 22.0 |
| Lead | 46.7 | 218 | 27.5 | 75.6 | 39.7 | 15.5 | 36.2 | 26.8 | 76.0 | 43.6 | 14.7 | 42.3 |
| Mercury | 0.15 | 0.71 | 0.06 | 0.42 | 0.18 | 0.12 | 0.17 | 0.00 | 0.49 | 0.17 | 0.12 | 0.16 |
| Nickel | 20.9 | 51.6 | 7.8 | 37.8 | 26.8 | 9.7 | 30.6 | 8.0 | 36.0 | 25.1 | 8.2 | 28.0 |
| Silver | 1 | 3.7 | 0.1 | 0.8 | 0.3 | 0.2 | 0.2 | 0.1 | 1.0 | 0.4 | 0.2 | 0.4 |
| Zinc | 150 | 410 | 35 | 125 | 88.0 | 31.4 | 98.0 | 19 | 144 | 92.9 | 31.7 | 94.0 |
| Organic compounds (ppb) | | | | | | | | | | | | |
| Acenaphthene | 16 | 500 | 1.2 | 59 | 9.6 | 15.4 | 3.1 | 1.2 | 49 | 11.6 | 13.7 | 6.3 |
| Acenaphthylene | 44 | 640 | 3.4 | 113 | 19.4 | 23.5 | 11.8 | 9.9 | 89 | 24.6 | 19.7 | 22.5 |
| Anthracene | 85.3 | 1100 | 4.5 | 180 | 37.1 | 48.8 | 15.0 | 7.9 | 170 | 47.1 | 46.8 | 37.5 |
| Fluorene | 19 | 540 | 2.9 | 125 | 20.2 | 29.5 | 8.6 | 4.7 | 98 | 22.5 | 23.2 | 14.0 |
| 2-Methyl naphthalene | 70 | 670 | 3.8 | 63 | 14.5 | 15.7 | 9.2 | 3.1 | 81 | 16.8 | 18.7 | 10.0 |
| Naphthalene | 160 | 2100 | 6.1 | 89 | 21.3 | 23.7 | 13.8 | 5.2 | 110 | 26.4 | 26.8 | 18.5 |
| Total LMW PAH | 552 | 3160 | 26.7 | 707 | 126.4 | 158.6 | 73.8 | 29.5 | 531 | 132.4 | 125.6 | 92.9 |
| Benzo(a)anthracene | 261 | 1600 | 26.1 | 446 | 110.6 | 125.0 | 49.1 | 31.0 | 740 | 158.4 | 167.9 | 105.0 |
| Benzo(a)pyrene | 430 | 1600 | 36.4 | 658 | 136.2 | 155.3 | 74.4 | 44.0 | 900 | 192.6 | 201.6 | 130.0 |
| Chrysene | 384 | 2800 | 38.8 | 523 | 135.8 | 145.7 | 68.5 | 52.0 | 1000 | 202.1 | 218.1 | 135.0 |
| Dibenzo(a,h)anthracene | 63.4 | 260 | 2.8 | 91 | 22.5 | 25.7 | 10.6 | 6.7 | 170 | 29.3 | 35.8 | 19.0 |
| Fluoranthene | 600 | 5100 | 73 | 1018 | 265.1 | 289.2 | 128.1 | 100 | 2200 | 386 | 435.6 | 275.0 |
| Pyrene | 665 | 2600 | 66 | 1094 | 251.8 | 281.4 | 126.7 | 78 | 1700 | 333 | 353.0 | 230.0 |
| Total HMW PAH | 1700 | 9600 | 362 | 5748 | 1442.3 | 1561.0 | 699.0 | 501 | 10,314 | 2061 | 2196.2 | 1407.7 |
| Total PAH | 4022 | 44,792 | 388 | 6157 | 1568.7 | 1710.8 | 768.1 | 530 | 10,663 | 2193 | 2298.9 | 1509.3 |
| p,p'-DDE | 2.2 | 27 | 0.4 | 3.6 | 1.2 | 1.0 | 0.9 | 0.4 | 3.0 | 0.7 | 0.9 | 0.5 |
| Sum total DDT | 1.58 | 46.1 | 1.3 | 17.4 | 4.9 | 5.2 | 2.9 | 0.9 | 18.6 | 4.8 | 5.1 | 3.1 |
| Total PCB | 22.7 | 180 | 6.0 | 503 | 43.9 | 99.7 | 15.9 | 2.4 | 53 | 18.0 | 15.8 | 13.8 |
| West Bay 1991 (n = 9) | | | | | | | | | | | | |
| West Bay 2000/2001 (n = 10) | | | | | | | | | | | | |
| Trace elements (ppm) | | | | | | | | | | | | |
| Arsenic | 8.2 | 70 | 4.8 | 19.6 | 12.4 | 2.0 | 13.0 | 4.0 | 16.0 | 11.5 | 2.7 | 12.0 |
| Cadmium | 1.2 | 9.6 | 0.1 | 0.5 | 0.3 | 0.1 | 0.3 | 0.1 | 0.5 | 0.3 | 0.1 | 0.3 |
| Chromium | 81 | 370 | 35.0 | 100.0 | 76.4 | 10.2 | 78.0 | 33.0 | 97.0 | 71.5 | 12.1 | 74.0 |
| Copper | 34 | 270 | 7.0 | 26.2 | 18.3 | 2.6 | 19.5 | 7.0 | 25.0 | 16.7 | 2.8 | 17.0 |
| Lead | 46.7 | 218 | 20.5 | 37.6 | 28.0 | 3.4 | 28.4 | 20.8 | 37.7 | 27.2 | 3.5 | 27.4 |
| Mercury | 0.15 | 0.71 | 0.02 | 0.10 | 0.07 | 0.02 | 0.08 | 0.01 | 0.13 | 0.06 | 0.02 | 0.06 |
| Nickel | 20.9 | 51.6 | 9.7 | 38.6 | 30.7 | 4.0 | 30.8 | 11.0 | 34.0 | 26.5 | 5.3 | 28.0 |
| Silver | 1 | 3.7 | 0.1 | 0.4 | 0.2 | 0.1 | 0.2 | 0.1 | 0.4 | 0.3 | 0.1 | 0.3 |
| Zinc | 150 | 410 | 34 | 140 | 91.2 | 21.1 | 92.0 | 37 | 107 | 81.0 | 14.3 | 84.0 |

| Organic compounds (ppb) | East Bay 1991 (n = 10) | | | | | | | | | | East Bay 2000/2001 (n = 13) | | | | | | | | | |
|-------------------------|------------------------|-------------------------|----------------------------|---------|---------|---------|-----------|--------|---------|---------|-----------------------------|-----------|--------|--|--|--|--|--|--|--|
| | Guidelines | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median | | | | | | | |
| Acenaphthene | 16 | 500 | | 0.2 | 2 | 9.6 | 15.4 | 3.1 | 0.5 | 4 | 1.8 | 0.5 | 1.9 | | | | | | | |
| Acenaphthylene | 44 | 640 | | 1.1 | 10 | 19.4 | 23.5 | 11.8 | 1.8 | 15 | 9.3 | 3.5 | 8.4 | | | | | | | |
| Anthracene | 85.3 | 1100 | | 1.2 | 13 | 37.1 | 48.8 | 15.0 | 2.0 | 16 | 8.9 | 2.6 | 9.6 | | | | | | | |
| Fluorene | 19 | 540 | | 0.7 | 6 | 20.2 | 29.5 | 8.6 | 1.3 | 10 | 4.5 | 1.4 | 4.4 | | | | | | | |
| 2-Methyl naphthalene | 70 | 670 | | 0.8 | 8 | 14.5 | 15.7 | 9.2 | 0.8 | 10 | 4.6 | 2.2 | 4.6 | | | | | | | |
| Naphthalene | 160 | 2100 | | 1.0 | 10 | 21.3 | 23.7 | 13.8 | 1.20 | 18 | 7.7 | 4.3 | 7.6 | | | | | | | |
| Total LMW PAH | 552 | 3160 | | 6.3 | 55 | 126.4 | 158.6 | 73.8 | 8.2 | 69 | 40.0 | 15.7 | 43.9 | | | | | | | |
| Benz(a)anthracene | 261 | 1600 | | 4.2 | 51 | 110.6 | 125.0 | 49.1 | 8.0 | 62 | 36.7 | 10.5 | 37.5 | | | | | | | |
| Benzo(a)pyrene | 430 | 1600 | | 6.0 | 89 | 136.2 | 155.3 | 74.4 | 9.4 | 77 | 45.1 | 13.6 | 44.0 | | | | | | | |
| Chrysene | 384 | 2800 | | 6.6 | 67 | 135.8 | 145.7 | 68.5 | 12 | 93 | 49.4 | 15.4 | 48.2 | | | | | | | |
| Dibenzo(a,h)anthracene | 63.4 | 260 | | 1.0 | 37 | 22.5 | 25.7 | 10.6 | 1.2 | 10 | 6.5 | 2.4 | 6.3 | | | | | | | |
| Fluoranthene | 600 | 5100 | | 13 | 124 | 265.1 | 289.2 | 128.1 | 20 | 170 | 88 | 24.2 | 88.5 | | | | | | | |
| Pyrene | 665 | 2600 | | 12 | 117 | 251.8 | 281.4 | 126.7 | 15 | 140 | 81 | 22.7 | 81.0 | | | | | | | |
| Total HMW PAH | 1700 | 9600 | | 70 | 904 | 1442.3 | 1561.0 | 699.0 | 111 | 856 | 488 | 140.9 | 502.5 | | | | | | | |
| Total PAH | 4022 | 44,792 | | 76 | 959 | 1568.7 | 1710.8 | 768.1 | 119 | 924 | 528 | 153.0 | 558.6 | | | | | | | |
| p,p'-DDE | 2.2 | 27 | | 0.1 | 0.8 | 0.6 | 0.2 | 0.7 | 0.2 | 1.1 | 0.1 | 0.1 | 0.1 | | | | | | | |
| Sum total DDT | 1.58 | 46.1 | | 0.1 | 2.9 | 1.3 | 0.6 | 1.6 | 0.3 | 2.9 | 0.8 | 0.4 | 0.6 | | | | | | | |
| Total PCB | 22.7 | 180 | | 1.3 | 14 | 8.9 | 3.7 | 9.3 | 0.3 | 148 | 5.6 | 2.5 | 5.9 | | | | | | | |

| Chemical | East Bay 1991 (n = 10) | | | | | | | | | | East Bay 2000/2001 (n = 13) | | | | | | | | | |
|-------------------------|------------------------|-------------------------|----------------------------|---------|---------|---------|-----------|--------|---------|---------|-----------------------------|-----------|--------|--|--|--|--|--|--|--|
| | Guidelines | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median | | | | | | | |
| Trace elements (ppm) | | | | | | | | | | | | | | | | | | | | |
| Arsenic | 8.2 | 70 | | 3.2 | 19.6 | 12.1 | 4.2 | 13.3 | 6.0 | 17.0 | 11.5 | 4.0 | 12.0 | | | | | | | |
| Cadmium | 1.2 | 9.6 | | 0.1 | 1.3 | 0.5 | 0.4 | 0.4 | 0.1 | 1.5 | 0.5 | 0.5 | 0.3 | | | | | | | |
| Chromium | 81 | 370 | | 29.0 | 105.0 | 91.2 | 11.2 | 94.0 | 51.0 | 110.0 | 76.5 | 20.4 | 70.0 | | | | | | | |
| Copper | 34 | 270 | | 5.6 | 37.0 | 18.8 | 6.9 | 19.9 | 9.0 | 30.0 | 18.8 | 7.6 | 19.0 | | | | | | | |
| Lead | 46.7 | 218 | | 13.6 | 37.0 | 29.7 | 5.4 | 31.9 | 19.8 | 37.3 | 29.2 | 5.7 | 28.2 | | | | | | | |
| Mercury | 0.15 | 0.71 | | 0.05 | 0.18 | 0.12 | 0.05 | 0.12 | 0.05 | 0.20 | 0.11 | 0.05 | 0.10 | | | | | | | |
| Nickel | 20.9 | 51.6 | | 8.4 | 38.4 | 28.3 | 6.9 | 29.0 | 18.0 | 41.0 | 28.8 | 8.0 | 27.0 | | | | | | | |
| Silver | 1 | 3.7 | | 0.1 | 0.3 | 0.2 | 0.1 | 0.2 | 0.2 | 0.5 | 0.3 | 0.1 | 0.3 | | | | | | | |
| Zinc | 150 | 410 | | 28 | 105 | 82.7 | 19.3 | 89.5 | 60 | 119 | 85.4 | 20.5 | 81.0 | | | | | | | |
| Organic compounds (ppb) | | | | | | | | | | | | | | | | | | | | |
| Acenaphthene | 16 | 500 | | 1.4 | 12 | 4.8 | 2.5 | 4.1 | 2.2 | 15 | 5.1 | 3.6 | 3.4 | | | | | | | |
| Acenaphthylene | 44 | 640 | | 6.6 | 53 | 22.8 | 11.9 | 19.4 | 13.0 | 91 | 30.6 | 21.2 | 21.0 | | | | | | | |
| Anthracene | 85.3 | 1100 | | 7.2 | 97 | 33.0 | 23.9 | 25.8 | 16.0 | 150 | 42.2 | 38.1 | 26.0 | | | | | | | |
| Fluorene | 19 | 540 | | 4.1 | 59 | 12.2 | 7.6 | 10.1 | 5.2 | 35 | 12.4 | 8.2 | 9.1 | | | | | | | |
| 2-Methyl naphthalene | 70 | 670 | | 4.0 | 28 | 11.4 | 6.2 | 9.6 | 3.6 | 19 | 7.7 | 3.1 | 6.9 | | | | | | | |
| Naphthalene | 160 | 2100 | | 5.13 | 35 | 15.3 | 7.5 | 13.5 | 7.10 | 30 | 12.8 | 5.5 | 11.0 | | | | | | | |
| Total LMW PAH | 552 | 3160 | | 32.7 | 214 | 88.9 | 47.3 | 75.5 | 41.0 | 213 | 84.2 | 44.5 | 70.4 | | | | | | | |
| Benz(a)anthracene | 261 | 1600 | | 31.8 | 326 | 117.4 | 78.1 | 93.0 | 67.0 | 530 | 151.9 | 131.7 | 100.0 | | | | | | | |
| Benzo(a)pyrene | 430 | 1600 | | 46.4 | 359 | 136.8 | 83.4 | 109.0 | 94.0 | 480 | 170.5 | 118.6 | 120.0 | | | | | | | |
| Chrysene | 384 | 2800 | | 43.8 | 350 | 136.4 | 79.9 | 117.8 | 81 | 480 | 162.4 | 114.8 | 110.0 | | | | | | | |
| Dibenzo(a,h)anthracene | 63.4 | 260 | | 6.9 | 45 | 19.2 | 10.4 | 16.8 | 11 | 64 | 21.2 | 14.4 | 16.0 | | | | | | | |
| Fluoranthene | 600 | 5100 | | 78 | 566 | 208.4 | 110.8 | 186.9 | 150 | 580 | 238 | 132.4 | 190.0 | | | | | | | |
| Pyrene | 665 | 2600 | | 74 | 508 | 206.7 | 112.2 | 180.4 | 140 | 600 | 235 | 142.4 | 180.0 | | | | | | | |
| Total HMW PAH | 1700 | 9600 | | 464 | 3219 | 1260.4 | 726.1 | 1099.0 | 890 | 4200 | 1538 | 979.0 | 1087.3 | | | | | | | |
| Total PAH | 4022 | 44,792 | | 498 | 3433 | 1349.3 | 773.0 | 1172.9 | 931 | 4413 | 1623 | 1021.8 | 1164.7 | | | | | | | |

(continued on next page)

Table 1 (continued)

| Chemical | Guidelines | | East Bay 1991 (n = 10) | | | | | East Bay 2000/2001 (n = 13) | | | | |
|-------------------------|-------------------------|----------------------------|-------------------------|---------|---------|-----------|--------|------------------------------|---------|---------|-----------|--------|
| | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median |
| <i>p,p'</i> -DDE | 2.2 | 27 | 0.3 | 1.7 | 1.0 | 0.5 | 1.1 | 0.3 | 1.3 | 0.2 | 0.2 | 0.2 |
| Sum total DDT | 1.58 | 46.1 | 0.7 | 3.8 | 2.1 | 1.2 | 2.0 | 0.6 | 3.5 | 1.6 | 0.9 | 1.3 |
| Total PCB | 22.7 | 180 | 8.1 | 35.8 | 18.2 | 9.7 | 15.6 | 2.2 | 18.1 | 9.2 | 3.8 | 9.1 |
| Chemical | Guidelines | | Cape Small 1991 (n = 7) | | | | | Cape Small 2000/2001 (n = 8) | | | | |
| | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median |
| Trace elements (ppm) | | | | | | | | | | | | |
| Arsenic | 8.2 | 70 | 5.0 | 13.7 | 8.1 | 3.7 | 5.7 | 3.0 | 10.0 | 5.4 | 2.3 | 4.5 |
| Cadmium | 1.2 | 9.6 | 0.0 | 0.2 | 0.1 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 |
| Chromium | 81 | 370 | 37.0 | 93.0 | 61.6 | 18.0 | 61.0 | 37.0 | 59.0 | 44.8 | 7.1 | 44.0 |
| Copper | 34 | 270 | 2.5 | 21.6 | 6.6 | 6.7 | 4.4 | 4.0 | 12.0 | 6.6 | 2.6 | 6.5 |
| Lead | 46.7 | 218 | 14.1 | 32.4 | 20.0 | 5.9 | 17.8 | 14.3 | 22.7 | 18.0 | 3.2 | 17.2 |
| Mercury | 0.15 | 0.71 | 0.01 | 0.19 | 0.04 | 0.07 | 0.02 | 0.00 | 0.04 | 0.02 | 0.02 | 0.02 |
| Nickel | 20.9 | 51.6 | 12.9 | 30.6 | 17.0 | 6.1 | 15.2 | 13.0 | 24.0 | 15.6 | 3.5 | 14.5 |
| Silver | 1 | 3.7 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 0.2 |
| Zinc | 150 | 410 | 31 | 88 | 44.4 | 19.8 | 38.0 | 38 | 66 | 44.0 | 9.6 | 40.0 |
| Organic compounds (ppb) | | | | | | | | | | | | |
| Acenaphthene | 16 | 500 | 0.1 | 7.8 | 1.6 | 2.8 | 0.6 | 0.0 | 2.8 | 1.1 | 1.0 | 1.0 |
| Acenaphthylene | 44 | 640 | 0.1 | 35.7 | 6.9 | 12.8 | 2.2 | 0.6 | 12.0 | 6.7 | 4.4 | 6.5 |
| Anthracene | 85.3 | 1100 | 0.1 | 50.0 | 9.2 | 18.1 | 2.4 | 0.5 | 12.0 | 5.6 | 4.0 | 4.9 |
| Fluorene | 19 | 540 | 0.1 | 15.6 | 3.1 | 5.5 | 1.0 | 0.0 | 5.3 | 2.3 | 1.9 | 2.1 |
| 2-Methyl naphthalene | 70 | 670 | 0.3 | 14.3 | 3.1 | 5.0 | 1.3 | 0.3 | 4.4 | 2.5 | 1.4 | 2.9 |
| Naphthalene | 160 | 2100 | 0.5 | 17.7 | 4.1 | 6.1 | 1.5 | 0.6 | 7.8 | 4.4 | 2.7 | 4.6 |
| Total LMW PAH | 552 | 3160 | 2.3 | 121 | 25.8 | 42.6 | 8.9 | 1.8 | 37 | 21.6 | 12.7 | 22.4 |
| Benzo(a)anthracene | 261 | 1600 | 0.5 | 182 | 35.0 | 65.3 | 13.0 | 2.0 | 53 | 26.2 | 18.5 | 21.5 |
| Benzo(a)pyrene | 430 | 1600 | 0.5 | 218 | 43.6 | 78.0 | 15.0 | 1.8 | 60 | 28.1 | 20.4 | 23.5 |
| Chrysene | 384 | 2800 | 0.6 | 201 | 39.5 | 71.8 | 16.1 | 1.8 | 56 | 28.6 | 20.0 | 24.5 |
| Dibenzo(a,h)anthracene | 63.4 | 260 | 0.1 | 32 | 7.3 | 11.4 | 2.7 | 0.3 | 7 | 4.1 | 2.5 | 3.8 |
| Fluoranthene | 600 | 5100 | 1.4 | 266 | 53.7 | 95.0 | 18.2 | 2.8 | 92 | 40 | 30.9 | 33.0 |
| Pyrene | 665 | 2600 | 1.4 | 286 | 57.1 | 102.2 | 21.7 | 2.7 | 92 | 39 | 30.8 | 32.0 |
| Total HMW PAH | 1700 | 9600 | 8.2 | 1826 | 374.9 | 649.6 | 138.1 | 19.0 | 559 | 265 | 189.5 | 221.6 |
| Total PAH | 4022 | 44,792 | 11.9 | 1948 | 400.7 | 692.2 | 146.7 | 20.8 | 596 | 287 | 201.6 | 244.0 |
| <i>p,p'</i> -DDE | 2.2 | 27 | 0.0 | 0.6 | 0.1 | 0.2 | 0.0 | 0.0 | 0.3 | 0.0 | 0.0 | 0.0 |
| Sum total DDT | 1.58 | 46.1 | 0.0 | 1.3 | 0.3 | 0.5 | 0.1 | 0.0 | 0.6 | 0.2 | 0.2 | 0.1 |
| Total PCB | 22.7 | 180 | 0.3 | 27.6 | 5.5 | 9.8 | 1.6 | 0.5 | 4.9 | 2.0 | 1.4 | 1.8 |
| Chemical | Guidelines | | Outer Bay 1991 (n = 14) | | | | | Outer Bay 2000/2001 (n = 13) | | | | |
| | Effects range low (ERL) | Effects range median (ERM) | Minimum | Maximum | Average | Std. Dev. | Median | Minimum | Maximum | Average | Std. Dev. | Median |
| Trace elements (ppm) | | | | | | | | | | | | |
| Arsenic | 8.2 | 70 | 5.0 | 20.5 | 12.1 | 3.6 | 11.8 | 2.0 | 15.0 | 10.4 | 2.8 | 10.0 |
| Cadmium | 1.2 | 9.6 | 0.0 | 0.6 | 0.2 | 0.1 | 0.2 | 0.0 | 0.3 | 0.2 | 0.1 | 0.2 |
| Chromium | 81 | 370 | 43.0 | 93.0 | 80.4 | 12.6 | 83.5 | 21.0 | 85.0 | 68.0 | 11.1 | 69.5 |
| Copper | 34 | 270 | 6.9 | 26.2 | 16.2 | 4.1 | 15.8 | 4.0 | 20.0 | 14.8 | 3.7 | 15.0 |
| Lead | 46.7 | 218 | 25.5 | 40.7 | 33.6 | 4.2 | 34.3 | 17.3 | 35.1 | 30.4 | 3.1 | 30.9 |

| | | | | | | | | | | | | |
|-------------------------|------|--------|------|------|-------|-------|-------|------|-------|------|-------|-------|
| Mercury | 0.15 | 0.71 | 0.05 | 0.14 | 0.09 | 0.03 | 0.09 | 0.00 | 0.10 | 0.06 | 0.02 | 0.06 |
| Nickel | 20.9 | 51.6 | 14.5 | 39.8 | 29.0 | 6.3 | 28.3 | 8.0 | 33.0 | 25.1 | 5.7 | 25.5 |
| Silver | 1 | 3.7 | 0.1 | 0.3 | 0.2 | 0.0 | 0.2 | 0.1 | 0.3 | 0.3 | 0.1 | 0.3 |
| Zinc | 150 | 410 | 43 | 109 | 81.9 | 14.6 | 82.0 | 22.0 | 99.0 | 77.0 | 14.7 | 81.5 |
| Organic compounds (ppb) | | | | | | | | | | | | |
| Acenaphthene | 16 | 500 | 2.0 | 5 | 3.0 | 1.0 | 2.6 | 0.1 | 4.6 | 2.8 | 1.1 | 2.6 |
| Acenaphthylene | 44 | 640 | 7.5 | 26 | 13.2 | 5.2 | 11.9 | 1.0 | 24.0 | 13.6 | 5.8 | 12.0 |
| Anthracene | 85.3 | 1100 | 10.8 | 41 | 17.3 | 7.9 | 13.9 | 1.2 | 23.0 | 15.0 | 5.3 | 15.0 |
| Fluorene | 19 | 540 | 5.3 | 14 | 7.5 | 2.4 | 6.5 | 0.6 | 9.3 | 6.3 | 1.9 | 6.1 |
| 2-Methyl naphthalene | 70 | 670 | 5.8 | 17 | 8.9 | 3.1 | 8.0 | 0.4 | 7.6 | 5.0 | 1.6 | 4.8 |
| Naphthalene | 160 | 2100 | 8.5 | 18 | 12.0 | 2.5 | 11.9 | 2.1 | 12.0 | 8.4 | 2.5 | 9.0 |
| Total LMW PAH | 552 | 3160 | 45 | 109 | 64.8 | 19.6 | 59.5 | 5.8 | 77.2 | 49.0 | 15.6 | 44.2 |
| Benz(a)anthracene | 261 | 1600 | 42 | 152 | 64.2 | 29.0 | 56.6 | 5.8 | 83.0 | 52.9 | 20.7 | 58.0 |
| Benzo(a)pyrene | 430 | 1600 | 49 | 196 | 85.7 | 39.1 | 74.5 | 4.5 | 88.0 | 62.9 | 22.5 | 68.0 |
| Chrysene | 384 | 2800 | 47 | 168 | 79.8 | 31.3 | 71.8 | 6.6 | 100 | 64.9 | 24.3 | 70.0 |
| Dibenzo(a,h)anthracene | 63.4 | 260 | 8 | 68 | 15.5 | 10.1 | 11.9 | 0.6 | 14 | 8.8 | 3.8 | 8.8 |
| Fluoranthene | 600 | 5100 | 91 | 239 | 131.9 | 39.7 | 122.7 | 11 | 150 | 106 | 36.4 | 120.0 |
| Pyrene | 665 | 2600 | 85 | 247 | 126.8 | 43.8 | 116.4 | 11 | 140 | 100 | 34.5 | 110.0 |
| Total HMW PAH | 1700 | 9600 | 524 | 1875 | 833.3 | 324.1 | 727.6 | 60 | 889 | 639 | 225.2 | 698.7 |
| Total PAH | 4022 | 44,792 | 569 | 1964 | 898.2 | 342.4 | 784.4 | 65 | 966 | 688 | 237.3 | 742.9 |
| p,p'-DDE | 2.2 | 27 | 0.5 | 1.2 | 0.7 | 0.2 | 0.7 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 |
| Sum total DDT | 1.58 | 46.1 | 1.1 | 3.4 | 1.7 | 0.6 | 1.7 | 0.0 | 455.5 | 0.9 | 0.5 | 1.1 |
| Total PCB | 22.7 | 180 | 5.8 | 26.2 | 15.4 | 5.9 | 15.5 | 0.7 | 23.9 | 9.5 | 6.5 | 7.9 |

data from the 1980s precludes trends analysis compared to the 1990s and 2000s data sets.

3.1. Total organic carbon (TOC)

The total organic carbon (TOC) and grain size are measured in sediments as descriptive properties of the sediment. Total organic carbon content of sediments may be related to the contaminant content or to the availability of the contaminant to organisms. Casco Bay sediments were characterized as fine-grained sediments with median TOC greater than or equal to 2%, except in the Cape Small area where sandy sediments with a median TOC concentration of 0.2% were found (Kennicutt et al., 1994). The shallow water sediments were generally coarser grained and had a median TOC concentration of 1.5%. Coarser grained sediment in the shallow water is expected since tidal and wave activity can transport the finer material away from shore. The available grain size data from all sources range from four fractions (gravel, sand, silt and clay) to two fractions (sand and silt/clay); we are limiting our discussions to these two fractions (and have converted data as appropriate) in order to incorporate the largest number of sites possible. Grain size was typically related to organic contaminant concentrations with higher concentrations associated with the finer grained (silt and clay) fraction. Many trace elements were also in higher abundance in silt and clay compared to sand. The frequency distribution for the two sampling periods indicated TOC is unchanged when the entire bay is considered (Wade and Sweet, 2005). The sand fraction or the silt and clay fraction did not exhibit any apparent trend between sampling periods. The geographic distribution of TOC and grain size was similar at most sites but there were some changes at specific sites (Fig. 3). This is likely due to the heterogeneity of the sediments.

3.2. Polycyclic aromatic hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons are one of the most widespread contaminants associated with the utilization of fossil fuels and related products. Polycyclic aromatic hydrocarbons are among the primary agents causing toxic effects attributed to petroleum exposure (Thomas et al., 2002; Klerks et al., 2004); although Barron et al. (1999) demonstrated that low aromatic content oil can be highly toxic. They are ubiquitous environmental contaminants being generated by natural combustion processes, oil seepage and anthropogenic inputs. Polynuclear aromatic hydrocarbons can enter the environment as a result of oil spills, ship traffic, urban run-off, wastewater and industrial discharges and by atmospheric deposition from vehicle exhaust and industrial stack emissions. The environmental concern regarding PAH is due to their carcinogenic and mutagenic potential (Thomas et al., 2002). These aromatic compounds, due to their low water solubility, tend to be associated with particles and are deposited in sediments. Thus, sediments represent an important PAH reservoir that may continue to be a source to organisms. Sediment and bivalve concentrations are normally higher in proximity to large

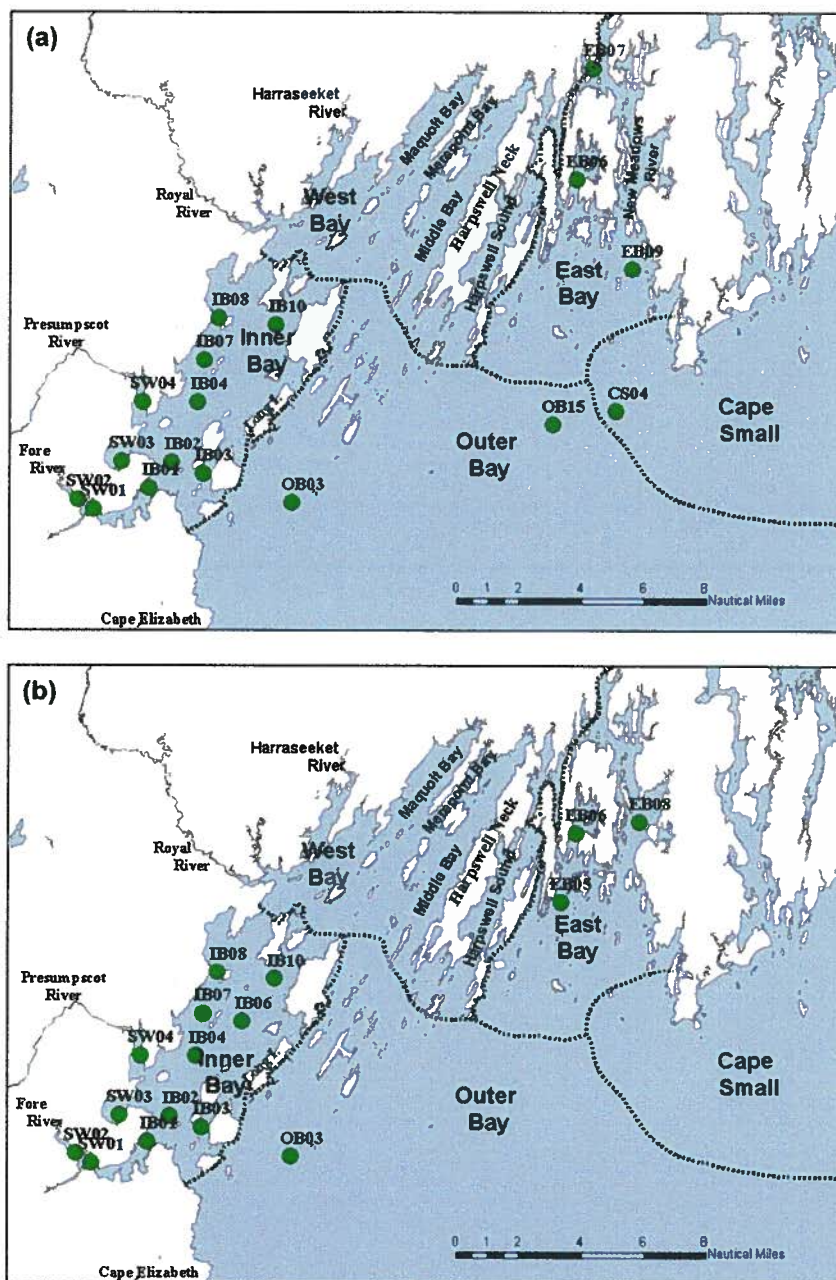


Fig. 2. Location of the highest 25% of (a) organic contaminants and (b) inorganic contaminants collected in 1991.

population centers (Jackson et al., 1994). Casco Bay has higher sediment PAH concentrations in near-shore sediments (Kennicutt et al., 1994). The intensity of hydrocarbon contamination generally decreases with increasing distance from areas of the highest population density. Localized sites of contamination are associated with cities, effluent outfalls, and spills. A recent study suggests atmospheric deposition is also a significant direct contributor of PAH to the Bay (Golomb et al., 2001). The predominance of high molecular weight PAH (HMW PAH) found in sediments adjacent to urban and industrialized locations in Casco Bay is indicative of pyrogenic sourced (i.e., car exhaust, urban run-off, etc.) material (Kennicutt et al., 1994).

The high PAH concentrations detected in Inner Bay sediments were similar to other contaminated estuaries (Macauley et al., 1994; USEPA, 1997), such as Hudson-Raritan Bay and Boston Harbor. Two sites in this region from the 1991 sampling, SW01 and SW02, had PAH sediment concentrations greater than the toxic effects response low (ERL), below which toxic effects are rarely found in marine benthic organisms, i.e., total PAH ≥ 4022 ppb (Long et al., 1995), while five sites (IB01, SW01, SW02, SW03, and IB08) from the 2000/2001 sampling had PAH sediment concentrations greater than the ERL. None of the sites from any of the samplings were above the toxic effects response median (ERM), above which toxic effects are frequently found (see Table 1).

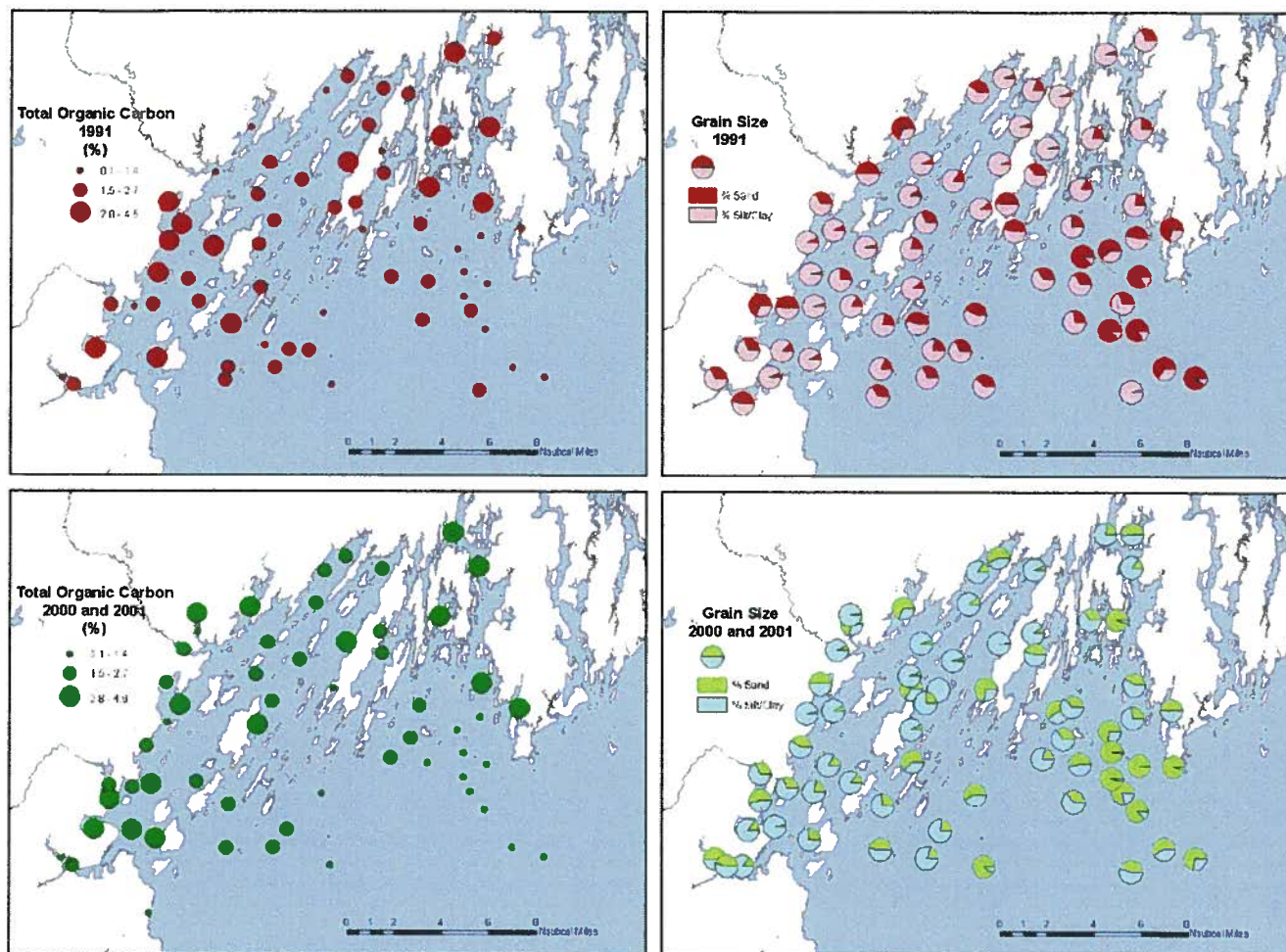


Fig. 3. Geographic distribution of total organic carbon and grain size from both sampling periods.

The mode of occurrence of PAH has been shown to vary widely depending on original source. Coal or soot associated combustion PAH are often tightly bound or occur in the interiors of particles. This mode of occurrence may render these PAH largely inert to organisms. In contrast, equivalent concentrations of liquid hydrocarbons such as oil or creosote induce more toxicological effects. Biological availability is important in determining whether a contaminant evokes a biological response. A majority of PAH detected in Casco Bay were combustion related (dominated by HMW PAH) and may be sequestered in fine particulates reducing the toxic potential. The remainder of the PAH were weathered residues of petroleum contributed by spills and run-off, based on the relative abundance of low molecular weight PAH (LMW PAH) and HMW PAH.

Evidence of toxic effects on organisms was apparent in the inner Fore River where the benthic (bottom-dwelling) infaunal community was altered and, at some sites, greatly reduced. Many of the organisms had oil on their parapodia (legs) (Doggett, DEP, 1989, personal communication). Mussels analyzed by the Casco Bay Estuary Project and Maine DEP indicated that, in general, PAH and other contaminants were more

elevated in the Portland Harbor area compared to the rest of the bay (Doggett, DEP, personal communication).

PAH concentrations in Casco Bay as a whole were very similar between 1991 and 2001. It is important to note that the relative percent difference (RPD) from replicate samples from the same site ranged from less than 10% to as high as 162% indicating the patchy distribution of PAH in the environment. This complicates detection of temporal or spatial trends. The frequency distributions for 1991 and 2000/2001 with ERL and ERM guidelines for total PAH, LMW PAH and HMW PAH are plotted in Fig. 4a–c. These plots have an “S” shaped curve indicating a normal distribution on a log scale. These curves have very similar distributions; if one sampling period had significantly different concentrations, the curves would be separated from one another. Aromatic hydrocarbon concentrations were consistently below the ERM guidelines, LMW PAH were below the ERL guidelines, with the exception of one station in 1991 (Inner Bay Station SW01), and HMW PAH were above the ERL for 15% and 20% of the stations from 1991 and 2001/2001, respectively. The geographical distributions of LMW PAH and HMW PAH, for the 1990s and 2000s, are very similar when plotted on a map of Casco Bay (Fig. 5).

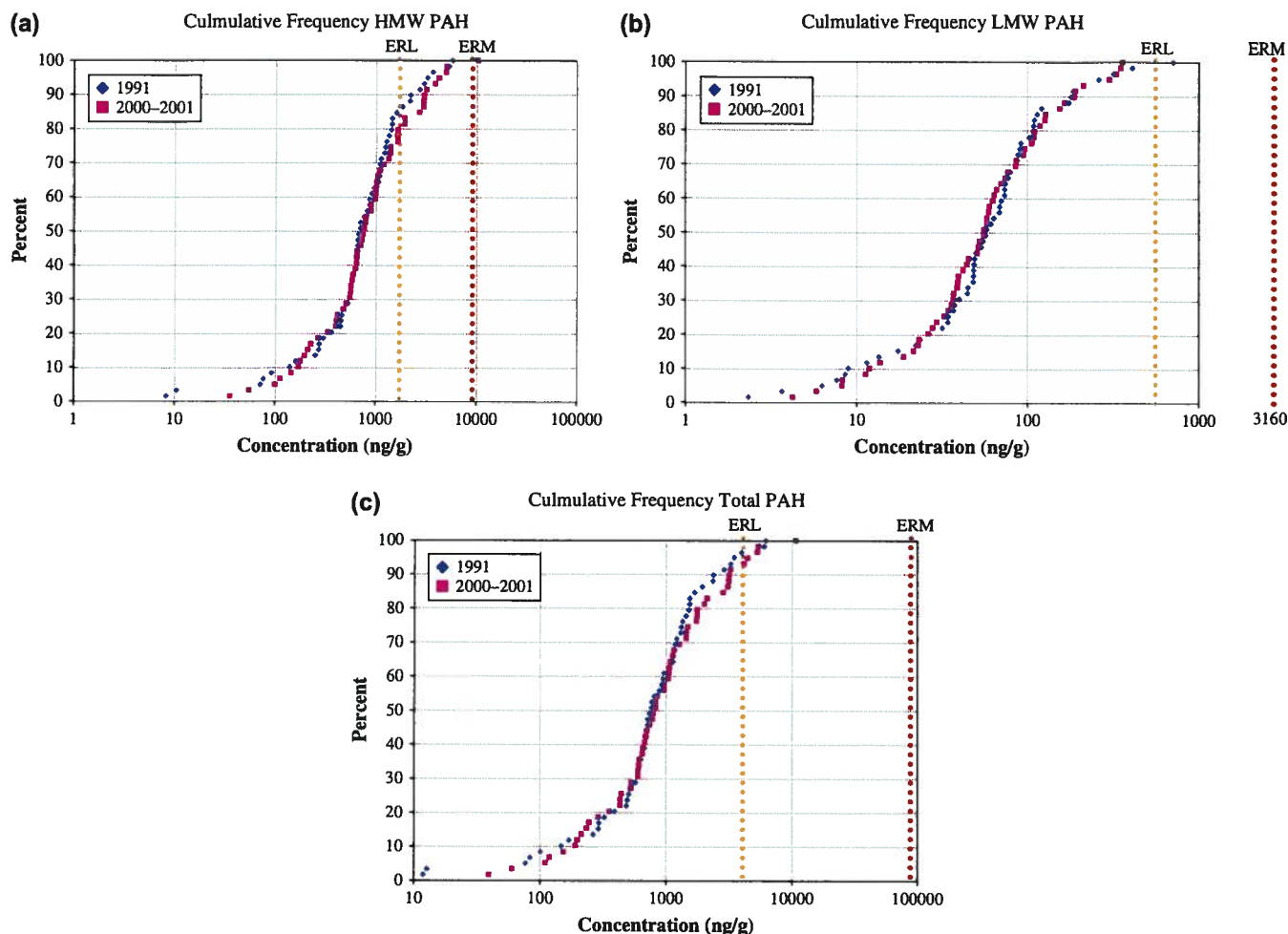


Fig. 4. Cumulative frequency distributions of (a) HMW PAH, (b) LMW PAH, (c) total PAH for both sampling periods with effects range low (ERL) and effects range median (ERM) guidelines plotted (Long et al., 1995).

3.3. Pesticides and polychlorinated biphenyls (PCB)

Organochlorine pesticides and PCB are ubiquitous environmental contaminants that are found in nature only due to anthropogenic activities as there are no known natural sources. Like PAH, pesticides and PCB enter ecosystems like Casco Bay from run-off and atmospheric deposition (Jarnberg et al., 1993). The organochlorine pesticides analyzed include aldrin, alpha-chlordane, DDT compounds, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, hexachlorobenzene, heptachlor, heptachlor epoxide, lindane, mirex, *trans*-nonachlor, and toxaphene. The organochlorine pesticides have been banned from use and PCB are restricted to sealed containers; therefore, it is expected that the concentrations of these contaminants will decrease with time. However many of these contaminants have long environmental half-lives, on the order of 10–20 years, and may continue to be added to the bay from run-off and atmospheric deposition. PCB concentrations above 180 ppb (dry weight) in sediments have been shown to elicit a median toxic response in some benthic organisms,

only one site was above this threshold, located in the Fore River (SW02, shallow water station 2, see Fig. 2a).

Generally, the concentrations of most pesticides were consistently low; the trend was for pesticides to decrease with time as shown for total pesticides in Fig. 6a. The total pesticide concentration was dominated by 2,4-dichlorodiphenyldichloroethane (DDD) and 4,4-DDD (110 ng/g and 330 ng/g, respectively). While none of the pesticides from both samplings were found at concentrations at or above the ERM, the number of locations at or above the ERL for total DDT decreased from roughly 59% to 34% from the 1990s to the 2000s, respectively (Fig. 6b). Individual PCB congener concentrations were also consistently low, with total PCB concentrations decreasing with time (Fig. 6c). The total PCB concentrations were all below the ERM, with concentrations at or above the ERL of roughly 20% and 15% for 1991 and 2000/2001, respectively. The PCB appears to be a mixture of several aroclors (e.g., 1242, 1254, 1260) with PCB 153 and PCB 138 as the predominant PCB congeners. Larsen et al. (1984) reported a mixture of aroclors 1242 and 1254

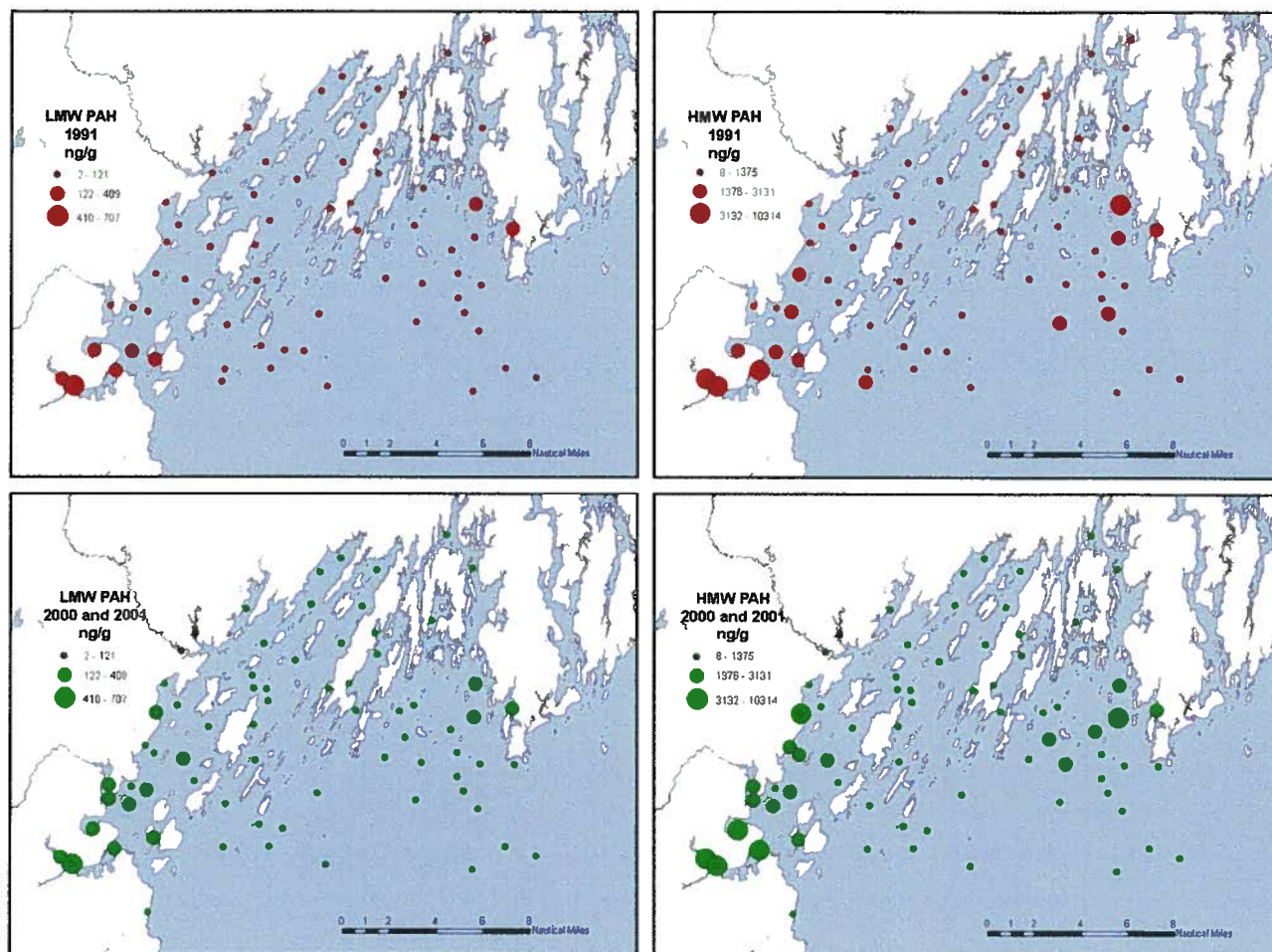


Fig. 5. Geographic distribution of HMW PAH and LMW PAH from both sampling periods.

for surficial sediments from stations located in Portland Harbor. While PCB congener patterns were similar throughout Casco Bay for both sampling periods, they were not identical. This may be the result of multiple inputs and different analytical techniques.

The geographical distributions of total DDT and PCB are shown in Fig. 7. Total DDT tend to be elevated in areas near shore and near Portland. The concentration of total DDT was lower in 2000/2001 especially in West Bay and Outer Bay. DDT concentrations in Casco Bay sediments were low compared to concentrations known to cause a median toxic response in most benthic organisms (Long et al., 1995) with the exception of one site, located off Cape Elizabeth that had the highest total pesticide concentration but was only sampled in 2000/2001 (Fig. 7). The highest concentrations of PCB were in the vicinity of Portland for both sampling periods, with the Fore River site (SW02) exhibiting a marked decrease between sampling periods.

3.4. Dioxins, furans, and planar PCB

Dioxins and furans are toxic unwanted by-products of industrial chlorination processes and waste incineration (Spiro

and Thomas, 1994). They have been called the most toxic man-made chemicals inadvertently released to the environment. Due to their low toxicity threshold the concentrations of dioxins and furans are measured at the pg/g or parts per trillion levels. The most toxic congeners of the dioxins and furans contain four (tetra) chlorines, 2,3,7,8-TCDF and 2,3,7,8-tetrachloro-*p*-dioxin (TCDD). The concentration of 2,3,7,8-TCDD was consistently low, less than 2 pg/g, for all samples from both samplings. There was no conclusive evidence that 2,3,7,8-TCDD concentrations have changed over the last decade.

It is anticipated that over the long term, dioxin/furan concentration in the environment will decrease in response to regulations lowering their production. The geographic distribution of dioxins and furans was similar to that of other contaminants. Fig. 8 shows the spatial distribution of total dioxins and total furans from both sampling periods. The spatial distributions of dioxins and furans, by chlorination level have been reported (Wade et al., 1997; Wade and Sweet, 2005). In general, the higher concentrations were found in the vicinity of Portland and other near-shore highly populated and industrialized areas. The concentrations were highest near potential input sources. For example, PCDD/PCDF and especially TCDD/TCDF had

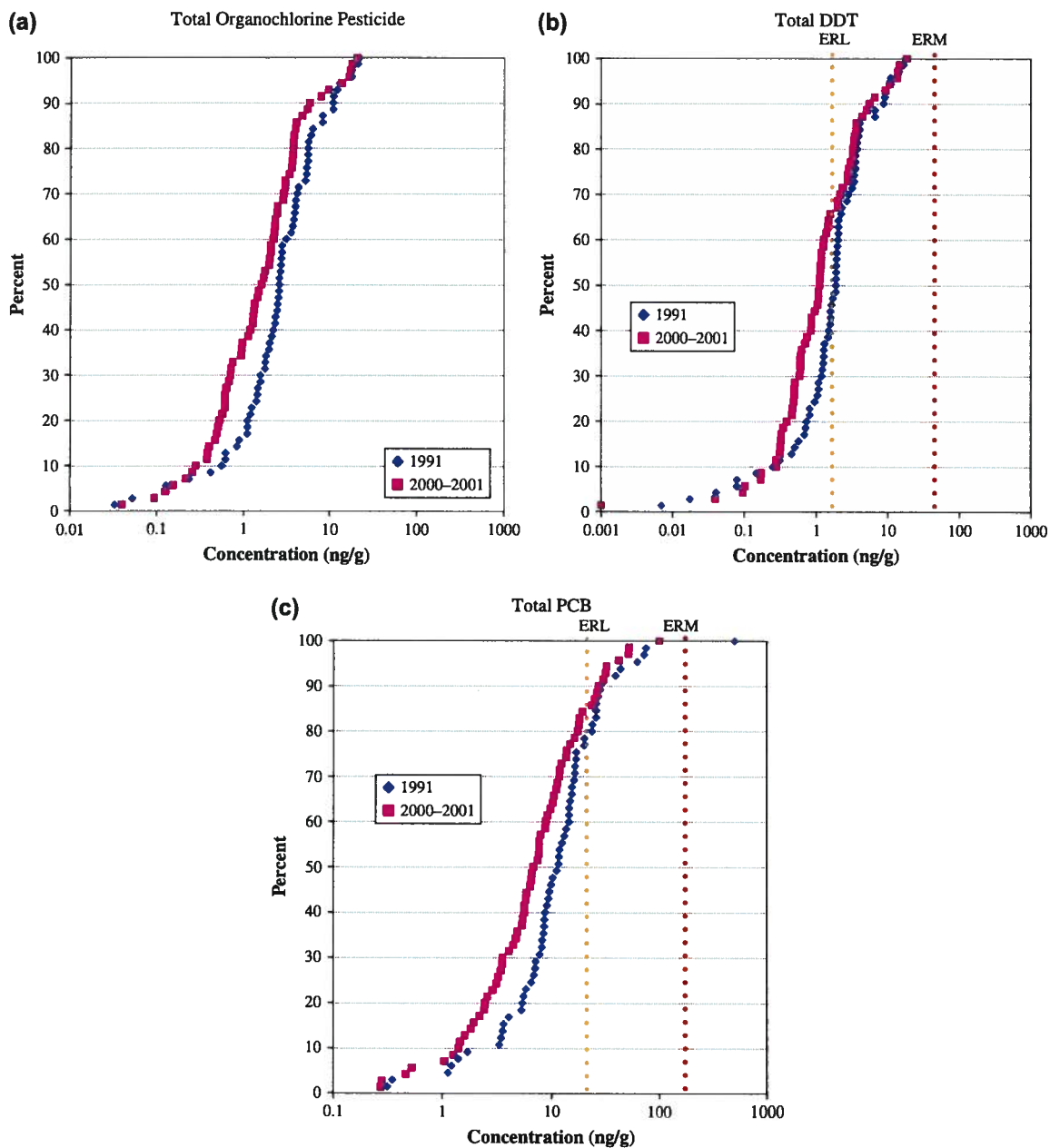


Fig. 6. Frequency distribution plots for (a) total pesticides, (b) total DDT, and (c) total PCB from both sampling periods with effects range low (ERL) and effects range median (ERM) guidelines plotted (Long et al., 1995).

higher concentrations near the Presumpscot River sites, 10 miles downstream of a pulp and paper mill. There are also exceptions, for example the higher PCDD/PCDF concentrations in East Bay are not near known point sources, but may be the result of transport into the bay from sources in the Kennebec/Androscoggin River or localized combustion sources (e.g., until recently, Harpswell operated an incinerator). While the geographic distributions of dioxins and furans were similar, it is apparent that the concentrations in the sediments at many sites have decreased between 1994 and 2001. The presence of elevated concentrations of contaminants in sediments represents a potential source of contaminants to organisms, which may

lead to adverse environmental and/or human health effects. For example, the detection of TCDD and TCDF in lobster tomalley has resulted in a human consumption advisory for Casco Bay (Mower, 1994). The concentrations of PCDD/PCDF and planar PCB found in Casco Bay sediments are in the range expected when compared to similar estuarine areas (Finley et al., 1990; Clarke et al., 1994; Fiedler, 1994).

Planar PCB are minor components of the Aroclors used in the United States, but they have characteristic toxicities similar to the dioxins and furans. Planar PCB 77 concentrations did not significantly differ between sampling periods (Wade and Sweet, 2005). The concentration of PCB 126 decreased

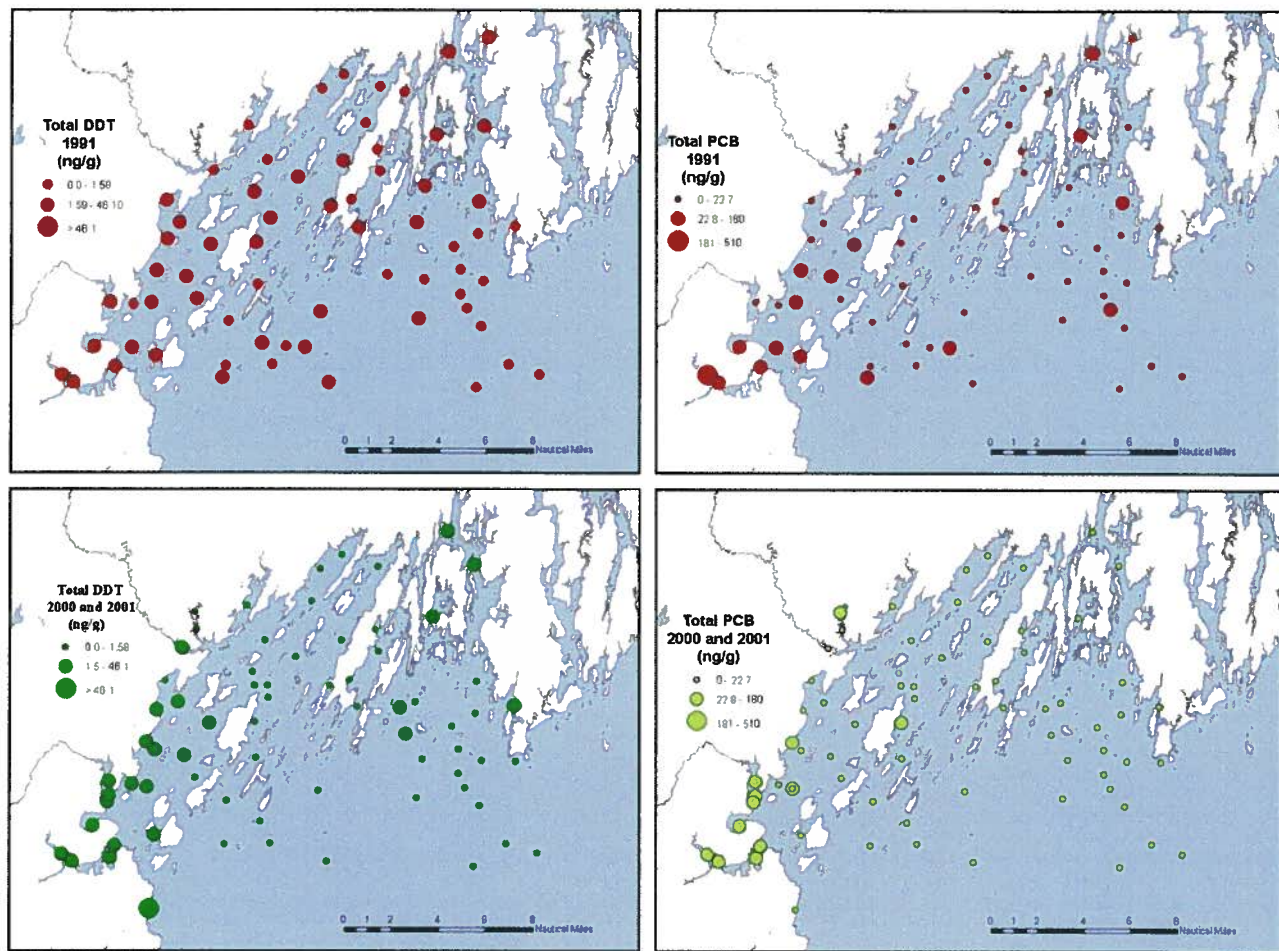


Fig. 7. Geographic distribution of total DDT and total PCB from both sampling periods.

slightly between sampling periods. There were not enough samples where planar PCB 169 was detected to observe any trends. Planar PCB 81 was not reported for 1994, but was likely present at concentrations lower than PCB 77. The geographic distribution of planar PCB was similar to that of other contaminants (Wade and Sweet, 2005). The higher concentrations were found in the vicinity of Portland and other near-shore highly populated and industrialized areas. While the geographic distributions of concentrations were similar, it is apparent that the concentrations at many sites have decreased between 1994 and 2001.

3.5. Butyltin compounds

Butyltins found in the environment include tetrabutyltin (4BT), tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT). The source of tetrabutyltin in sediment is usually from paint chips where 4BT is a minor component. TBT is the active ingredient used in marine paints that prevent fouling of marine vessel bottoms by the growth of barnacles and other organisms on solid surfaces immersed in sea water (Laughlin et al., 1984; Wade et al., 1991). Fouling increases roughness of the vessel surface increasing the fuel consumption. Sediment

sites near boating activities are expected to contain the highest concentrations of TBT. Dibutyltin and monobutyltin are minor components of anti-fouling paints and are also degradation products of TBT. Dibutyltin is also used as a stabilizer for polyvinylchloride plastics and as a catalyst in the production of polyurethane foams (Laughlin et al., 1984; Muller et al., 1989). Only limited butyltin data were available for Casco Bay before the 1994 study. In 1990, sediments from the Fore River were sampled and analyzed for butyltins. The concentration of TBT ranged from 24 ng Sn/g to 693 ng Sn/g in the surficial sediments. Dibutyltin concentrations ranged from 15 ng Sn/g to 453 ng Sn/g. The highest concentrations of butyltins were observed in the sediments collected near shipyards (Ozbal, 1992). Three individual butyltin species TBT, MBT and DBT were analyzed during both periods, however; the concentrations of 4BT were not reported in 2001. Detectable concentrations of 4BT were only found at 8 of 31 sites in 1991 and were present at low concentrations (less than 0.7 ng Sn/g). Tributyltin has generally decreased with time; over half of the sites that had detectable TBT concentrations in 1994 were below the limits of detection in 2000/2001. The three sites where TBT did not decrease were collected from the Fore River, where many commercial vessels, including oil tankers,

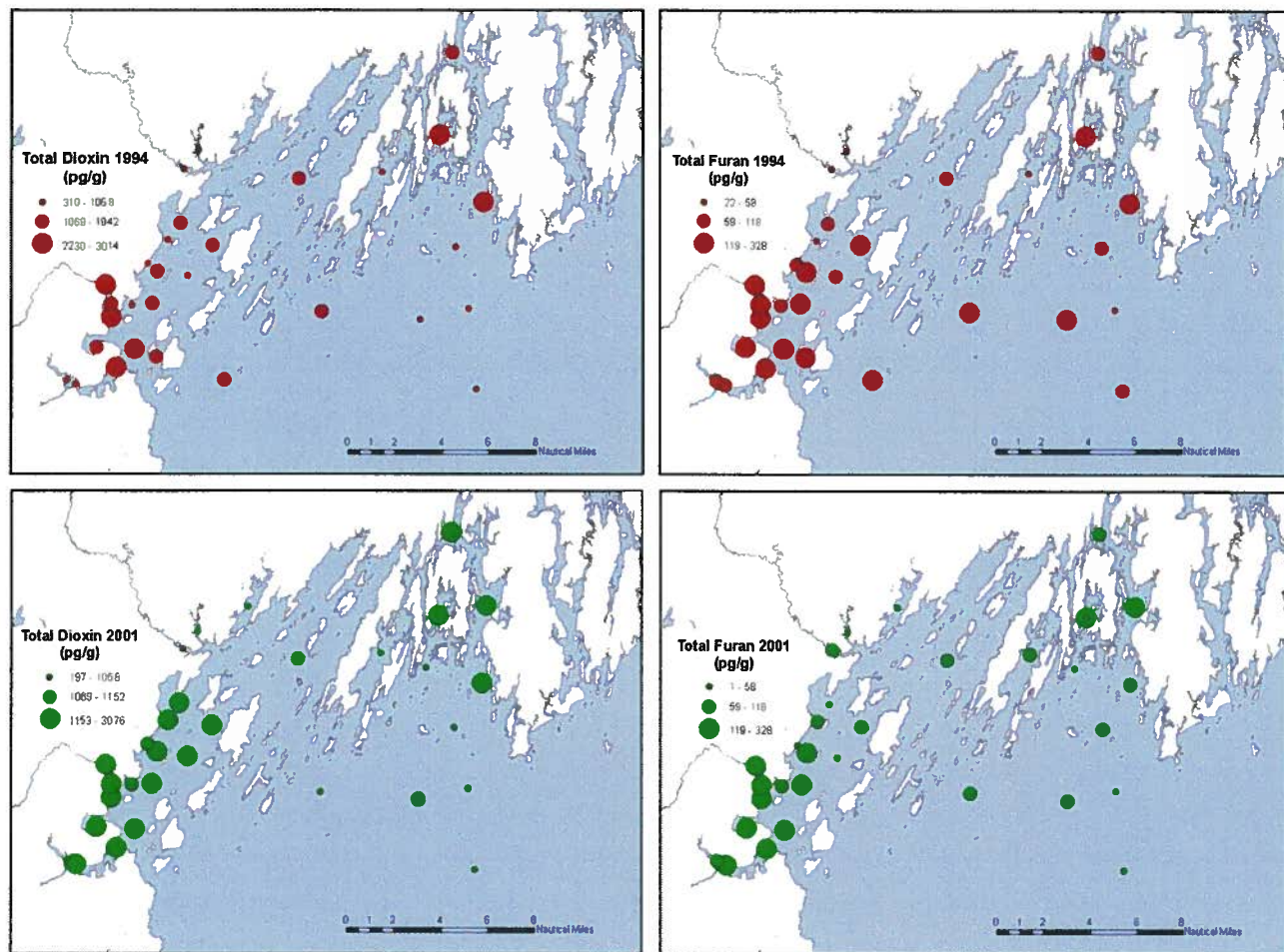


Fig. 8. Geographic distribution of total dioxins and total furans from both sampling periods.

container ships, cruise ships and large fishing vessels are anchored. The interpretation of DBT and MBT results is complicated by different method detection limits (MDL) between the 1994 and 2000/2001 sampling periods and the low concentrations present in the sediments. Toxicity guidelines for TBT have been reported based on data from Puget Sound (USEPA, 1996) using TOC normalized TBT concentrations resulting in screening values of $515 \mu\text{g Sn/kg TOC}$ and $7204 \mu\text{g Sn/kg TOC}$ used as approximations for the ERL and ERM, respectively. Fig. 9 shows the TOC normalized TBT from the 1990s and 2000s. There were no concentrations approaching the ERM, while the percentage of stations at or exceeding the ERL was roughly 75% for 1994 and 30% for 2000/2001. The geographic distributions of total butyltin and TBT are shown in Fig. 10. The distributions indicate a rather dramatic decrease in total butyltin and tributyltin between the two sampling periods. The rapid decline of butyltins is consistent with bivalve studies for US coastal areas (Jackson et al., 1998).

3.6. Trace elements

Trace elements are a natural component of sediments. Their concentrations can be increased by the activities of humans

and then become a pollution concern. Some trace elements are required for the healthy growth of organisms, but concentrations exceeding thresholds can be toxic. Metal concentrations present in Casco Bay sediments were comparable to those in uncontaminated sediments. The concentrations of

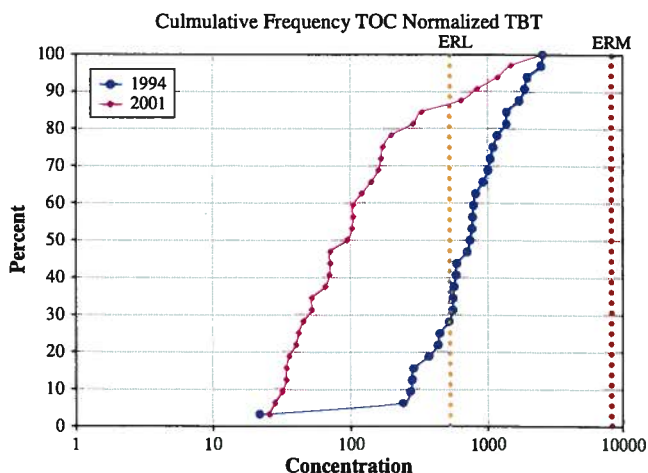


Fig. 9. TOC normalized total BT from both sampling periods.

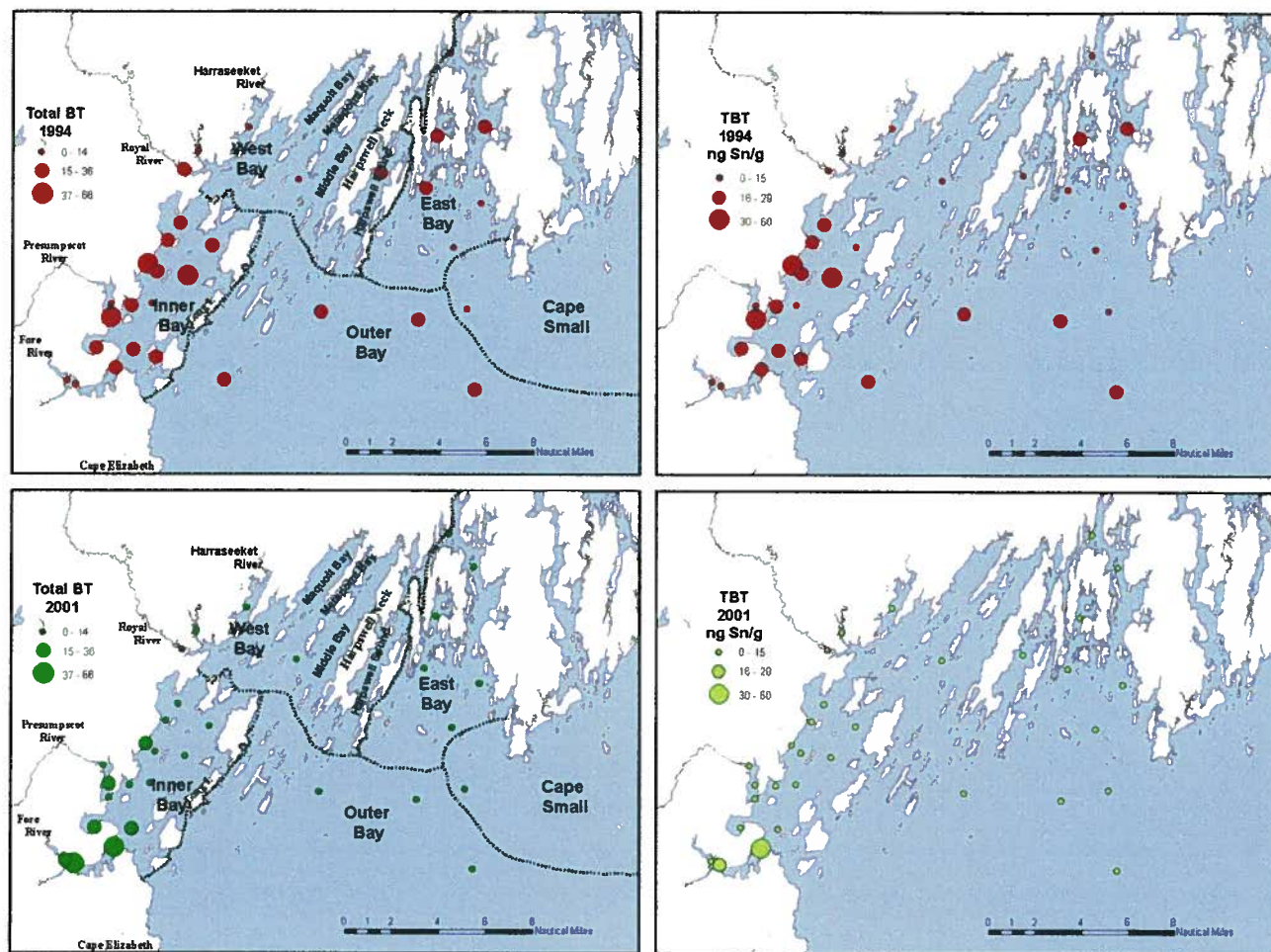


Fig. 10. Geographic distribution of total BT and TBT from both sampling periods.

trace metals known to elicit toxic biological responses are much higher than the concentrations present in Casco Bay sediments. Ag, Cd, Pb, Zn, and Hg concentrations suggest anthropogenic inputs have occurred at a few locations. However, even the few elevated trace metal concentrations in Casco Bay were much lower than those reported for highly contaminated sediments from Hudson-Raritan, Long Island Sound, Boston Harbor, and urban water bodies (Kennicutt et al., 1994). It is unlikely that the trace metals present in the Casco Bay sediments result in measurable toxic effects to marine organisms. All of the trace elements were below the ERM, throughout Casco Bay (Table 1) and zinc was below the ERL throughout Casco Bay. Arsenic concentrations were above the ERL for 72% and for 70% of the sites in the 1990s and 2000s, respectively. Cadmium levels were above the ERL for 2% and for 2.5% of the sites in the 1990s and 2000s, respectively. Mercury levels were above the ERL for 28% and for 29% of the sites in the 1990s and 2000s, respectively. Copper concentrations were above the ERL for 3% and for 10% of the sites in the 1990s and 2000s, respectively. Lead concentrations were above the ERL for 10% and for 20% of the sites in the 1990s and 2000s, respectively. Silver was present at all locations in low concentrations below the ERL with

the exception of one station in the Inner Bay (IB02) where the concentration was at the ERL (1 ppm). There were decreasing concentrations at the majority of sites for chromium, nickel, and selenium. Chromium was above the ERL for 50% and for 25% of the sites in the 1990s and 2000s, respectively. Nickel was above the ERL for 77% and for 65% of the sites in the 1990s and 2000s, respectively.

The geographical distributions of iron normalized trace elements are, in general, slightly elevated in the vicinity of Portland and at many near-shore sites (Wade and Sweet, 2005). This is due to the overprinting of small anthropogenic trace element concentrations on the natural concentrations from the crustal material of these sediments. This geographic pattern was similar to that of other contaminants that have sources in highly populated and industrial areas.

4. Summary and conclusions

Contaminant concentrations of sediment samples collected approximately 10 years apart were compared to establish the current status of contaminant concentrations in Casco Bay and to determine the spatial and temporal status and trends as they relate to contaminant concentrations. This process is

complicated by the potential of re-suspension of older sediment back to the surface, the non-homogeneity of sediments, low concentrations for some analytes and variability of different analytical methods. The top 2 cm of sediments can reflect different time periods for different locations that have significantly different sedimentation rates. The sediments can also be re-disturbed by natural processes (e.g., storms). Concentrations of many contaminants were low and the lower the measured concentrations of analytes, the greater the uncertainty of their concentrations. It is also important to note that differences were normally of less than a factor of 2 increase or decrease in concentration. However, with the large number of sites analyzed, the overall changes in the concentrations observed are given more credibility. In spite of these complications several observations are noteworthy.

As was expected most of the contaminants were either static or tending to decreasing concentration as a function of time. In general, for PAH there was no significant change between 1991 and 2000/2001. There were individual PAH that do suggest increasing concentrations (e.g., benzo(b)fluoranthene) as well as decreasing concentrations (e.g., 2,6-dimethylnaphthalene) from 1991 to 2000/2001, but most PAH do not indicate any differences. It is not unreasonable that PAH concentrations in sediments may be increasing at selected sites and decreasing at others. There is a continuing increased use of fossil fuels that is balanced by increasing regulatory controls that lower PAH inputs as well as small scale oil spills at random sites. Total pesticides, total PCB, as well as 4,4-dichlorodiphenyldichloroethylene (DDE), 4,4-DDD and total DDT indicate a decreasing trend. There were decreasing concentrations at the majority of sites for chromium, nickel, and selenium and no apparent trend for arsenic, cadmium, mercury, copper, lead, silver, and zinc. Tributyltin and total butyltin are trending toward lower concentrations. Dioxins/furans do not indicate a significant change between sampling periods. The planar PCB indicates no change (PCB 77) or decreasing concentrations (PCB 126). The geographic distribution of sediment contaminants was similar to that of mussel tissue reported by the Casco Bay Estuary Project and Maine DEP. Most contaminants in Casco Bay were found at relatively low concentrations, are decreasing, and are not at concentrations that are expected to adversely affect the biota.

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