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The chemical response of particle-associated contaminants in aquatic sediments to urbanization in New England, U.S.A.

A.T. Chalmers [a,*], P.C. Van Metre [b], E. Callender [c]

[a] U.S. Geological Survey, P.O. Box 628, Montpelier, VT 05601, USA
[b] U.S. Geological Survey, 8027 Exchange Drive, Austin, TX 78754-4733, USA
[c] 2 Schumann Rd., Westerly, RI 02891, USA

Abstract

Relations between urbanization and particle-associated contaminants in New England were evaluated using a combination of samples from sediment cores, streambed sediments, and suspended stream sediments. Concentrations of PAHs, PCBs, DDT, and seven trace metals (Cd, Cr, Cu, Hg, Ni, Pb, Zn) were correlated strongly with urbanization, with the strongest relations to percentage commercial, industrial, and transportation (CIT) land use. Average PAH and metal concentrations in the most urbanized watersheds were approximately 30 and 6 times the reference concentrations, respectively, in remote, undeveloped watersheds. One-quarter to one-half of sampling sites had concentrations of PAHs, Cu, Pb, or Zn above the probable effects concentration, a set of sediment quality guidelines for adverse effects to aquatic biota, and sediments were predicted to be toxic, on average, when CIT land use exceeded about 10%. Trends in metals in cores from urban watersheds were dominantly downward, whereas trends in PAHs in a suburban watershed were upward. A regional atmospheric-fallout gradient was indicated by as much as order-of-magnitude-greater concentrations and accumulation rates of contaminants in cores from an undeveloped reference lake in Boston compared to those from remote reference watersheds. Contaminant accumulation rates in the lakes with urbanization in their watersheds, however, were 1–3 orders of magnitude greater than those of reference lakes, which indicate the dominance of local sources and fluvial transport of contaminants to urban lakes. These analyses demonstrate the magnitude of urban contamination of aquatic

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* Corresponding author. Tel.: +1 802 828 4511; fax: +1 802 828 4465.
  E-mail address: chalmers@usgs.gov (A.T. Chalmers).

systems and air sheds, and suggest that, despite reductions in contaminant emissions in urban settings, streams and lakes will decline in quality as urbanization of their watersheds takes place.

1. Introduction

Elevated concentrations of particle-associated contaminants (PACs), including metals and persistent organic compounds, often are associated with urban areas (Lopes et al., 1997; Rice, 1999; Wong et al., 2000). The magnitude of changes in concentrations and the relative importance of transport pathways of PACs across different types and intensities of urban land use, however, are not well known. Urban sources of PACs to aquatic environments have both atmospheric and fluvial pathways. Sources of polycyclic aromatic hydrocarbons (PAHs) and trace metals with atmospheric pathways include fossil fuel combustion, waste incineration, and industrial emissions from plating, smelting, and refining (Christensen et al., 1993; Nriagu, 1996). Volatilization of these contaminants and chlorinated hydrocarbons from soils and urban surfaces also contributes to urban air pollution (Gingrich and Diamond, 2001). Sources with fluvial pathways to aquatic environments include wastewater discharges, releases of contaminants by various means to the land surface (e.g. pesticide use, disposal of waste, spills), wear of infrastructure (e.g. asphalt roads, parking-lot sealants, roofing materials, galvanized metals), and erosion of historically contaminated soils. With the exception of wastewater discharges, these sources are transported to aquatic systems primarily by storm runoff. Additionally, atmospheric fallout on the watershed can be transported to aquatic environments by runoff.

Urban and industrial development in New England, U.S.A., has a long history. The Boston and Providence metropolitan areas are recognized as the birthplace of the American industrial revolution from the late 1700s to early 1900s. During this early industrial period air or water-quality regulations were minimal; most industrial and sewage wastes were discharged directly to the air and to rivers, lakes, and harbors. As a result, extensive contamination occurred in many streams and lakes from textile dyes, metal plating, and machine operations (Shanahan, 1994), and chemical and leather industries (Spliethoff and Hemond, 1996). The effects of the early industrial period have been seen in sediment cores. Rapid increases in the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) (Spliethoff and Hemond, 1996), and PAHs (Gschwend and Hites, 1981) were found in sediment cores at depths corresponding to periods of intense industrial activity of the early 1900s in the Boston and Providence metropolitan areas. Also during this early industrial period, a large number of dams were built for operating mills. At its peak, the Blackstone River (in the Providence and Boston metropolitan areas) had an average of one dam every mile (Shanahan, 1994). Contaminants have accumulated in fine sediments behind impoundments in the region and remain in place today (Shanahan, 1994; Spliethoff and Hemond, 1996). Resuspension of these contaminated sediments during high flows, dredging, or removal of dams remains a major water-quality concern for the area (Rhode Island Department of Environmental Management, Division of Water Resources, 1994; Massachusetts Department of Environmental Protection, Division of Water Pollution Control and Office of Watershed Management, 1995). As industrial emissions and point sources have come under stricter controls in recent decades, nonpoint sources of metals (Callender and Rice, 2000) and PAHs (Van Metre et al., 2000) have gained attention.

This study investigated concentrations and accumulation rates of PACs in aquatic sediments in relation to urbanization in New England. Three different sediment media were sampled: bottom sediments from streams, suspended sediments in streams, and sediment cores from lakes and reservoirs (hereinafter, referred to as lakes except where the distinction is warranted). The study area extends from the Providence, RI, and Boston, MA, metropolitan areas in the south to central New Hampshire and western Maine in the north (Fig. 1). The population density of the study area ranges from less than 10 people/km^2 in the north to more than 20,000 people/km^2 in the metropolitan areas in the south. The study was conducted as a part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) program (Robinson et al., 2004).
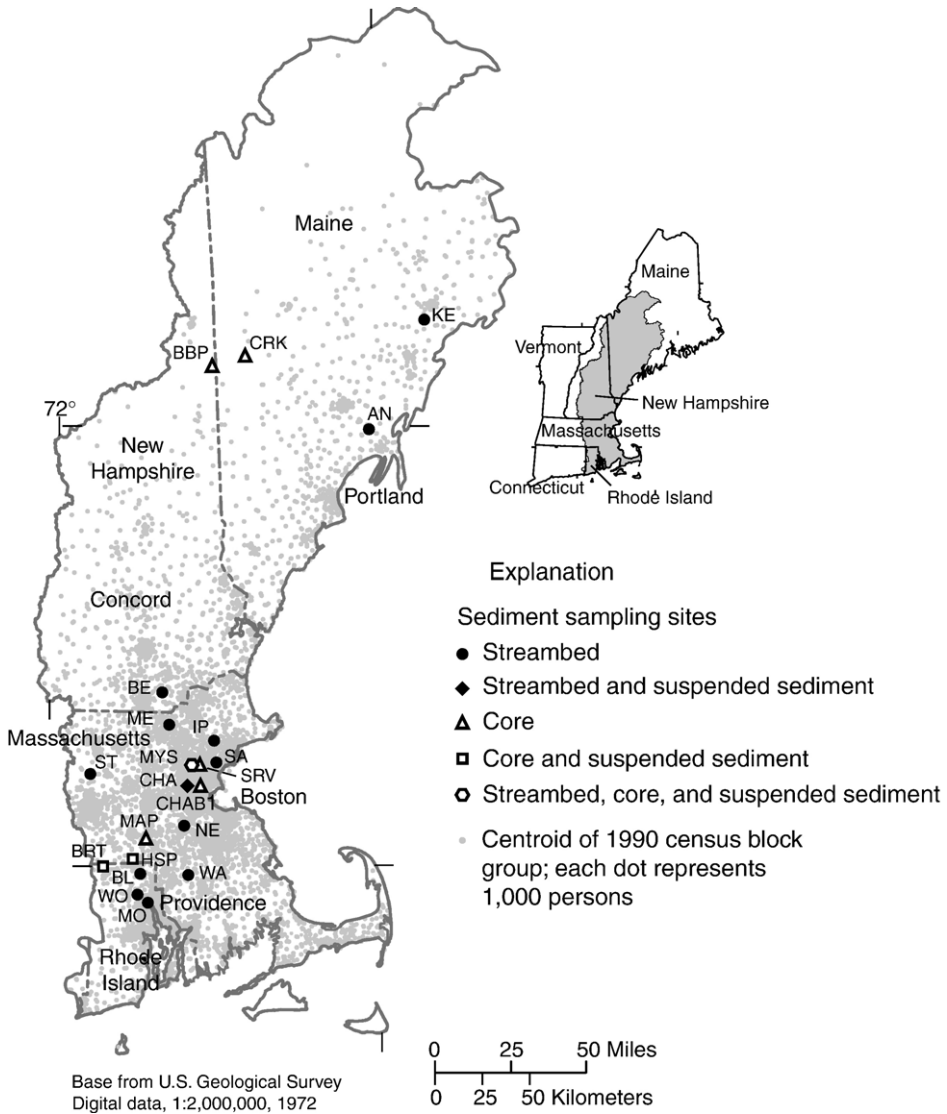

Fig. 1. Study area and locations of sampling sites. Site codes are in Table 1. The study area is the New England Coastal Basins study unit of the USGS National Water-Quality Assessment Program.

2. Methods

Twenty-one sites were selected along an urban land-use gradient, in watersheds having from 0% to 97% urban land use, from Maine to Rhode Island (Fig. 1 and Table 1). Data were collected along this urban gradient to describe PAC occurrence, trends, and sources in streams and lakes in relation to urbanization. Occurrence was indicated by concentrations of PACs in suspended sediments and recently deposited streamed and lake sediment (top 0–3 cm of surficial material in streams or core samples age-dated 1990 and younger). Trends were indicated by concentration profiles in age-dated sediment cores. Sources were implied by correlations of all sediment samples with different urban land uses and comparisons of contaminant mass accumulation rates (MARs) among coring sites. Coring sites without anthropogenic contaminant sources in the watershed, with the exception of long-range fallout, were selected as atmospheric reference sites (in italic) (*BRT, SRV, BBP,* and *CRK*). Other coring sites were selected to represent recently urbanizing (suburban, in bold) watersheds (**MAP** and **HSP**) and older, dense urban watersheds (MYS and CHA). Land use (Table 1) was calculated using the "sediment" contributing watershed, an area that excludes areas above impoundments upstream from the sampling site if those impoundments were considered large enough to be efficient sediment traps. In most cases, the sediment contributing area included the entire watershed; only CHAB1, CHA, **BL**, **SA**, **WO**, and

Table 1
Site characteristics

Map ID	Site type	Site name	Samples collected	Land-use			Pop density (people/ km²)
				Urban	CIT	Res	
MYS	Urban	Upper Mystic Lake at Winchester, MA	BS, C, SS	91	31	60	1195
CHAB1	Urban	Charles River at Boston, MA	C	96	29	67	3420
CHA	Urban	Charles River at Watertown, MA	BS, SS	97	26	71	1802
MO	Urban	Moshassuck River at Providence, RI	BS	58	22	37	1453
BL	**Suburban**	**Blackstone River at Manville, RI**	**BS**	**38**	**10**	**27**	**517**
SA	**Suburban**	**Saugus River at Saugus, MA**	**BS**	**77**	**9.5**	**68**	**1129**
IP	**Suburban**	**Ipswich River at South Middleton, MA**	**BS**	**64**	**9.1**	**54**	**481**
WO	**Suburban**	**Woonasquatucket River at Centerdale, RI**	**BS**	**63**	**8.8**	**54**	**531**
NE	**Suburban**	**Neponset River at Norwood, MA**	**BS**	**45**	**6.5**	**39**	**490**
MAP	**Suburban**	**Charles River at North Bellingham, MA**	**C**	**42**	**6.0**	**35**	**522**
BE	**Suburban**	**Beaver Brook at North Pelham, NH**	**BS**	**34**	**5.4**	**28**	**349**
WA	**Suburban**	**Wading River near Norton, MA**	**BS**	**19**	**4.4**	**14**	**226**
ME	**Suburban**	**Merrimack River at Lowell, MA**	**BS**	**11**	**2.8**	**8**	**119**
HSP	**Suburban**	**Upper Harris Pond near Blackstone, MA**	**C, SS**	**20**	**2.0**	**18**	**237**
AN	*Rural*	*Androscoggin River near Lisbon Falls, ME*	*BS*	*1.9*	*0.54*	*1.3*	*19*
BRT	*Rural*	*Big Round Top Pond at Round Top, RI*	*C, SS*	*2.2*	*0.50*	*1.7*	*51*
KE	*Rural*	*Kennebec River at North Sidney, ME*	*BS*	*1.2*	*0.45*	*0.7*	*10*
ST	*Rural*	*Stillwater River near Sterling, MA*	*BS*	*1.8*	*0.40*	*1.4*	*62*
SRV	*Rural*	*South Reservoir at Winchester, MA*	*C*	*0.6*	*0.00*	*0.6*	*0*
CRK	*Rural*	*Crocker Pond near Bethel, ME*	*C*	*0.0*	*0.00*	*0.0*	*4*
BBP	*Rural*	*Basin Brook Pond near Gilead, ME*	*C*	*0.0*	*0.00*	*0.0*	*4*

Types of samples collected include streambed sediment (BS), sediment cores (C), and suspended sediment (SS).
Sites are characterized by population density (Pop density) and percentages of urban land uses: total urban (Urban); commercial, industrial and transportation (CIT); and residential (Res).
Sites defined as urban (CIT>20) are in non-bold, non-italic, suburban (CIT 1–10) in bold, and rural (includes reference coring sites) (CIT<1) in italic. Sites are ordered from highest to lowest % CIT land use.

WA had impoundments above the sampling site that were large enough to be considered sediment traps.

2.1. Sample collection

Three types of sediment samples were collected: surficial streambed sediments, sediment cores, and suspended sediments. Streambed-sediment samples were collected from the top 2–3 cm of submerged sediments in depositional areas during low-flow conditions following NAWQA program protocols (Shelton and Capel, 1994). Each sample is a composite of about 10 grab samples that are combined and wet-sieved in the field (2-mm sieve for organic-compound sample and 63-μm sieve for major and trace element sample) prior to analysis. Samples were chilled and shipped wet to the laboratory.

Sediment cores were collected from areas of lakes and reservoirs thought to be continuously depositional and unlikely to have been disturbed, following the approach of Van Metre et al. (2004). Sampling locations typically were in the deepest part of the lake or reservoir. Cores were collected using a 14-cm square box corer or a 6.7-cm diameter gravity corer. Cores were vertically extruded and sectioned on site into 0.5-cm or 1-cm intervals in most cases for analysis of major and trace elements, radionuclides, and organic compounds. Samples for analysis of organic compounds were chilled and shipped to the laboratory. Samples for other analyses were weighed, freeze-dried, weighed again, ground to a powder, and shipped to the laboratory. Wet and dry weights of known volumes of sediment were used to calculate porosity and density of solids.

Suspended-sediment samples were collected in 200-l PTFE-lined plastic drums using automatic samplers. Samples were a composite of subsamples collected over the duration of a storm. Samples were processed according to the methods of Mahler and Van Metre (2003). Organic-compound samples were filtered using a 298-mm diameter stainless steel plate filter with 0.45-μm PTFE filter, and major- and trace-element samples were filtered using a 145-mm acrylic filter holder with 0.45-μm PTFE filter. Once clogged, the filter was placed in a sealable plastic bag with a few milliliters of distilled water and massaged until all the sediment was removed from the filter and was suspended in the small volume of water. Samples for analysis of organic compounds were placed in baked-glass containers and shipped chilled to the laboratory. Samples for analyses of major and trace elements were freeze-dried and ground to a power prior to shipment to the laboratory. Samples for determination of suspended-sediment concentrations were collected before and after each sample.

2.2. Chemical analyses

Streambed- and suspended-sediment samples analyzed for major and trace elements were completely digested using a mixture of hydrochloric–nitric–perchloric–hydrofluoric acids and analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) (Briggs and Meier, 2002). Sediment core samples analyzed for major and trace elements were completely digested using nitric–hydrofluoric acids in microwave pressure vessels and analyzed by inductively coupled plasma–atomic emission spectrometry (ICP/AES) (Arbogast, 1996) and by graphite furnace atomic adsorption spectrometry (GF/AAS) (As and Cd, only) (Aruscavage and Crock, 1987). Mercury (Hg) in all samples was analyzed by cold vapor atomic absorption spectrometry (Arbogast, 1996).

Streambed-sediment samples analyzed for chlorinated hydrocarbons and PAHs were extracted, isolated, and analyzed using the procedures of Foreman et al. (1995) and Furlong

et al. (1996). Core and suspended-sediment samples were analyzed for chlorinated hydrocarbons and PAHs by modified versions of the same methods (Noriega et al., 2004; Olson et al., 2004). In brief, sediment was extracted overnight with dichloromethane in a Soxhlet apparatus and split into two aliquots. The first aliquot was analyzed for PAHs and alkyl–PAHs by capillary–column gas chromatography with detection by mass spectrometry. The second aliquot was analyzed for chlorinated hydrocarbons by dual capillary–column gas chromatography with electron capture detection. $\sum$PAH reported here is the sum of 12 of the 13 PAHs (1-methyl naphthalene was not analyzed) used to represent total PAH in the consensus-based sediment quality guidelines (Ingersoll et al., 2000). PCBs in streambed- and suspended-sediment samples were quantified as total PCBs. PCBs in core samples were quantified as Aroclor equivalents 1016/1242, 1254, and 1260. The former and the sum of the latter are reported here as $\sum$PCB. $\sum$DDT reported here is the sum of p,p'-DDT, p,p'-DDD, and p,p'-DDE. In computing sums, non-detections were treated as zeros.

Cesium-137 (^{137}Cs) activity was measured by counting freeze-dried sediments in fixed-geometry with a high-resolution, intrinsic germanium detector gamma-spectrometer (Robbins and Edgington, 1976). Activity concentrations of lead-210 (^{210}Pb) and radium-226 (^{226}Ra) were measured by high-precision gamma-ray spectrometry (Baskaran and Naidu, 1994).

Quality assurance for major and trace element analyses was provided by analyzing several standard reference materials (SRMs), an environmental duplicate, and a blank sample with each batch of as many as 20 samples. The two methods used for elements both performed well, on the basis of analyses of four of the same SRMs. Median relative percent difference (RPD) for all elements for all SRMs was 2.3% for ICP/AES (and GF/AAS for Cd and As) and 4.4% for ICP/MS. Twenty-nine bottom-sediment duplicate samples had a median RPD of 3.3%. Median RPD for elements was 1.0% for two suspended-sediment samples. Median RPD for elements was 6.9% for one environmental duplicate streambed-sediment sample.

Quality assurance for organic-compound analyses was provided by analyzing an environmental duplicate sample, a blank sample, a spiked sample, and a certified reference material (CRM), and by monitoring recovery of surrogate compounds with each set of 12 environmental samples (Noriega et al., 2004; Olson et al., 2004). Median spike recoveries for sample sets that included core and suspended-sediment samples from this study were 81% for PAHs and 85% for chlorinated hydrocarbons. Although the methods were the same for the core and suspended-sediment samples, sample mass was small for suspended-sediment samples, which affected reporting levels and precision and limited the number of duplicates analyzed. Six environmental duplicates for organic compounds analyzed from this and similar suspended-sediment studies in Texas (Mahler and Van Metre, 2003; Van Metre et al., 2003b) had median RPDs of 36% for chlorinated hydrocarbons and 22% for PAHs. One environmental duplicate for streambed-sediment samples had a median RPD of 18.2% for chlorinated hydrocarbons and 40.9% for PAHs.

2.3. Data analysis

Three correlation approaches were used to evaluate relations between contaminants and urbanization: Spearman's ρ (a nonparametric rank test), Pearson's r with concentrations, and Pearson's r with logarithms of concentrations. Nonparametric rank correlations were used to show the association between contaminants and urbanization. These relations also were tested parametrically using Pearson's correlations, and it was assumed that the nature of the relation, linear or logarithmic, might provide additional information on potential sources. If a source is associated with a particular land use, then source strength should be a linear function of the

percent of the watershed in that land-use. The degree of urbanization was indicated by population density data from the 2000 U.S. Census Bureau decennial files, and land use land cover data available as Geographic Information and Retrieval and Analysis System (GIRAS) files (U.S. Geological Survey, 1990), updated with the U.S. Bureau of the Census 1990 population density data to reflect more accurately the 1990s extent of residential areas (Hitt, 1994).

Reference concentrations of trace metals and PAHs in sediments were computed using the mean concentration for samples from the three reference lake cores that are farthest from the Boston metropolitan area, *BRT*, *BBP*, and *CRK*. The mean was computed using all the samples from the shortest core (*BBP*), and an equivalent number of samples from the other two sites (*BRT*, *CRK*), so as not to bias the reference concentration relative to any of the three reference lakes. Reference concentrations used in this study were in reasonable agreement with concentrations measured at other reference sites in the eastern United States (Callender and Rice, 2000; Long et al., 2003).

Contaminant MARs in sediment cores were calculated for 1970–2000. Contaminant MARs were calculated by multiplying the contaminant concentration by the sediment dry mass per unit area in each sampling interval in the core to yield mass of contaminant per sample, summing that from 1970 to 2000, and dividing by 30 years to yield a 30-year mean contaminant MAR. When an interval was not analyzed, linear interpolation from intervals above and below was used to estimate concentrations and sediment dry mass.

2.4. Age dating and sediment focusing in cores

Sediment intervals in cores were dated using a combination of physical and chemical markers including reservoir impoundments dates, ^{210}Pb profile, peak ^{137}Cs (1963–1964), and date of core collection (July and August 2000). Details of age dating for these cores are presented elsewhere (Van Metre et al., 2004). Briefly, in lakes where dates were based on ^{137}Cs and other depth–date markers, mean MARs were calculated for the time intervals between markers by summing dry sediment mass per unit area of core for the interval then dividing by the number of years represented (g/cm^2 year). The MAR was then used to assign approximate deposition dates to samples from the interval. Dates for cores from *CRK*, *SRV*, and MYS were based on one of two ^{210}Pb dating models (Van Metre et al., 2004).

Relatively poor results were obtained for age dating cores from *BBP* and **MAP** because of post-depositional sediment mixing (Van Metre et al., 2004). Mixing and dating uncertainty in these cores could limit their utility for evaluating trends, although they were included in the trend testing done here. Even with mixing, average concentrations of persistent contaminants in the upper parts of these cores should be representative of the land-use setting in their watersheds and long-term (e.g. 30 years) mean contaminant MARs should be valid.

To interpret a contaminant MAR in a sediment core as a measure of fallout flux, sediment focusing must be accounted for. Focusing is the movement of sediments and associated contaminants from other parts of the lake and watershed to the coring site. One approach for evaluating focusing compares the ^{137}Cs burden in a core with the measured or estimated ^{137}Cs fallout at the site (Van Metre et al., 1997). A focusing factor (ratio of core burden to fallout) greater than 1 indicates sediment and associated contaminants have been transported from other areas and deposited at the site. Estimating sediment focusing from core burdens of ^{137}Cs is problematic for some of the cores collected in this study. Two (*BBP* and **MAP**) only extend back to about 1970, missing the major period of fallout; and loss of ^{137}Cs by desorption, a process reported elsewhere (Anderson et al., 1987), is suggested by profiles and burdens from the organic

carbon-rich sediments in *CRK* and *BBP* (Van Metre et al., 2004). It is possible, however, to estimate focusing using ^{210}Pb by dividing full-core burdens of excess ^{210}Pb by measured ^{210}Pb fallout in the region, an approach used here for the three lakes where ^{210}Pb was measured (*CRK*, *SRV*, and MYS).

3. Results

Concentrations of 13 PAHs and seven trace metals (Cd, Cr, Cu, Ni, Hg, Pb, Zn) were above detection levels at all 21 sampling sites and in all three sediment media, suspended sediment, bed sediment and sediment cores (Table 2). $\sum$PCB and $\sum$DDT were detected at 15 and 16 sampling sites, respectively, of the 19 sampling sites where organochlorine compounds were analyzed. The lowest contaminant levels were found in rural reference sites and the highest levels were in older, dense urban areas of Boston. Maximum PAH and metal concentrations were approximately 10 to 40 times greater than reference concentrations. Values above the probable effect concentration (PEC) (MacDonald et al., 2000) were common at the more urban sites (Table 2). The PEC is the consensus-based sediment quality guideline above which adverse effects on benthic biota are likely (MacDonald et al., 2000). Concentrations were below the PEC at all reference sites except for Pb at the reference site near central Boston (*SRV*). The close proximity of emissions (the dominant source of Pb) and the very low sedimentation rate in the lake probably explain the higher concentrations at this site.

3.1. Relations between contaminant occurrence and urbanization

Significant positive correlations (*p*-value<0.05) were found for most contaminants tested in relation to four different measures of urbanization (Table 3). All of the Spearman's rank correlations were significant at the 0.05 level, and most were significant at the 0.005 level. The strongest rank correlations (ρ about 0.8 or above) were for PAHs, PCBs, Cd, Cu, Pb, and Zn. Although all measures of urbanization correlated to contaminant concentrations, percent commercial, industrial and transportation (CIT) land use and population density had the strongest relations overall using rank correlation. Using linear (Pearson's *r* with concentrations) and log Pearson's *r* correlation, CIT land use and (total) urban land use had the strongest relations. Many of the strongest relations were linear relations to CIT land use, including PAH and most metals.

CIT land use was used in regressions to predict contaminant concentrations because of the strong linear correlations associated with this land use. Fig. 2 plots concentrations from streambed-sediment and suspended-sediment samples, and the median concentration in each core for samples dated as deposited in the 1990s (1990 to the top of the core), versus CIT land use. Regression lines (Fig. 2 and Table 4) are based on the data shown with the exception that for sites with multiple sample types (MYS, CHA, **HSP**, *BRT*), the median value was used to avoid biasing the regression relative to these sites. Outliers greater than three times the standard deviation from the mean that were suspected to be from point source contamination were excluded; one high outlier for Cd and one for Hg were thus excluded. Concentrations of Cu at SRV were not used because Cu was used as an algaecide at this site. Regressions with metals and $\sum$PAH are significant at greater than 99.9% confidence level (*p*-value<0.001) and r^2 values from 0.59 (Hg) to 0.85 ($\sum$PAH). Regressions with $\sum$PCBs and $\sum$DDT are significant at greater than 99% confidence levels (*p*-values<0.01) and r^2 values 0.39 and 0.35, respectively.

Enrichment factors (the ratio of contaminant concentration to reference concentration as used in Fig. 2) were calculated to evaluate contaminant response relative to location and land-use

Table 2
Concentrations of selected contaminants in sediment samples

Map ID	Sample type	∑PAH (µg/kg)	∑PCB (µg/kg)	∑DDT (µg/kg)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Ni (µg/g)	Hg (µg/g)	Pb (µg/g)	Zn (µg/g)	Mean PEC quotient
MYS	Bed sediment	**49 215**	**833**	227	**7.3**	**440**	**360**	46	**2.20**	**580**	**1500**	2.2
MYS	Core	**53 618**	215	94	**8.0**	**388**	**407**	47	**1.80**	**639**	**2015**	2.0
MYS	Suspended sediment	**66 446**	302	132	**6.8**	**368**	**331**	41	**1.30**	**515**	**1610**	2.3
CHAB1	Core	**66 882**	**1192**	267	3.5	**113**	**224**	**55**	**1.39**	**533**	638	2.0
CHA	Bed sediment	**32 546**	340	104	4.4	92	110	26	0.73	**250**	300	0.9
CHA	Suspended sediment	**24 172**	430	125	3.7	92	101	28	0.01	**327**	649	0.9
MO	Bed sediment	**32 414**	347	36	**6.4**	98	**280**	**67**	0.98	**590**	960	1.1
BL	Bed sediment	15 024	180	221	**18.0**	**220**	**270**	**50**	1.00	**240**	610	0.8
SA	Bed sediment	17 969	130	73	2.0	**140**	85	**57**	0.54	**200**	380	0.7
IP	Bed sediment	16 056	264	136	1.4	62	51	30	0.79	**180**	280	0.8
WO	Bed sediment	**24 737**	474	16	2.2	**210**	**160**	**57**	0.50	**290**	480	0.8
NE	Bed sediment	16 684	**766**	162	2.5	**140**	130	**83**	**2.80**	**460**	520	0.9
MAP	Core	2042	71	55	2.5	28	56	16	0.22	59	200	0.3
BE	Bed sediment	1620	<50	<2	1.2	53	24	28	0.15	60	160	0.2
WA	Bed sediment	3562	111	15	3.6	86	100	**50**	0.81	120	290	0.4
ME	Bed sediment	8752	45	9	1.6	78	42	20	0.32	82	180	0.3
HSP	Core	5452	139	22	0.5	42	58	18	0.21	58	209	0.3
HSP	Suspended sediment	17 109	320	50	1.4	49	44	20	na	90	334	0.7
AN	Bed sediment	3325	<50	<2	0.5	100	30	27	0.50	44	140	0.2
BRT	Core	1564	53	18	0.1	38	12	16	0.18	74	81	0.2
BRT	Suspended sediment	–	–	–	1.0	51	24	19	–	79	260	0.1
KE	Bed sediment	738	<50	<2	0.4	**120**	32	44	0.13	38	170	0.2
ST	Bed sediment	1241	<100	6	1.0	36	21	22	0.11	73	180	0.3
SRV	Core	9834	98	104	1.7	48	**258**	42	0.69	**337**	277	0.6
CRK	Core	3507	–	–	1.0	16	16	13	0.14	48	103	0.1
BBP	Core	373	–	–	0.4	29	14	9	0.14	45	144	0.1
PEC		*22 800*	*676*	*572*	*5.0*	*111*	*149*	*49*	*1.06*	*128*	*459*	
Reference concentration		1741	–	–	0.5	29	14	13	0.13	49	103	

Concentrations for sediment cores are the median of samples dated as 1990 to top of core. The consensus-based sediment quality guidelines probable effect concentrations (PEC) (MacDonald et al., 2000) are listed; concentrations above the PEC are in bold. PEC quotient for each site is the contaminant concentration divided by the PEC. PEC quotients for each of three groups – metals, chlorinated hydrocarbons, and PAHs – were computed, then the three values were averaged to compute the mean PEC quotient. Reference concentrations are the mean of samples from cores from three remote lakes with undeveloped watersheds (*BRT*, *BBP*, and *CRK*).

setting. Enrichment factors calculated for each site ranged from about 1 to 37 (Fig. 2). The highest enrichment factors were for PAHs and Cu. Dense urban sites (defined as CIT > 20%) typically had enrichment factors greater than 10. Suburban sites (CIT 1–10%) generally had enrichment factors between 1 and 10, and reference or rural sites (CIT < 1%) typically had enrichment factors between 1 and 2. Enrichment factors greater than 5 did occur at the near-Boston reference site (SRV) for contaminants with important atmospheric pathways (PAHs, Hg, and Pb).

The strong correlations between contaminants and CIT land use and the relatively even distribution of residuals about the regression lines (Fig. 2) support the use of regression analysis

Table 3

Correlations between contaminant concentrations in streambed, suspended, and lake core (median of 1990s) samples, as a group, and measures of urban land use

	n	Population density		Urban land use		CIT land use		Residential land use	
		ρ	p-value	ρ	p-value	ρ	p-value	ρ	p-value
$\sum$PAH	21	**0.85**	**0.0001**	**0.83**	**0.0002**	**0.83**	**0.0002**	**0.80**	**0.0004**
$\sum$PCB	19	**0.80**	**0.0007**	**0.79**	**0.0008**	**0.75**	**0.0015**	**0.76**	**0.0014**
$\sum$DDT	19	**0.68**	**0.0037**	0.64	0.0070	0.64	0.0064	0.61	0.0099
Cadmium	21	**0.82**	**0.0003**	**0.71**	**0.0015**	**0.80**	**0.0003**	**0.68**	**0.0025**
Chromium	21	0.54	0.0157	0.58	0.0097	**0.67**	**0.0027**	0.55	0.0132
Copper	20	**0.86**	**0.0002**	**0.79**	**0.0006**	**0.89**	**0.0001**	**0.74**	**0.0012**
Nickel	21	0.61	0.0066	0.55	0.0135	0.61	0.0066	0.55	0.0136
Mercury	21	**0.68**	**0.0022**	**0.64**	**0.0041**	**0.72**	**0.0013**	0.60	0.0071
Lead	21	**0.80**	**0.0003**	**0.69**	**0.0021**	**0.71**	**0.0015**	**0.66**	**0.0031**
Zinc	21	**0.87**	**0.0001**	**0.79**	**0.0004**	**0.84**	**0.0002**	**0.76**	**0.0007**

B	Pearson's r on concentration (linear correlation)								
	n	Population density		Urban land use		CIT land use		Residential land use	
		r	p-value	r	p-value	r	p-value	r	p-value
$\sum$PAH	21	**0.89**	**<0.0001**	**0.82**	**<0.0001**	**0.92**	**<0.0001**	**0.75**	**0.0001**
$\sum$PCB	19	**0.79**	**<0.0001**	**0.64**	**0.0029**	**0.62**	**0.0043**	0.61	0.0052
$\sum$DDT	19	**0.67**	**0.0018**	0.59	0.0074	0.59	0.0074	0.56	0.0131
Cadmium	20	0.60	0.0053	**0.69**	**0.0007**	**0.85**	**<0.0001**	0.60	0.0057
Chromium	21	*0.29*	*0.1972*	0.55	0.0104	**0.60**	**0.0041**	0.50	0.0220
Copper	20	0.60	0.0055	**0.66**	**0.0014**	**0.81**	**<0.0001**	0.57	0.0089
Nickel	21	*0.42*	*0.0567*	0.48	0.0275	*0.43*	*0.0536*	0.48	0.0295
Mercury	20	**0.62**	**0.0034**	**0.63**	**0.0028**	**0.77**	**<0.0001**	0.55	0.0126
Lead	21	**0.71**	**0.0003**	**0.70**	**0.0004**	**0.81**	**<0.0001**	**0.62**	**0.0028**
Zinc	21	0.54	0.0123	**0.67**	**0.0009**	**0.83**	**<0.0001**	0.57	0.0066

C	Pearson's r on logarithm of concentration (log correlation)								
	n	Population density		Urban land use		CIT land use		Residential land use	
		r	p-value	r	p-value	r	p-value	r	p-value
$\sum$PAH	21	**0.70**	**0.0004**	**0.79**	**<0.0001**	**0.76**	**<0.0001**	**0.76**	**<0.0001**
$\sum$PCB	19	**0.69**	**0.0011**	**0.76**	**0.0002**	**0.69**	**0.0011**	**0.74**	**0.0003**
$\sum$DDT	19	0.53	0.0188	0.60	0.0065	0.54	0.0177	0.59	0.0078
Cadmium	20	**0.64**	**0.0024**	**0.76**	**0.0001**	**0.79**	**<0.0001**	**0.70**	**0.0005**
Chromium	21	*0.38*	*0.0870*	0.58	0.0055	0.58	0.0058	0.55	0.0092
Copper	20	**0.65**	**0.0020**	**0.77**	**<0.0001**	**0.79**	**<0.0001**	**0.72**	**0.0004**
Nickel	21	0.44	0.0452	0.51	0.0174	0.46	0.0344	0.51	0.0197
Mercury	20	0.59	0.0062	**0.64**	**0.0025**	**0.69**	**0.0008**	**0.58**	**<0.0001**
Lead	21	**0.69**	**0.0006**	**0.74**	**0.0001**	**0.76**	**<0.0001**	**0.70**	**0.0004**
Zinc	21	**0.65**	**0.0013**	**0.78**	**<0.0001**	**0.85**	**<0.0001**	**0.72**	**0.0003**

Significant relations are $p\text{-value}<0.05$. Highly significant relations at $p\text{-value}<0.005$ are shown in bold. Relations that were not significant are in italic.

Cu at the urban reference site (SRV) was not used in correlations because it was added to control algae. One outlier value of Cd and Hg was removed prior to parametric correlations (B and C).

as a means of quantifying these relations. Regression equations using CIT as the independent variable predict that, on average, metal concentrations will double when a rural site becomes suburban, and concentrations will triple when a suburban site becomes urban (Table 4). PAH
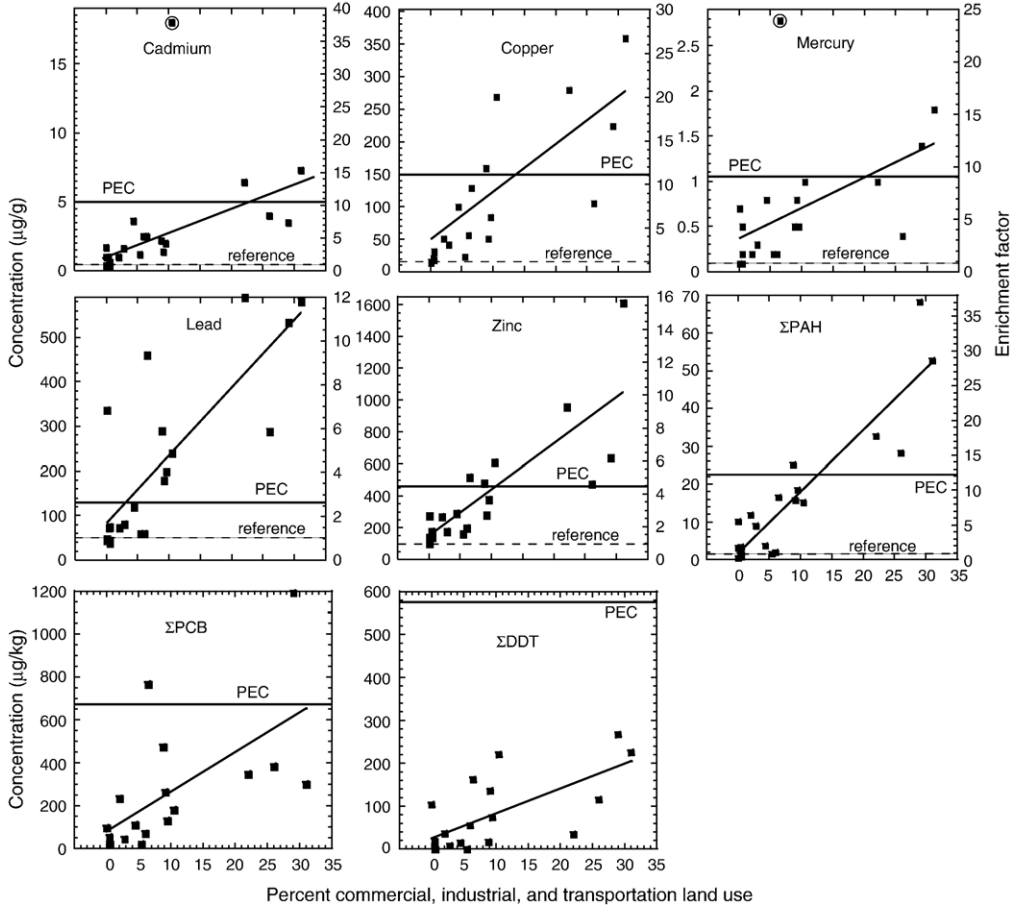
Fig. 2. Relations between concentrations of contaminants in sediments and urbanization, as indicated by percentage commercial, industrial and transportation land use. Median values were used for four sites with multiple sample media (streambed sediment, suspended sediment and/or sediment cores). Concentrations in sediment cores are median values for samples deposited during 1990–2000. Enrichment factors are the ratios of contaminant concentrations to calculated reference concentrations for metals and PAHs. Reference concentrations (the mean of concentrations for samples in cores from the three reference lakes farthest from the Boston metropolitan area, *BRT*, *BBP*, and *CRK*) are represented by a dashed line. Solid lines indicate sediment quality guidelines probable effect concentrations (PECs) (MacDonald et al., 2000). Two outliers (circled) were not included in regression equations.

concentrations are predicted to have a stronger response to urbanization than metals, increasing by a factor of 6 when a rural site becomes suburban, and increasing by a factor of 5 when a suburban site becomes urban. In all cases except ∑DDT, the regression equations predict contaminant values will exceed the PEC at 3% of the watershed as CIT (Pb) to about 30% (Hg, Cd, and PCB) and averaging about 15% (Fig. 2 and Table 4). On the basis of the strength of the relation to urban land use, the enrichment factors, and the relations to sediment quality guidelines, PAHs, lead, and zinc have the strongest response to urbanization among the contaminants tested.

One approach for evaluating overall sediment quality is to compute the mean PEC quotient, the mean of concentrations divided by the PEC for all contaminants considered to be "reliable" predictors of toxicity (MacDonald et al., 2000). Mean PEC quotients for each of three groups of

Table 4

Regression equations to predict concentrations of selected contaminants as a function of commercial, industrial and transportation (CIT) land use, and predicted enrichment factors for given levels of urban land use

| | Predicted cultural enrichment factors | | | | |
	Regression equation	r^2	Rural land becoming urban	Suburban land becoming urban	Threshold CIT% where concentrations exceed the PEC
∑PAH	$C = 1635x + 1610$	0.84	6.1	5.2	13
∑PCB	$C = 19x + 80$	0.39	2.2	3.7	31
∑DDT	$C = 4.66x + 30.89$	0.35	1.8	3.2	PEC not exceeded
Cd	$C = 0.16x + 0.93$	0.73	1.9	3.3	25
Cu	$C = 8.4x + 30.7$	0.66	1.7	3.1	14
Hg	$C = 0.035x + 0.25$	0.59	1.7	3.1	23
Pb	$C = 15.3x + 83.5$	0.65	1.9	3.4	3
Zn	$C = 29.4x + 149$	0.69	2.0	3.5	10

Rural land use is defined as having no CIT, suburban 5% CIT, and urban 30% CIT land use. Predicted cultural enrichment factors are the ratio of contaminant concentrations predicted for the current level of land use relative to concentrations predicted at the previous level of land use.

contaminants – metals, chlorinated hydrocarbons (PCBs and DDE) – and ∑PAHs were computed. Those three values were averaged to compute the overall mean PEC quotient. MacDonald et al. (2000) found that a mean PEC quotient greater than 1 was a reliable predictor of toxicity; 92% of 143 cases tested with mean PEC > 1 were toxic to sediment-dwelling organisms. As expected, mean PEC quotients computed for sediment samples in this study correlate strongly to urban land use (Fig. 3). The regression equation for the line in Fig. 3 is

$$\text{Mean PEC quotient} = 0.216 + 0.049\text{CIT} \quad (r^2 = 0.80)$$

The regression line crosses the line representing a mean PEC quotient of 1 at CIT land use of 16%. A similar equation developed for total percent urban land use crosses the line representing a mean PEC quotient of 1 at 65% ($r^2 = 0.66$).

3.2. Trends

Trends in concentrations of seven metals (Cd, Cr, Cu, Ni, Pb, Zn, and Hg) and three organic compound groups (∑PAH, ∑PCB, and ∑DDT) in sediment cores were tested from 1965 to 2000 using Kendall's τ (Helsel and Hirsch, 1992). Trends were considered significant if the p-value was less than or equal to 0.05. The starting point of 1965 was chosen because it approximately coincides with major environmental legislation in the United States (U.S. Environmental Protection Agency, 2004) and with peak concentrations in several important environmental contaminants, including Pb, DDT, and PCBs (Callender and Van Metre, 1997; Van Metre et al., 1998). Because age dates were assigned on the basis of the ^{137}Cs peak and a constant MAR or a ^{210}Pb model that results in a constant MAR, sediment MARs were constant between 1965 and 2000 in all of the sediment cores. In this case, trends in contaminant accumulation rates will be the same as trends in concentrations.

Trends in metal concentrations since 1965 were significantly downward at most of the suburban and urban coring sites and a few of the reference sites (Table 5). Treating each metal at each site as a case, 48% of metals trends were downward and only 7% were upward. Among the suburban and urban lakes, 71% were downward and only 4% were upward. Downward trends
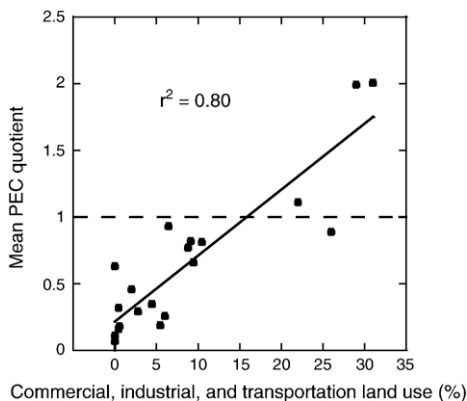
Fig. 3. Relation between overall sediment quality, as indicated by the mean probable effect concentration (PEC) quotient, and commercial, industrial, and transportation (CIT) land use. PEC quotient for each site is the contaminant concentration divided by the PEC. PEC quotients for each of three groups – metals, chlorinated hydrocarbons, and PAHs – were computed, then the three values averaged to compute the mean PEC quotient.

might reflect reductions in releases brought about by changing industrial practices since the 1960s and by regulations such as the Clean Air and Clean Water Acts.

Many of the urban sites are in areas affected by early industrial activity (late 1800s to early 1900s), in particular Upper Mystic Lake, MA. Trends in the core from Upper Mystic Lake (MYS) are indicative of the industrial history of the watershed and improvements in contaminant discharges in recent decades (Fig. 4). Most metals and the organic contaminants $\sum$PCB and $\sum$DDT peak in concentration about 1965, then decline consistently to the present (2000). A period of larger concentrations in several metals (Cd, Cu, Hg, and Zn) also is indicated in the late 1940s or early 1950s. Age control on this core is relatively poor prior to about 1960 (Van Metre et al., 2004), so this earlier peak possibly could be a result of industrialization during and after World War II.

Downward trends were observed for $\sum$PCB (MYS and CHAB1) and $\sum$DDT (MYS) only at the most densely urban sites (Table 5). Extensive use of these compounds began in the 1940s and 1950s and peaked between 1960 and 1970; concentrations in sediment cores typically peak in the 1960s, then decrease (Van Metre et al., 2004), similar to trends in the MYS core (Fig. 4). The lack of trends at suburban and reference sites could result from the relative lack of development in these watersheds during peak use of these compounds in the 1950s and 1960s and also could be affected by post-depositional sediment mixing in the cores, which will tend to "flatten" the temporal trends in cores.

PAH trends were downward at the Boston reference site (SRV) and upward at the suburban site (HSP), and there was a general lack of trends at the other sites (Table 5). Other researchers have reported downward trends in PAHs in remote and urban lakes in recent decades and attributed the decreases to reduced use of coal for home heating, industrial emissions controls, and increased efficiency of power plants (Hites et al., 1981; Christensen et al., 1993; Huntley et al., 1995). Van Metre et al. (2000), however, investigated PAH trends in 10 urban lakes and concluded that most were increasing coincident with urbanization and increases in vehicle traffic in the watersheds. Decreases in atmospheric emissions and fallout, as indicated by trends in SRV, and increases coincident with rapid urban growth, as indicated by trends in HSP, are consistent with findings of these other studies.

Table 5
Trend testing results for selected contaminants in sediment cores

	Remote reference sites				Rural reference site		Urban reference site	
	BBP		CRK		BRT		SRV	
	τ	p-value	τ	p-value	τ	p-value	τ	p-value
	$n=6$		$n=9$		$n=16$		$n=10$	
Cadmium	**0.733**	**0.039**	−0.222	0.404	0.258	0.123	**−0.734**	**0.002**
Chromium	0.333	0.348	−0.197	0.459	−0.317	0.058	**−0.524**	**0.025**
Copper	0.276	0.437	**−0.889**	**0.001**	0.324	0.053	**−0.818**	**0.001**
Nickel	−0.600	0.091	−0.028	0.916	0.216	0.196	−0.273	0.243
Lead	0.000	>0.999	0.444	0.095	**0.435**	**0.009**	0.055	0.815
Zinc	**0.867**	**0.015**	**−0.648**	**0.015**	−0.219	0.190	**−0.564**	**0.016**
Mercury	0.690	0.052	**−0.722**	**0.007**	0.207	0.215	0.322	0.195
	$n=5$		$n=8$		$n=4,5$		$n=5$	
∑PAH	0.000	>0.999	0.143	0.621	0.000	>0.999	**−0.733**	**0.039**
∑PCB	na	na	na	na	−0.400	0.327	−0.200	0.624
∑DDT	na	na	na	na	−0.738	0.071	−0.600	0.142
	Suburban sites				Urban sites			
	HSP		MAP		CHAB1		MYS	
	τ	p-value	τ	p-value	τ	p-value	τ	p-value
	$n=15$		$n=15$		$n=17$		$n=21$	
Cadmium	**0.628**	**0.001**	**−0.612**	**0.002**	**−0.662**	**0.000**	**−0.552**	**0.000**
Chromium	**−0.767**	**<.0001**	−0.174	−0.904	0.015	0.933	**−0.836**	**<.0001**
Copper	**−0.800**	**<.0001**	**−0.733**	**0.000**	**−0.578**	**0.001**	**−0.753**	**<.0001**
Nickel	−0.202	0.276	**−0.676**	**0.000**	0.074	0.680	**−0.409**	**0.006**
Lead	**−0.564**	**0.002**	−0.299	0.121	**−0.574**	**0.001**	**−0.787**	**<.0001**
Zinc	0.202	0.276	**−0.676**	**0.000**	**−0.578**	**0.001**	**−0.929**	**<.0001**
Mercury	**−0.573**	**0.002**	**−0.539**	**0.005**	**−0.459**	**0.010**	−0.213	0.155
	$n=11$		$n=9$		$n=6$		$n=9,8$	
∑PAH	**0.545**	**0.014**	0.056	0.835	−0.333	0.293	0.167	0.532
∑PCB	−0.225	0.366	−0.444	0.095	**−1.000**	**0.002**	**−0.571**	**0.048**
∑DDT	−0.068	0.784	−0.333	0.211	−0.524	0.099	**−0.571**	**0.048**

Test is the Kendall's τ for the period 1965 to top of core (about 2000). Trend considered significant (in bold) at a 95% confidence level (p-value<0.05).

3.3. Contaminant mass accumulation rates and fallout fluxes

Contaminant MARs in sediment cores were computed for 1970–2000 to evaluate atmospheric fallout as a function of distance from metropolitan Boston and to compare atmospheric versus fluvial contaminant inputs to the lakes across the urban–rural gradient. Contaminant MARs vary greatly among cores with the highest values in the dense urban sites and the lowest values in the remote reference sites (Table 6). The contaminant MARs at the most urban sites (MYS, CHA) were 2–3 orders of magnitude higher than the MAR at a remote reference site (CRK) and about an order of magnitude higher than the MAR at a nearby urban-reference site (SRV). The order of MARs for most contaminants was CHA (urban site)>MYS (urban site)>**HSP** (suburban site)=**MAP**
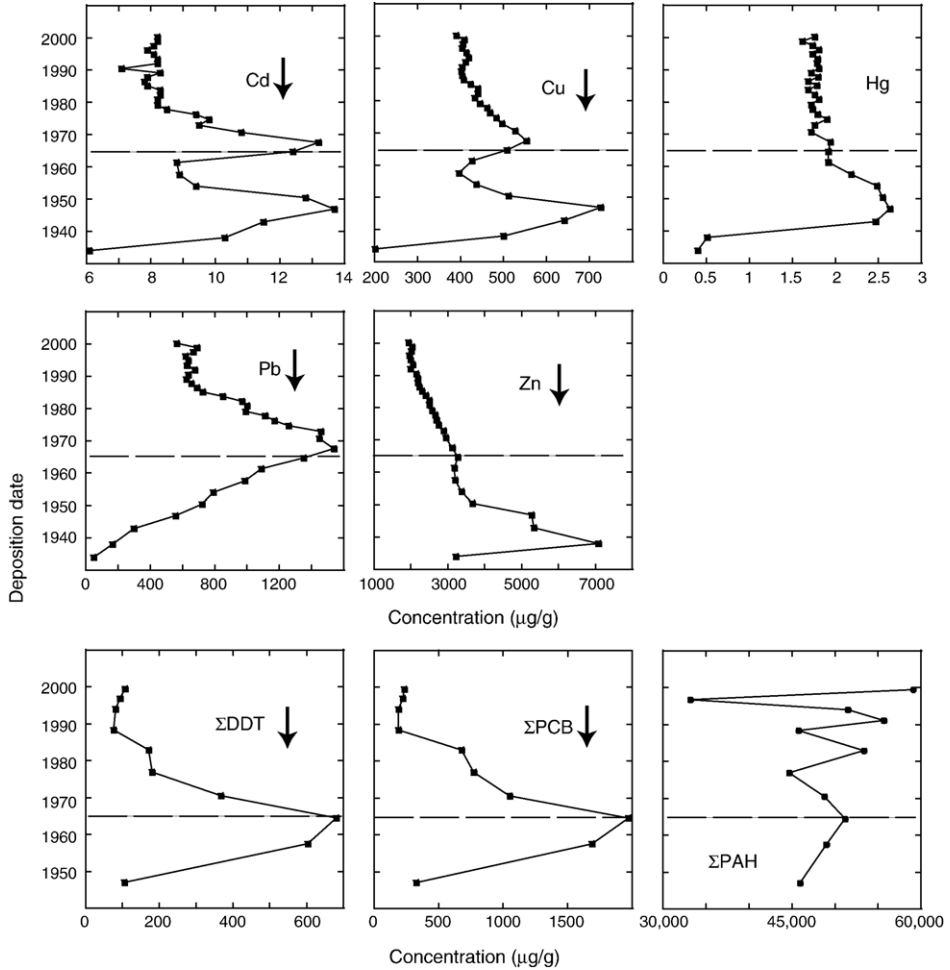
Fig. 4. Trends in selected metals and organic compounds in a core from Upper Mystic Lake, MA. Dashed line at 1965 marks start of trend testing time period used. Arrow indicates direction of a statistically significant trend.

(suburban site)>*SRV* (urban-reference site)>*BRT* (rural reference site)>*BBP* (remote reference site)>*CRK* (remote reference site).

One objective in sampling reference lakes is to assess atmospheric fallout. The four reference lakes sampled in this study comprise a transect from near central Boston (*SRV*), to about 60 km southwest of Boston (*BRT*), to about 200 km north in eastern New Hampshire and western Maine (*BBP* and *CRK*). To interpret a contaminant MAR in a sediment core as a measure of fallout flux, sediment focusing and, for metals and PAHs, the contribution from natural sources in the watershed must be accounted for. Focusing for the three lakes where ^{210}Pb was measured (*CRK*, *SRV*, and MYS) was estimated using ^{210}Pb. The annual fallout of ^{210}Pb was estimated as 0.92 dpm/cm^2 year ($\pm$0.09 dpm/cm^2 year) at New Haven, CT, on the basis of wet- and dry-fall monitoring over a 3-year period (Turekian et al., 1977). This estimate is in reasonable agreement with estimates from soil profiles in the eastern United States (Connecticut, Maryland, and

Table 6
Mean sediment and contaminant mass accumulation rates (MAR) at sediment coring sites over 30 years, 1970–2000

| | Mar (1970–2000) | | | | | | | | | | |
	Sediment (g/cm² year)	Cd (µg/cm² year)	Cr (µg/cm² year)	Cu (µg/cm² year)	Hg (µg/cm² year)	Ni (µg/cm² year)	Pb (µg/cm² year)	Zn (µg/cm² year)	∑PAH (ng/cm² year)	∑PCB (ng/cm² year)	∑DDT (ng/cm² year)
CRK	0.01	0.01	0.19	0.19	0.002	0.14	0.48	1.2	13	–	–
BBP	0.03	0.01	0.90	0.42	0.003	0.38	1.4	3.9	34	–	–
BRT	0.04	0.01	1.6	0.43	0.006	0.55	2.6	3.3	50	1.9	0.75
SRV	0.02	0.03	0.78	4.4	0.010	0.66	5.4	4.6	190	1.7	2.1
HSP	0.17	0.04	5.3	7.6	0.025	2.2	7.0	23	860	28	3.8
MAP	0.11	0.33	2.7	8.8	0.027	2.4	6.3	26	240	11	7.4
MYS	0.15	1.6	93	78	0.307	8.9	170	420	8500	99	31
CHA	0.70	2.9	85	190	1.45	42	470	530	48000	1140	210
Urban land-use gradient: ratio of urban to suburban and reference lakes (%)											
MYS/HSP	0.88	38	18	10	12	4.0	24	18	10	3.5	8.2
MYS/MAP	1.4	4.8	34	8.9	11	3.7	27	16	35	9.1	4.3
MYS/SRV	10	53	120	18	30	13	31	92	45	59	15
		Anthropogenic flux (1970–2000)									
CRK		0.01	0.04	0.02	0.001	0.05	0.19	0.36	22	–	–
SRV		0.03	0.58	4.2	0.010	0.54	4.9	3.4	170	1.7	2.1
	Focusing factor	Atmospheric fallout flux (1970–2000)									
CRK	1.20	0.01	0.03	0.02	0.001	0.04	0.16	0.30	18	–	–
SRV	1.17	0.02	0.49	–	0.008	0.46	4.2	2.9	145	1.4	1.8
Air-shed gradient: ration of near-urban to remote reference lake (%)											
SRV/CRK		3.3	16	–	10	11	26	9.7	7.9		
	Focusing factor	Atmospheric versus fluvial flux to MYS									
Atmospheric	3.50	0.08	1.7	–	0.029	1.6	15	10	510	5.0	6.2
Fluvial		1.5	92	–	0.278	7.3	160	410	8000	94	25
Fluvial inputs (%)		95	98	–	91	82	94	98	94	95	80

Atmospheric fallout flux was not calculated for Cu at the urban reference site (*SRV*) because Cu was added to control algae.

Pennsylvania) ranging from 0.8 to 1.2 dpm/cm^2 year (Turekian et al., 1977, and references therein). Adjusting the measured fallout in New Haven by the ^{210}Pb decay constant yields an estimate of the expected ^{210}Pb burden of 29.2 dpm/cm^2. Core burdens for the two reference lakes with ^{210}Pb data, CRK and SRV, are 35.1 and 34.3 dpm/cm^2, resulting in focusing factors of 1.20 and 1.17, respectively, or about 1.2 for both cores, considering the uncertainties. The third site with ^{210}Pb analyses is MYS, with a core burden of 103 dpm/cm^2 and a focusing factor of 3.5. With a relatively much larger watershed, dense urbanization, and a higher sediment MAR, the greater focusing factor at MYS is reasonable.

If a core extends back to the pre-industrial era in New England, background levels of metals in lake sediments can be estimated and subtracted from more recent concentrations to allow estimates of anthropogenic concentrations. Only one core collected by this study, CRK, extends far enough back in time (early 1800s) that background concentrations might be represented. Background concentrations were estimated for the core using the lowest concentration among the deepest three samples in the core. With only a few exceptions (e.g. Cr in two samples, Cu in three samples, and Pb in one sample), these concentrations were equal to or lower than any more recent concentrations. To compute the anthropogenic flux, background concentration was subtracted from total, multiplied by dry mass, summed for samples deposited after about 1970 (30 years), and divided by 30 years (Table 6). The only two reference lakes for which focusing factors could be calculated are CRK and SRV. SRV extends back to about 1930, so pre-industrial background is not known there. As an approximation, the background concentrations in sediment from CRK were used for SRV to estimate anthropogenic concentrations. Background was a small fraction of total concentration in most intervals in SRV. These fluxes for both cores were then divided by the ^{210}Pb focusing factors to yield estimates of fallout flux (Table 6).

4. Discussion

4.1. Urban–rural fallout gradient

The interpretation of contaminant MARs in lakes can indicate the relative magnitude of fluvial and atmospheric fluxes to the lakes. Each of the four reference lakes (BBP, CRK, BRT, and SRV) has little (BRT at 2.1%) or no developed area in the watershed. Using contaminant MARs in the cores as an indication of fallout flux, these four reference lakes define a pronounced increasing gradient in fallout of PAHs and metals with decreasing distance from metropolitan Boston (Table 6). Anthropogenic contaminants in these cores can come either from direct fallout on the lake surface or transport of fallout on the watershed to the lake. Metals and PAHs also occur naturally in soils, so fluxes of these to the lake will also come from erosion and transport of uncontaminated soil. A study of a small mountain lake in Scotland used multiple cores and monitored fallout and inflows and outflows from the lake (Yang et al., 2002). They estimated that 78% of the Hg and 91% of the Pb being delivered to the lake were from the watershed (fluvial inputs) and that 77% of the Hg and 90% of the Pb deposited since the 1860s and stored in watershed soils are from anthropogenic sources. Thus, to use a core MAR to evaluate fallout flux, both natural inputs and sediment focusing must be accounted for.

Fallout flux was estimated for two lakes, CRK and SRV, using a background correction to estimate anthropogenic flux and ^{210}Pb focusing correction to account for transport of anthropogenic fallout on the watershed to the coring location. Fallout fluxes estimated for CRK and SRV indicate a large increase in fallout in Boston compared with about 200 km north, from about 3-fold (Cd) to about 26-fold (Pb), ignoring Cu, which by these calculations had almost

no anthropogenic fallout at *CRK* and a point source at *SRV* (Table 6). The magnitude of the regional gradient for PAHs and Hg, both of which have important atmospheric pathways, is about 10. The gradient in fallout fluxes of metals and PAHs indicates the existence of a relatively contaminated urban air shed in the Boston area.

PAH MARs in the reference lakes are consistent with those reported in the literature (see Fernandez et al., 1999, and references therein). Using the sum of PAH in Fernandez et al. (1999) (phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzofluoranthenes, benzo[*e*] pyrene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene), in $\mu g/m^2$ year, PAH MARs in this study are 160, 510, 740, and 2500 $\mu g/m^2$ year at *BBP*, *CRK*, *BRT*, and *SRV*, respectively. Fernandez et al. (1999) reported fluxes (similar to MARs used here) of 38–130 $\mu g/ m^2$ year in relatively uncontaminated high mountain lakes in Western Europe and 820–1500 $\mu g/ m^2$ year in more contaminated mountain lakes in Eastern Europe. Furlong et al. (1987) reported PAH fluxes in remote lakes in the eastern United States in the range of 105–680 $\mu g/m^2$ year. MARs determined in New England (this study) are in the ranges of these other studies, with the possible exception of *SRV*, which is somewhat greater. Greater fallout a few kilometers from the center of a major urban area than in any remote mountain lakes is not unexpected.

Metal fluxes have been determined in numerous studies, particularly for Pb (e.g. Callender and Van Metre, 1997, and references therein) and Hg (Perry et al., 2005, and references therein). Callender and Van Metre (1997) summarized published atmospheric Pb fallout for the years 1965–1975, which had a mean of 0.7 $\mu g/cm^2$ year ($\pm 0.4 \ \mu g/cm^2$ year) at rural sites and 14.5 $\mu g/ cm^2$ year ($\pm 11 \ \mu g/cm^2$ year) at urban sites. That time period coincides with maximum Pb fallout in the United States caused largely by the use of lead in gasoline. Eisenreich et al. (1986) measured precipitation fluxes of Pb in Minnesota for 1979–83, soon after Pb was removed from most gasoline in the United States, and found ranges of 0.4–2.0 $\mu g/cm^2$ year at urban sites and 0.1–0.3 $\mu g/cm^2$ year at rural sites. In comparison, 30-year average fluxes computed here are 0.16 $\mu g/cm^2$ year (*CRK*) and 4.2 $\mu g/cm^2$ year (*SRV*), about one-third the means reported by Callender and Van Metre (1997) and similar to the values of Eisenreich et al. (1986). All of these data show the strong urban–rural gradient in Pb fallout.

The National Atmospheric Deposition Program (NADP) has a Mercury Deposition Network (MDN) site at Bridgton, ME, about 40 km southeast of *CRK*, where wet deposition of Hg has been monitored since 1997 (NADP, 2005). The average annual Hg deposition at the MDN site during 1997–2004 was 6.35 $\mu g/m^2$ year, 23% less than the estimated fallout flux of 8.2 $\mu g/ m^2$ year at *CRK* (note difference in units from Table 6). The MDN sites monitor wet deposition only, whereas a lake will collect wet and dry deposition (minus volatilization); thus, somewhat larger average flux is expected in a lake core. Considering the differences in sampling methodologies and data uncertainties, the flux determined from the core is in close agreement with the measured Hg deposition. The 30-year average fallout flux at *SRV* was 82 $\mu g/m^2$ year, a 10-fold increase in fallout in the metropolitan area relative to *CRK*. Engstrom and Swain (1997) reported an approximate 10-fold increase in Hg accumulation rates in urban lakes compared with rural lakes in Minnesota, although the urban lakes they sampled were in watersheds dominated by residential development.

4.2. The urban land-use gradient

Urban lakes transecting the metropolitan area (**HSP**, **MAP**, CHAB1, MYS) (Fig. 1) suggest an urban gradient in contaminant inputs with an even larger range in magnitude than the atmospheric gradient, and at a much greater scale (Table 6). The least urban of these lakes, **HSP**

and **MAP**, had MARs roughly 2 to 10 times larger than *SRV*, the most contaminated of the reference lakes, even though they are located on the outskirts of Boston, about 40 km from the city center. The highest contaminant MARs were found at the dense urban sites (MYS, CHAB1). Contaminant MARs at MYS were about 15 times greater, on average, than at the suburban sites (**MAP** and **HSP**) and were about 50 times greater than at the nearby urban reference site (*SRV*) The MAR for PAHs at CHAB1 was nearly 300 times higher than *SRV*, and more than three orders of magnitude higher than the MAR at *CRK* (remote reference site). These comparisons indicate the dominating affect of watershed sources and fluvial inputs of contaminants to lakes in urban settings.

Using the ^{210}Pb focusing factors for *SRV* and MYS, an estimate can be made of the relative amounts of atmospheric and fluvial inputs to MYS. Correcting contaminant MARs for background concentrations and sediment focusing assumes that the contaminant is delivered to the watershed by fallout, not local point or nonpoint sources. The fallout fluxes calculated for *SRV* provide estimates of fallout to central Boston. Multiplying these fluxes times the focusing factor of 3.5 calculated for MYS yields estimates of the contaminant accumulation rates expected from atmospheric fallout on Upper Mystic Lake and its watershed. Comparing these estimates with total MARs in MYS suggests that from about 80% (DDT) to 98% (Cr) of contaminant accumulation in the core is from within watershed sources, and the remainder is from atmospheric fallout (Table 6).

4.3. Effects of urbanization on sediment quality

Both correlation and regression analyses indicate that contaminant levels are strongly related to urban land use. In a study of suspended-stream and lake-core sediments in Fort Worth, TX, Van Metre et al. (2003a) found similarly strong correlations between CIT land use and metals and PAHs, but found that organochlorine pesticides correlated more strongly to residential land use. Although there are subtle differences in the strength of the correlations between the various measures of urbanization and contaminants in this study, population density and CIT had the strongest relations to contaminants overall, including that for ∑DDT, the only pesticide widely detected.

The nature of the regression relations, linear or logarithmic, might provide additional information on potential sources. If a source is associated with a particular land use, then source strength should be a linear function of the percentage of the watershed in that land use. For most contaminants, the strongest relations were for (linear) concentrations versus CIT (Table 5). These relations suggest that CIT could be an indicator of some of the more important sources of these contaminants.

The strong association of many contaminants with urbanization and the rapid urbanization occurring in the Boston metropolitan area could be offsetting (per capita) reductions in releases of many pollutants since the 1970s caused by improved environmental regulations and technological change. Concentrations of many contaminants in settings with stable land use but improved regulation of releases, like metals and chlorinated hydrocarbons at Upper Mystic Lake, are decreasing. This might not be the case, however, in watersheds undergoing rapid urbanization and for contaminants with largely unregulated nonpoint sources (e.g. PAH). Urban land use in 2001 accounted for about 5.3% of total land area of the 48 contiguous states or about 43 million ha, a 46% increase since 1982 (NRCS, 2001). The strong relations between urban land use and contaminant concentrations presented here indicate that as urban areas expand, streams and lakes in these newly urbanizing areas are likely to decline in quality.

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