

Chapter 5

Metals, Organic Compounds, and Nutrients in Long Island Sound: Sources, Magnitudes, Trends, and Impacts

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5.1 Introduction

Long Island Sound (LIS) is a relatively shallow estuary with a mean depth of 20 m (maximum depth 49 m) and a unique hydrology and history of pollutant loading. These factors have contributed to a wide variety of contamination problems in its muddy sediments, aquatic life, and water column. The LIS sediments are contaminated with toxic compounds and elements related to past and present wastewater discharges and runoff. These include nonpoint and stormwater runoff and groundwater discharges, whose character has changed over the years along with the evolution of its watershed and industrial history. Major impacts have resulted from the copious amounts of nutrients discharged into LIS through atmospheric deposition, domestic and industrial waste water flows, fertilizer releases, and urban runoff. All these sources and their effects are in essence the result of human presence and activities in the watershed, and the severity of pollutant loading and their impacts generally scales with total population in the watersheds surrounding LIS. Environmental legislation passed since the mid-to-late 1900s (e.g., Clean Air Act, Clean Water Act) has had a beneficial effect, however, and contaminant loadings for many toxic organic and inorganic chemicals and nutrients have diminished over

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the last few decades (O'Shea and Brosnan 2000; Trench et al. 2012; O'Connor and Lauenstein 2006; USEPA 2007). Major strides have been made in reducing the inflow of nutrients into LIS, but cultural eutrophication is still an ongoing problem and nutrient control efforts will need to continue. Nonetheless, LIS is still a heavily human impacted estuary (an "Urban Estuary," as described for San Francisco Bay by Conomos 1979), and severe changes in water quality and sediment toxicity as well as ecosystem shifts have occurred since the European colonization in the early 1600s (Koppelman et al., 1976). The Sound has seen the most severe environmental changes over the last 400 years during its 10,000 year history (Lewis, this volume), suggesting that human impacts have overwhelmed the natural forces at play.

The main rivers that discharge into LIS are the Housatonic and Connecticut Rivers on the north, and the Thames River at the northeastern end of LIS, with the Quinnipiac and several other smaller rivers also coming in from Connecticut. The East River, a tidal strait connecting with New York Harbor through the heart of the New York City metropolitan region, is at the head of LIS at its western boundary. The Housatonic, Quinnipiac, Connecticut, and Thames river basins drain agricultural, urban, and industrial lands in a watershed that extends from Connecticut north to Canada. The Sound receives contaminants from many sources within and outside its contributing watershed, including direct discharges from coastal industries, wastewater treatment facilities (WWTF), urban runoff, and atmospheric deposition. New England has a long history of industrial activity, with factories that once crowded its riverbanks and shores now having succumbed to economic forces that drove manufacturing overseas. Relict deposits with legacy pollutants in upland sediments persist and combined with modern runoff sources from an increasingly densely populated watershed, continue to be a source of contaminants for LIS. While toxic exposure from legacy and active sources has diminished over the years as wastewater treatment has improved and industries are closed or moved away, pockets of contamination still have consequences for many embayments and coves, particularly near urbanized areas of western LIS.

The loading of nutrients and carbon has been of recent concern in LIS because of the extensive impacts observed since the mid-1980s. Excess nutrients not only create inhospitable conditions for higher forms of aquatic life through reduced oxygen levels and disrupting trophic dynamics, but also by altering the local biogeochemistry. As a result, the release of toxic substances into the water column may be enhanced in hypoxic waters, thus exerting a toxic effect or enhancing incorporation of toxic pollutants into the food web, and exacerbating bioaccumulation and biomagnification in tissues of various species, including those consumed by humans. This combined human impact is not unique to LIS, but common to many urban estuaries worldwide.

Urban estuaries worldwide are beset by a host of environmental problems. Environmental problems of other US urban estuaries were reviewed in detail, e.g., for the Chesapeake Bay (e.g., Smith 2003; Boesch et al. 2001; Cooper and Brush 1993; Kemp et al. 2005; Jackson et al. 2002); Puget Sound (e.g., Puget Sound Partnership 2011, <http://www.psp.wa.gov/scienceupdate.php>); San Francisco Bay (e.g., Kuivila and Foe 1995; Flegal et al. 1996); as well as from LIS (Mitch and Anisfeld 2010).

This chapter reviews and synthesizes the sources and distribution of contaminants and pollutants in LIS, and some of their impacts on the biosphere. We use the terms “contaminants” (substances or elements that occur above their local natural background) and “pollutants” (contaminants whose elevated concentrations have an impact on the local ecosystem) as originally accepted by GESAMP (<http://www.gesamp.org/>) interchangeably throughout the text. This chapter starts with a discussion of the sources of the various pollutants, followed by a section on metal concentrations in the sediment of LIS basin-wide, and a short section on metal concentrations in embayments and harbors. The next section reviews and discusses organic pollutants, sediment toxicity, and pollutant concentrations in biota, followed by a section that reviews the nutrient fluxes into LIS and their variations over time, and nutrient concentrations in the water column. The last section reviews core data for carbon and nitrogen, and puts the current data into a historical context. The chapter ends with recommendations for further research and data needs.

5.2 Data Sources

5.2.1 *Metals and Organic Compounds*

A limited number of peer-reviewed papers have been published on contaminants in LIS, the most recent by Mitch and Anisfeld (2010). Contaminants data are available in many governmental and technical reports (e.g., EPA, NOAA, and Brownawell et al. 1991). Mitch and Anisfeld (2010) reviewed the literature and available databases on metal and organic contaminant levels in sediment and biota in LIS. They discussed discrepancies among the data sources, examined trends over the last few decades, compared sediment contaminant levels with benchmark levels for toxicity, and provided an overview of contaminant issues within the region.

Metal pollutants in LIS sediment were discussed by Mecray and Buchholtz ten Brink (2000) and Varekamp et al. (2000, 2003, 2004, 2005), and studies on metal contamination in the fringing saltmarsh sediments were provided by Cochran et al. (1998) and Varekamp (1991). Buchholtz ten Brink et al. (2000) discussed the presence of WWTF effluents in LIS sediment using spores of *Clostridium perfringens*, and Turekian and co-workers traced WWTF effluents using Osmium and its isotopic composition (Cuomo et al. Chap. 4, in this volume).

The primary data sources on contaminants in LIS come from federally funded monitoring programs. These programs generally focus on determining concentrations of organic contaminants in sediments, and resident mussels, and/or measures of sediment toxicity. The programs initially reported levels of a suite of metals, chlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and in some cases polychlorinated dibenzodioxins and furans and polybrominated diethyl ethers (PBDEs). NOAA's National Status and Trends (NS&T) Program monitors levels of organic and inorganic contaminants in surface

sediments and blue mussels (*Mytilus edulis*) collected from coastal embayments during the winter, in efforts commonly referred to as the Benthic Surveillance and Mussel Watch Programs, respectively. The NS&T program provides the longest dataset collected on a regular basis throughout US coastal areas since 1986, with the most recent available data online from 2008. There are nine NS&T sites within LIS, although samples were not consistently collected from all sites each year. NS&T program data were reviewed by O'Connor and Lauenstein (2006) and most recently by Kimbrough et al. (2009).

The USEPA's National Coastal Assessment (NCA) collected surface sediments from a large number of sites during each summer between 2000 and 2006. There were 488 discrete sediment samples collected from the Connecticut and New York waters covered in the NCA. About 50 of the Connecticut stations were in LIS or in tidal portions of rivers feeding into LIS; about half of the 50 New York NCA sites were located in LIS, mostly located in coastal embayments on the New York side of the western sections of LIS. The NCA measured contaminant concentrations in sediments and performed amphipod (*Ampelisca abdita*) sediment toxicity tests on the collected sediments. The NCA data collected between 2000 and 2002 were reviewed in a report on the entire national program (USEPA 2008) and in a more focused report on LIS (USEPA 2007). Data up through 2006 are available online at <http://www.epa.gov/emap/nca/html/regions/ne0006/index.html>.

An earlier, large survey of organic contamination and effects was conducted within USEPA's Environmental Monitoring and Assessment Program (EMAP) during the early 1990s (Paul et al. 1999). Monitoring programs for the New York–New Jersey Harbor Estuary Program conducted by NOAA in 1991 and 1993 as part of the NS&T program were reviewed by Long et al. (1995). Other surveys were conducted in 1993, 1998, 2003, and 2008, as part of USEPA, Regional EMAP or REMAP programs, of which the first two were discussed by Adams et al. (1998) and Adams and Benyi (2003). During those surveys, surface sediments were collected for analysis of metals and organic pollutants, and amphipod sediment toxicity tests were conducted. A special issue of the journal *Estuaries* (*Estuaries* 14(3), September 1991) reviewed many aspects of contaminant loadings, distributions, and effects on selected biota in LIS.

The USGS conducted an extensive sampling campaign to evaluate the distribution of trace metals and elements in surface sediments and selected sediment cores in 1996. Their reports and analyses of sedimentary properties were published in a special issue of the *Journal of Coastal Research* (Knebel et al. 2000). The USGS compiled a database of LIS sediment properties and contaminant levels, which is available online (Mecray et al. 2003). A map was compiled by Mitch and Anisfeld (2010; Fig. 5.1) of sampling locations from these national programs as well as for sites sampled for dredged material management purposes housed in the Sediment Quality Information database (SQUID) maintained by the Connecticut Department of Energy and Environmental Protection (CTDEEP). Also indicated in Fig. 5.1 are the boundaries among the three basins of LIS, Western LIS (WLIS) extending from the East River to a line between the mouth of the Housatonic River in Connecticut and Port Jefferson Harbor in New York, central LIS (CLIS) extending from WLIS to

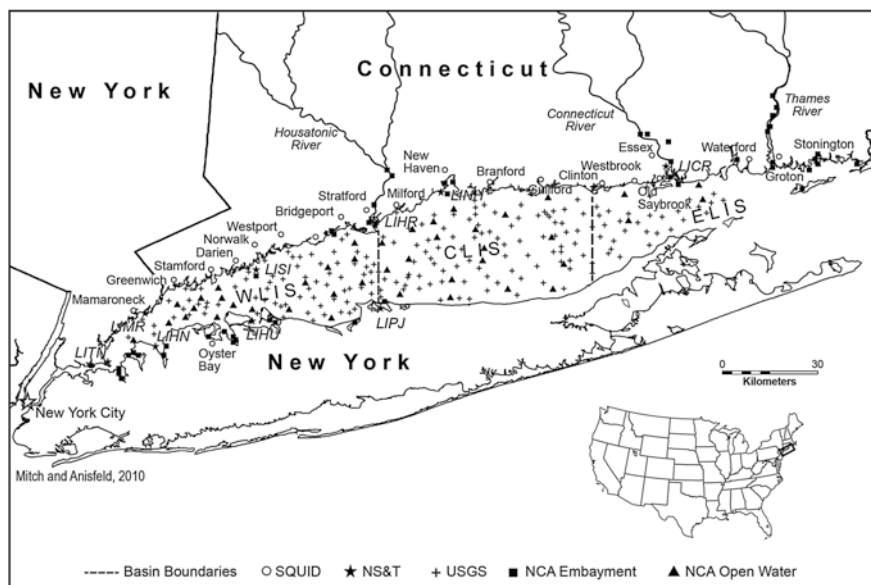


Fig. 5.1 Map of LIS showing the three major basins: western LIS (WLIS), central LIS (CLIS), and eastern LIS (ELIS), and the sampling locations within LIS sampled by several large national and local monitoring programs including the State of Connecticut Sediment Quality Information Database (SQUID), the National Status and Trends Program (NS&T) of NOAA, the National Coastal Assessment (NCA) of the USEPA. Two types of sites, embayment, and open water, are shown for the NCA study. Abbreviations for the NS&T sites from west to east are as follows: Throgs Neck (LITN), Mamaroneck (LIMR), Hempstead Harbor (LIHH), Huntington Harbor (LIHU), Sheffield Island (LISI), Port Jefferson (LIPJ), Housatonic River (LIHR), New Haven (LINH), and Connecticut River (LICR). Map from Mitch and Anisfeld 2010

a line between Clinton, CT and Mattituck, NY, and eastern LIS (ELIS), the area east of CLIS out to The Race between Plum and Fishers Islands.

We reviewed these primary data sources on metals and organic contaminants in LIS surface sediment, including a treatment of the historical record of contamination based on sediment core data from LIS, as well as from surface sediment samples taken over the last 25 years. Body burdens of contaminants in LIS biota were reviewed within the context of the limited data available on toxicity benchmarks, data on sediment toxicity tests discussed, as well as the very limited data available on sublethal effects observed in resident biota. Data from original research reports were also included in our analysis, e.g., an analysis of recent data on the metal distribution in several Connecticut embayments (Conklin 2008; Church 2009; Lee 2010; Titus 2003). The record of mercury contamination is discussed in some detail because of the abundance of studies and data on this element in the LIS region. It should be noted that chemical contaminant data are reported in various ways, usually normalized to the dry weight of sample (either tissue or sediment) as a mass unit per unit dry weight (dw). Although particularly for tissue samples,

values are often reported normalized to wet weight (ww) or sometimes lipid weight (lw), as body burdens of organic contaminants can be strongly influenced by lipid content of an organism (McElroy et al. 2011). When not otherwise indicated, the reader can assume concentrations are expressed on a basis of dry weight.

5.2.2 Nutrients and Related Pollutants

Macronutrient (N, P, Si) sources into LIS have been the topic of many state and government reports, and are a major focus of the National Estuary Program's Long Island Sound Study (LISS). These data have been used to establish the Total Maximum Daily Load (TDML) as a means to improve LIS water quality, especially the hypoxia in WLIS (USEPA 2000; NYSDEC and CTDEP 2000). Both N and P have received increasing attention and control as a national priority for management under the Clean Water Act. Despite meaningful reductions in WWTF N fluxes into the Sound (36 % overall reduction by 2011 compared to 1990) each summer, portions of CLIS and most of WLIS are hypoxic from as early as June to as late as September (Fig. 5.2a).

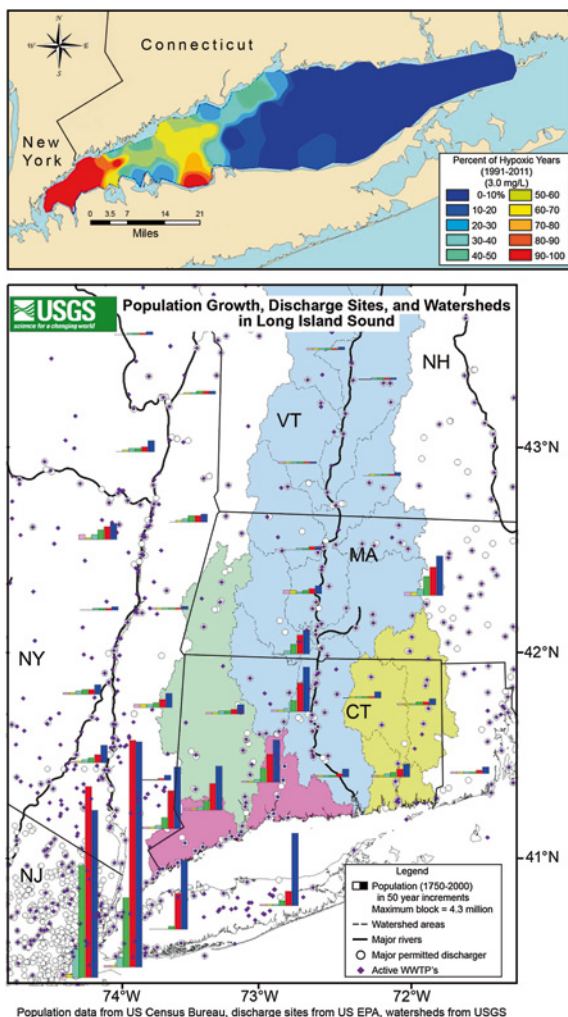
Anthropogenic sources of nutrients and organic carbon-based biological oxygen demand (BOD) are primary drivers of cultural eutrophication that has significantly disrupted the LIS ecosystem. After the massive fish kills of the 1970s and 1980s, more subtle ecosystem changes have been documented (Lopez et al. Chap. 6, in this volume). A short overview on sediment burdens of organic carbon, carbon sources, and carbon isotope data complements the more in-depth analysis of nutrient loading. Concentrations of N species and isotopes in LIS sediment and water-column samples are considered as well. Water quality monitoring data from the USGS and CTDEEP for macronutrients and organic carbon at stream gaging stations throughout the Connecticut watershed were discussed by Sprague et al. (2009). Here, we provide an in-depth analysis of the 40-year history of these element fluxes from the main rivers that discharge into LIS as well as from the WWTFs that discharge directly into LIS from data compiled by CTDEEP for their Nitrogen Credit Exchange Program, and discuss the potential implications for local primary productivity and carbon storage in the LIS sedimentary system. We also summarize some data from recent theses related to nutrient dynamics and impacts in LIS (Boon 2008; Andersen 2005; Lugolobi 2003).

5.3 Contaminant Sources to LIS Sediments

5.3.1 Metal Loading to Sediments

Many point and nonpoint source discharges contribute metals to LIS sediment. A review of sources of toxic contaminants to LIS by the Long Island Sound Study (1994) indicated that upstream riverine sources contributed most to delivery of the

Fig. 5.2 A: Frequency of hypoxia in LIS from 1991 to 2011 (From CTDEEP) 2B: Geography of the LIS watershed, with the main river basins feeding into LIS, locations of major permitted discharges, and WWTFs that discharge directly or indirectly into LIS and bars of population growth over the period 1750–2000 (in 50 year increments – yellow bar is 1750–1800, pale blue bar 1800–1850, and so on). From: The United States Geological Survey http://www.odshole.er.usgs.gov/project-pages/longislandsound/Research_Topics/Contaminants.htm



majority of toxic metals to LIS, except for lead (Pb) which has a major source from urban runoff. Significant sources of copper (Cu) and zinc (Zn) once existed along the Housatonic River and along some embayments (e.g., Bridgeport and New Haven). Connecticut was the center for brass production in the 1700–1800s, with Waterbury and Naugatuck as the two leading centers (Weigold and Pillsbury, [Chap. 1](#), in this volume; Varekamp et al. 2005). Brass sheet metal and wire as well as clocks, buttons, and weaponry were all made in the Brass Valley of the Naugatuck River watershed. According to Andersen (2004), by the early 1900s, nearly 4,000 manufacturers were active in Connecticut, with 381 factories lining the rivers of the Brass Valley.

The Remington Company in Bridgeport has made ammunition and weapons in extensive factories since 1867, and may have been an important source

of Cu, Zn, and Pb to the local watershed. Eli Whitney's development of interchangeable parts in the manufacturing of arms was a boon to the arms industry in Connecticut, along with the success of his Whitney Armory, which became the Whitney Arms Company in 1863 and provided arms for the American Civil War. Parker's Meriden Machine Company was also under Union contract to produce 10,000 repeating rifles and 15,000 Springfield rifles. Whitney Arms was eventually sold to the Winchester Repeating Arms Company in New Haven, which was active in the 1800s and closed only recently. Other plating and metal industries were active in Hartford and Springfield (MA), and discharged part of their waste into the Connecticut River. Meriden and Wallingford (CT) were known as "silver cities" due to the large number of sterling flatware, hollowware, and related silver (Ag) plated and other products that were manufactured there by companies such as International Silver, Wallace Silversmith, and Meriden Cutlery. Connecticut has been and continues to be a center of the metal industry, and waste fluids rich in metals have been discharged over the centuries into the main rivers draining into LIS.

Danbury and surrounding towns (Bethel) were the center of the hat-making industry, with the town of Norwalk as a second focus. The manufacturing of felt, initially from beaver fur and later from rabbit fur, involves sprinkling a solution of mercury (Hg) nitrate on the fur before it is hot pressed into felt and then formed into hats. The Hg-nitrate apparently makes the larger hairs crinkly and they wrap around the finer hairs to make a dense mat of felt. The subsequent heating process decomposes the Hg-nitrate again, leading both to the Hg exposure of hat-makers as well as constituting a significant source of environmental elemental Hg contamination. The resulting felt hat is relatively mercury-free and presumably almost all Hg used in the process is thus lost to the environment. The elemental Hg was possibly oxidized and then became attached to particles, providing a reservoir of strongly contaminated sediment in the uplands in Danbury around the former hat-making factories and in the Still River and Housatonic River. Similarly, in Norwalk several hat-making factories existed in the old center around Water Street and provided contaminated upland soils that were eroded over time and transported into the Norwalk River. A second atypical source of concentrated mercury pollution possibly existed in the HELCO power plant in Hartford, CT that used mercury vapor (instead of steam) as the working fluid in the plant. Spills during recharge and accidents may have provided mercury to Connecticut River sediment (Varekamp 2011). Other, lesser Hg sources relate to the use of Hg bearings in some WWTFs and discharges from companies making switches and thermostats.

Most WWTFs (locations shown in Fig. 5.2b) process a variety of waste water streams, including sewage that contains human fecal matter, industrial waste fluids, and liquid household waste. Studies of suspended solids in WWTF fluids and in sludges report high levels of Ag, Hg, Zn (Scancar et al. 2000; Sañudo-Wilhelmy and Flegal 1992) and a variety of other elements and compounds (e.g., Osmium; see Cuomo et al., Chap. 4, in this volume), reflecting the omnipresence of many metallic elements in common household and hospital products. Particularly, concentrations of Cu, cadmium (Cd), Zn, Pb, chromium (Cr), and Hg can be high. After the 1988 federal law that banned ocean dumping of sewage sludge, currently most

sludge from around LIS is disposed of through incineration (CT) or transformed into biopellets as a fertilizer (NY) or exported for landfill storage to other states. Some fine-grained matter and dissolved fractions escape with the fluids, providing a flux of metals to LIS. In addition, runoff from urban areas may contain metals, which wash off paved areas and from contaminated soils. In some urban areas, including New York City, stormwater passes through combined sewer overflow systems (CSOs) and may contribute to relatively high metal fluxes into rivers and estuaries. Sediments in some LIS embayments are strongly contaminated with metals, usually related to local sources (e.g., Pb and Cr contamination in the sediments of the Mill River in the Southport section of Fairfield, CT, from the former Exide Battery plant) and one cove also showed low-level contamination with radioisotopes from the nuclear power industry (Benoit et al. 1999). Small patches of highly contaminated sediment removed from urban harbors around LIS occur at the dredge material disposal sites in LIS, although most of these have been capped with clean sand to minimize environmental threats (Fredette et al. 1992; Fredette and French 2004).

5.3.2 Organic Contaminant Loadings to Sediments

Primary sources of organic contaminants to LIS are direct inputs from WWTFs, urban runoff, CSOs, and atmospheric deposition. Riverine inputs, particularly in Connecticut and the East River, extend the range of contaminant sources, as these rivers, in addition to serving inland population centers, also historically have functioned as corridors for industrial activity. Generally only organic contaminants that are sufficiently hydrophobic to become associated with sediment particles are analyzed in monitoring programs, so very little is known about the sources or distributions of dissolved organic contaminants in LIS, and these will not be discussed in this chapter. A map of population density over the period 1750–2000, location of WWTFs, major discharges, and watersheds for the region (Fig. 5.2b) clearly shows the sources of anthropogenic contaminants in WLIS. Wolfe et al. (1991) cited LIS riverine discharges and WWTFs as primary sources of nutrients and metals, with urban runoff as the primary source for most organic contaminants and lead. They recognized atmospheric deposition as another important source, both for distribution of new organic contaminants and redistribution of more volatile compounds. In contrast, the WWTF inputs of organic contaminants were considered to be secondary to river inputs in the CCMP, but are still significant. Sources for polycyclic aromatic hydrocarbons (PAH) in the New York/New Jersey estuary were mainly urban runoff, while atmospheric deposition was a significant source for PAHs with molecular weights of <200 g/mol (Rodenburg et al. 2010). Reviews by the National Academy of Sciences (NAS 1985, 2003) showed that urban runoff was also a major source of petroleum hydrocarbons to the sea. The PCBs that enter LIS largely follow the same pathways as the PAHs; significant sources of PCBs in the upper reaches of the Housatonic River to the north and from the Hudson River to the west do not seem to reach LIS

(Pringle et al. 2011). Chlorinated pesticides such as DDT and its metabolites, DDE, dieldrin, and chlordane, although banned in the 1970s and 1980s, are still found at appreciable concentrations in upland soils and LIS sediments in some locations; these legacy sources continue to enter LIS through pathways similar to those described for PAHs and PCBs. Once in the system, particle reactive and/or hydrophobic contaminants will tend to be associated with fine, organic-rich sediments. Although all but the largest sediment-sorbed contaminants (those with log octanol water coefficients >6.5) are generally available for bioaccumulation by resident biota, only those that cannot be broken down via metabolism biomagnify to top predators through trophic interactions.

5.3.3 *Macronutrients*

The nutrients N and P are essential for primary productivity and Si for diatoms as well because they use silica in their skeletons. The flux of N and P into LIS has increased dramatically over the last two centuries, leading to eutrophication (e.g., Lugolobi et al. 2004) though recent management efforts have significantly reduced point source loadings of N and P from WWTFs. A direct record of current and past nutrient fluxes is provided by monitoring data of rivers (USGS) and WWTFs (CTDEEP), whereas longer term, more indirect data can be extracted from sediment core analyses for particle-reactive species (Varekamp et al. 2004). The N and P fluxes today have a strong anthropogenic component, whereas the Si fluxes are only modulated by human activity (e.g., dam building; Triplett et al. 2008) but are not a human-caused effluent (derived from rock weathering processes).

The sources of N and P include atmospheric deposition (Luo et al. 2002), non-point and stormwater discharge from the human-altered landscape (Mullaney et al. 2002), excess fertilizer flows, excess particulate organic carbon from the land that becomes oxidized in LIS to release its N and P, but most of all, nutrient releases from WWTFs, especially those in the highly populated environs of New York City (Fig. 5.2b). Presently, the WWTF's in New York and Connecticut with discharge into LIS and its tributaries contribute an average of 61,200 kg of N per day, down from a baseline value of 95,250 kg N/day in 1990, but still quite significant (CTDEEP 2011). The effluents of the WWTFs are monitored and a TMDL has been established to meet dissolved oxygen water quality standards in Connecticut and New York by limiting the N inputs into the Sound (CTDEP and NYSDEC 2000). The TMDL target is to reduce the input of N into the Sound by 58.5 % (relative to a ca. 1990 "average" baseline load) by 2014. Reductions are accomplished primarily by upgrading WWTF's to tertiary or advanced wastewater treatment. This process presently reduces rates of ammonium discharge at some plants by an order of magnitude and DIN concentrations by as much as 70 % (CTDEEP 2011). Additional upgrades at many plants are planned which may further increase the efficiency of the removal process.

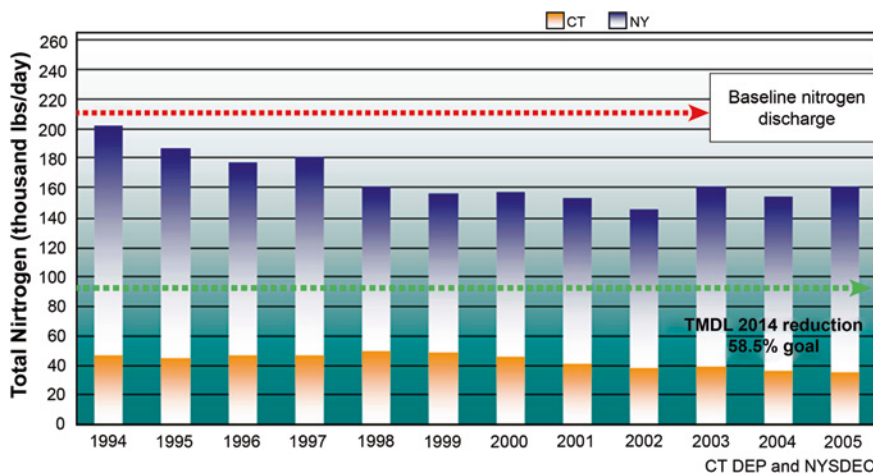


Fig. 5.3 Total N loadings of LIS from CT and NY from 1994 to 2005, showing a steady decrease over the first 9 years. Taken from CTDEP and NYSDEC data

Progress toward that total N target of 39,900 kg N/day is measured against a baseline flux of 95,250 kg N/day (Fig. 5.3). To reach the target, the phased (5 year increments) management of WWTF effluents in Connecticut and New York is emphasized and accomplished using a variety of regulatory tools including a “bubble” permit approach in New York City and N “trading” in Connecticut (CTDEEP, 2011). As of 2011, NY and CT had accomplished approximately 70 % of this goal; additional upgrades are scheduled, including several New York City plants coming online between 2012 and 2014. In terms of concentration, reductions are required from >8 mg/L total N in WWTF fluids to a final goal of 5.6 mg/L total N.

5.4 Metal Contamination

5.4.1 Spatial Patterns of Metal Contamination in LIS Surface Sediment

The absolute concentrations of contaminants in sediment are strongly influenced by grain size and organic carbon contents, and these tend to be correlated to each other in many environments as well (Windom et al. 1989). The association of metal contaminants with fine-grained organic-rich sediment thus impacts the spatial distribution of contaminants as well as the distribution of their maximum and minimum concentration values. Trace metal concentrations in LIS sediment show a wide range, caused by these sedimentary factors and variations in local anthropogenic source inputs. The mean and maximum values for a suite of trace metals, together with their preindustrial (background) values (after Mccray and Buchholtz

Table 5.1 Mean and maximum concentrations ($\mu\text{g/g}$) for metallic contaminants in LIS surface sediment (upper 2 cm).

	Ag	Cu	Cd	Hg	Pb	As	Zn	Cr	V	Ni	Ba
Mean	1.5	117	2	0.7	83	6	160	78	101	26	230
Maximum	10.1	7720	35	17	3284	61	4800	2000	160	665	445
Background	0.05	8	0.2	0.1	23	2.5	68	59	90	25	377
Mean EF	29.8	14.6	9.9	6.5	3.6	2.5	2.4	1.3	1.1	1.0	0.6

The natural background values are after Mecray and Buchholtz ten Brink 2000 and the Enrichment Factor (EF) is the mean value divided by the natural background concentration (for Arsenic few core data exist, background value estimated from the USGS surface sediment data base for relatively unpolluted sediment)

ten Brink 2000) and mean enrichment factors (EF), are shown in Table 5.1. Silver is the most strongly enriched metal (30x), followed by Cu, and then Cd and Hg. Barium, vanadium (V), and nickel (Ni) have close to natural background values. The high EF for Ag probably reflects the large inputs from WWTFs (Sañudo-Wilhelmy and Flegal 1992) and the high EF value for Cu reflects the inputs from the Housatonic River, which drains the historically industrialized Naugatuck River, and several smaller sources located along local embayments (Breslin and Sañudo-Wilhelmy 1999). Metal concentrations in LIS sediment increase with proximity to New York City, and higher concentrations are associated with fine-grained deposits that expectedly have higher surface-to-volume ratios relative to larger size fractions (Mitch and Anisfeld 2010; Mecray and Buchholtz ten Brink 2000; Greig et al. 1977; Long Island Sound Study 1993). The concentration maps for Cu and Pb exemplify this trend (Fig. 5.4), with some patchiness, but clearly higher values are found in the central and western parts of the Sound. Sediment grain size generally decreases from east to west (Knebel et al. 2000), with depositional sedimentary environments in CLIS and WLIS. To correct metal abundances for these grain size influences, we normalized the metal data on their sample Fe concentrations, which has been shown to correlate closely with grain size (Fig. 5.5). We then evaluated the resulting Fe-normalized east–west patterns for different metals.

Nickel has only modest contributions from anthropogenic sources, but non-normalized Ni concentrations show a clear increase from east to west (Fig. 5.6a). The Fe-normalized Ni concentrations show a much flatter east–west trend (Fig. 5.6b), however, indicating that Ni concentrations in LIS sediment are probably largely controlled by natural processes. In contrast, Fe-normalized trends for Cu, Hg, Ag, and Cr (Fig. 5.7a–d) show increases from east to west, indicating that metal sources increase to the west. Sources near the central and western part of the Sound are the industrial sources in the Housatonic River basin for Cu, Zn, and Hg, and urban sources along the East River (Ag, Hg). In particular, many large WWTFs that discharge directly into central and western LIS or a short distance up tributary rivers may be responsible for the Ag enrichment in sediment.

Element ratios that are characteristic of specific sources can be used to trace the metal origins. These source signals were determined from metals analyses

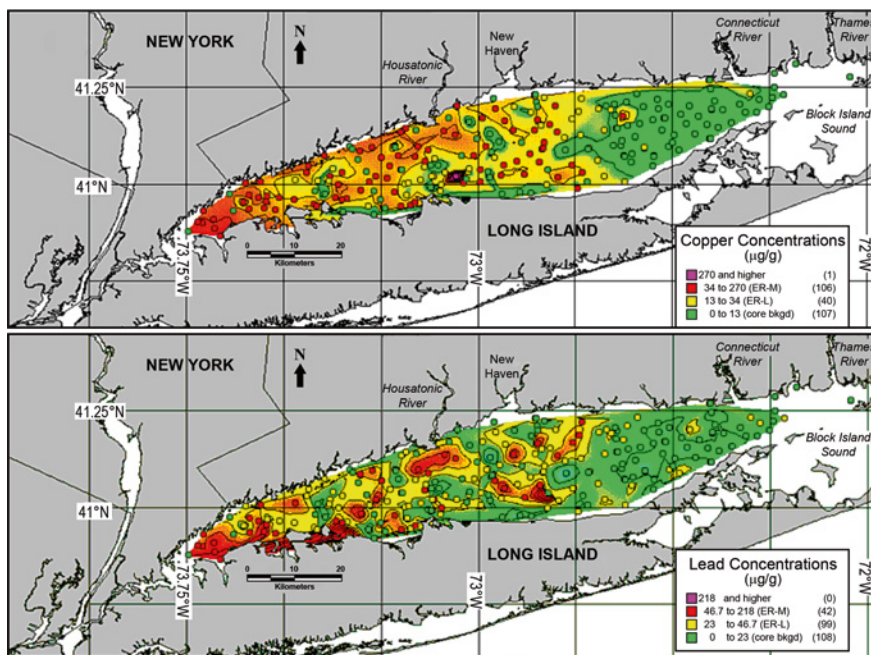
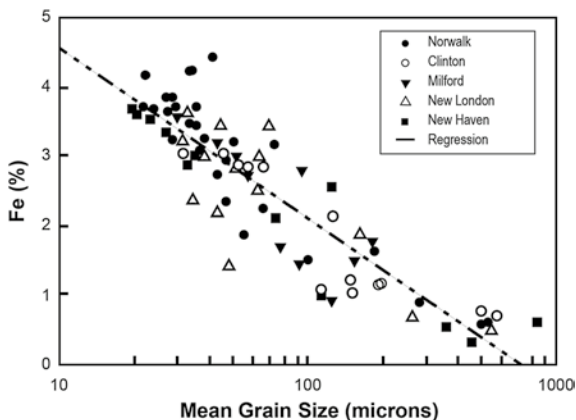


Fig. 5.4 Lead and Copper concentrations in LIS surface sediments, showing the highest concentrations in the western section of LIS, with a more patchy pattern in central LIS. Data source: <http://pubs.usgs.gov/of/2000/of00-304/htmldocs/chap06/index.htm>

Fig. 5.5 Relationship between sediment iron content and mean grain-size for LIS embayments (Lee 2010; Church 2009 and unpublished data). Similar results were obtained for ‘open LIS’ surface sediment data (Varekamp et al. 2000)



in the sediment of the Housatonic River estuary, which carries the characteristic source signals of the metal industry in the Brass Valley (Cu, Cr) and the Hg from the hat-making industry in Danbury and surrounding areas (mainly the Still River effluents). Connecticut River metals were characterized from sediment cores

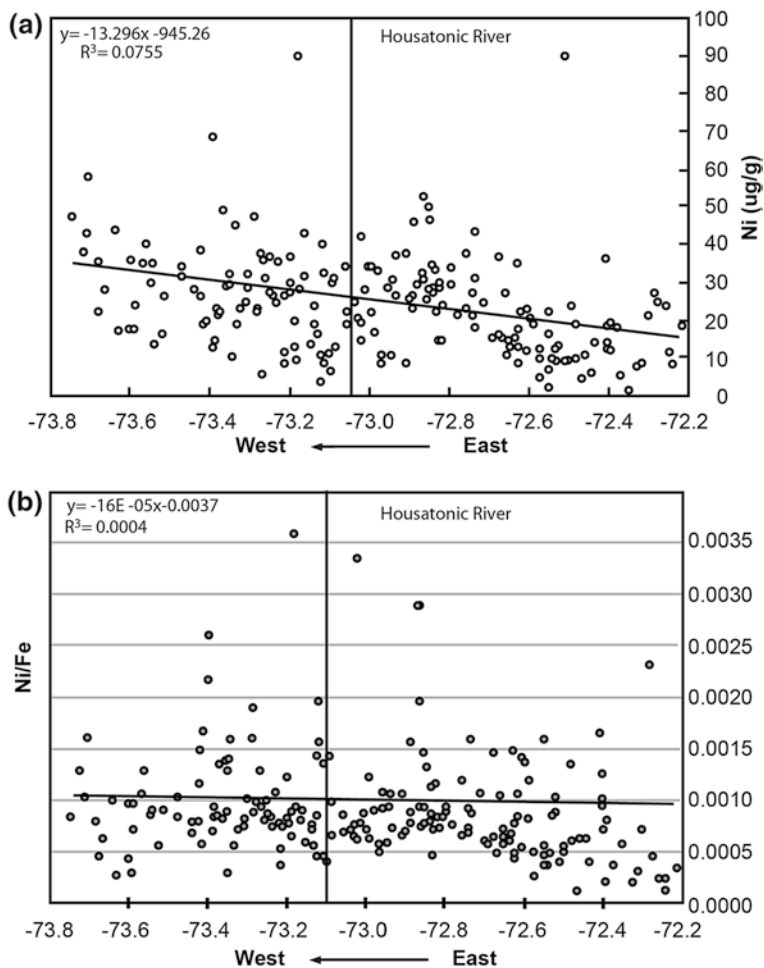


Fig. 5.6 Spatial distribution of Ni in LIS surface sediments. **a** Ni concentrations based on dry weight sediment, **b** Ni concentrations normalized to Fe concentrations. Much of the E–W trend in Ni concentrations is an artifact of the grain size differences between the east and west sections of LIS. Data source: <http://pubs.usgs.gov/of/2000/of00-304/html/docs/chap06/index.htm>

taken from Chapman Pond, a small cove south of East Haddam, and Great Island in the mouth of the Connecticut River estuary. Metal concentrations in sewage sludge were estimated from sediment samples taken in the New York Bight where a large amount of sewage sludge had historically been disposed until passage of the Ocean Dumping Ban Act of 1988, which ended sludge disposal in 1991 (e.g., <http://pubs.usgs.gov/fs/fs114-99/fig3.html>), using correlations between sewage indicators and metal concentrations.

In addition to Cu and Zn, sediment upstream of the Housatonic River estuary has up to 7,000 mg Cr/kg (Varekamp et al. 2005), providing a Cr-rich sediment

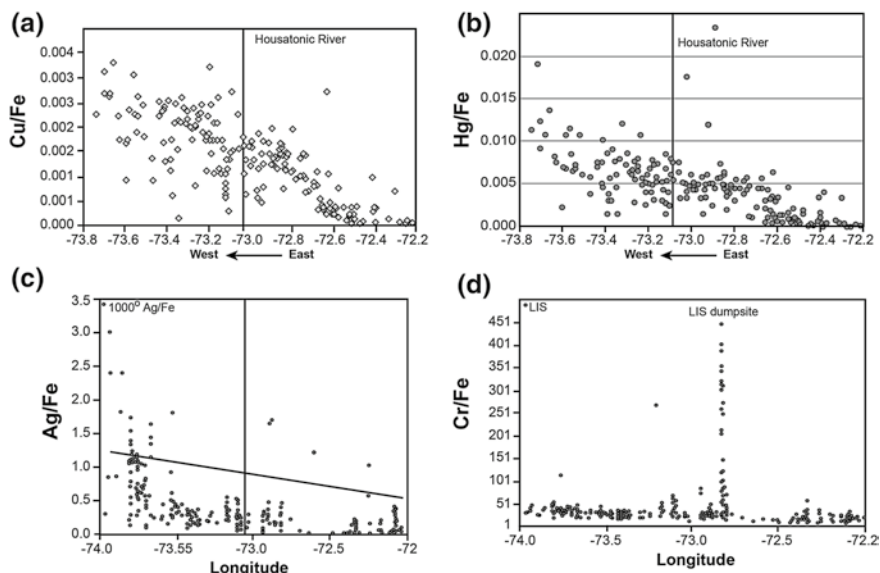


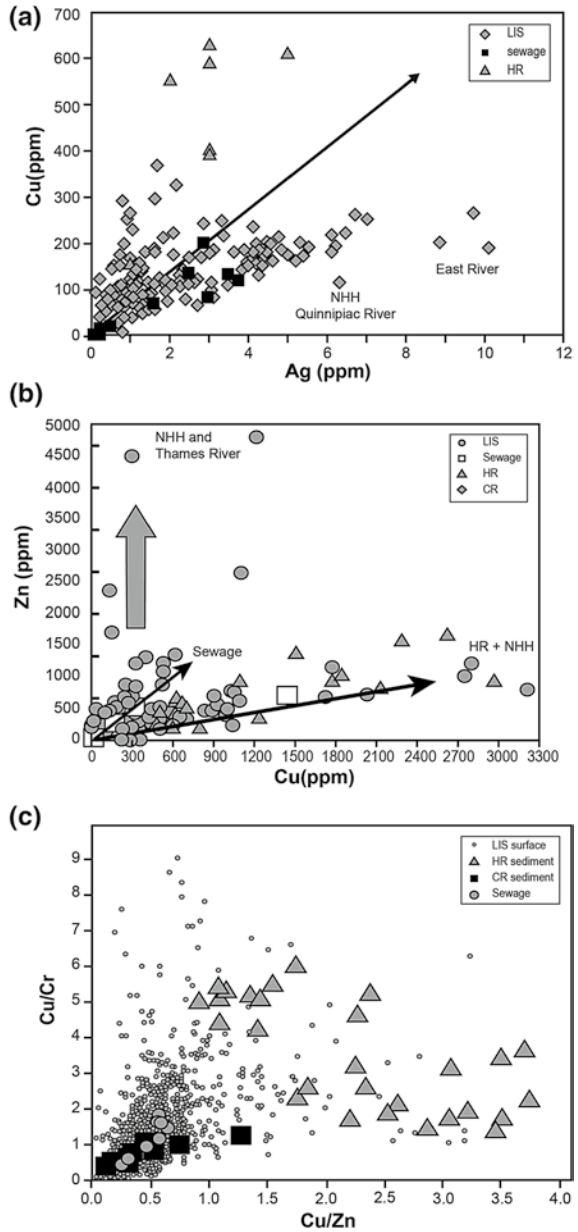
Fig. 5.7 Spatial distribution of Metal/Fe ratios in LIS surface sediments for Cu, Hg, Ag, and Cr. These elements show a significant E to W trend after normalization on Fe, (in contrast to Ni, Fig. 5.6), indicating the presence of strong metal sources along central and western LIS

source for LIS. The Cr/Fe in LIS sediment indeed increases from east to west (Fig. 5.7d). The area around the CLIS dredge material disposal site also shows high Cr/Fe and these sediments are presumably partially derived from dredged Housatonic River sediment. Many LIS sediments have Cu/Ag similar to sewage, but a group of LIS sediments with high Cu/Ag must have additional contributions from Cu-rich Housatonic River sediment. A similar pattern to Cr emerges for Cu and Zn concentrations (Fig. 5.8). Mixing calculations based on element ratios (Fig. 5.9) indicate that up to 20 % of Housatonic River sediment can explain the high Cr and Cu concentrations in many LIS sediment samples, with extremes carrying up to 40 % of the highly metal-polluted Housatonic River sediment.

5.4.2 Metal-Laden Sediments in Coastal Embayments

Harbor or embayment sediments may have much higher metal concentrations than open LIS sediment due to the restricted water circulation and the proximity to multiple sources of industrial and municipal wastewater (Breslin and Sañudo-Wilhelmy 1999; Rozan and Benoit 2001; Luoma and Phillips 1988). Most embayments are characterized by a variety of sedimentary environments

Fig. 5.8 Element ratios in LIS surface sediment and some of the sources of these metals: Cu–Ag, Cu–Zn, Cu/Cr–Cu/Zn



with high concentrations of Zn, Cu, Pb, and Cd (Breslin and Sañudo-Wilhelmy 1999; NOAA 1994; Rozan and Benoit 2001). The high metal loadings are a concern, particularly in embayments that support commercial and recreational shellfish industries (O'Connor 1996). The mean and median sediment Zn and

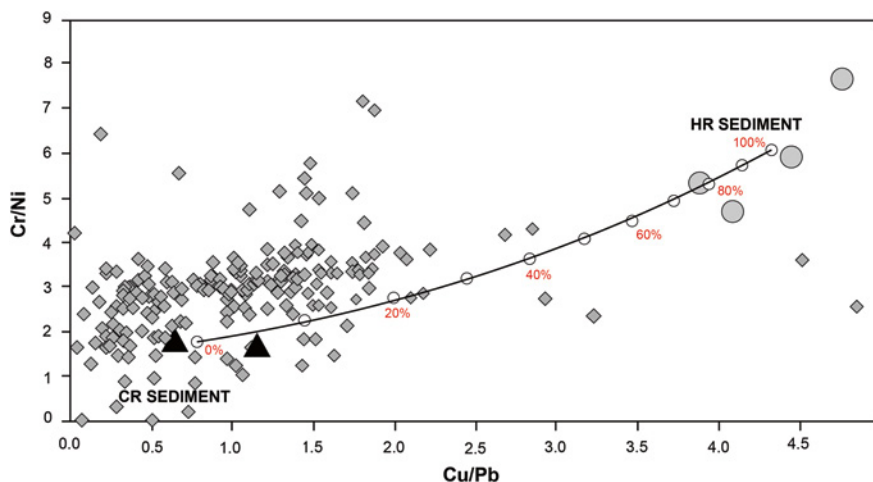


Fig. 5.9 Calculated potential contributions of Housatonic river (HR) and Connecticut River (CR) sediment to LIS metal contaminant budgets

Cu concentrations for several Connecticut embayments (Table 5.2 and Fig. 5.10) all exceed natural background values and display a much greater variability than open LIS sites. Sediment metal contents in Port Jefferson Harbor, NY for instance vary by over an order of magnitude over distances of only 50–500 m (Breslin and Sañudo-Wilhelmy 1999), suggesting highly variable sedimentary environments or the influence of local discharges. With the exception of Clinton Harbor (Cu and Zn) and the Housatonic River (median Zn), all mean and median Cu and Zn values are similar to or exceeded NOAA Effects Range Low (ERL) thresholds. For most Connecticut embayments, both mean and median sediment Zn concentrations are similar to the ERL Zn threshold. Only Clinton Harbor (below the ERL) and the Bridgeport and Norwalk Harbors (above the ERL) differ significantly from the ERL Zn threshold. Both Cu and Zn concentrations were similar to or exceed NOAA Effects Range Median (ERM) thresholds for one or more locations in four of the eight harbors examined in ELIS (New London), CLIS (New Haven), and WLIS (Bridgeport and Housatonic River; Fig. 5.10). The ERL and ERM values were set based on empirical data gathered across the country by NOAA linking sediment contaminants levels with observed toxicity, where the ERL corresponds to the 10th and the ERM the 50th percentiles, respectively, of toxicity effects (Long and Morgan 1990). Hot spots in embayments are defined as locations where sediment Cu and Zn concentrations exceed the 90th percentile values. The number of hot spots identified within Connecticut embayments range from one (Clinton, Branford, and Milford) to eight (New Haven).

Linear regression analyses of the sediment Cu and Zn concentrations within each harbor show that Cu and Zn co-vary, with regression coefficients from

Table 5.2 Comparison of copper and zinc concentrations in Connecticut harbors with previously published data and reference levels

Harbor	Stations	Copper (mg/kg)			Zinc (mg/kg)		
		Range	Mean	Median	Range	Mean	Median
New London ^a	n = 35	3.2–252	62	61	10.0–642	156	165
Clinton ^b	n = 14	0.4–49	22	13	10.1–247	108	70
Branford ^c	n = 18	17.2–148	67	67	35.7–274	159	156
New Haven ^d	n = 128	6.3–405	82	74	7.5–463	151	146
Milford ^b	n = 11	19.9–104	67	70	37.0–236	147	161
Housatonic River ^e	n = 31	6.3–685	146	93	11.3–517	159	104
Bridgeport ^d	n = 26	18.5–491	182	146	5.6–677	234	196
Norwalk ^f	n = 30	6.9–218	99	98	33.0–387	174	170
ELIS ^g	n = 302	2.8–96	53		23.5–186	110	
CLIS ^g	n = 323	8.6–185	84		43.3–221	137	
WLIS ^g	n = 453	14.8–216	116		39.2–315	183	
Effects Range Low ^h			34			150	
Effects Range Median ^h			270			410	
Natural Background ⁱ			8			68	

^aLee (2010)^bChurch (2009)^cBreslin et al. (2005)^dTitus (2003) and unpublished data^eConklin (2008)^fUnpublished data^gData from Mitch and Anisfeld (2010) compiled from multiple sources. Range represents 10th and 90th percentile values^hEffects Range data from NOAA (1999)ⁱNatural background from Mecray and Bucholtz ten Brink (2000)

0.73 for Norwalk Harbor to 0.96 for Clinton Harbor. For most Connecticut harbors, the slope of the regression line defining the relationship between Cu and Zn was similar for ELIS and CLIS harbors in this study (0.22–0.49). In contrast, the slope of the regression line increased (0.58–0.81) for WLIS harbors (Bridgeport, Housatonic, and Norwalk) indicating a disproportionately higher sediment Cu content relative to Zn content for these harbors (Table 5.3). Linear regression analysis shows that Cu is strongly correlated with both sediment Loss on Ignition (LOI) (a proxy for organic matter) and sediment Fe (= Iron %) for all Connecticut harbors/ rivers studied (Fig. 5.11a and b; Table 5.3). Steeper slopes of the Cu versus LOI and Cu versus Fe relationships indicate disproportionately higher source strength for Cu within WLIS river estuaries and embayments, such as the Housatonic River.

Mecray and Bucholtz ten Brink (2000) showed a significant correlation between metal concentrations and % fines in open LIS sediment, whereas the Mitch and Anisfeld (2010) analysis of the National Coastal Assessment 2000–2002 and State of Connecticut Sediment Quality Information Database (SQUID) showed no strong relationship between sediment metal concentration and grain size. The coastal embayments generally show a greater range of sediment Cu and Zn variability compared to their respective open water sediment location in LIS

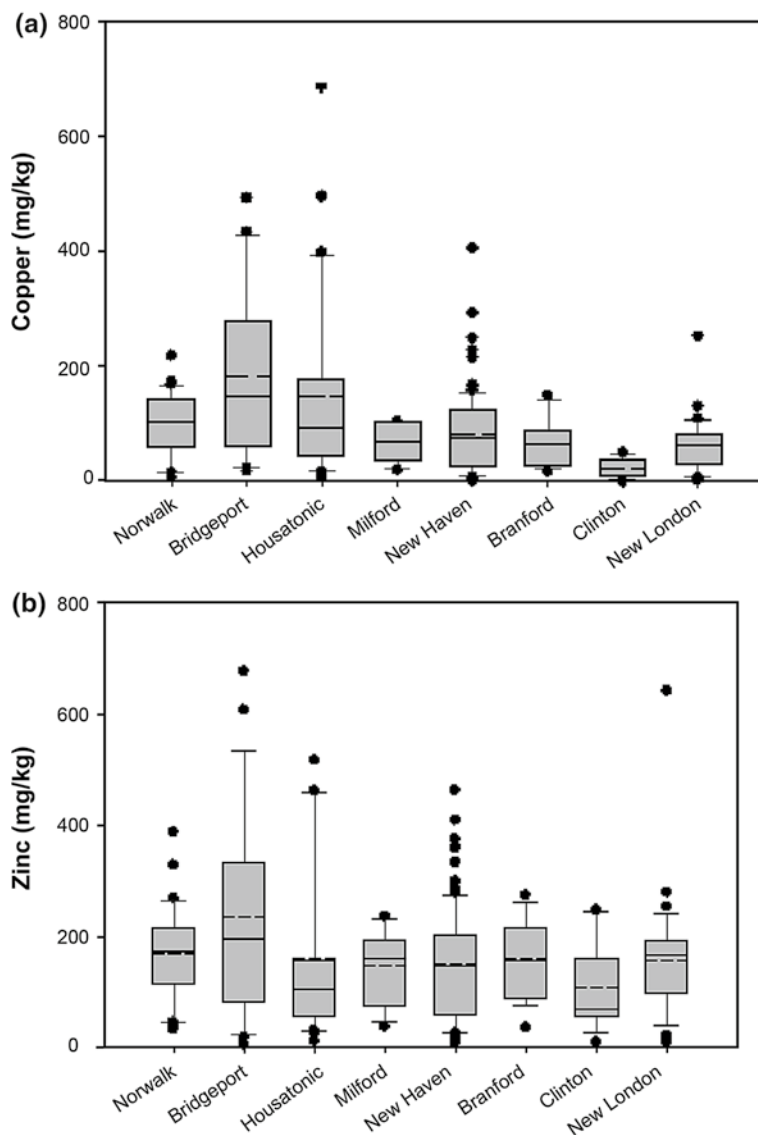


Fig. 5.10 Comparison of copper (a) and zinc (b) sediment metal concentrations in Connecticut harbors. Embayments are arranged along the X-axis from left to right, west to east. The whiskers indicate the 10th and 90th percentile values. The bottom and top of each *box* indicate the 25th and 75th percentile values, respectively. The *solid line* within the *shaded box* indicates the median concentration and the *dashed line* indicates the mean concentration. The *solid circles* represent outliers; sediment metal values higher or lower than the 90th and 10th percentiles

(Mitch and Anisfeld 2010), which is here largely explained by variations in sediment physical properties and local depositional environment. The “hot spots” are characterized by the presence of fine-grained, high-LOI sediment, and are most

Table 5.3 Coefficients of determination^a (r^2) and p -values for testing the population slope (β_1) = 0 between sediment copper and zinc, copper and iron, and copper and loss on ignition for Connecticut embayment datasets

Harbor	Cu vs Zn			Cu vs Fe ^b			Cu vs LOI ^c		
	r^2	Slope	p	r^2	Slope	p	r^2	Slope	p
New London	0.92	0.41	<0.001	0.68	31.0	<0.001	0.32	5.1	<0.001
Clinton	0.96	0.22	<0.001	0.93	16.5	<0.001	0.95	5.7	<0.001
Branford	0.88	0.53	<0.001	0.49	29.9	0.001	0.51	5.1	<0.001
New Haven	0.74	0.49	<0.001	0.62	28.7	<0.001	0.52	12	<0.001
Milford	0.83	0.42	<0.001	0.93	30.9	<0.001	0.79	7.1	0.001
Housatonic River	0.94	0.81	<0.001	0.79	121	<0.001	0.84	39	<0.001
Bridgeport	0.88	0.71	<0.001	0.72	71.6	<0.001	0.66	25.7	<0.001
Norwalk	0.73	0.58	<0.001	0.51	35.2	<0.001	0.68	14.9	<0.001
Port Jefferson, NY ^d	0.96	0.51	<0.001	0.74	26.6	<0.001			

^aCoefficient of Determination (r^2) and slope estimates derived from a linear regression analysis of the dataset for each harbor in Table 5.2. The number of stations (n) analyzed for each regression analysis for each harbor is given in Table 5.2

^bRegression analysis for sediment copper versus iron shown for each harbor in Fig. 5.11b

^cRegression analysis for sediment copper versus loss on ignition shown for each harbor in Fig. 5.11a

^dCoefficient of Determination (r^2) and slope estimates derived from a linear regression analysis of data available in Breslin and Sañudo-Wilhelmy (1999)

frequently located in the inner (northern) reaches of the harbors (dredged channels, river mouths, river coves) proximate to contaminant sources. Copper and Zn sediment concentrations at these “hot spot” locations in the harbors throughout LIS exceed ERL and ERM thresholds. The two main WLIS harbors (Housatonic River and Bridgeport) have disproportionately high sediment Cu concentrations compared to other LIS harbors, showing the influence of the Housatonic River inputs from the “Brass Valley” industries of the past. The correlation of high Cu and Zn with LOI may reflect metal association with particulate organic carbon, and if so, microbially mediated repartitioning and mobilization of these elements to more bioavailable forms in the solution phase, may then be a management concern.

5.4.3 Core Records of Historic Metal Contamination

Many sediment cores in LIS have been dated with radioisotopes and thus provide a time record of metal contamination in LIS (Buchholtz TenBrink, personal communication; Varekamp and Thomas 2010). Examples for several metals are shown for two cores, positioned on the A transect of the USGS coring cruise of 1996 (Fig. 5.12a). Core A4C1 is positioned in shallow water close to the Connecticut coast, whereas core A1C1 is located in the middle part of CLIS. Sediment accretion

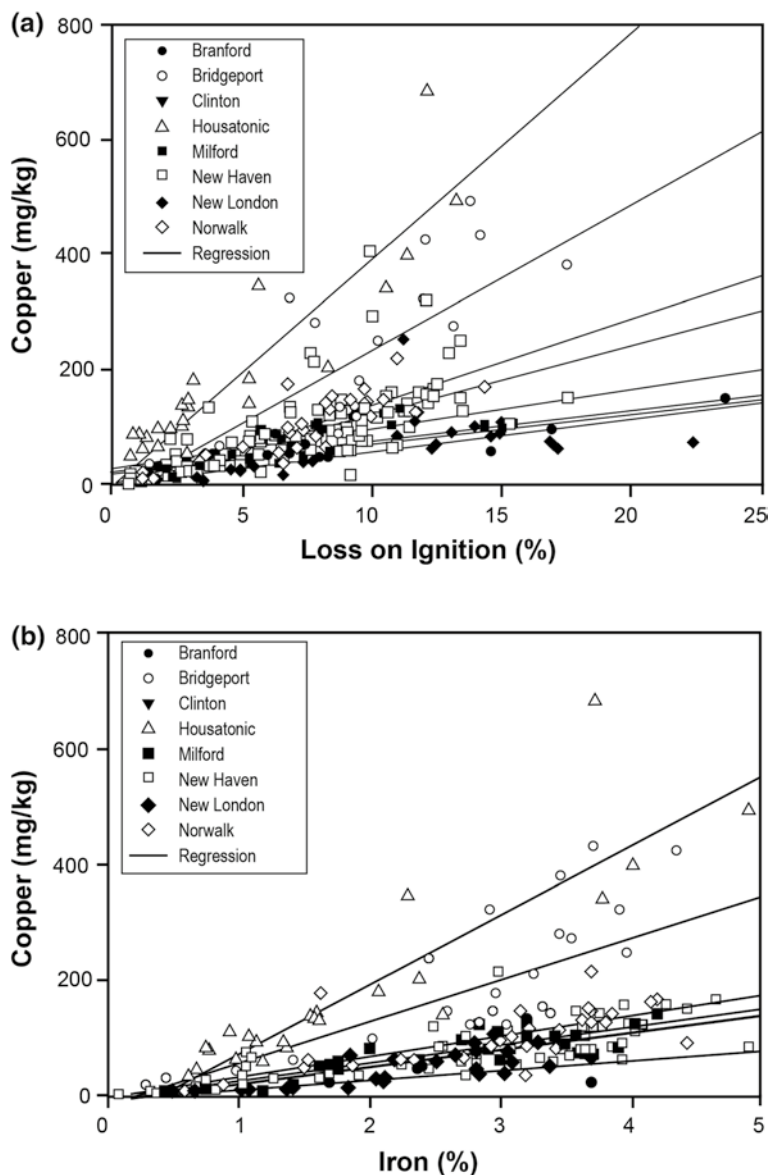


Fig. 5.11 Co-variance between sediment Cu concentrations and **a** sediment loss on ignition (LOI) and **b** sediment Fe concentrations for Connecticut harbors and embayments

rates in core A1C1 (0.6 mm/year mean sedimentation rate) are much lower than those in A4C1 (2 mm/year), providing a higher time resolution in core A4C1.

The metal profiles versus age (Fig. 5.12b) show background concentrations in precolonial times and gentle increases in concentration in the early to mid-1800s

and stronger enrichments in the 1900s. In most cores, metal concentrations decreased between 1980 and 2010, the period of enhanced environmental control required by the Clean Water Act. The metals Ag, Cu, Zn, Cr, Hg, and Pb show EFs over natural background values ranging from ~3 to 15. The element Ni shows no enrichment in sediment deposited since 1850 and appears to have no major anthropogenic contributions. A similar conclusion for Ni was obtained earlier in the Ni/Fe values along the longitudinal transect of LIS. Core A4C1 shows a strong concentration spike in Cu, Zn, Cr, and Hg around 1955, a period when two hurricanes hit central Connecticut. This distribution of elements is characteristic for sediment from the Housatonic River, and this thin metal-enriched layer was caused by a 100 year hurricane flood deposit in the central LIS area (Varekamp et al. 2005).

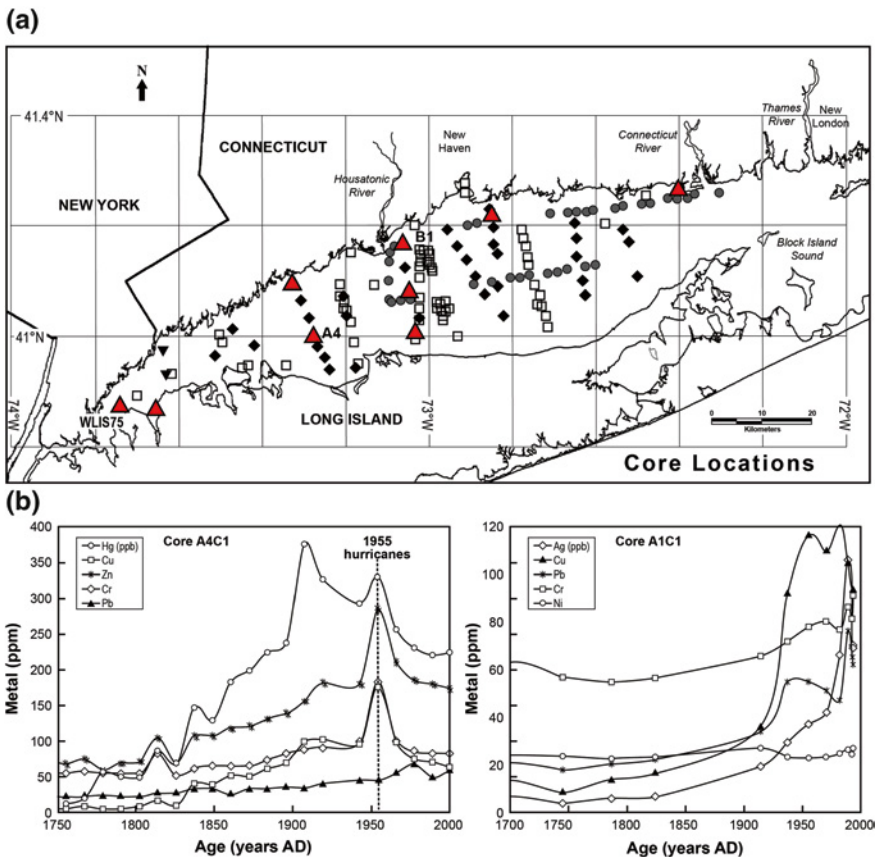


Fig. 5.12 Core profiles of metal concentration versus age in LIS cores A1C1 and A4C1 (see index map for locations) a Cu, Zn, Cr, Pb, and Hg in core A4C1 (location A4, core 1) b Ag, Cu, Cr, Pb, and Ni in core A1C1 (location A4, core 1)

5.4.4 Mercury Contamination in LIS

The geochemistry of mercury (Hg) as a contaminant in LIS has been studied extensively over the last 20 years. Sediment concentrations range from low ppb (ng Hg/gr dry sediment) Hg values in the east up to 800 ppb Hg in WLIS (Figs. 5.13a, 5.14a). The Hg/Fe values also trend higher going west (Fig. 5.7b), like many other metals with sources in WLIS. Most LIS core profiles for Hg show a large increase in the mid-1800s (in dated cores based on ^{210}Pb and ^{14}C ages), which correlates with the concentration increase in spores of *Clostridium perfringens* (Fig. 5.13b), a sewage indicator (Buchholtz ten Brink et al. 2000; Varekamp et al. 2000, 2003). This synchronicity between sewage input and Hg enrichment is not necessarily causal: Both relate to industrialization and the increase in population density over the last 150 years.

Besides the common far-field Hg sources such as coal and solid waste incineration, western Connecticut has a large Hg point source in the historic hat-making industry (Varekamp et al. 2005). Upland sediments around the old hat-making towns of Danbury and Norwalk have mercury concentrations in the thousands to hundred thousands ppb Hg. These sediments are remobilized in a steady state fashion at low level, but more intensely during major rain storms, hurricanes, and extended wet periods. The marshes and mudflats of the Housatonic River estuary are strongly enriched in Hg (Varekamp et al. 2005; Table 5.4), and the offshore delta deposits also show a strong spike at about the 1955 level, which is the time of major flooding in Connecticut (two hurricanes in 2 weeks; Fig. 5.14b, c). In western LIS, a core near Execution Rock (core WLIS75GGC1) shows a strongly Hg-enriched layer that is directly underlain by a coarser deposit with small coal and debris fragments (Fig. 5.14d). Most likely, this is also part of a hurricane deposit, possibly from the 1955 hurricanes, although the direct source of this Hg

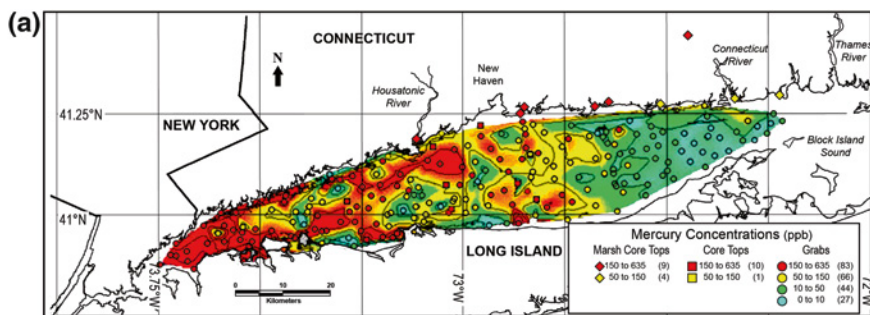


Fig. 5.13 **a** Mercury contamination pattern in LIS surface sediment and **b** with two core records for Hg and **c** perfringens versus depth (Core A7C1 is the most southerly coring site on the A transect of Fig. 5.12). The core concentration profiles show the strong increase in Hg and a retreat in the top of the core, whereas the C. perfringens concentrations remain high also in the core top. Data source: <http://pubs.usgs.gov/of/2000/of00-304/htmldocs/chap06/index.htm>

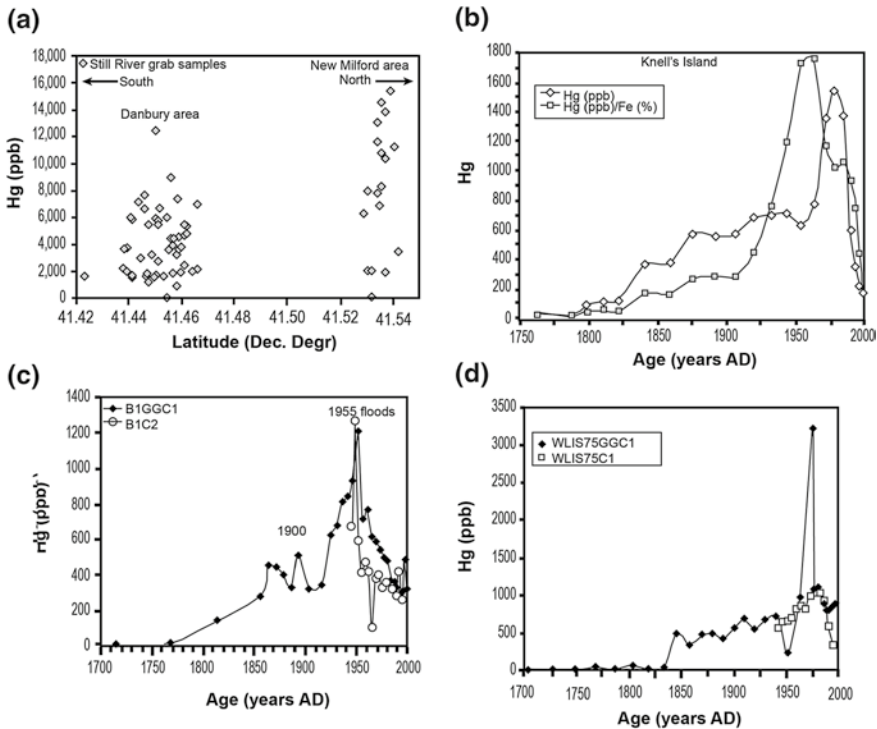


Fig. 5.14 Mercury data from the Housatonic River watershed and western LIS. **a** High mercury concentrations in the Still river that drains the main hat-making area in CT (Danbury) **b** Mercury profile of core KI from Knells Island in the Housatonic River estuary **c** Mercury profile from cores at the B1 site on the Housatonic River delta **d** Mercury profile from the WLIS75 coring site near Execution Rock in WLIS (Fig. 5.13b). All cores show evidence for a steep rise in Hg in the mid-1800s, and spikes around 1955 from hurricane activity

Table 5.4 Mercury concentrations in cores from LIS, salt marshes, and coves around LIS; the Housatonic River (HR) shows strong contamination from the uplands with the hat-making industry near Danbury, CT (after Varekamp et al. 2000, 2003)

	Hg peak range (ng Hg/gr)	Inventory excess Hg (ng/cm ²)
LIS	Up to ~800	2120–9200
Salt marshes (excluding HR)	160–470	490–3770
HR marshes	1500–7000	>5000

in the far western Sound is not known. The Connecticut River has carried Hg-rich fine-grained sediment to the Sound over the last 60–80 years, presumably from various industrial sources and possibly from an experimental power plant that used Hg as its working fluid (Varekamp 2011). Clay deposits in small coves and inlets on the river flood plain contain up to 3,000 ppb Hg (Varekamp 2011). Presumably,

this fine-grained sediment was also carried into the Sound over the years, constituting a heretofore unrecognized Hg source for LIS.

Core profiles in LIS and its surrounding marshes show that sediments deposited in the 1960–1970s periods display the strongest Hg contamination. These cores show a decrease in Hg concentrations in the core tops, whereas concentrations of *C. perfringens* increased also over these last 50 years (Fig. 5.13b), because WWTF effluent discharges kept increasing in volume over this time. Besides the direct hurricane layers, many LIS and coastal salt marsh cores show a double peak in Hg concentrations, one at ~1900 and the second peak in the 1960–1970s. The late 1800s and early 1900s were a very wet period and presumably more Hg was exported from the heavily contaminated watersheds of the Housatonic and Norwalk Rivers. The wet climate also possibly enhanced the “flush out” of Hg from the atmospheric reservoir (Varekamp et al. 2003).

Records of Hg deposition from ponds on Block Island, RI, east of LIS (i.e., in Block Island Sound), where the primary source of Hg is atmospheric, show a different pattern than the open LIS core records (Fig. 5.15). These Block Island records were obtained from a freshwater pond and a freshwater marsh on an island with no local Hg contamination sources (Neurath 2009) and no influx from LIS sediment. These records show only a very gentle increase in Hg concentration over the last part of the nineteenth century (from 30–60 ppb Hg). The first large increase in Hg concentrations (from 70 to 200–300 ppb Hg) and Hg accumulation rates only starts in ~1935–1940 in these cores dated with ^{210}Pb , ^{137}Cs , and ^{14}C . This relatively recent and rapid increase in Hg contamination is also found in some ice core records (Schuster et al. 2002) and other remote lake records (Perry et al. 2005), and reflects far-field atmospheric deposition of Hg. These results contrast strongly with almost all records from the open LIS basin and its coastal marshes with their steep rise in Hg in the mid-1800s. The substantial local Hg sources from the hat-making industry started at the beginning of the nineteenth century, and have influenced the Hg distribution in LIS for more than 200 years, overwhelming the variations in the strength of the far-field atmospheric input. The latter is deposited both in situ on the Sound and in the watershed, the latter focused through the watersheds and then transported through riverine sediment into LIS. If the hat-making Hg has such a large influence on the Hg distribution patterns and concentrations in most of CLIS, we have to assume that fine-grained sediment is circulated throughout the Sound with the strong tidal currents. Satellite images of the sediment plume of the Connecticut River during Hurricane Irene (September 2011) clearly show that the river sediment plume is dispersed dominantly to the west but to a lesser degree also to the east-southeast.

Wastewater treatment facilities provide a flux of Hg into the Sound and correlations with the abundance of the sewage tracer *C. perfringens* spores (Fig. 5.16) suggest that up to 25 % of total Hg in Sound sediment was derived from WWTF effluents (Varekamp et al. 2003). The hat-making Hg may have been responsible for 20–30 %, based on Cu-based mass flux constraints of Housatonic River sediment, whereas the remainder may have come in with the sediment from the Connecticut River and smaller watersheds.

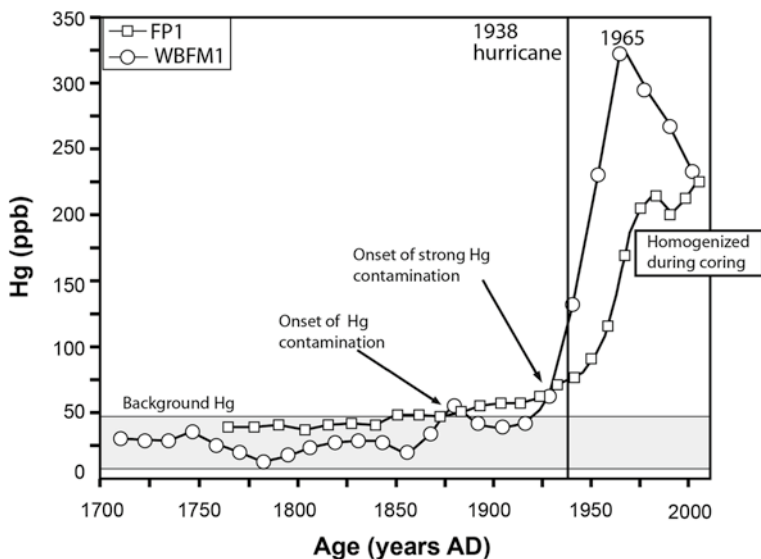


Fig. 5.15 Mercury concentrations in two bogs (FP1 and WBFM1) on Block Island (Rhode Island) to the east of the LIS map in Fig. 5.12), showing a very different pattern compared to those from LIS (see text for discussion; Fig. 5. after Neurath 2009)

A modern Hg budget for LIS was presented by Balcom et al. (2004), who considered the Hg inputs and outputs to LIS and cycling within LIS (Fig. 5.17). The inorganic pool of dissolved Hg and Hg adsorbed onto fine particulate matter from the main rivers feeding LIS (East River, Connecticut River, Thames River and Housatonic River) provides the dominant input flux (close to a 1,000 mol/year), whereas the WWTFs along the LIS coastline supply a much smaller amount (~60 mol/year). Atmospheric deposition is a sizeable source term at 130 mol/year, but rather surprising is the magnitude of the estimate of the volatile elemental Hg(0) escape from LIS into the atmosphere (~400 mol/year). The inorganic Hg that is brought in by the various sources may become reduced during aqueous bacterial reactions; this leads to a buildup of Hg⁰ (aq) (Rolfhus and Fitzgerald 2001; Tseng et al. 2003) that ultimately escapes to the atmosphere. The estimated flux of Hg from LIS waters back into the atmosphere is about three times as large as the estimated direct atmospheric Hg deposition rate (Balcom et al. 2004). Thus, the evasion of elemental Hg from the surface waters of LIS is a return pathway of Hg that was brought into LIS associated with particles through rivers from a variety of point and nonpoint sources. Mercury may also escape from coastal salt marsh areas through reduction and vapor evasion, but the magnitude of that flux is not well-known (Lee et al. 2000). The LIS coastal zone thus is an area with active processing of Hg, where the input consists of focused atmospheric deposition from the watershed, in situ deposition on LIS, and point source Hg in dissolved and particulate form. Bacterial reduction in the water column with subsequent evasion to the atmosphere forms an important Hg return flux.

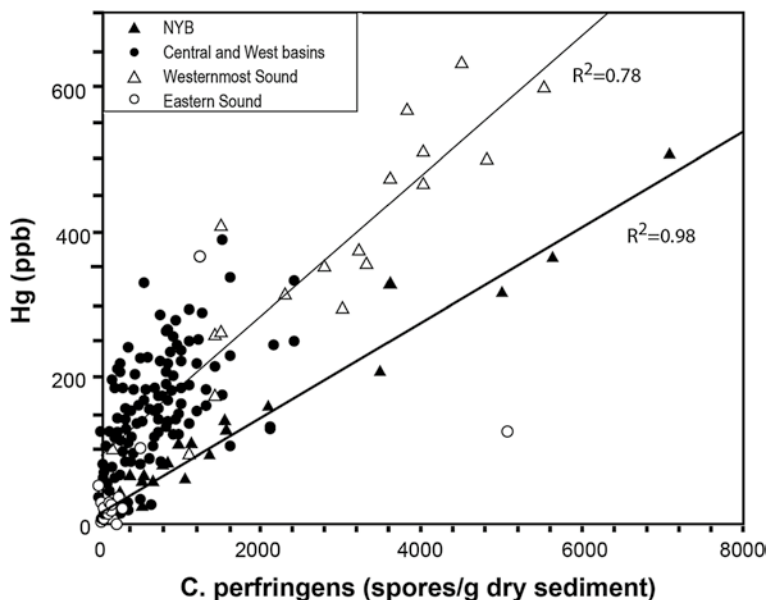


Fig. 5.16 Correlation between Hg and *C. perfringens* for LIS surface samples. Most data points plot above the sewage correlation line (heavy black line associated with NYB points, data from NY bight sewage dumpsite), indicating that sources other than sewage contribute to the Hg loadings in LIS

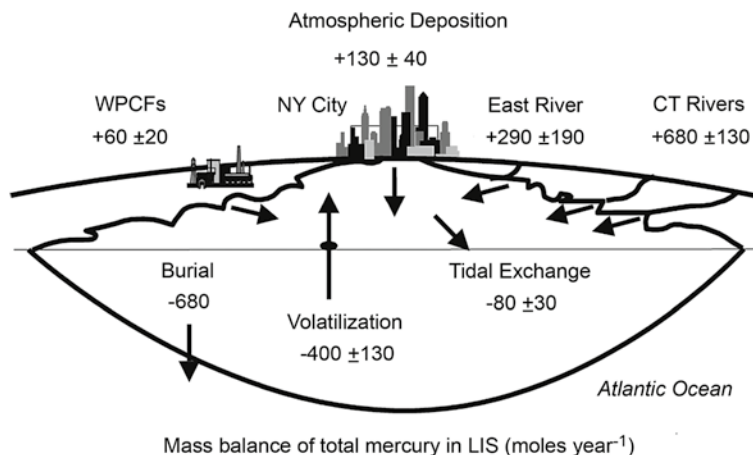


Fig. 5.17 Mercury budget for LIS based on measured fluxes from rivers, WWTFs and atmospheric deposition (after Balcom et al. 2004). The Hg revolatilization flux from LIS surface water into the atmosphere is substantial (three times the atmospheric Hg deposition flux)

Methylation and ecosystem uptake occur in LIS and marsh fringes, and methylation rates in marsh environments can be substantial (Langer et al. 2001). Fish in LIS have Hg enrichments up to 1 mg/kg wet weight (Skinner 2009), suggesting

that a fraction of the inorganic mercury has been transformed into methylmercury through bacterial reactions (Whalin et al. 2007). The methylation of Hg in LIS depends on the substrate that carries the Hg and presence of bacteria capable of sulfate or Fe reduction and methylation. Sediment in WLIS with high Hg concentrations has the lowest methylation rates (Hammerschmidt et al. 2008; Fitzgerald et al. 2000), believed to be the result of the presence of abundant organic carbon that tightly binds the Hg to the substrate. With potential decreases in eutrophication in the future, the deposition rate of organic carbon may decrease, which may lead to higher methylation rates and hence increased trophic transfer of Hg in that part of the Sound (i.e., the concept of “growth dilution” for Hg in reverse; Fitzgerald et al. 2007; Ward et al. 2010), although sulfide abundances in waters also play a role in the kinetics of these Hg conversions.

5.5 Organic Contaminants (PAHs, PCBs, and Chlorinated Pesticides)

5.5.1 *Spatial Patterns of Organic Contaminants in LIS Surface Sediment*

The USGS, as part of their comprehensive evaluation of sediment contamination in LIS sediments begun in 1995, gathered all available data on sediment contaminant levels for priority pollutants from federal and state monitoring programs as well as dredge material permits and published papers. Their dataset is available online at <http://pubs.usgs.gov/of/2003/of03-241/>. An overview of spatial patterns in the toxic fraction of petroleum hydrocarbon contaminant levels in sediments was obtained by calculating total PAHs by summing all 23 PAHs analyzed in the dataset after removing data reported as being below the limit of detection, and data from nonpeer-reviewed studies conducted as part of dredge permitting applications (e.g., SQUID). The PAH values were grouped into four categories, showing low levels approximately corresponding to the 85th percentile ranking of all values reported by NOAA's NS&T program (<2,000 ng/g dry weight) in blue, slightly higher levels (from 2,000 to 4,000 ng/gdw) in green, levels exceeding the ERL (4000–45,000) in yellow, and levels exceeding the ERM (<45,000) in red (Fig. 5.18). Particularly in ELIS and CLIS, most sediment sampled showed PAHs levels below 2,000 ng/gdw (blue symbols), indicating that they rank among the least contaminated sites throughout the United States. In ELIS and CLIS, values exceeding the NS&T 85 % percentile (green symbols) are only seen near the CLIS dredge material disposal site in central LIS and at coastal locations, particularly in Connecticut, although it should be noted that there is a paucity of data along the eastern shore of Long Island. In WLIS, there are many more data points and clear evidence of organic contaminant pollution. In this region, most sediment PAH levels exceed the NS&T 85 % percentile, and many exceed the ERL (yellow),

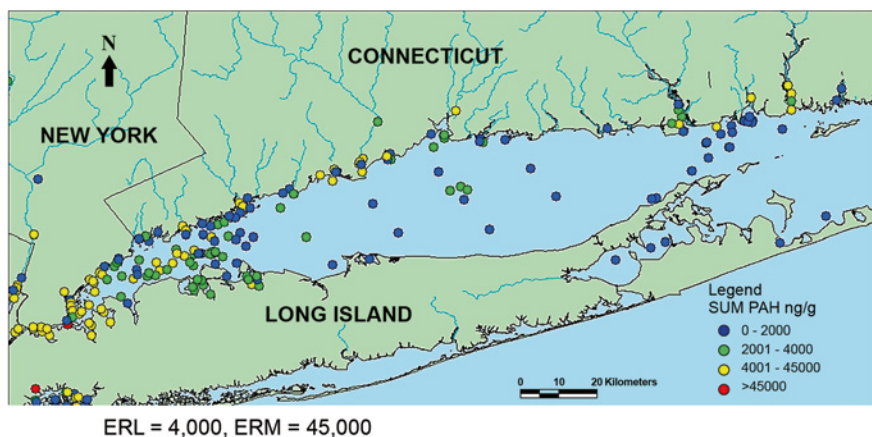


Fig. 5.18 Total PAH concentrations in LIS surface sediments (USGS database, years 1975–2000) ERL (effects range low), and ERM (effects range medium) specify the 10th and 50th percentile values of a given pollutant that have a noticeable biological effect, Long and Morgan (1990)

not only along the coast, but also in samples taken along the main stem of LIS. Sediment samples exceeding the ERL are also found in some coastal embayments along the Connecticut shore, particularly New Haven Harbor, and in some river samples in mid- and central LIS. Total PAH levels exceeding the ERM are found only in the extreme western Sound and outlet of the upper East River.

The USGS dataset contains data for 18 individual PCB congeners, but none of the more toxic co-planar PCBs. Toxic reference values for total PCBs are much lower than for total PAHs, with the ERL at 23 and the ERM at 180 ng/gdw, so data were plotted showing levels below the ERL (blue), between the ERL and ERM (green), values exceeding the ERM but <500 ng/g (yellow), and values exceeding 500 ng/g (red) (Fig. 5.19). Generally, a similar distribution pattern is observed for PCBs as for PAHs, with the lowest sediment concentrations (blue) observed in open waters of ELIS and CLIS with the exception of the former mud dump site, and elevated levels exceeding the ERL common at coastal Connecticut locations. In contrast, sediment PCB levels exceeding the ERL are routine both in coastal areas and open waters of WLIS. Sediment PCB levels exceeding the ERM are fairly common in WLIS and in a number of coastal areas further east in Connecticut. Extremely high levels (>500 ng/g) are only found closer to the Hudson River and in one site on the Mystic River.

These overall patterns were also reported in more recent data compilations such as Mitch and Anisfeld (2010), who reviewed contaminant data derived from the period 1994–2006, pooling all data for WLIS, CLIS, and ELIS (Table 5.5). Values within each sub-basin were reported as percentile values, and as overall means for each area. Mean levels of sediment PAHs, PCBs, and DDT generally decreased from west to east, although some very high levels of PAHs were observed in CLIS, leading to a very high

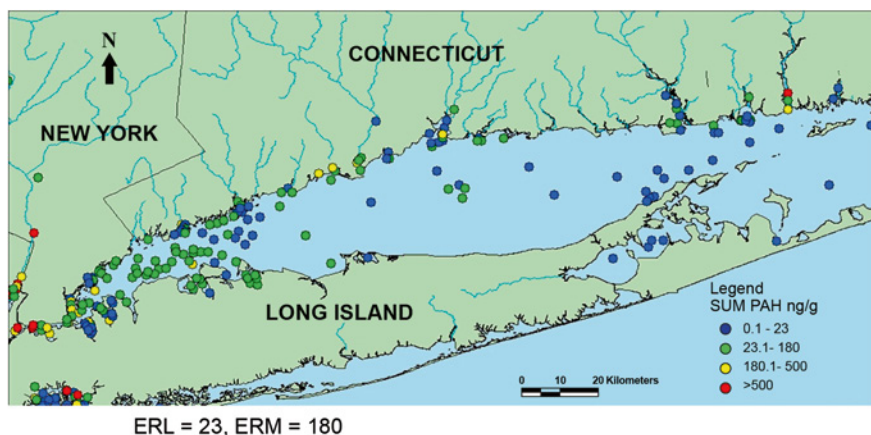


Fig. 5.19 Total PCB levels in LIS surface sediments (from USGS data base, 1975–2000 all years combined)

90th percentile value of 10,900 ng/g, and a mean value of 2,860 ng/g, higher than that observed in WLIS (2,470 ng/g). Concentrations at the 90th percentile exceeded ERL values for all three groups of contaminants in all three LIS areas. In WLIS, values in the 50th percentile exceeded ERL values for DDT and PCBs, but not PAHs. The dataset for metals is much more extensive than those for organic contaminants, but generally, the two datasets show the same trends, with more WLIS stations having sediments that exceed the ERL values. Metal ERM values were only exceeded for Hg in WLIS.

Mitch and Anisfeld (2010) also compared sediment data from embayments with those from open-water regions of LIS for PAHs, PCBs, and DDT and found no significant differences between these two regions. This conclusion contradicts the indications from earlier datasets, and the much larger datasets compiled by the USGS. This apparent lack of coastal enrichment in organic contaminants could have been driven by the preponderance of open water NCA sampling sites in WLIS, or the high variability in values observed for most contaminants. In a comparison of sediment contaminant levels reported by NS&T from 1994 to 2004, only the Housatonic River, Mamaroneck and Throgs Neck showed levels of PAHs or PCBs exceeding the NS&T 85th percentile value (1870 and 14.5 $\mu\text{g/g}$, respectively). Mitch and Anisfeld, comparing EMAP data from 1990 to 1992 to NCA data from 2000 to 2002, reported no significant changes in sediment PCB concentrations, while sediment PAH concentrations fell by a factor of approximately three during this period. These temporal patterns are consistent with the more persistent nature of PCBs compared to PAHs, which are more easily metabolized. Mitch and Anisfeld also evaluated data on chlorinated pesticides, including total chlordanes, chlorpyrifos, total DDT and total dieldrin, total endosulfan, and total hexachlorocyclohexane (Lindane). They reported levels exceeding the NS&T 85th percentile value for almost all pesticides in the Housatonic River, the Mamaroneck, and the Throgs Neck sites. These same three sites also had high levels of the contaminant metals Cr, Cu, Pb, Hg, Ag, and Sn. A

Table 5.5 Summary of sediment concentrations of organic and inorganic contaminants 1994–2006. Microgram per gram dry weight for metals; nanogram per gram dry weight for organics

Contaminant	Area of Long Island Sound														
	WLIS						CLIS						ELIS		
	N	10th	50th	90th	Mean	N	10th	50th	90th	Mean	N	10th	50th	90th	Mean
Arsenic	366	ND	6.85	12.2	6.68	193	ND	4.98	10.56	5.69	268	ND	3.75	11.2	4.92
Cadmium	452	ND	0.63	2.6	1.18	311	ND	0.21	2.16	0.92	304	ND	0.2	2.37	0.82
Chromium	453	13.4	64	110	64.9	288	20.7	51.4	108	62	310	9.2	30.1	69.3	36.1
Copper453	14.8	89	216	116	323	8.6	51.7	185	83.8	302	2.8	33.2	96.3	52.5	
Lead	453	12.6	57	162	87	322	9.0	37	85.9	45.6	306	4.8	24.8	82.2	43.9
Mercury	454	0.02	0.3	1.00	0.49	300	0.02	0.15	0.47	0.21	302	ND	0.12	0.56	0.24
Nickel	451	7.4	23	37.6	23.9	306	6.8	19.4	37	22.5	303	5.6	15.2	30	18.1
Selenium	56	ND	ND	5.3	1.3	34	ND	0.2	3.91	2.22	26	ND	0.03	2.12	0.74
Silver	142	0.05	0.54	2.05	0.97	164	ND	0.31	1.65	0.71	60	ND	0.06	0.6	0.25
Tin	36	1.65	5.54	9.8	5.88	23	1.11	2.94	5.34	6.77	18	0.45	1.51	7.95	2.99
Zinc	450	39.2	164	315	183	305	43.3	113	221	137	299	23.5	82.2	186	110
DDTs	72	ND	3.71	15.3	6.37	39	ND	ND	3.68	2.22	30	ND	ND	3.95	1.29
PAHs	72	61.1	880	4350	2370	36	69.1	561	10900	2860	30	ND	463	4610	1810
PCBs	72	3.21	36.5	174	162	36	ND	2.75	35.3	32.6	30	ND	1.37	31	15.2

>ERL = Bold, >ERM = Bold, >NS&T national 85th percentile value = *Italics*

Adapted from Mitch and Amisfield (2010)

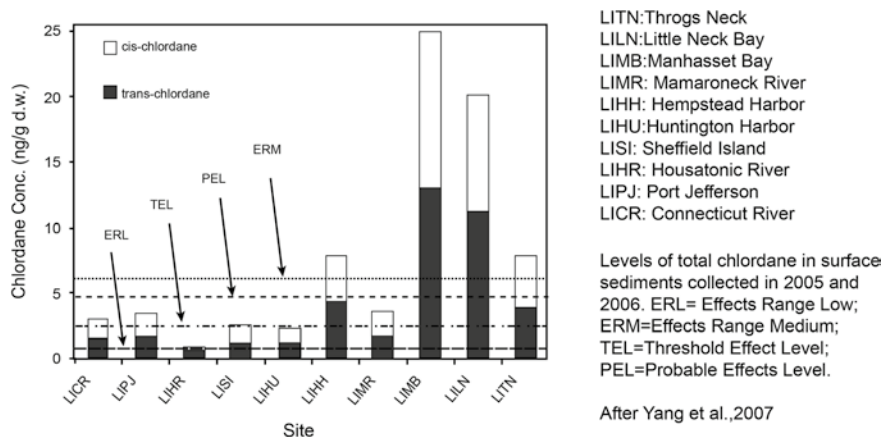


Fig. 5.20 Chlordane in LIS surface sediments (data from LIS NS&T sites)

recent evaluation of the chlordane data by Yang et al. (2007) indicates that levels of this persistent but banned hydrophobic insecticide have not consistently diminished over the past 2 decades. Most concentrations are higher in WLIS, exceeding those thought to cause toxicity (Fig. 5.20).

Butyltins resulting from use in antifouling paints are another organic contaminant of concern, particularly in port and harbor areas where boats are moored and serviced. Unfortunately, data on butyltins in sediment samples from LIS are scarce, and the NS&T data portal only contains values collected in 1995 and 1996. Despite their ban, periodic sampling for this important group of contaminants in coastal sediments is needed, particularly given recent increases in butyltin concentrations in biota from some areas discussed below.

5.5.2 Sediment-Associated Emerging Contaminants

All the studies discussed previously report on priority pollutants that have been the focus of monitoring programs over the last 20–30 years. Until recently, emerging contaminants have received relatively little attention. The only relatively new contaminants that have been added to national monitoring programs are the polybrominated diethyl ethers (PBDEs), a family of recently recognized persistent bioaccumulative toxic compounds widely used as fire retardants until they were banned by international treaty during the last 10 years. Due in part to their propensity to bioaccumulate, most of the monitoring associated with tracking PBDEs in the environment has been conducted on tissue samples. Recently released NOAA data from the Mussel Watch program reported concentrations of mono to hepta PBDEs in mussel tissue and sediment from around the country (Kimbrough et al. 2009). Unfortunately, PBDEs were not measured in any samples from LIS, but those collected in New York Harbor ranged from 19–41 ng/gdw, some of the highest concentrations measured nationwide. Concentrations of PBDEs

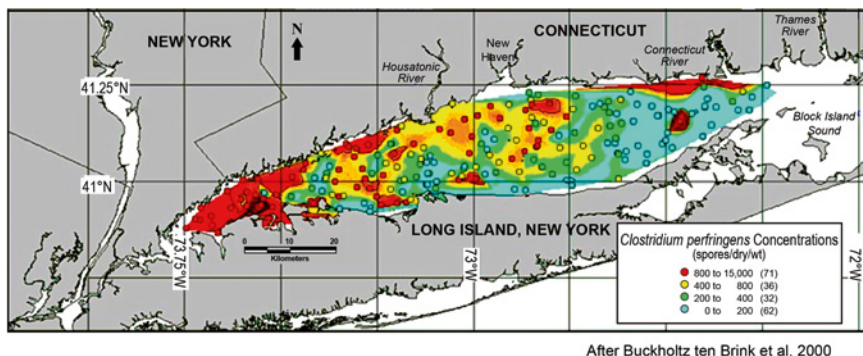


Fig. 5.21 Distribution of *C. perfringens* in LIS surface sediment, with highest values in western LIS and some patchy zones in eastern and central LIS

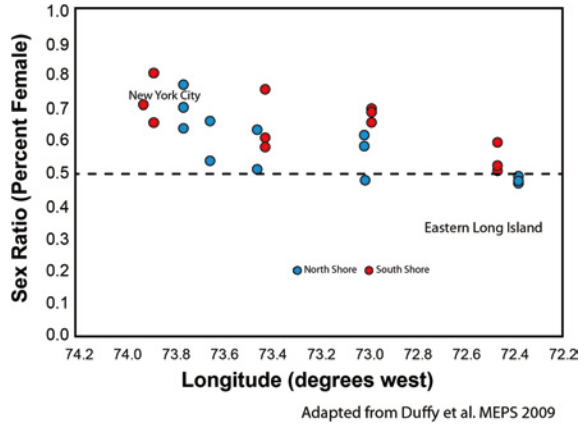
measured in mussels collected from LIS are discussed below. Use of these lower molecular weight PDBEs has now been banned in the United States and throughout much of the world. However, use of the deca PBDEs is still allowed.

Data collected as part of the USGS survey characterizing sediment properties of LIS in 1996 mapped the distribution of *C. perfringens* spores in LIS sediments (Buchholtz ten Brink et al. 2000) as a marker for sewage inputs to the system (Fig. 5.21). The *C. perfringens* spores are abundant in WLIS as well as in pockets of elevated spore counts at locations near the Connecticut and New York coasts and smaller areas in the main stem of LIS. Due to their persistence and density, spores are likely to be distributed with fine sediments throughout LIS.

Brownawell's research group has recently measured a new group of sewage tracer compounds, a class of disinfectants called quaternary ammonium compounds or QACs. In a transect of surface sediments along the main stem of LIS from near the Throgs Neck Bridge to Mt. Sinai, NY, concentrations of total QACs decreased from a high of almost 14 $\mu\text{g/gdw}$ to $<1 \mu\text{g/gdw}$, clearly indicating the relative significance of sewage input to WLIS (Brownawell, SBU unpublished data). The WWTFs are also a source of natural and synthetic hormones as well as hormone mimics such as the detergent breakdown products, alkylphenol polyethoxylates. No comprehensive survey of these compounds has yet been conducted in LIS. However, a recent examination of sex ratios in local Atlantic silversides (*Menidia menidia*) from coastal areas around Long Island (Duffy et al. 2009) reported a significant correlation between longitude and sex ratio with fish from the western, more urban portions of Long Island showing female biased sex ratios (Fig. 5.22).

A reconnaissance study could be a useful option for evaluating other emerging organic contaminants of potential concern. Chief among these are perfluorinated compounds (PFCs), including perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS), which are components of many nonstick and stain resistant coatings with known Immunotoxicant and endocrine disrupting potential (DeWitt et al. 2009). Although production of some of these materials ended in the United States and most of Europe, a review of recent data indicates that levels in biota continue to increase in some

Fig. 5.22 Sex ratio in *Menidia menidia* as a function of distance from the East River entrance into LIS (after Duffy et al. 2009). Sex ratio regressed onto longitude ($P < 0.001$, adj. $R^2 = 0.478$ of arcsin transformed data). Dotted line represents a 1:1 sex ratio



areas (Houde et al. 2011). Even more troubling is the almost exponential increase in PFC levels in the United States population identified by the National Health and Nutrition Examination Survey (NHANES) (Kao et al. 2011). Given the potential for PFCs to bioaccumulate and biomagnify, analysis of levels in LIS biota is clearly warranted.

Also of interest are pharmaceuticals and personal care products (PPCPs). The QACs discussed above belong to this group. Newer analytical techniques using mass spectroscopy (MS) with or without prior separation using liquid chromatography (LC), principally MS/MS and LC/MS–MS, facilitate measurement of these compounds with highly diverse structures and physical chemical properties. As evident from the USGS’s landmark national reconnaissance study (Kolpin et al. 2002), with better detection, these compounds are now being found in surface waters in many parts of the United States. A corresponding study of coastal waters and coastal sediments has not been attempted. Considering the proximity of LIS to the New York metropolitan area, and the relatively high density of people and urban areas throughout the LIS coastline, the potential for inputs of human-derived PPCPs is high. Given, the very low levels detected in surface waters by the USGS, it is unlikely that the individual compounds are present at concentrations high enough to have a biological impact in coastal water. The potential for interactive effects with other PPCPs or other types of legacy contaminants exists, so there is a need to at least determine their ambient levels.

5.6 Contaminants in Biota and Their Effects

5.6.1 Organic and Inorganic Contaminants in Biota

Data on levels of contaminants in tissues of LIS aquatic species are limited. The largest dataset consists of tissue contaminant levels in blue mussels collected at nine sites (Connecticut River, Hempstead Harbor, Housatonic River, Huntington

Table 5.6 Comparison of Contaminants in LIS with other Urban Estuaries in the USA

Location	Sediments number of sites	Mussels		
		Number of values in top 20	Number of sites	Number of values in top 10
Hudson/Raritan Estuary	6	81	6	32
Boston/Salem Harbors	6	56	5	20
Los Angeles coast	9	33	5	16
Long Island Sound	7	22	9	17
Sand Diego Bay and coast	6	18	5	14
Tampa Bay	7	13	ND	ND
San Francisco Bay	9	13	5	9
Puget Sound	10	12	3	5
Delaware Bay	9	5	ND	ND
Galveston Bay	7	3	ND	ND

Adapted from Robertson et al. (1991)

ND No data

Harbor, Mamaroneck, New Haven, Port Jefferson, Sheffield Island, and Throgs Neck) as part of the NS&T program, annually from 1986 to 1994, and every other year since then. Data for the Mussel Watch Program from NS&T collected since 1989 are available on an easily searched data portal (<http://egisws02.nos.noaa.gov/nsandt/index.html#>).

Robertson et al. (1991) conducted a detailed assessment of contaminant status in LIS as it related to national trends for both inorganic and organic contaminants in mussels and sediments from the 1986–1988 NS&T data. Data for the nine Mussel Watch stations and the two Benthic Surveillance stations in WLIS and ELIS were plotted on cumulative distributions for the entire country for both sediment and mussel tissue contaminant data. Several patterns are evident from these plots. LIS sites tend to rank low for inorganic contaminants compared to other sediment sites on the national distribution, with no site standing out as being highly contaminated on a national basis. In contrast, organic contaminants generally show higher rankings, with most LIS sites ranking above national means. A summary of national rankings for all contaminants is provided in Table 5.6, which shows that with regard to sediment or mussel contaminants, LIS ranked fourth highest in the nation, behind only the Hudson/Raritan estuary, Boston/Salem Harbors and the Los Angeles coast, but ranking above San Diego, Tampa Bay, San Francisco Bay, Puget Sound, Delaware Bay, and Galveston Bay. The Throgs Neck station in extreme WLIS ranked particularly high in this assessment for tPAHs, tClordane, tPCBs, tDDT, and Pb, being more than one standard deviation above the national mean, thus ranking in the top 16 % of values nationwide.

Turgeon and O'Connor (1991) reviewed Mussel Watch data for LIS from 1986 to 1988, focusing on comparisons among sites within LIS, and reported contaminant

Table 5.7 Time trends in LIS mussel watch data; analysis by spearman rank correlation

Location	N	Lind	tClD	tDDT	tDld	tPCB	tTBT	tPAH	As	Cd	Cu	Hg	Pb
Connecticut river	11	NT	**	**	NT	*	NT	*	NT	NT	NT	NT	NT
New Haven	13	**	**	**	**	**	*	NT	NT	*	NT	NT	NT
Housatonic river	12	NT	**	NT	**	NT	**	NT	NT	NT	NT	NT	NT
Sheffield island	10	NT	**	**	NT	**	NT	NT	NT	NT	NT	NT	NT
Mamaroneck	12	**	**	**	NT	**	**	**	NT	NT	*	NT	NT
Throgs neck	13	**	**	**	NT	**	**	**	NT	NT	**	N	**
Hempstead harbor	13	**	**	**	NT	**	**	NT	NT	**	**	NT	**
Huntington harbor	12	**	**	**	**	**	**	NT	NT	NT	*	NT	NT
Port jefferson	13	**	**	**	**	**	**	**	#	NT	NT	#	NT

Lind Lindane, *tClD* total chlordanes, *tDDT* total DDTs, *tPCB* total PCBs, *tTBT* total organotins, *tPAH* total PAHs

NT no significant time trend

** Decreasing trend with 95 % of confidence

* Decreasing with 90 % confidence

Increasing with 90 % confidence

Adapted from O'Connor and Lauenstein (2006)

levels in mussels from WLIS (particularly the Throgs Neck site) to be high relative to national standards. Median concentrations at the Throgs Neck site were 4,900, 1,300, and 210 $\mu\text{g/gdw}$ for total PAH, PCB, and DDT, respectively, for the 3-year period studied, higher than any other LIS site. O'Connor and Lauenstein (2006) published a detailed analysis of the National Mussel Watch dataset analyzing time trends in data from 1986 to 2003. For the organic contaminants Lindane, tClordane, tDDT, tPCB, tPAH, and tButyltin, significant decreases were observed at most LIS sites for most contaminants with the exception of tDieldrin and tPAHs, for which no significant time trends were observed for five out of the nine sites (Table 5.7). In contrast, very few of the metals showed time trends, with only Cd, Cu, and Pb showing significant decreases at a couple of sites. Interestingly, As and Hg showed statistically significant increasing trends at Port Jefferson over time. Coal combustion can be a source of both As and Hg to the environment, but there are no data to support why this would be a factor in Port Jefferson Harbor as coal has not been used at the power plant there for decades. If these trends continue, attempts should be made to identify the source. For the organic contaminants analyzed, national median values during these periods (1988–2003 for tPAHs, and 1989–2003 for tButyltin) decreased on average by a factor of four, with tButyltin showing the largest decrease (8x) while tDDT, tPCB, and tPAH only decreased by a factor of two to three. The enhanced reduction of tButyltin is likely due to legislation banning its use on vessels <25 m in length beginning in 1988, and the voluntary “sunsetting” of the United States production in 2001. These trends were significant at the 95 % level for each of these groups of contaminants. Of contaminant metals, only Cd showed significantly decreasing trends over this period, by a factor of only 1.5.

A closer inspection of all available data for PAHs and butyltins in LIS, including the 2004–2008 data from the NS&T data portal, suggests that although levels are now lower than observed in the 1980s, decreasing trends are no longer evident.

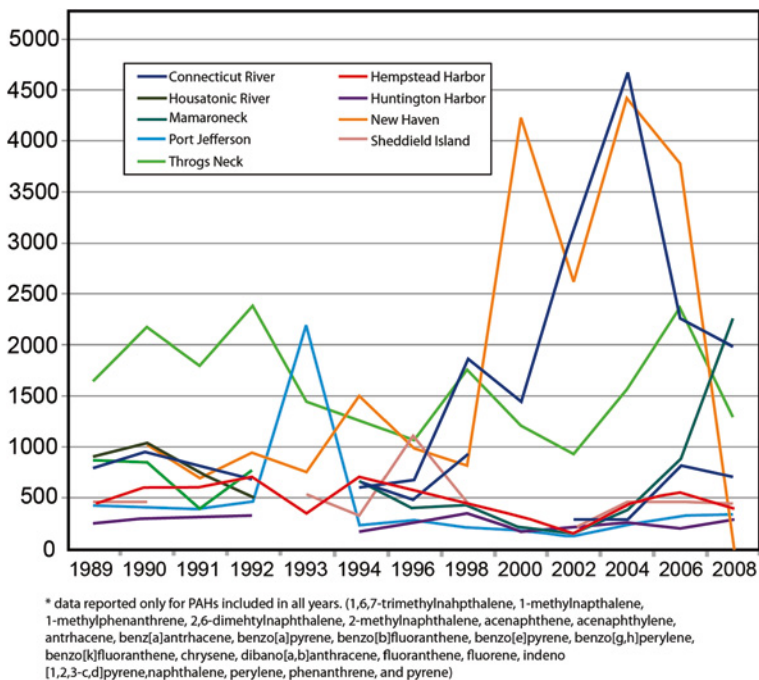


Fig. 5.23 Time trends in median total PAH concentrations in mussel tissue from NS&T sites in LIS over the period 1989–2008. Concentrations in ng/gdw

Furthermore, there appear to be differences emerging at some sites where levels could be increasing, and overall levels from the WLIS sites are not necessarily the highest observed Sound-wide. Some contaminants at some of the LIS sites are no longer decreasing nor are values from the WLIS necessarily still the highest for individual contaminants in all cases. These points out the need for continued monitoring, and more process-oriented work at some sites to determine potential sources of these contaminants to particular environments.

Data for tPAHs in mussel tissue from NS&T over the period 1989–2008 (Fig. 5.23) show median values over this entire period from a low level of 314 ng/gdw in Port Jefferson to a high level of 1,580 ng/gdw at Throgs Neck. Median levels for the period exceed 1,000 $\mu\text{g/g}$ for both the Housatonic River and New Haven Harbor, including some of the highest values recently measured. Median values for all LIS sites exceeded the national median of 220 ng/gdw reported by O'Connor and Lauenstein (2006) for 2002–2003. These accumulated body burdens are still well below values predicted to cause acute toxicity (around 100 $\mu\text{g/gdw}$), although some PAHs can act via receptor-mediated mechanisms, leading to developmental effects at much lower levels (McElroy et al. 2011). The observed trend of increasing tissue concentration values for tPAH is a cause for concern. Since mussels filter particulates from the water column, current values in these organisms should be reflective of recent trends in water column bulk concentrations of these

contaminants. The presence of increasing body burdens could reflect increasing inputs to the watershed or at least enhanced resuspension of relict polluted sediments.

Data for butyltins in the NS&T Mussel Watch program illustrate spatial trends unlike those observed for most other organic contaminants in that the Throgs Neck site is not the most contaminated. In an early review looking at data from 1986 to 1989, Turgeon and O'Connor (1991) found the highest levels at Mamaroneck (500 ng/gdw), Port Jefferson (300 ng/gdw), and then Huntington Harbor (250 ng/gdw) with lower levels at the six other sites. Throgs Neck ranked fifth among the sites sampled. These levels were considered low from a national perspective, approximately 10 times less than concentrations observed in oysters or mussels at sites near marinas in other parts of the country. Recent NS&T data for butyltins (mono-, di-, tri-, and tetra-butyltin, 1989–2008) were only available from five of the Mussel Watch sites (Hempstead Harbor, Mamaroneck, Huntington Harbor, Port Jefferson, and Throgs Neck). Tetra-butyltin was not detected in any sample. But of the three organotin compounds measured, tributyltin (TBT) usually accounted for the majority of the residues with dibutyltin, a metabolic breakdown product of tributyltin, sometimes found at levels approaching tributyltin. Data for the sum of mono-, di-, and tributyltin for 1989 through 2010 are shown in Fig. 5.24. Maximum levels were generally observed in 1989 or 1990, with the highest levels (exceeding 500 ng/gdw) observed in Mamaroneck and Port Jefferson. Peak levels (about 400 ng/g) were observed later (1993) at Throgs Neck. Port Jefferson experienced a secondary peak of almost 100 in 1994, with periodic increases observed throughout the sampling period, including

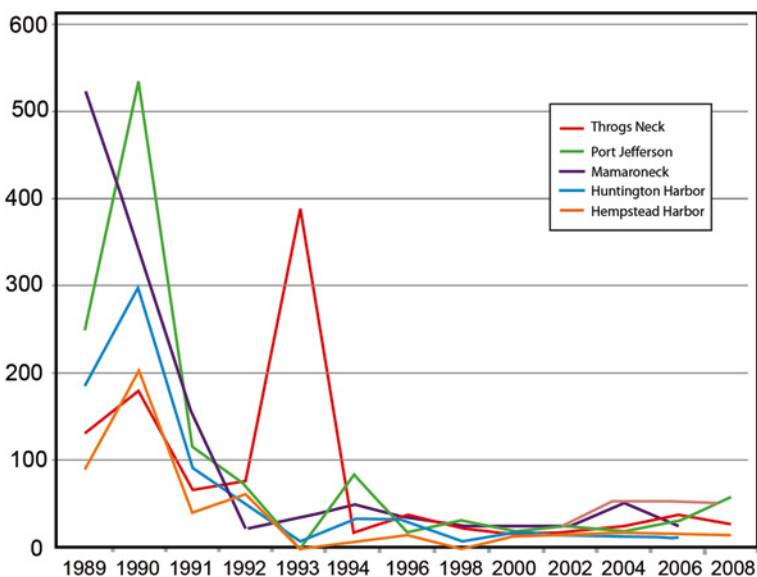


Fig. 5.24 Time trends in Butyltin (mono + di + tri) concentrations in mussel tissue from five locations in western LIS (from NS&T Mussel Watch Stations) over the period 1989–2008. Units: ng/gdw

the most recent data available in 2008, where levels of 56 ng/g were reported. Throgs Neck and Mamaroneck mussels still contain butyltins at levels exceeding 25 ng/g, whereas most other sites have dropped to <15 ng/g. Patterns observed in butyltin levels in mussel tissues likely reflect decreasing environmental concentrations resulting from the 1988 partial ban of TBT antifouling paints in the United States. More recent spikes at Throgs Neck and Port Jefferson indicate either new sources or remobilization of high TBT sediment reservoirs, continuing well past the partial ban. Although body burdens of butyltins in mussels are still well below levels known to cause mortality (48,000 ng/gdw), growth impairment (3200 ng/gdw), or even imposex in sensitive neogastropod species (320 ng/gdw) (Meador 2006), increased levels despite the ban are a cause for concern. Sources could include resuspension of older more heavily contaminated harbor sediments due to dredging projects or potentially more recent inputs from either illegal use of TBT paints or from vessels exempt from the 1988 ban.

Apart from the NS&T data, there are only limited and sporadic additional data available on levels of organic or inorganic contaminants in LIS organisms. Most of the additional data have resulted from periodic surveys conducted by the NYSDEC, often in partnership with CTDEEP, NYSDOH, CTDOH, and the USEPA, which has monitored PCB levels primarily not only in striped bass (*Morone saxatilis*), but also in bluefish (*Pomatomus salatrix*). More recently, as part of a large survey done in 2006 and 2007 funded by the LISS (Long Island Sound Study), PCBs and mercury were analyzed in striped bass, bluefish, American eel (*Anguilla rostrata*), weakfish (*Cynoscion regalis*), and American lobster (*Homarus americanus*) hepatopancreas, as well as Cd, dioxins, and furans in lobster hepatopancreas from LIS (Skinner et al. 2009). The majority of data on PCB levels in fish has been collected as part of the NYSDEC striped bass monitoring program, which has been focused on samples from the Hudson River. However, periodic sampling of striped bass from LIS has occurred since 1984, with the most recent comprehensive survey completed in 2006 and 2007, introduced above (Skinner et al. 2009). In evaluating these recent samples, Skinner et al. also reviewed the earlier data and trends in PCB levels in striped bass and bluefish. For PCBs, no significant differences were observed between sampling areas roughly corresponding to WLIS, north and south regions of CLIS, and ELIS in any of the fish species sampled, although collections of eel and weakfish were insufficient to test for differences among all four of the areas sampled. The PCB body burdens were not correlated with wet weight of striped bass, although large bluefish (>508 mm) had significantly higher body burdens. Average concentrations of PCBs were 0.333, 0.110, 0.565, and 0.512 $\mu\text{g/g}$ wet weight (gww) for striped bass, small (305–508 mm) bluefish, large (>506 mm) bluefish, American eel, and weakfish, respectively. Levels of PCBs reported for striped bass declined by >80 % from levels observed in 1985 on a wet weight basis (from >2 $\mu\text{g/gww}$ to <0.5 $\mu\text{g/gww}$); during this period the lipid content also dropped significantly (Fig. 5.25). On a lipid-normalized basis, PCB levels dropped by 50 % on average between the mid-1980s and 2006–2007. Combining all the data for the entire record, PCB body burdens were significantly correlated with lipid content. Similar time trends were observed with bluefish, where declines of 70 % in wet weight normalized in tissue levels were observed, while no significant declines in

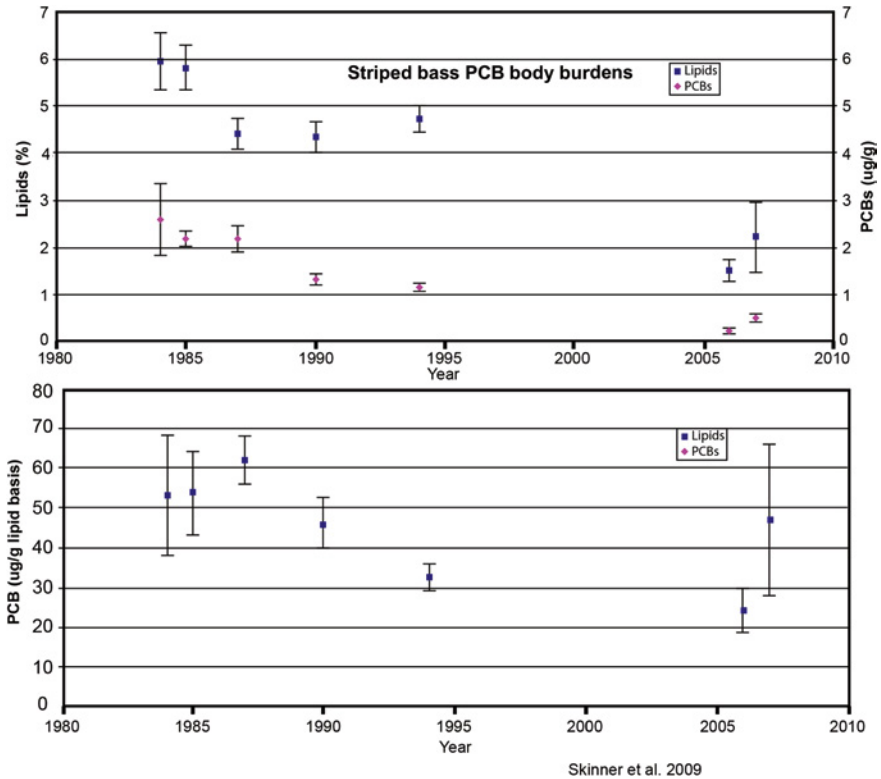


Fig. 5.25 The PCB body burdens in striped bass over the period 1984–2007 (after Skinner et al. 2009)

lipid-normalized body burdens were found for the same period. Skinner concluded from these analyses that ambient levels of PCBs in the LIS environment have not significantly changed since the mid-1980s. Insufficient data on American eel and weakfish prevent any conclusions regarding temporal differences. In the NYSDEC 2006–2007 study, the mean concentration of PCBs in lobster hepatopancreas for LIS was $1.31 \mu\text{g/gww}$. Interestingly, significantly higher concentrations were observed in male lobsters, possibly due to depuration by female lobsters through egg production. The differences between concentrations in males and females created more complex special patterns. On a wet weight basis, lobsters from ELIS appeared to have lower PCB concentrations, but this pattern was not apparent when body burdens were normalized to lipid content. Skinner did not comment on temporal trends in PCB concentrations over time due to insufficient data.

Although mean body burdens of PCBs in all species analyzed were below the FDA action limit of 2 mg/kgww (2 ppm), it is important to note that significant individual variation in PCB content was observed in all species analyzed. Maximum PCB levels in some species approached or exceeded the FDA limit. Maximum PCB concentrations observed were 1.45 , 3.17 , 1.85 , and $2.83 \mu\text{g/gww}$ for striped bass,

Table 5.8 Total PCB concentrations (ng/gr wet weight tissue) in LIS marine organisms (From NCA data 2000–2006)

	Mean	SD	Maximum	N
Blue crab	31	27.3	87.3	27
Lobster	9.4	7.1	20.9	5
Summer flounder	56.1	55.3	421	92
Winter flounder	38.4	43.3	216	41
Scup	28.6	27.4	137	64
White perch	660	513	1680	8

large (>508 mm) bluefish, weakfish, and lobster hepatopancreas, respectively. This implies some health risk to both wildlife and humans in consuming these species.

Tissues of blue crab (*Callinectes sapidus*), American lobster, scup (*Stenotomus chrysops*), summer flounder (*Paralichthys dentatus* also commonly called fluke or Northern fluke), winter flounder (*Pseudopleuronectes americanus*), bluefish, brown bullhead (*Ameiurus nebulosus*), channel catfish (*Ictalurus punctatus*), and white perch (*Morone americana*) were also analyzed as part of the NCA assessment, although analysis of these data has not been published to our knowledge. In most cases, filets were analyzed, but sometimes the viscera, also known as “offal” or whole organisms, were analyzed. Data on PCB body burdens in fish and shellfish collected were examined as part of this review. Twenty-one individual PCB congeners were analyzed, including three of the more toxic, co-planer PCBs (IACUC# 77, 118, and 126). Polychlorinated biphenyls were detected in most but not all samples analyzed. Sums of all PCBs in filets with five or more samples (Table 5.8) indicate average concentrations in filets were generally low relative to the FDA action limit of 2000 mg/kgww, with average body burdens below 100 mg/kgww for all species except white perch. Although only eight white perch specimens were analyzed, the maximum value recorded (1,680 mg/kgww) was within 20 % of the FDA action limit. The NCA data are for filet or muscle tissue only, so they cannot be directly compared to the hepatopancreas data reported in the NYDEC study for lobsters. The NCA dataset on PCB body burdens is not extensive, but it does provide data on species that are prominent members of the local sport fishery for which we have no other recent data. Individual variability in this dataset is also large with coefficients of variation approaching or exceeding 100 %. Despite this, the very low levels reported indicate minimal human exposure to PCBs as a result of the consumption of these species, with the exception of white perch for which maximum values are close to the FDA limit.

The PBDEs are similar in structure and chemical properties to PCBs, and are a more recently recognized bioaccumulative organic toxicant, particularly in urban areas. Kimbrough et al. (2009) recently reviewed the limited data available as part of the NS&T program on PBDE levels in bivalves. Elevated levels were found in mussel tissue collected near urban areas in many parts of the country, including Seattle, Los Angeles, Boston, and Baton Rouge, but the largest concentrations of hot spots on the national map were associated with the New York/New Jersey Harbor Estuary and LIS. Elevated PBDE levels were observed in 57 locations

nationwide in samples collected in 1996 or between 2004 and 2007, and five were in LIS. Concentrations (expressed in ng/g lipid) were 697 at Throgs Neck, 495 at New Haven, 493 at the Housatonic River, 350 at the Connecticut River, and 334 at Hempstead Harbor. Mussels from sites in the Hudson River and New York/New Jersey Harbor estuary generally showed higher levels, ranging from 2190 ng/g lipid at Governor's Island in the Hudson River to 594 ng/g lipid in Raritan Bay. Six of the 10 highest levels nationwide were reported from mussels collected in this area. Using the national dataset, Kimbrough determined there was a statistically significant relationship between population density and PBDE levels in local bivalves. Given the relatively high levels observed in LIS biota and the high population density in the LIS watershed, continued sampling for PBDEs in biota is warranted.

The NYSDEC also measured total Hg in striped bass, bluefish, weakfish, American eel, and lobster tissues as part of their 2006–2007 survey in LIS (Skinner et al. 2009). In both striped bass and bluefish, total Hg levels in muscle tissue were significantly correlated with size, with the highest concentrations being observed in the north portion of CLIS due to the greater numbers of larger fish caught in this area. Mean tissue Hg concentrations in Area 2 were 0.528 $\mu\text{g/gww}$ in striped bass, and 0.400 $\mu\text{g/gww}$ in bluefish. Mercury levels were lower in weakfish (0.141 $\mu\text{g/gww}$) and American eel (0.110 $\mu\text{g/gww}$). The smaller sample size for these two species prevented spatial comparisons to be made. Mercury was also measured in the hepatopancreas of American lobster. Regardless of location, all values were found to be <200 ng/gww. Lobsters from ELIS showed a small but statistically significant elevation in Hg concentrations (111 vs. 61 ng/gww) as compared to lobsters from the WLIS and ELIS combined. This was not considered to be extremely meaningful, given the overall low levels. Mercury, as a class B metal, strongly binds to sulfhydryl functional groups of proteins (Kuwabara et al. 2007), and evaluation of Hg levels in lobster muscle rather than hepatopancreas may have yielded higher concentrations. Comparison of striped bass Hg data collected in 1985 by the NYSDEC to values obtained in 2006–2007 indicated no significant differences in mean Hg concentrations over this 20-year period.

Hammerschmidt and Fitzgerald (2006) quantified both total Hg and methylmercury (MeHg) levels in four species of fish (alewife (*Alosa pseudoharengus*), winter flounder, bluefish, and tautog (*Tautoga onitis* also known as blackfish)) as well as American lobster collected from CLIS in 2002. Virtually all (98 %) Hg recovered from animal tissue was in the form of MeHg, allowing relatively straightforward comparison between their data on MeHg with the data on total Hg reported by NYSDEC. Mean MeHg levels in muscle were similar in bluefish and tautog (137 and 191 ng/gww), but much lower in winter flounder muscle (21 ng/gww), and in whole bodies of alewife (27 ng/gww). Levels in lobster tail muscle (140 ng/gww) were similar to those found in bluefish and tautog. Collectively, these data indicate no significant spatial trends for Hg body burdens in fish or shellfish from LIS. However, given the relatively high levels observed in some of the species evaluated, unrestricted human consumption is ill-advised with a consumption advisory set by the USEPA of 300 ng/gww (USEPA 2001). Research to develop an improved quantitative understanding of Hg trophic transfer in LIS seems advisable.

5.6.2 Toxicity of LIS Sediments and Health Impacts on Resident Biota

Assessment of toxicity can be inferred by comparison to body burdens associated with toxicity in other studies. However, potential or realized effects can also be directly measured through sediment toxicity tests or analysis of local fauna. In support of the LISS NOAA conducted contaminant toxicity assessment in LIS during the period 1988–1991. Wolfe et al. (1994) published the first comprehensive analysis of these data. Sediment samples were collected at 20 coastal stations along the entire coast of Connecticut, and from the WLIS coast out to Cold Spring Harbor, and 11 stations along the main stem of LIS from the west to a point north-east of Montauk. At each sampling location, three sediment samples were collected and three independent toxicity assays were performed: the 10-day whole sediment toxicity test with *A. abdita*, a 48 h sediment elutriate test embryo test with *Mulinia lateralis*, and a microbial bioassay (MicrotoxTM¹) performed on organic sediment extracts.

The *A. abdita* toxicity test, which exposes organisms to bedded sediments, is probably the most realistic exposure scenario for sediment-sorbed contaminants. About 80 % of samples collected from the coastal embayments showed significant toxicity in this assay, while tests of samples from the main stem of LIS with the exception of a site in CLIS showed little to no toxicity. The *M. lateralis* test was less sensitive, yielding fewer toxic sites. The MicrotoxTM assay identified a similar number of toxic sites as the amphipod test, yet the results were not correlated, indicating these tests are responding to different sediment properties. Sites that show toxicity in 1, 2, or 3 toxicity tests are given in the data summary (Fig. 5.26). Coastal embayments in the WLIS, including Little Neck Bay, Oyster Bay, and Manhasset, showed the most significant toxicity in this survey, although sites in extreme WLIS as well as sites in most coastal embayments along Connecticut showed some evidence of sediment toxicity as well (Fig. 5.26).

The *A. abdita* test is also being used as part of the NCA program. Results obtained from 2000 to 2006 showed significant mortality (60–80 % of control survival) in 19 out of 310 tested samples (Fig. 5.27; data taken from <http://www.epa.gov/emap/nca/html/regions/ne0006/index.html>). Also shown in this map are samples with even greater mortality (<60 % of control survival). Despite the general reduction in toxic sites identified, the NCA data indicate that toxic sediments are still present throughout coastal embayments along both the New York and Connecticut shores of LIS with approximately equal numbers of toxic sites in each state. The presence of toxic sediments in coastal sites throughout LIS is also indicated by data from McElroy's group who analyzed sediment toxicity using the Mictorox test on extracts of LIS sediments collected in 2002. This test measures reduction in light emission from luminescent bacteria in response to test solutions.

¹ Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

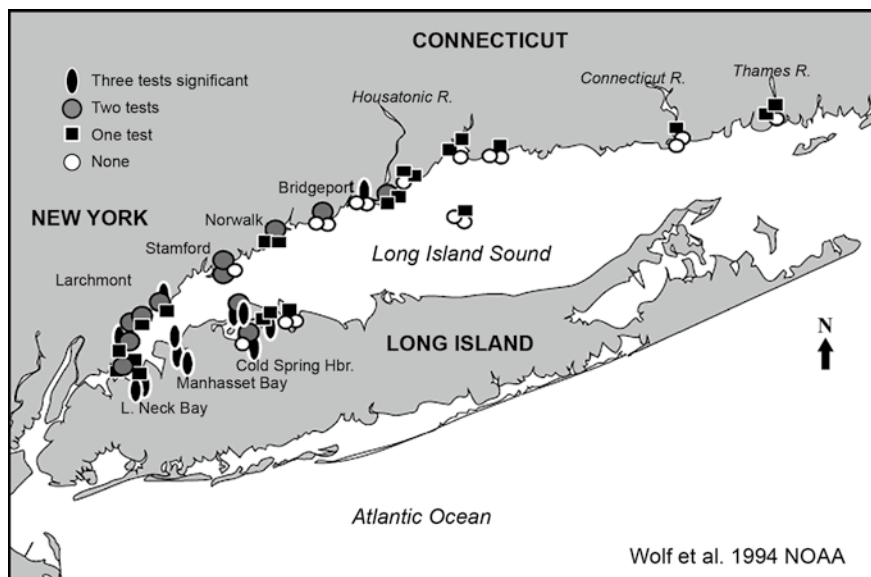


Fig. 5.26 Toxicity of surface sediment in LIS with one, two or three tests done (Wolfe et al. 1991)

It is considered a nonspecific general indicator of relative toxicity among samples. Evidence of sediment toxicity is fairly widespread in LIS (Fig. 5.28). The Mutatox™ assay uses a dark mutant of these bacteria that no longer is capable of producing light. After a suitable incubation period of the dark mutant with a test substance, mutations leading to restoration of the light emitting phenotype indicate that the test substance is mutagenic. Results from the Mutatox™ assay indicate that some solvent extractable materials in these sediments are also capable of causing mutations in bacterial test species, and thus represent a potential mutagenic risk to higher organisms.

Toxicity studies on indigenous species were performed as part of the NS&T assessment in the late 1980s, and were reported in the 1991 special editions of *Estuaries*. Few related studies have been conducted since that time. Nelson et al. (1991) evaluated reproductive success of winter flounder from Shoreham, Madison, New Haven, Milford, Norwalk, and Hempstead in comparison to flounder from two sites near WWTF outfalls in Boston Harbor in 1986 through 1988 by examining egg and larval properties. Evaluation of % fertilization, embryo lipid content, and larval size indicated New Haven Harbor to be the most impacted of the study sites in LIS, although fish from both Shoreham and Milford scored poorly in some indices. The embryos from all LIS sites were in better condition than those sampled from Boston Harbor. Within LIS there were no differences in sediment, adult liver, or embryo PCB concentrations, nor was there any apparent correlation between embryo PCB concentrations and embryo health measures. No significant site specific differences in PCB concentrations in flounder livers were

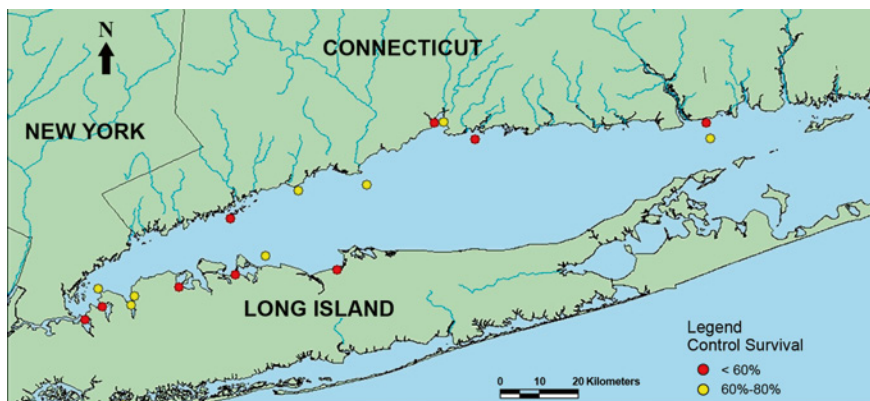


Fig. 5.27 Toxicology of various coastal LIS sites using *Ampelisca abdita* tests, with <60 % survival rate indicated as the most toxic sites. Data taken from USEPA 2010, USEPA, National Coastal Assessment Northeast 2000–2006 Summary Data at <http://www.epa.gov/emap/nca/html/regions/ne0006/index.html>

observed in LIS, and all were lower than those from fish collected near WWTF outfalls in Boston Harbor. No correlation was found between embryo or sediment metal concentrations and toxicity. Their data indicate that some other factors, such as a contaminant not analyzed, or other environmental or biological variables likely contributed to the toxicity observed. Nelson et al. (1991) concluded that winter flounder reproduction was impaired at some LIS locations, but that neither PCBs nor metals appeared to be linked to the health status of the fish. A related study examined sublethal abnormalities in winter flounder embryos and found developmental deficits and elevated incidence of cytotoxicity and DNA damage in fish embryos (Perry et al. 1991). Fish embryos from New Haven were most significantly affected, although abnormalities were also observed in embryos from Hempstead, Shoreham, and the Boston Harbor sites.

Gronlund et al. (1991) reported on a more detailed study assessing overall health of winter flounder collected at three of the NS&T sites: New Haven, Niantic and Norwalk. Histological examination of liver from adults indicated fish from the New Haven site to be most severely impacted with almost 90 % showing some measure of histological lesions. Flounder from Norwalk ranked next, with 70 % showing lesions, while only about 20 % of fish from Niantic showed liver lesions. Levels of DNA adducts were highest in fish from New Haven, which had prevalences around 35 %, similar to that observed in Boston Harbor. Fish from both Norwalk and Niantic had levels of hepatic DNA adducts of <10 %. Of the three sites examined, New Haven had the highest levels of chemical contaminants including PAHs, PCBs, Ag, Ni, Pb, Cu, Cr, and Zn. Although no cause and effect relationships could be determined from this study, levels of PAHs at the New Haven site of 4000 ng/gdw were similar to those associated with liver lesions in other flounder species at other sites.

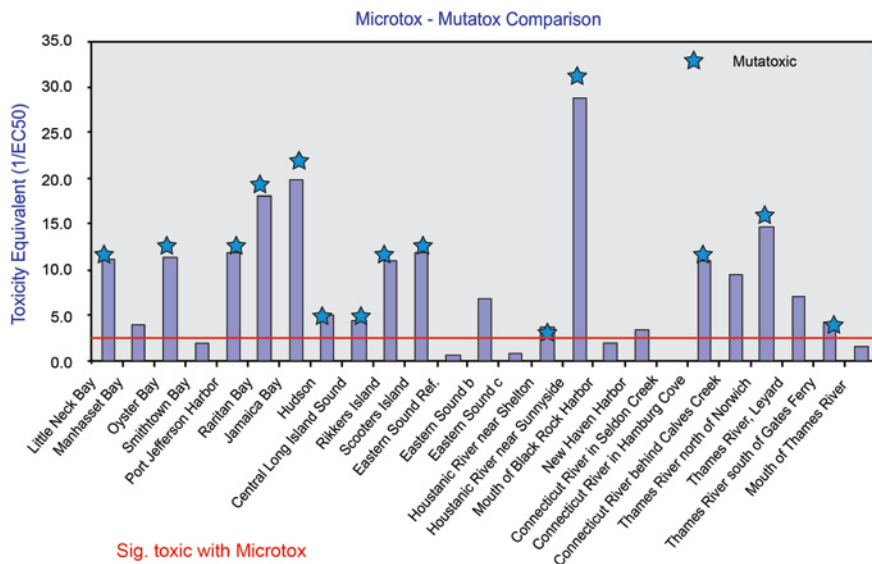


Fig. 5.28 Toxicity equivalent comparison for various locations using the Microtox™ and Mutatox™ luminescent bacterial assays (McElroy, unpub. data)

Cytochrome P450 monooxygenase (Cyp1a) has been used as a biomarker of exposure to organic contaminants, particularly PCBs and PAHs in fish for almost 30 years. Monosson and Stegeman (1994) evaluated Cyp1a activity in livers of winter flounder from a variety of locations throughout the Northeast, including LIS, in the early 1990s. Their analysis indicated widespread exposure to chemicals that induce Cyp1a throughout the region. As measured by Cyp1a catalytic activity, only fish from Georges Bank appeared to be free of contamination. Fish from Hempstead Harbor and Niantic in LIS were evaluated as part of this study. Hempstead Harbor fish expressed the highest levels of any examined in this study, and activity at both sites exceeded that observed in Boston Harbor fish. Cyp1a activity correlated with PCB concentrations in liver from the same fish.

A more comprehensive study, part of NOAA's Benthic Surveillance Program (Collier et al. 1998), reported Cyp1a data on winter flounder from samples collected from 1988 to 1994 at 22 sites around the Northeast, and demonstrated that with the exception of Maine, Cyp1a induction was widespread throughout the region. Furthermore, there appears to be no evidence of diminished responses in the more recently collected fish samples. The results of this study indicate that exposure to organic contaminants is widespread in fish collected from urban areas throughout the northeast. More recent work in McElroy's lab examining Cyp1a gene expression in livers from young-of-the-year winter flounder collected in 2008 and 2009 from Port Jefferson, Oyster Bay, Manhasset Bay, and Little Neck Bay in LIS, and Shinnecock and Jamaica Bay on Long Island's south shore also indicates widespread evidence of exposure to organic contaminants in LIS fish (Romany 2010).

5.7 Nutrient and Carbon Patterns and Trends

Like so many other urban estuaries, LIS suffers from nutrient and carbon pollution, creating directly (carbon) or indirectly (nutrients) a large biogenic oxygen demand (e.g., Diaz 2001; Boesch et al. 2001; Bricker et al. 2003). The direct effect of the enhanced nutrient fluxes is cultural eutrophication with the recurring effect of seasonal hypoxia–anoxia in WLIS and CLIS (O’Shea and Brosnan 2000; Welsh and Eller 1991; Parker and O’Reilly 1991; Lee and Lwiza 2008).

5.7.1 *Currently Measured and Estimated Nutrient Fluxes*

The magnitude of the various nutrient fluxes and their relationship to cultural eutrophication impacts today can be estimated and measured directly from river data. River loads quantify the aggregated contributions of nutrients from all sources within the watershed, and are a starting point for their allocation among specific sources such as WWTFs, urban, and agricultural runoff, and atmospheric deposition that comprise the major contributors of nutrient enrichment (NYSDEC and CTDEP 2000). Groundwater nutrient fluxes are less well-known but may be significant as well.

We estimated atmospheric wet deposition of inorganic N to LIS watersheds, an area of approximately 4.3 Mha, for calendar years 1994–2009 using data from the National Atmospheric Deposition Program (NADP 2009). The data from the NADP have been synthesized into a gridded format based on interpolation at each of the monitoring locations. The mean deposition rate was calculated for each year by taking the average of the gridded data for the LIS watershed, including the Pawcatuck River basin. The watershed area used did not include the surface of LIS, because the grids were clipped to the coastlines.

Wet deposition of inorganic N on the LIS watershed, generally referred to as “indirect deposition,” as opposed to direct deposition on the waterbody’s surface, generally decreased since the mid-1990s. This decrease is parallel to decreases in emissions of N oxides from vehicles and electrical power generation. The declines in atmospheric deposition of reactive N are primarily in the form of nitrate, whereas emissions of NH₃ do not appear to have significant trends, indicating that reduced forms of N are becoming a larger fraction of the atmospheric N budget (Pinder et al. 2011). Estimated wet deposition of inorganic N ranged from 28 Mkg/year (6.5 kg/ha/year) in 1996 to 15 Mkg/year in 2009 (3.5 kg/ha/year) (Fig. 5.29). The direct atmospheric input of N onto LIS is estimated at ~2.5 Mkg/year (Castro and Driscoll 2002).

The loading of the other nutrients such as Si (an essential element for diatoms, the main primary producer in the Sound) and P is largely determined by the river fluxes, where the element originates through weathering of rocks on land. Secondary Si fluxes may stem from phytoliths (small silica grains in plants) in

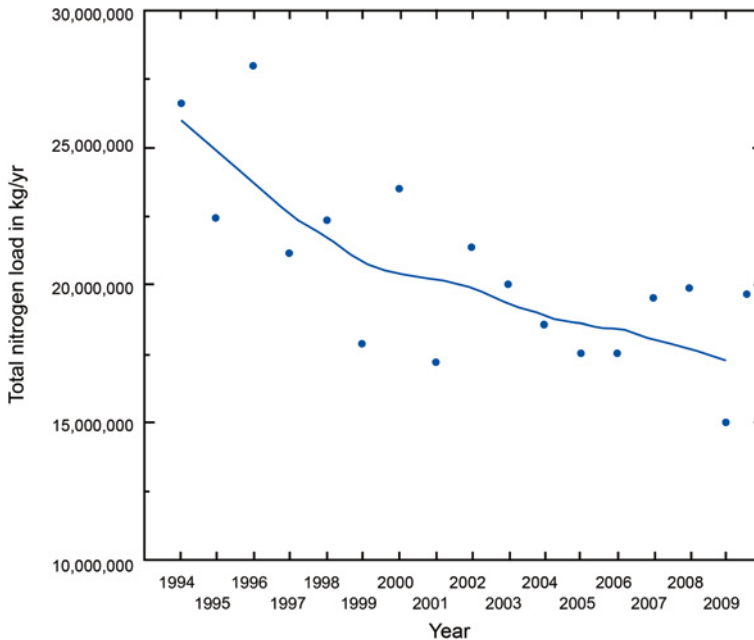


Fig. 5.29 Atmospheric wet deposition of inorganic N, averaged for the LIS Watershed, 1994–2009 (data from National Atmospheric Deposition Program 2009)

association with particulate organic matter discharge. The combined annual flux of Si from the Connecticut and Housatonic Rivers is estimated at 1,500 Mkg Si/year, while the WWTF silica flux is estimated at ~1 % of the riverine flux (Boon 2008). The total P load derived from rock weathering and WWTFs is estimated at 0.55 Mkg P/year.

5.7.2 Trends in Nutrient Fluxes over the Last 40 Years

The United States Geological Survey has maintained a network of stream gages and water quality monitoring sites in the LIS watershed, such as NASQAN (Ficke and Hawkinson 1975) and USGS National Water Quality Assessment or NAWQA (Gilliom et al. 1995), summarized in Fig. 5.30. These long-term monitoring sites are largely stations above the tidal influence (“fall line” stations), and nutrient loads below these stations are not measured. The monitoring sites on the major rivers (Connecticut, Farmington, Housatonic, Naugatuck, Quinnipiac, Shetucket, and Quinebaug) represent 82 % of the drainage area of the LIS watershed; however, the majority of the point sources of nutrients (N and P) are in coastal areas, downstream of these sites. Data on the loads and trends of N and P have

previously been summarized by Mullaney et al. (2002), Colombo and Trench (2002), Trench and Vecchia (2002), Trench (1996, 2000), and Sprague et al. (2009). Data for selected water-quality monitoring stations and associated flow data from USGS stream gaging sites were analyzed to estimate the N, P, Si, and total particulate organic carbon loads from 1974 to 2008. Loads were calculated using the linear regression method LOADEST developed by Runkel et al. (2004). Given a time series of streamflow and constituent concentration, LOADEST assists the user in developing a regression model for the estimation of constituent load. Explanatory variables in the regression model include various functions of streamflow, decimal time, and additional user-specified data. The formulated regression model then is used to estimate loads over a user-specified time interval. Several trend types were analyzed, including flow-adjusted trends in concentrations and loads, and nonflow-adjusted trends in concentrations and loads. These trend analysis methods were presented in detail by Sprague et al. (2009).

Our analysis shows that the concentrations and loads of total N have declined during the 1974–2008 study period, probably related to the implementation of the Federal Clean Water Act (CWA) of 1972 and the related benefits of management actions taken under its authority. Trends in flow-adjusted concentrations and loads and nonflow-adjusted concentrations and loads are shown in Table 5.9. Significant flow-adjusted trends in concentrations and nonflow-adjusted concentrations of total N were observed at most selected sites, with the exception of the Quinnipiac River at Wallingford and the Saugatuck River at Redding (Table 5.9). The Quinnipiac River is dominated by point source N discharges from three wastewater treatment facilities totaling 26,500 m³/day (Mullaney et al. 2002). Mullaney et al. (2009) estimated that about 360 ha of impervious area were added to this watershed from 1985 to 2002 as a result of urbanization. The Saugatuck River watershed at Redding (Fig. 5.30) has remained mostly forested and rich in wetlands (80.7 %) (Fig. 5.30). This station is an example of concentrations and loads of N that can be expected in similar, mostly forested watersheds of the LIS basin.

Downward trends in N loads were significant at seven of the 11 sites selected for this summary (Table 5.9). The Housatonic, Norwalk, Quinnipiac, and Saugatuck River sites showed no significant trends. Total N loads (nonflow-adjusted) declined significantly from the other seven stations, averaging 1.08 %/year over the period of record. Although over this long period of analysis (water years 1974–2008) there are significant downward trends in total N, concentrations generally showed no significant trend in later years, as described by Sprague et al. (2009).

Total N loads from the seven major fall line stations described above declined dramatically during the period of study, from about 21 Mkg/year to 15 Mkg/year. The most notable 5 decreases occurred at the Connecticut, Farmington, Naugatuck, Quinebaug, and Shetucket Rivers (Fig. 5.31; Tables 5.9, 5.10). Yields (loads/watershed area/time) of N during the study period ranged from 3.0 kg/ha/year for watersheds with minimal development to 21.4 kg/ha/year in watersheds with dense urban development and major wastewater discharges. Nitrogen yields are strongly correlated with percent of impervious surface in each watershed, which serves as a measure of the overall urban development and magnitude of wastewater discharge (Fig. 5.32).

Table 5.9 Trends in nutrient constituents at USGS fall-line monitoring stations on rivers in Connecticut 1974–2008 [*p*-values in bold indicate significance at the = 0.05 level]

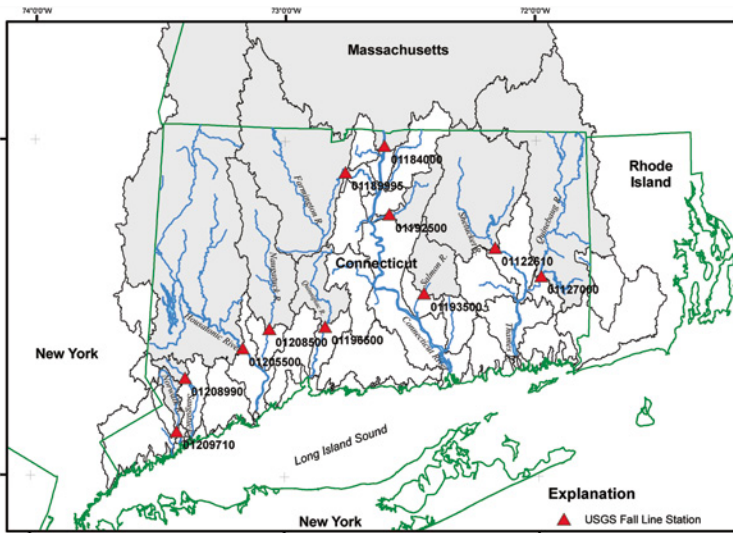
Rivers ^a	Trend in flow-adjusted concentration or load, in percent/year	Flow-adjusted trend in load, in kg/day/year	<i>p</i> value for flow-adjusted trend in load	Trend in concentration, in percent/year	<i>p</i> -value for non-flow-adjusted concentration	Trend in load, in percent/year	Trend in load, in kg/d/year	<i>p</i> -value for trend in load
<i>Total nitrogen</i>								
Shetucket	-0.92	-10.21	<0.0001	-0.90	<0.0001	-0.97	-10.83	0.0032
Quinebaug	-0.84	-23.97	<0.0001	-0.78	<0.0001	-1.20	-34.23	<0.0001
Connecticut	-1.04	-325.63	<0.0001	-1.06	<0.0001	-0.94	-295.47	<0.0001
Farmington	-0.46	-11.82	0.0004	-0.42	0.0173	-0.53	-13.54	0.0361
Hockanum	-1.21	-11.49	0.0001	-1.37	<0.0001	-0.96	-9.09	0.0118
Salmon	-0.65	-1.12	0.0030	-0.68	0.0019	-0.96	-1.64	0.0417
Quinnipiac	-0.16	-2.07	0.2337	-0.16	0.4141	-0.15	-2.00	0.5184
Housatonic	-0.67	-21.89	<0.0001	-0.67	<0.0001	-0.22	-7.11	0.6938
Naugatuck	-1.96	-79.65	<0.0001	-1.88	<0.0001	-2.03	-82.38	<0.0001
Saugatuck	0.02	0.00	0.9492	0.01	0.9567	-0.05	-0.01	0.9471
Norwalk	-1.02	-0.84	<0.0001	-1.01	<0.0001	-0.98	-0.81	0.0662
<i>Total phosphorus</i>								
Shetucket	-1.97	-1.75	<0.0001	-1.97	<0.0001	-2.00	-1.77	<0.0001
Quinebaug	-2.02	-5.69	<0.0001	-2.01	<0.0001	-2.18	-6.14	<0.0001
Connecticut	-1.61	-36.78	<0.0001	-1.62	<0.0001	-1.54	-35.17	<0.0001
Farmington	-1.39	-4.41	<0.0001	-1.36	<0.0001	-1.42	-4.50	<0.0001
Hockanum	-1.90	-1.94	<0.0001	-2.06	<0.0001	-1.71	-1.75	0.0005
Salmon	-1.51	-0.07	0.0005	-1.56	0.0003	-1.72	-0.09	0.0022
Quinnipiac	-1.46	-2.90	<0.0001	-1.46	<0.0001	-1.46	-2.89	<0.0001
Housatonic	-1.66	-2.66	<0.0001	-1.64	<0.0001	-1.38	-2.22	0.0058
Naugatuck	0.27	0.86	0.2934	0.62	0.0949	0.10	0.32	0.7187
Saugatuck	-1.03	-0.01	0.0097	-1.03	0.0095	-1.07	-0.01	0.1204
Norwalk	-1.28	-0.05	0.0003	-1.27	0.0005	-1.24	-0.05	0.0562
<i>Total organic carbon</i>								

(continued)

Table 5.9 (continued)

Rivers ^a	Trend in flow-adjusted concentration or load, in percent/year	Flow-adjusted trend in load, in kg/day/year	p value for flow-adjusted trend in load	Trend in concentration, in percent/year	p-value for non-flow-adjusted concentration	Trend in load, in percent/year	Trend in load, in kg/d/year	p-value for trend in load
Shetucket	-0.45	-25.77	0.0008	-0.47	0.0026	-0.55	-31.38	0.2675
Quinebaug	-0.59	-91.85	0.0001	-0.62	<0.0001	-1.07	-164.79	0.0037
Connecticut	-0.65	-916.20	<0.0001	-0.63	<0.0001	-0.49	-692.30	0.1274
Farmington	-0.64	-64.11	<0.0001	-0.65	<0.0001	-0.74	-75.02	0.0560
Hockanum	-0.60	-7.85	0.0941	-0.59	0.0982	-0.10	-1.35	0.8506
Salmon	-0.60	-7.34	0.0016	-0.66	0.0013	-0.95	-11.66	0.0641
Quinnipiac	-1.01	-23.75	<0.0001	-1.01	<0.0001	-1.00	-23.61	0.0027
Housatonic	-0.65	-94.05	0.0010	-0.62	0.0018	-0.16	-22.83	0.7956
Naugatuck	-1.34	-91.58	<0.0001	-1.32	<0.0001	-1.55	-106.20	<0.0001
Saugatuck	-0.85	-2.23	<0.0001	-0.86	<0.0001	-0.90	-2.36	0.1608
Norwalk	0.55	1.65	0.0188	0.56	0.0320	0.62	1.86	0.4056
<i>Silica</i>								
Shetucket	0.05	5.14	0.5726	0.05	0.6026	-0.05	-4.55	0.9172
Quinebaug	-0.32	-43.29	0.0290	-0.37	0.0127	-0.87	-117.99	0.0282
Connecticut	0.45	740.40	0.0004	0.47	0.0003	0.69	1126.18	0.0591
Farmington	0.16	21.06	0.2582	0.15	0.2682	0.03	3.51	0.9480
Hockanum	-0.26	-6.28	0.2774	-0.30	0.2090	0.21	5.08	0.6349
Salmon	0.16	3.70	0.0581	0.19	0.0376	-0.20	-4.46	0.6497
Quinnipiac	0.30	12.92	0.0438	0.29	0.0552	0.30	13.29	0.3893
Housatonic	0.70	64.15	0.0731	0.86	0.0448	1.63	149.09	0.0906
Naugatuck	-0.22	-15.68	0.0219	-0.21	0.0277	-0.61	-43.31	0.0572
Saugatuck	0.42	1.59	0.0246	0.42	0.0240	0.35	1.33	0.6248
Norwalk	-0.43	-2.56	0.1898	-0.42	0.2011	-0.38	-2.27	0.5627

^a Shetucket R. at S. Windham, CT, 01122610; Quinebaug R. at Jewett City, CT, 01127000; Connecticut R. at Thompsonville, CT, 01184000; Farmington R. at Tariffville, CT, 01189995; Hockanum R. near East Hartford, CT, 01192500; Salmon R. near E. Hampton, CT, 01193500; Quinnipiac R. at Wallingford, 01196500; Housatonic R. at Stevenson, CT, 01205500; Naugatuck R. at Beacon Falls, CT, 01208500; Saugatuck R. near Redding, CT, 01208990; Norwalk R. at Winnipauk, CT, 01209710



USGS station number	USGS station name	Drainage area (km ²)	Period of record used (water years)	Urban land use, in percent	Agricultural land use, in percent	Forested land cover, in percent	Wetlands, in percent	Impervious area, in percent	2000 population density, in people/km ²
01122610	Shetucket River at South Windham, Conn.	1,060	1974-2008	10.0	7.6	68.7	10.0	1.8	99
01127000	Quinebaug River at Jewett City, Conn.	1,850	1974-2008	11.4	10.1	60.9	13.6	2.6	98
01184000	Connecticut River at Thompsonville, Conn.	25,000	1974-2008	6.9	6.8	78.0	3.5	1.6	45
01189995	Farmington River at Tariffville, Conn.	1,490	1974-2008	13.7	5.8	71.3	4.9	3.1	126
01192500	Hockanum River near East Hartford, Conn.	190	1990-2008	41.4	9.8	40.9	5.2	13.2	515
01193500	Salmon River near East Hampton, Conn.	259	1974-2008	11.3	8.3	62.5	14.6	1.8	101
01196500	Quinnipiac River at Wallingford, Conn.	298	1974-2008	53.2	2.8	36.9	4.1	17.5	534
01205500	Housatonic River at Stevenson, Conn.	4,000	1974-2008	10.4	13.4	66.6	5.0	2.3	88
01208500	Naugatuck River at Beacon Falls, Conn.	673	1974-2008	25.5	8.9	59.4	2.9	8.6	358
01208990	Saugatuck River near Redding, Conn.	54	1974-2008	13.2	3.7	75.2	5.5	1.3	129
01209710	Norwalk River at Winnipauk, Conn.	86	1981-2008	27.6	2.7	63.2	4.6	6.8	279

Fig. 5.30 Water-quality stations in Connecticut used for flux monitoring by USGS. (Land use/land cover data interpreted from The United States Environmental Protection Agency (2001a, b))

Nitrogen loads from Connecticut’s WWTFs were generally lower in 2010 than in 1995. Nitrogen loads from these point sources have been declining, particularly since 2002, when the Nitrogen Credit Exchange (NCE) program began (CTDEEP 2011). Nitrogen loads from wastewater treatment facilities in Connecticut and New York have been managed in watershed-based zones (Fig. 5.33). End-of-pipe discharge of N is an order of magnitude greater in management zones 8 and 9 in the New York City area, compared to other management zones in Connecticut and New York (graphs of these zones are highlighted in the Fig. 5.5 because they are at a different scale). End-of-pipe N loads averaged 21,000 kg/day in Connecticut and 64,000 kg/day in New York in 1995. In 2010, they totaled 11,300 kg/day, and

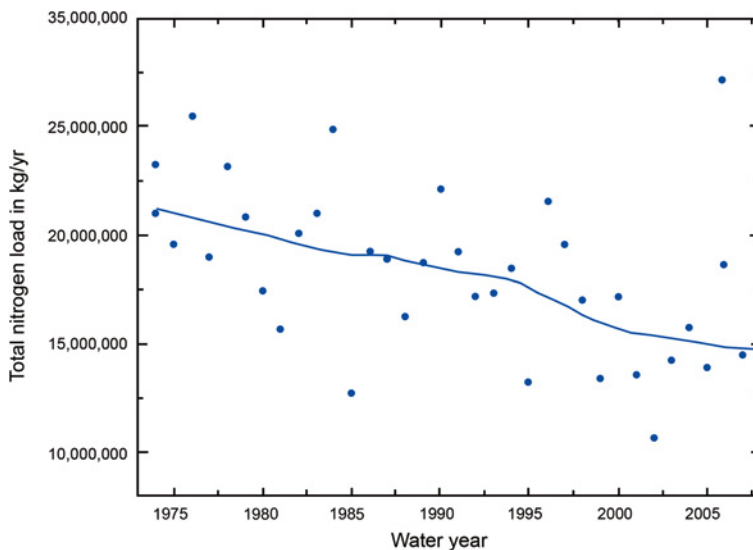


Fig. 5.31 Sum of estimated total N loads for fall-line stations in Connecticut, water years 1974–2008 (Stations include Connecticut River (01184000), Farmington River (01189995), Quinnipiac River (01196500), Housatonic River (01205500), Naugatuck River (01208500), Shetucket River (01122610), and Quinebaug River (01127000), fitted line is a Lowess smooth curve)

50,000 kg/day, respectively (Joseph Salata, USEPA Long Island Sound Office, written communication, March 3, 2011).

Total P concentrations and loads (Fig. 5.34) have also declined in the majority of stations analyzed for this summary (Tables 5.9, 5.10), probably due to improvements in wastewater treatment practices that are required by state and federal law, and state bans on phosphate in most detergents (Litke 1999). Total P loads (nonflow-adjusted) declined significantly at eight stations, averaging 1.6 %/ year over the period of record. Significant downward trends in total P occurred over this long period of analysis (water years 1974–2008), but there are indications of increases in P concentrations and loads toward the end of the record. Analysis of data water years 1993–2003 (Sprague et al. 2009) indicates significant increasing flow-adjusted and nonflow-adjusted trends in total P at five of these stations. Phosphorus yields ranged from 0.1 kg/ha/year in watersheds with minimal development to 3.3 kg/ha/year in the past at sites with high-density urban development and major wastewater discharge (Table 5.10). Total P loads from the seven major fall line stations described above declined during the period of study, from about 2.5 Mkg/year to 1.3 Mkg/year. The trends identified by these analyses indicate large declines in N and P loads during 1974–2008 with associated changes in the ratios of these nutrients. Although changes in Si/N ratios were initially implicated as a cause for shifts away from diatom dominance in coastal waters, changes in TN/TP may also have implications for the dominant phytoplankton in LIS (diatoms and dinoflagellates; Sommer 1994; Hodgkiss and Ho 1998). The TN/TP

Table 5.10 Loads and yields of nutrient constituents at USGS fall-line monitoring stations on rivers in Connecticut, water years 1974, 1990, 2000, and 2008 [Loads in kg/year, yields in kg/ha/year]

Water Year	1974 ^b	1990	2000	2008	2008
River ^a	Load ^d	Yield ^e	Load	Yield	Load
<i>Total nitrogen</i>					
Shetucket	1,420,000	7.7	1,300,000	7.0	988,000
Quinebaug	633,000	6.0	612,000	5.8	438,000
Connecticut	14,400,000	5.8	14,600,000	5.8	11,500,000
Farmington	973,000	6.5	1,270,000	8.5	1,030,000
Hockanum			341,000	17.9	364,000
Salmon	120,000	4.6	146,000	5.6	92,300
Quinnipiac	589,000	19.8	638,000	21.4	542,000
Housatonic	2,660,000	6.7	2,870,000	7.2	2,270,000
Naugatuck	1,420,000	21.1	1,410,000	20.9	802,000
Saugatuck	19,900	3.7	21,000	3.9	16,000
Norwalk	34,100	4.0	50,400	5.9	37,200
<i>Total phosphorus</i>					
Shetucket	166,000	0.9	87,100	0.5	52,600
Quinebaug	71,400	0.7	29,000	0.3	19,100
Connecticut	1,780,000	0.7	1,080,000	0.4	789,000
Farmington	162,000	1.1	110,000	0.7	87,500
Hockanum			43,100	2.3	32,400
Salmon	5,830	0.2	4,840	0.2	2,670
Quinnipiac	98,900	3.3	67,600	2.3	51,300
Housatonic	214,000	0.5	118,000	0.3	87,200
Naugatuck	185,000	2.7	154,000	2.3	151,000
Saugatuck	1,020	0.2	982	0.2	599
Norwalk	1,950	0.2	3,230	0.4	2,140
<i>Total organic carbon</i>					
Shetucket	8,790,000	47.6	8,040,000	43.5	5,940,000
Quinebaug	4,740,000	44.9	3,840,000	36.3	2,870,000

(continued)

Table 5.10 (continued)

Water Year	1974 ^b	1974	1990 ^c	1990	2000	2000	2008	2008
River ^a	Load ^d	Yield ^e	Load	Yield	Load	Yield	Load	Yield
Connecticut	95,100,000	38.0	86,300,000	34.5	72,400,000	28.9	94,100,000	37.6
Farmington	5,840,000	39.1	5,460,000	36.5	4,520,000	30.2	4,810,000	32.2
Hockanum			506,000	26.6	637,000	33.5	547,000	28.8
Salmon	974,000	37.6	966,000	37.3	668,000	25.8	736,000	28.4
Quinnipiac	1,760,000	59.1	1,360,000	45.7	950,000	31.9	1,160,000	39.0
Housatonic	14,100,000	35.3	12,300,000	30.8	11,400,000	28.5	13,000,000	32.5
Naugatuck	4,320,000	64.2	3,010,000	44.7	2,090,000	31.0	2,160,000	32.1
Saugatuck	247,000	45.4	207,000	38.1	145,000	26.7	154,000	28.3
Norwalk	98,600	11.5	271,000	31.7	216,000	25.3	257,000	30.1
<i>Silica</i>								
Shetucket	9,150,000	49.5	8,670,000	46.9	6,450,000	34.9	6,770,000	36.7
Quinebaug	6,080,000	57.5	6,080,000	57.5	4,910,000	46.5	5,070,000	48.0
Connecticut	90,800,000	36.3	109,000,000	43.6	104,000,000	41.6	123,000,000	49.2
Farmington	6,920,000	46.3	7,530,000	50.4	6,710,000	44.9	6,920,000	46.3
Hockanum			944,000	49.7	1,060,000	55.8	1,030,000	54.2
Salmon	1,420,000	54.8	1,560,000	60.2	1,250,000	48.3	1,290,000	49.8
Quinnipiac	1,920,000	64.5	2,370,000	79.6	2,090,000	70.2	1,970,000	66.2
Housatonic	12,400,000	31.0	14,800,000	37.0	13,400,000	33.5	17,400,000	43.5
Naugatuck	3,780,000	56.1	3,770,000	56.0	3,070,000	45.6	3,240,000	48.1
Saugatuck	282,000	51.8	325,000	59.7	274,000	50.4	273,000	50.2
Norwalk	181,000	21.2	431,000	50.4	350,000	40.9	397,000	46.4

^a Shetucket R. at S. Windham, CT; 01122610; Quinebaug R. at Jewett City, CT; 01127000; Connecticut R. at Thompsonville, CT; 01184000; Farmington R. at

Tariffville, CT; 01189995; Hockanum R. near East Hartford, CT; 01192500; Salmon R. near E. Hampton, CT; 01193500

^b Quinnipiac R. at Wallingford, 01196500; Housatonic R. at Stevenson, CT; 01205500; Naugatuck R. at Beacon Falls, CT; 01208500

Saugatuck R. near Redding, CT; 01208990; Norwalk R. at Winnipauk, CT; 01209710

^c Norwalk River, beginning water year is 1981

^d Hockanum River, beginning water year is 1992

^e Load is the amount delivered from the basin upstream from the monitoring station over the course of the water year

Yield is the annual load divided by the drainage area, and allows for comparisons among stations

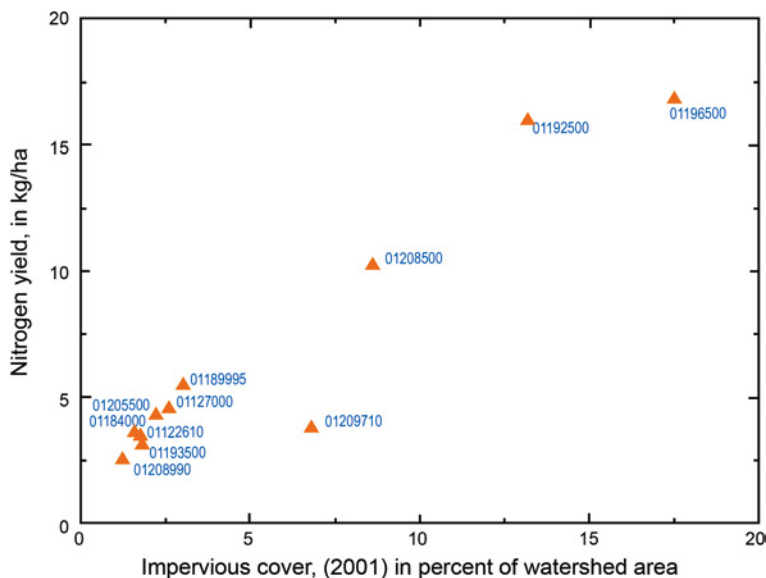


Fig. 5.32 Relationship between impervious cover and N yield in selected watersheds that drain into LIS (Impervious cover data interpreted from The United States Environmental Protection Agency 2001)

ratios were lowest (11–26) among sites with the most developed watersheds (Hockanum, Naugatuck, and Quinnipiac Rivers), and the highest ratios (43–76) were found for the least developed watersheds (Salmon and Saugatuck Rivers). The TN/TP generally increased from water years 1974 to the mid-1990s, and then began to decline until present. This is generally due to declines in TP loads relative to TN loads in the early part of the record followed by slightly increasing TP loads from the late 1990s through 2008 (Fig. 5.35).

Flow-adjusted concentrations and loads of total organic carbon (Fig. 5.36) declined significantly at most of the stations during the study period. Only three stations had significant declines in nonflow-adjusted loads of total organic carbon (Table 5.9).

The trends in Si loads (Fig. 5.37) and concentrations were not consistent over the time period of study (Table 5.9). The Quinebaug and Naugatuck Rivers had a significant decline in flow-adjusted concentrations and loads of Si, while the Connecticut, Quinnipiac, and Saugatuck Rivers had a significant increase in flow-adjusted Si concentrations and loads. Only the Quinebaug River site had a significant decline in nonflow-adjusted loads. The Connecticut River had a marginally significant ($p = 0.059$) increase in Si load that amounted to 0.69 %/year, or 24 % during the total studied period of record. Silica concentrations measured at the fall-line stations were similar to those commonly expected for natural waters (SiO_2) (Hem 1985), and ranged from about 3–12 mg/L as SiO_2 . The median yield of silica was 48 kg/ha/year, with an interquartile range of 37–57 kg/ha/year. The lowest yields occurred in the Connecticut and Housatonic Rivers, and the highest

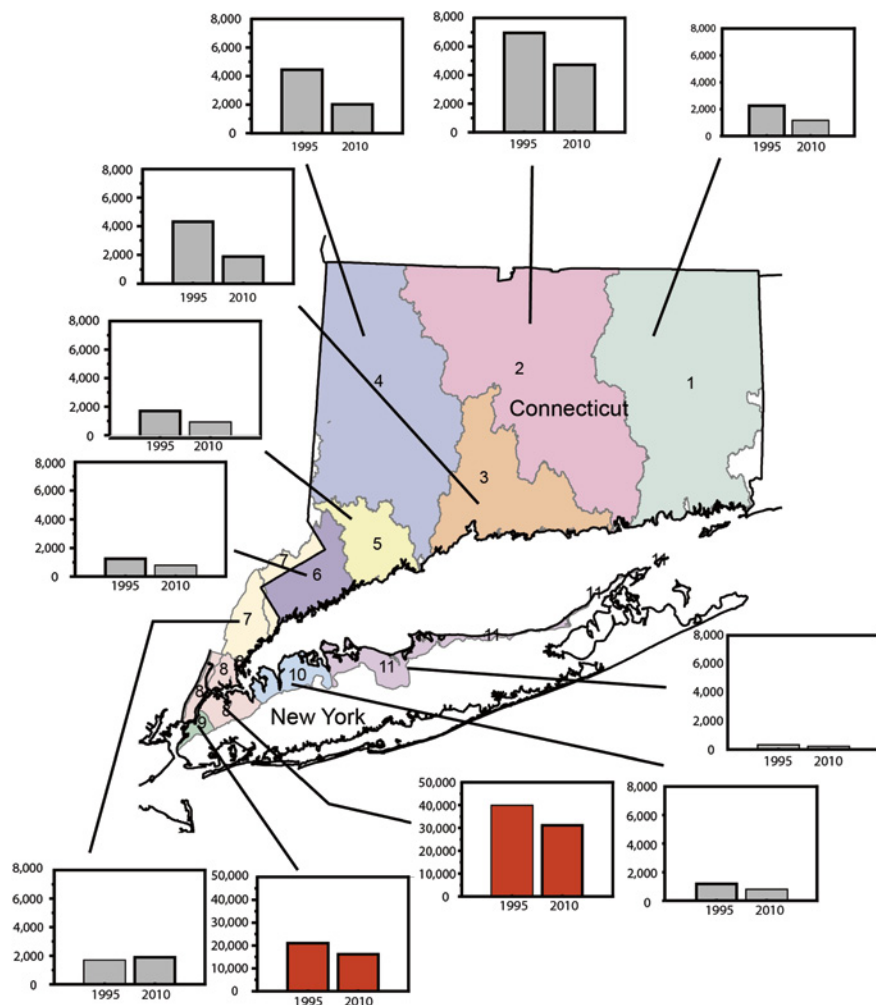


Fig. 5.33 Total N loads from WWTFs in N management zones for LIS, 1995 and 2010. The units along the Y axis are in mean kg/day (Data from Joseph Salata, USEPA Long Island Sound Office 2010, written communication)

yield was in the Quinnipiac River (Table 5.10). Lower yields of dissolved silica have been associated with the accumulation of biogenic silica from diatom productivity in the impoundments (Humborg et al. 2000; Triplett et al. 2008). The higher yields associated with the Quinnipiac River may be due to higher silica concentrations in groundwater in sediments of the Mesozoic Valley of Connecticut relative to sediments derived from other local bedrock types (Grady and Mullaney 1998). Increasing development of watersheds and climate change may affect the baseflow index and therefore the Si loads, due to the introduction of additional

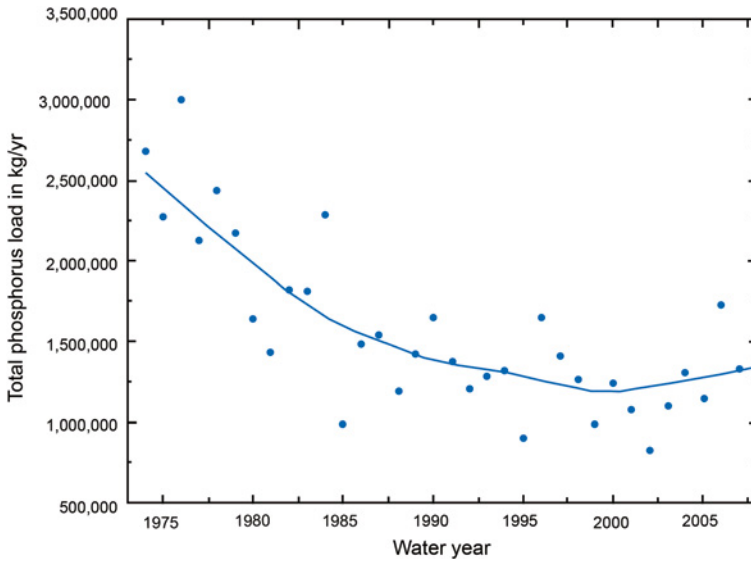


Fig. 5.34 Sum of estimated total P loads for fall-line stations in Connecticut, water years 1974–2008 (Stations include Connecticut River (01184000), Farmington River (01189995), Quinnipiac River (01196500), Housatonic River (01205500), Naugatuck River (01208500), Shetucket River (01122610), and Quinebaug River (01127000), fitted line is a Lowess smooth curve)

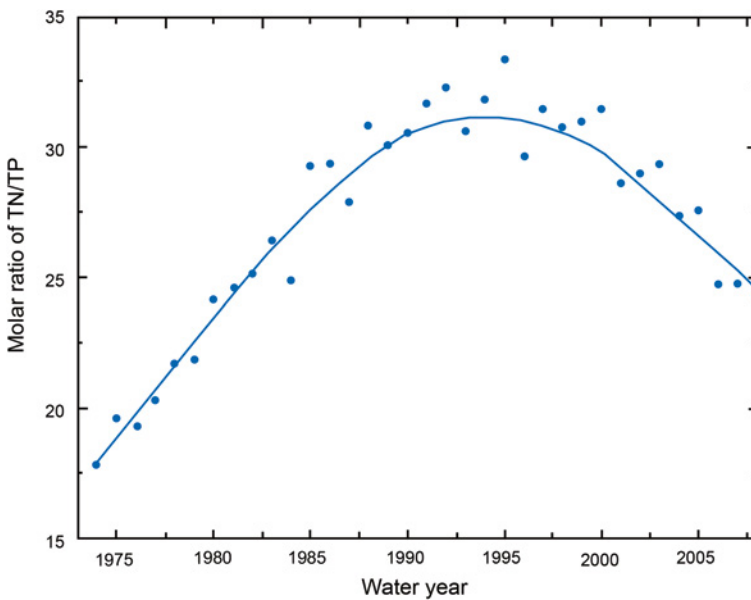


Fig. 5.35 The TN:TP ratios for combined fall-line stations in Connecticut, water years 1974–2008 (Stations include Connecticut River (01184000), Farmington River (01189995), Quinnipiac River (01196500), Housatonic River (01205500), Naugatuck River (01208500), Shetucket River (01122610), and Quinebaug River (01127000), fitted line is a Lowess smooth curve)

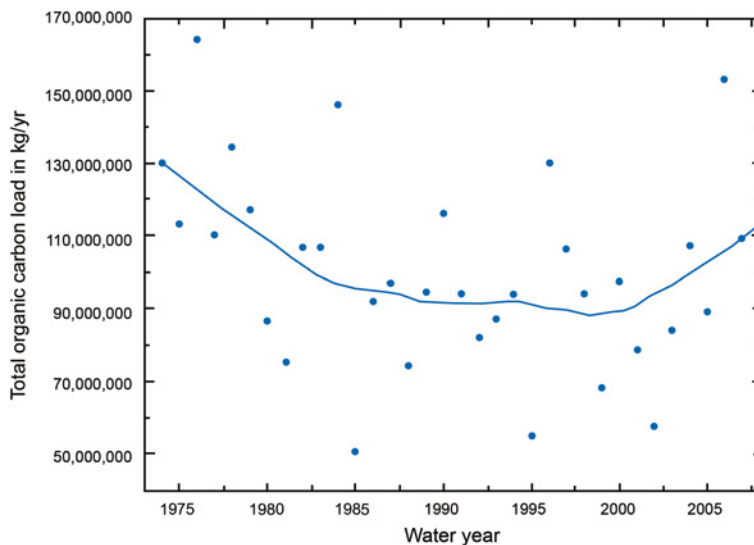


Fig. 5.36 Sum of estimated total organic C loads for fall-line stations in Connecticut, water years 1974–2008 (Stations include Connecticut River (01184000), Farmington River (01189995), Quinnipiac River (01196500), Housatonic River (01205500), Naugatuck River (01208500), Shetucket River (01122610), and Quinebaug River (01127000), fitted line is a Lowess smooth curve)

impervious areas (Loucaides et al. 2007), and changes in recharge rates and the time distribution of streamflow. Carey and Fulweiler (2011) report relations among land use/land cover and silica loads for streams in southern New England, with forested watersheds delivering the smallest loads and developed land delivering the largest loads. Further information on silica loading from the watershed is necessary to understand the mechanisms that control the loading of this nutrient.

Groundwater loading is an important transport mechanism of N entering LIS, more so than for P, which tends to be low in groundwater underlying urban development in Connecticut (Grady and Mullaney 1998). Phosphorus from groundwater can still constitute a substantial part of the watershed load of P (Mullaney 2007) and can be mobile under some geochemical conditions (Denver et al. 2010). Phosphorus loads from groundwater have not been studied extensively in the LIS watershed; most P is likely delivered by point sources and stormwater runoff. More information is needed to understand the loading of Si from direct and indirect (tributary) discharge of groundwater to LIS. Concentrations of Si in groundwater are similar to those in surface waters of the LIS watershed, and concentrations can be related to aquifer source material and land use (Grady and Mullaney 1998).

The loading of N from groundwater can be indirect, as a component of tributary loads (Mullaney 2007) or can be direct discharge to coastal embayments or LIS. Loading of N from groundwater may require different management mechanisms than the management of stormwater. The groundwater travel time from the

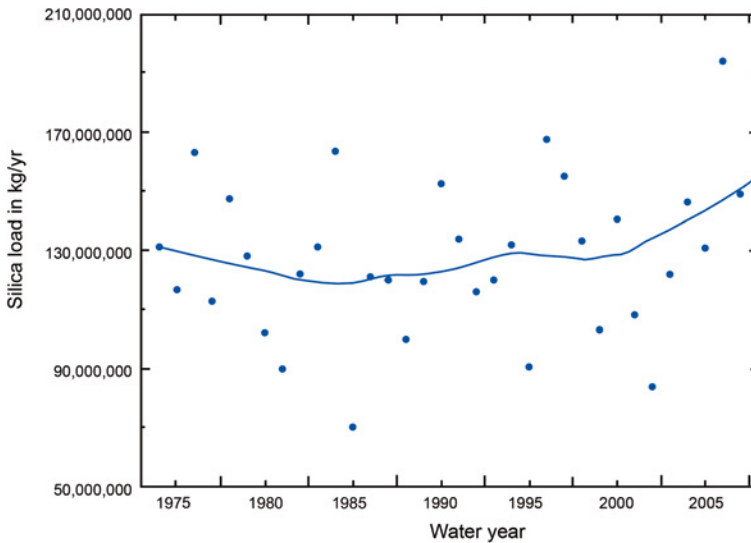


Fig. 5.37 Sum of estimated Si loads for fall-line stations in Connecticut, water years 1974–2008 (Stations include Connecticut River (01184000), Farmington River (01189995), Quinnipiac River (01196500), Housatonic River (01205500), Naugatuck River (01208500), Shetucket River (01122610), and Quinebaug River (01127000), fitted line is a Lowess smooth curve)

source of recharge to the tributary or embayment of LIS can be long (years to decades), delaying the effects of land-use changes or management actions on receiving waters. Loading of N from groundwater from Long Island to LIS was estimated at 0.75 Mkg/year (Scorca and Monti 2001). In Connecticut, the percent base flow of streams relatively unaffected by human activities is determined by the percentage of each watershed underlain by coarse-grained glacial stratified deposits (Mazzaferro et al. 1979). Connecticut is underlain by about 18 % coarse-grained glacial stratified deposits, which equates to a base-flow index of 46 % of total runoff, indicating that groundwater discharge may be a significant part of the tributary flow in Connecticut watersheds. Further research is needed to understand the importance of this groundwater source on both the Connecticut and New York parts of LIS, and the mechanisms of transport from the groundwater system to coastal waters. Information is lacking on the importance of residential and municipal on-site wastewater management in contributing to this subsurface load of nutrients.

In summary, total N loads from tributaries in Connecticut have declined relative to 1974, but appear to have stabilized or slightly increased in the more recent part of the record. Total P loads have generally declined, but may have increased slightly toward the end of the record for this study (2008). Silica loads appear to vary with discharge, but are possibly affected by impoundments in some of the tributaries. Changes to the time distribution of stream flow caused by withdrawals for public water supply, and increased impervious surfaces, and other changes to land cover may have an effect on the yields of silica as well.

Atmospheric wet deposition of inorganic N appears to have declined since 1994. Nitrogen yields from forested watersheds generally were smaller than the amount of wet deposition of inorganic N they received in 1994, indicating retention of N in these areas. In 2008, wet deposition of N was only slightly higher than the total N loss from forested watersheds. Questions remain about whether these areas will become saturated with N, increasing the losses of N from the watershed, similar to those described by Aber et al. (2003).

The data presented here are useful in understanding the loads of TN from the major tributaries. The TN load from the Connecticut River represents a large part of the overall tributary load. Other sources of N with limited information include the net flux of N from the East River in the western end of LIS, the importance of the loading of N from direct and indirect groundwater sources, and the processing of N in tidally affected rivers.

5.7.3 LIS Water Column Nutrient Data

The CTDEEP carries out biweekly surveys of water quality in LIS along a series of fixed stations. Analytical data from water samples from these and several other cruises provide a snapshot of the distribution of nutrient concentrations and $\delta^{15}\text{N}$ values in LIS in 2007 (Boon 2008). The nutrient concentrations and isotopic ratios in LIS waters are determined by the various inputs and by the sinks, mainly primary productivity, but also exchange with the open ocean through tidal exchange (Bowman 1977). The isotopic ratio of nitrogen ($\delta^{15}\text{N}$) shows the pathways that the N has gone through before arrival in LIS. Terrestrial soil fixed nitrogen (NO_3^-) usually has $\delta^{15}\text{N}$ values of 0–5 ‰ whereas atmospheric deposition nitrate has $\delta^{15}\text{N}$ of 0–3 ‰. Consumption of land plants by higher organisms leads to higher $\delta^{15}\text{N}$ values in their tissues and waste products. During denitrification (turning NO_3^- into N_2 gas), the bacteria prefer the light isotope and what remains behind is isotopically heavy. As a result, manure, animal remnants, and WWTF effluents tend to have relatively high $\delta^{15}\text{N}$ values (with values >10 ‰).

The concentrations of the various N species display differences for surface and bottom waters and a strong E–W trend with higher concentrations in WLIS (Table 5.11). Records from CTDEEP from 1991 to 2004 of TDIN (in mg N/L) versus time show the characteristic cyclic pattern of build-up during the winter and

Table 5.11 Ranges of nutrient concentrations ($\mu\text{mol/L}$) in LIS waters (after Gobler et al. 2006)

	East river	WLIS	CLIS	ELIS
TDIN	25–47	2.6–2.7	1.4–9.5	1.0–9.5
TDIP	1.5–3.8	0.6–2.8	0.4–2.1	0.5–1.5
DSi	26–78	10–85	13–78	15–41

TDIN total dissolved inorganic nitrogen, *TDIP* total dissolved inorganic Phosphorus, *DSi* dissolved silica

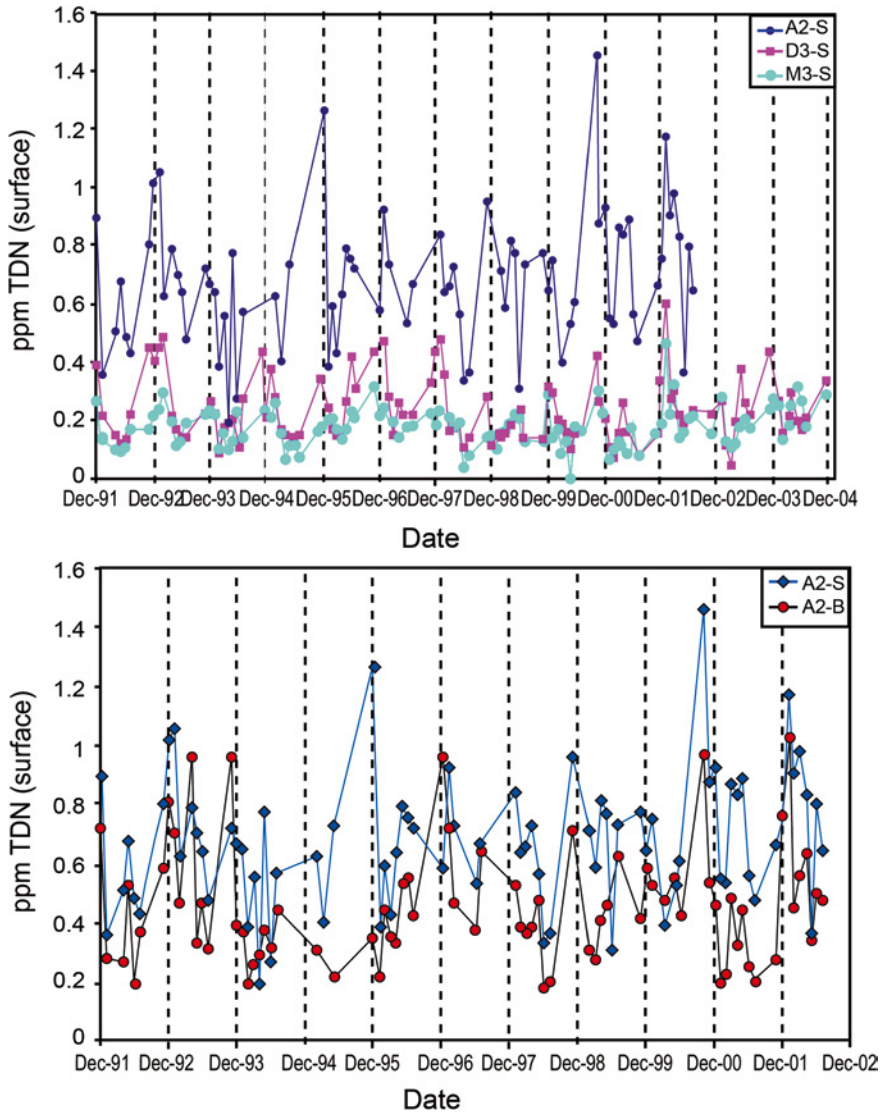


Fig. 5.38 a Temporal variations in total dissolved N in LIS surface waters in western LIS (A2), central LIS (D3), and eastern LIS (M3) over the period 1991 to 2002 (CTDEEP data). b Comparison of time trends in total N in surface and bottom waters at site A2 (western LIS)

withdrawal during the early spring bloom (Fig. 5.38). Phytoplankton (e.g., diatoms) blooms occur in late winter/early spring (sunlight induced algal blooms), and late summer and early fall from nutrient build-up, warm waters, and strong sun exposure. Nitrogen concentrations drop markedly during these blooms. Experiments with nutrient addition (Gobler et al. 2006) demonstrate that LIS primary production is largely N-limited. The NO_3/NH_3 ratio is determined by the various inputs

as well as by the extraction by photosynthesizing organisms, some preferring NH_3 , others NO_3 . The input of WWTF ammonia is an important factor as is the ammonia flux from the decomposition of organic material in the bottom waters (Cuomo et al. 2005). The molar ratios of nitrate to ammonium in the two main input rivers vary from 2.5 to 20 (with seasonal fluctuations), with a mean of ~ 10 , whereas WWTFs have much lower ratios (~ 1.5 – 2). The molar NO_3/NH_3 in LIS varies between 0.15 and 0.75, which is very different from the nitrate-dominated riverine environment. The variations over time for surface and bottom waters in station A2 indicate that in WLIS the surface waters tend to be enriched in TDIN with respect to the bottom waters, whereas the reverse may be true in waters from CLIS and ELIS.

The Si concentrations reach very low values during the blooms, and locally, Si-limitation may curb diatom productivity (Gobler et al. 2006; Boon 2008). A detailed analysis of the extensive dissolved nutrient data from LIS collected over the last few decades in conjunction with the measured inputs summarized above is a necessity for a better understanding of nutrient cycling and primary productivity in LIS over time, but is outside the scope of this chapter.

The spatial distribution of dissolved nitrogen, P, and silica in LIS varies with the season, but a snapshot is provided for the year 2007 (Figs. 5.39, 5.40). The WLIS surface and bottom waters are rich in P and ammonium, whereas the dissolved Si shows a simple variation with salinity (S) (indicating that most of the Si is brought in by rivers). The dissolved NO_x pattern is more complex, with depletions in CLIS (probably related to local productivity) and enrichments in WLIS.

The isotopic composition of nitrogen ($\delta^{15}\text{N}$) is a function of its ultimate source, with, in general, isotopically heavier N stemming from material higher up in the food chain (Cravotta 2002). In addition, the removal of N through photosynthetic activity may fractionate the N isotopes, and thus the resulting N isotope ratios are a complex function of N supply, speciation, and withdrawal. Denitrification is extensively used in WWTFs to remove N, and WWTF effluents may show $\delta^{15}\text{N}(\text{NH}_3) = +6\text{‰}$ to $+25\text{‰}$, and $\delta^{15}\text{N}(\text{NO}_3) = -9\text{‰}$ to $+16\text{‰}$ (Boon 2008). Riverine TDIN is a mixture of all N sources which include effluents of local WWTFs and has $\delta^{15}\text{N}(\text{NH}_3)$ from $+2$ to $+4\text{‰}$ and $\delta^{15}\text{N}(\text{NO}_3)$ from 0 to $+10\text{‰}$ (data from samples collected between February and August 2007 in the Connecticut River in various locations above the estuarine mixing zone; Boon 2008). In the Housatonic River, $\delta^{15}\text{N}(\text{NH}_3)$ ranges from $+2$ to $+10\text{‰}$ and $\delta^{15}\text{N}(\text{NO}_3)$ from $+4$ to $+12\text{‰}$ for the same period. The modern mean $\delta^{15}\text{N}$ of total riverine N is $\sim +5\text{‰}$, whereas that for WWTFs is heavier at $\sim +10$ to $+12\text{‰}$, albeit with large seasonal and local variations. The N isotope data thus can be used to broadly trace the N sources and possibly the fate of the relatively heavy WWTF N within the LIS foodweb, and ultimately in the buried remains of photosynthate in sedimentary marine organic matter. Observed $\delta^{15}\text{N}$ in nitrate in LIS waters ranges from -8.6‰ to $+5.7\text{‰}$ in surface waters, and in bottom waters from -2.7‰ to $+11.4\text{‰}$ (Fig. 5.39). The $\delta^{15}\text{N}$ values for dissolved NH_3 are not yet available, but presumably on the heavy end of the range, up to $+20\text{‰}$.

A study by Anisfeld et al. (2007) showed the origin of N compounds in the Quinnipiac and Naugatuck Rivers in Connecticut and apportioned the sources of

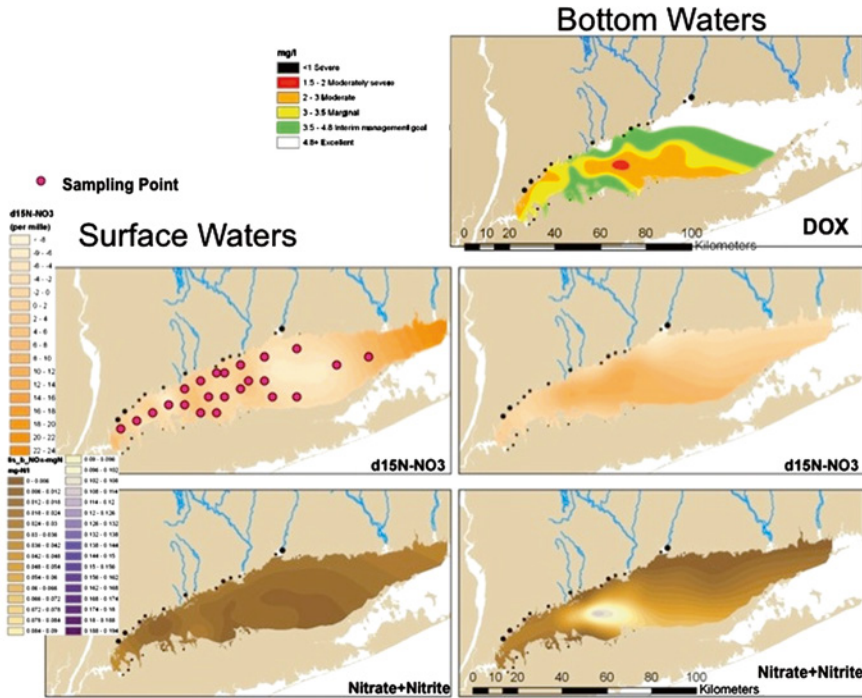


Fig. 5.39 Spatial trends in LIS during a period of water column stratification and hypoxia in bottom waters in August 2007. Samples collected during CTDEEP sampling cruise in central and western LIS (red dots are sampling points). Spatial patterns of dissolved oxygen (DOX) in bottom waters, $\delta^{15}\text{N}$ in nitrate, and nitrate+nitrite in surface and bottom waters are shown. The black dots along the coastlines are WWTPs, with the dot size reflecting their relative N-output. Colors at the eastern end of LIS are an artifact of the spatial interpolation model, most easterly data point is located just west of the mouth of the Connecticut River. Note the correlation between low dissolved oxygen and high dissolved nitrate+nitrite and high $\delta^{15}\text{N}$ in nitrate in the bottom waters of CLIS. Figure adapted from Boon, 2008; measurements made in the laboratory of Dr. Mark Altabet (SMAST, Univ. of Massachusetts, Dartmouth, MA)

N in these rivers based on the $\delta^{15}\text{N}$ and the $\delta^{18}\text{O}$ in nitrate. They found for these rivers that at base flow, the atmospheric deposition of N was a small contributor, whereas during storm flow a significant part of the N came from the atmospheric reservoir. The contributions from sewage were hard to determine from that study and the authors showed a very wide range in estimates of sewage contributions.

5.7.4 The Historic Record of Organic Productivity from Sediment Core Data

The modern LIS nutrient concentration data discussed above do not aid directly in the identification of trends in nutrient fluxes beyond the last 4 decades. The

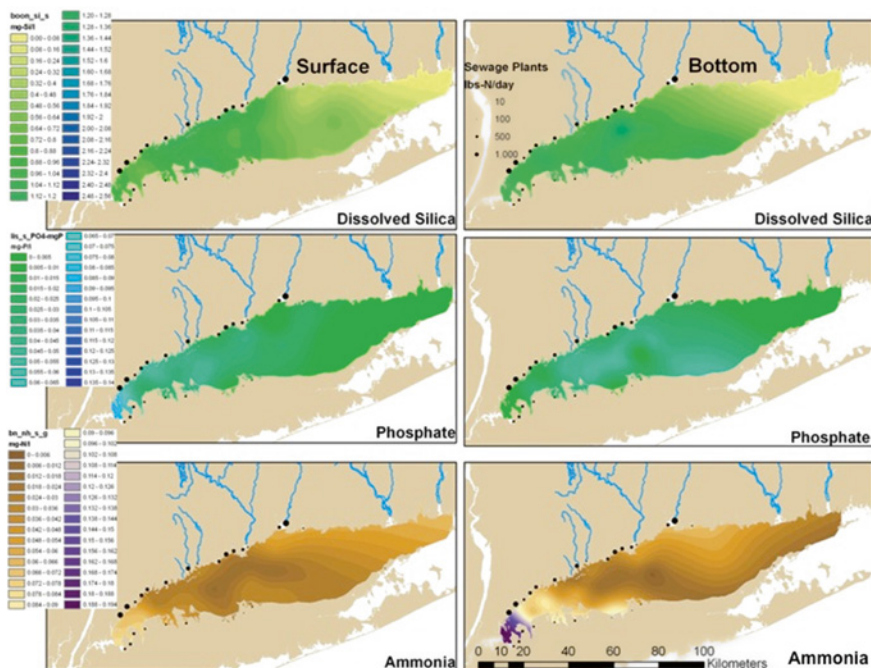


Fig. 5.40 Spatial trends in LIS for dissolved Si, P and NH_3 in surface and bottom waters of LIS in August 2007 (see caption of Figure 5.39 for sampling details). Note the high NH_3 concentrations in extreme western LIS

increased nutrient fluxes of the last 100–200 years probably enhanced the primary productivity in LIS, which in conjunction with global climate change (e.g., enhanced stratification of LIS; see O'Donnell et al. [Chap. 3](#), in this volume), led to the seasonal hypoxia in CLIS and WLIS. The hypoxic conditions of the last few decades are probably also impacted by the organic carbon that is now stored in the sediment bed, which provides a long-term oxygen sink. Many processes play a role in the creation of hypoxia, and one approach to unravel this multitude of drivers is to consider the historic record of eutrophication in sediment cores to assess when eutrophication started in conjunction with other factors that may have a causal role.

The organic carbon and N concentrations in sediment cores indicate the amount of buried organic matter, which is commonly recast as organic carbon accumulation rates ($\text{mg Corg/cm}^2 \text{ year}$) if the sedimentation mass accumulation rates are adequately known. These carbon accumulation rates are an indirect proxy for historic nutrient fluxes into the Sound because higher nutrient fluxes usually translate into higher rates of primary productivity (the system is N-limited; e.g., Gobler et al. [2006](#)) and higher burial rates of organic matter. Integration of core data over the whole bottom of the Sound to obtain LIS-wide burial rates of organic carbon and N is fraught with many uncertainties, but the trends in representative cores provide proxies for changes in the overall fluxes of carbon and N over time. The organic

fractions of sediment are mixtures of organic carbon imported from the watersheds (terrestrial carbon) and in situ production of marine algal matter. Mixing calculations based on $\delta^{13}\text{C}$ and N/C values (Perdue and Koprivnjak 2007) of the organic fraction of the sediment are used to deconvolute these mixtures, so pure marine organic matter accretion rates can be calculated (Varekamp et al. 2009). The burial rate of marine organic carbon is an indirect proxy for primary productivity and for the nutrient fluxes that sustained that productivity.

The isotopic composition of N in LIS sediment is, among others things, an indicator of the N sources, although the N isotopes are also fractionated during the photosynthetic process. The modern increase in N fluxes stems partly from enhanced WWTF flows, which have more positive $\delta^{15}\text{N}$ values than most other sources. Mapping the $\delta^{15}\text{N}$ in LIS water and sediment cores thus is another mode of tracing the magnitude of increased N fluxes. A caveat is that changes in the rates of denitrification and in the food chain may also cause changes in $\delta^{15}\text{N}$ in the buried organic matter. We present data on these aspects for two sediment cores: core WLIS75GGC1, taken near Execution Rock in the far western part of WLIS and core B1GGC2, taken on the delta of the Housatonic River in CLIS (Fig. 5.12).

Evidence is found in the sediment of hypoxia beginning in the early to mid-1800s, as indicated by lighter $\delta^{13}\text{C}$ values in carbonate (Lugolobi 2003; Lugolobi et al. 2004). The oxidation of photosynthate in the bottom waters and sediment porewaters leads to consumption of dissolved oxygen, but also to an isotopically lighter carbon pool of DIC in the bottom waters (the photosynthate is isotopically light compared to marine DIC). The presence of this isotopically light DIC is reflected in the lower values of $\delta^{13}\text{C}$ in carbonate tests of benthic foraminifera (Thomas et al. 2000, 2004). The records of $\delta^{13}\text{C}$ in carbonate of foraminifera from the two cores show more or less constant values during precolonial times, but then drop by 1–3 ‰ since the early 1800s. Part of this drop in $\delta^{13}\text{C}$ is a reflection of the isotopically lighter CO_2 in the atmosphere, which has decreased by about 1 ‰ over the last 150 years (Keeling et al. 2005). That decreasing trend is also shown in marine carbonates in various other studies (e.g., Bohm et al. 2002). After correction for this atmospheric isotopic change, it appears that most cores in WLIS show an additional decrease in $\delta^{13}\text{C}$ in foraminiferal carbonate of about 1 ‰, indicating potentially the onset of eutrophication and associated hypoxia in WLIS about 150 years ago. This time scale is coincident with the increase in population density and growth in industrialization around LIS and, presumably, increased nutrient fluxes.

Particulate organic carbon (POC) is a contaminant in LIS because it creates biological oxygen demand that ultimately is one of the causes of the hypoxia. The POC in LIS stems from the local marine primary productivity (marine organic carbon or CORGM) and from import from land (terrestrial carbon or CORGT) as well as a particulate CORG flux from WWTFs (CORGWW). The three forms of POC can be distinguished based on their $\delta^{13}\text{C}$, C/N, and $\delta^{15}\text{N}$ values (Meyers 1997; Varekamp et al. 2009), although we do not distinguish explicitly here the CORGWW component (similar in C/N to marine organic matter with C/N~8). The CORGM accumulation rates in sediment cores are a proxy for marine primary productivity although the cores only represent the buried (and preserved) fraction of the total marine organic

Fig. 5.41 Total organic C accumulation rates in cores from central and western LIS (see Fig. 5.12 for locations). Data sources: Varekamp et al. 2009; Varekamp and Thomas 2010; Varekamp unpublished data)

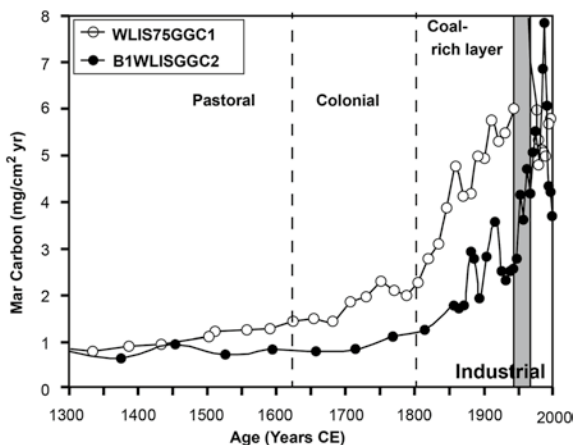
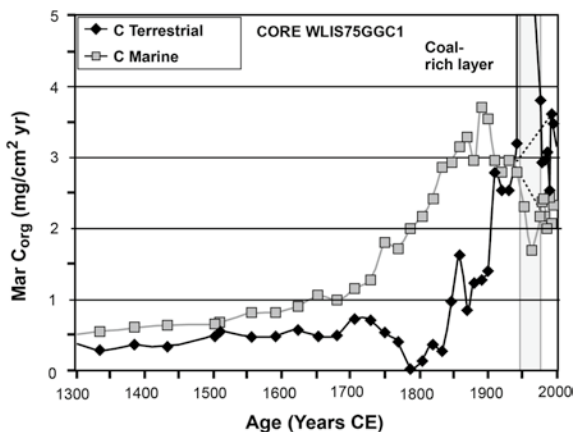


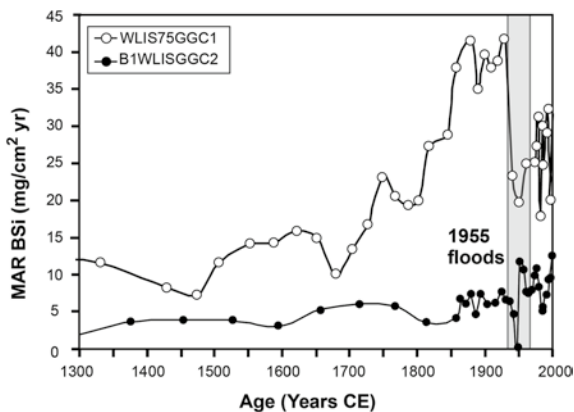
Fig. 5.42 Terrestrial and marine organic C accumulation rates for core WLIS75 in the extreme western end of LIS. Data sources: same as Fig. 5.41



productivity. Other fractions of the marine productivity are consumed higher up in the food chain and possibly exported from LIS (fish catch, movement of fish to other areas). Most LIS cores show higher CORG concentrations in the more recent sediment, and bulk CORG accumulation rates increased five to eight times from precolonial background levels to recent times (Fig. 5.41).

The CORGM accumulation record in the WLIS core WLIS75GGC1 shows a strong increase in late colonial times, but decreased strongly over the last 100 years (Fig. 5.42). The CORGT dropped to almost zero in the mid- to late 1700s, most likely the result of the extensive deforestation at that time. After 1800, the CORGT flux increases again and by 1900, the CORGT and CORGM accumulation rates are roughly equal, and CORGT is the dominant form of organic carbon in core sediments deposited over the last 50 years. The Housatonic River delta core BIGGC2 record has a similar pattern, be it less extreme, and the CORGT in the sediment dominates over the last 100 years (Varekamp et al. 2000).

Fig. 5.43 Biogenic silica accumulation rates in two cores from western and central LIS, showing strong increases between late 1700s and mid 1900s, followed by a strong decline (after Andersen 2005)



Obviously, the contributions of both marine and terrestrial organic matter to LIS have fluctuated strongly over the last few hundred years, a reflection of changes in landscape and nutrient fluxes. The common hypothesis that increased nutrient fluxes drove up the marine primary productivity of the Sound and thus caused hypoxia is not the complete story; the impact of the abundant CORGT on the occurrence of hypoxia should probably be considered as well (see e.g., Latimer et al. 2003). The accumulation rates of biogenic silica (BSi) were measured in many LIS cores (Andersen 2005) and have increased strongly since 1800, but decreased over the last 50 years (Fig. 5.43). The Execution Rock core had higher background (4–5x) and much higher peak (10x) BSi accumulation rates compared to those in the Housatonic delta core. Higher nutrient concentrations may have been common in the western Sound over time, which seems to translate into higher sedimentary BSi values. Apparently, the productivity of diatoms decreased, presumably as a result of silica limitation, and possibly other species took over (e.g., dinoflagellates; see Lopez et al. Chap. 6, in this volume).

The sedimentary N content and its isotopic composition provide a direct insight into sources of N over time, and in the following section we present preliminary, unpublished data from two cores. The sedimentary N increased simultaneously with CORG concentrations over time as has the $\delta^{15}\text{N}$ of the bulk sediment (Fig. 5.44). The precolonial $\delta^{15}\text{N}$ background values differ by $\sim 1\text{‰}$ in between the two studied cores, but both cores show an increase of 1.0–1.5‰ over the last 150–200 years. This strongly suggests the arrival of heavier N in LIS waters, most likely sewage-derived N. This may have created, possibly with enhanced fluxes of carbon as CORGWW, higher $\delta^{15}\text{N}$ values in the Sound waters over the last 150 years. The bulk $\delta^{15}\text{N}$ values of the CORG in sediment represent a mixed signal, however, influenced by the proportions of CORGT and CORGM in the sediment. The $\delta^{15}\text{N}$ signature of the bulk CORG was once more deconvoluted into that of CORGM, using a $\delta^{15}\text{N}$ of +2.5‰ for CORGT, using the proportions of the two types of CORG calculated before. These values provide a detailed record of the $\delta^{15}\text{N}$ of locally produced marine organic matter and presumably CORGWW over the last few hundred years (Fig. 5.45).

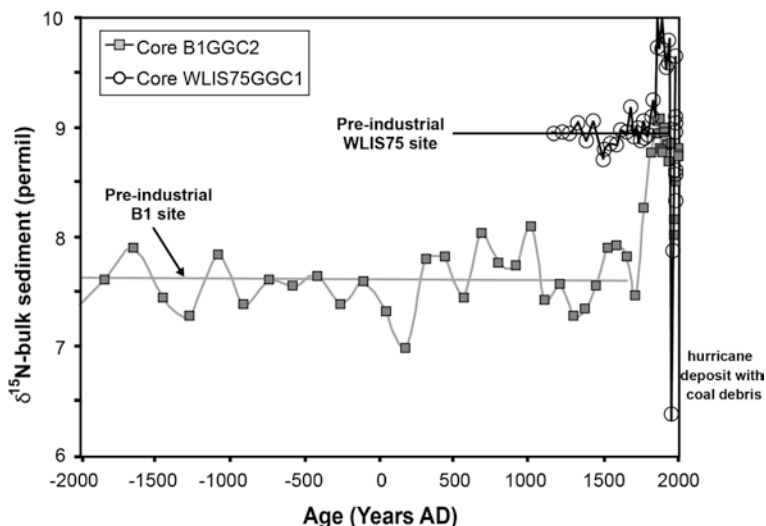
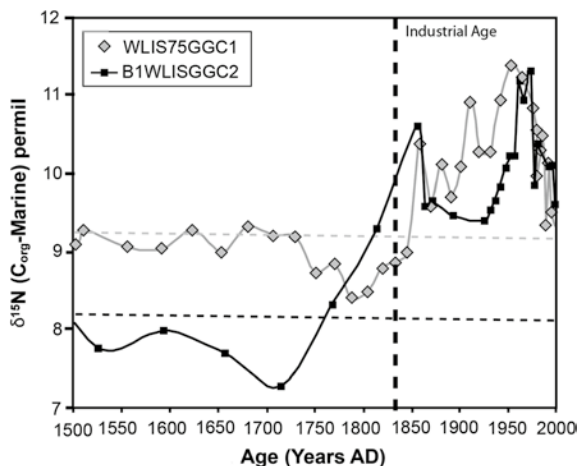


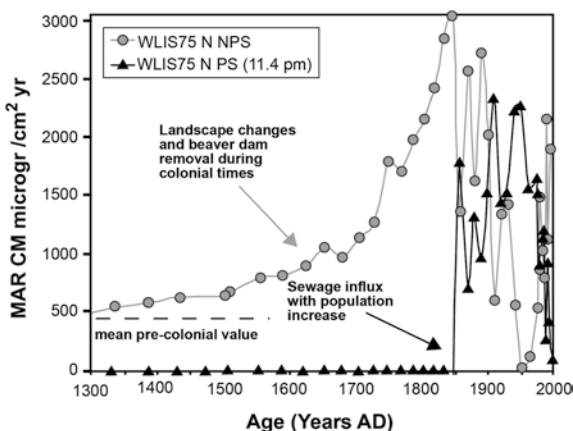
Fig. 5.44 Nitrogen isotope composition of bulk organic matter in the same two cores from LIS. Both cores show isotopically heavier N in sediments deposited since ~1800 AD. Data sources: same as Fig. 5.41

Fig. 5.45 Nitrogen isotope trends in marine organic carbon in sediment samples from the same two cores. Note the increase in the early 1800s, and the decline in N isotope ratio since the mid twentieth century in both cores. Data sources: same as Fig. 5.41



The two cores show very similar records and the precolonial $\delta^{15}\text{N}$ in CORGM from the Housatonic River delta core is $\sim+8.2\text{‰}$ (based on a 4000 year record in this core; Varekamp et al. 2000) and rose to $\sim+10\text{‰}$ by 1850. The $\delta^{15}\text{N}$ in CORGM of the Execution Rock core rose from $\sim+9.2\text{‰}$ in the precolonial background to $\sim+10.2\text{‰}$ in industrial times. Both core records show a decrease in $\delta^{15}\text{N}$ in marine organic matter of $\sim-1\text{--}1.5\text{‰}$ over the last 50 years. The latter is a puzzling observation that seems to contradict the simple scenario of strong

Fig. 5.46 Marine organic C accumulation records, driven by two separate N sources: WWTFs and nonpoint source N similar to precolonial N. Data sources: same as Fig. 5.41



primary productivity stimulation by the abundant N from WWTFs with high $\delta^{15}\text{N}$ for the last half century. This aspect needs more study.

On a more speculative basis, we estimated the burial rate of marine organic matter partitioned according to N derived from WWTFs and N from nonpoint sources. These calculations do not consider the N isotope fractionations (or changes in those over time) during photosynthesis, and these estimates are also sensitive to the assumed mean value of $\delta^{15}\text{N}$ in bulk WWTF effluents. The observed mean value for $\delta^{15}\text{N}$ in WWTF effluent in 2007 was +10 ‰, but the final value had to be taken equal to or larger than the heaviest $\delta^{15}\text{N}$ value in the core records. We used +11.4 ‰ as the mean for $\delta^{15}\text{N}$ in WWTF effluents and assumed a zero WWTF N flux prior to 1850. We use the precolonial $\delta^{15}\text{N}$ values in each core as representative of the $\delta^{15}\text{N}$ from nonpoint source N, although we realize that those values may have changed over time as well.

The mass accumulation rates of marine organic carbon productivity driven by nonpoint source N inputs in the Execution Rock core sediment show an increase in the 1600–1700 periods, probably as a result of landscape changes and beaver dam removal (Varekamp 2006), and continued to rise until 1850. This is followed by a decrease between 1850 and 1950 till almost zero contributions, but rising strongly again since the mid-twentieth century. The WWTF N-driven productivity increased since 1850 and became dominant between 1900 and 1950, but then again decreased to low values as found today.

The CORGM record of the Housatonic River delta core partitioned according to N source is similar to that of W LIS75GGC1, with recent productivity equally divided between WWTF and nonpoint source N (Fig. 5.46). A shift in primary productivity from diatoms to dinoflagellates over the last 50 years may have both impacted the rate of marine carbon burial in western LIS (Dortch et al. 2001) as well as changed the $\delta^{15}\text{N}$ of the buried organic matter (Lopez et al. Chap. 6, in this volume).

In conclusion, nutrient pollution of the Sound is ongoing, although both riverine and direct WWTF inputs of N and P have been diminishing over the last few decades. The environmental effects of these processes are obvious in the seasonal hypoxia that

occurs with variable intensity in mid- to late summer in CLIS and WLIS. The trends in cores on stored organic carbon and its isotopic signatures indicate that the flux of terrestrial carbon into LIS may also be an important driver for hypoxia, although terrestrial carbon may be more refractory than marine carbon (Meyers 1997). The records also show that the increased marine productivity over the last 150 years is related to both enhanced N fluxes from land as well as from WWTFs.

5.8 Summary of Data and Research Needs and Recommendations

Long Island Sound represents an estuarine system significantly impacted by anthropogenic activities. Data from sediment cores show without any doubt the profound human impacts on the water and sediment quality of LIS since pre-colonial times. Inputs of both organic and inorganic contaminants increased steadily during the first three quarters of the twentieth century and peaked during the 1960–1970s. Fortunately, with implementation of upgraded sewage treatment associated with the Clean Water Act, and laws regulating use and releases of persistent toxic contaminants such as PCBs and chlorinated pesticides, general water quality has improved in LIS since the mid-1980s. However, despite these improvements, there remains a legacy of persistent contaminants in LIS sediments, and measurable contaminants are found in many LIS biota. Contaminant levels remain elevated in WLIS and CLIS relative to ELIS, and hot spots for various contaminants remain in coastal embayments, particularly along the Connecticut shores of LIS receiving inputs from major cities and/or rivers. A summary with broad sediment quality indicators (Fig. 5.47) show that in WLIS, almost 50 % of the habitat areas can still be rated as “poor.” Recent trends in contaminant levels in indigenous bivalves in some cases show that levels are no longer decreasing, and in some cases appear to be on the rise again, albeit much below than those found in the 1980s. Of particular concern are methylmercury levels in biota. In addition to continuing inputs from atmospheric deposition and “legacy Hg” from the watersheds, decreased degrees of eutrophication in some areas may lead to diminished organic carbon burial (an important stable host for Hg) and thus could accelerate the release of methylmercury from LIS sediments. Despite reductions in contaminant concentrations in surface sediments, low level sediment toxicity appears to still be common in many areas of WLIS, but also in a number of coastal bays. Data from the NCA, as well as several smaller independent research projects, indicate that the potential for negative impacts on organisms throughout LIS still exists. These trends are illustrated in a recent survey comparing sediment quality indices estimated from levels of contaminants in sediment, sediment toxicity as measured by the *A. abdita* test, and organic carbon content for the three subareas of LIS using data collected from 2000 to 2004 as part of the NCA (USEPA 2008). This analysis indicated from 9 to 46 % of the area within each sub-basin was in poor condition (mainly WLIS) while between 18 and 69 % of the area was in good condition (Fig. 5.17a; USEPA 2008).

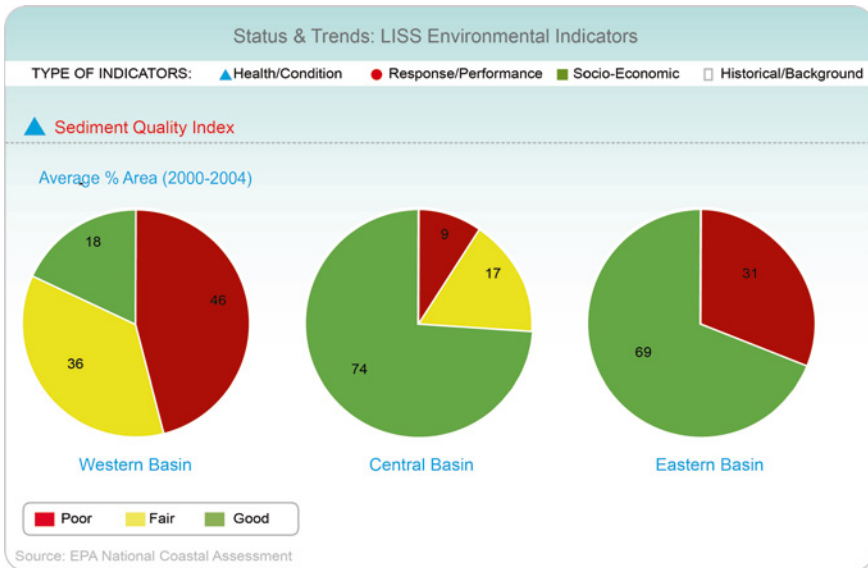


Fig. 5.47 Broad sediment quality indicators in the three LIS zones over the period 2000–2004. From: USEPA National Coastal Condition report (2008)

Of all human impacts, one of the most pervasive and disrupting has been the increase in nutrient fluxes into LIS. The loading of nutrients to LIS has been dynamic over time, but especially over the last 40 years. Actions to control the effects of wastewater discharges have been initiated, affecting the loads and ratios of N and P in the major tributaries. Remarkable success has been observed in the decrease in N loads from many sources, yet the occurrence and extent of hypoxia continue. The onset and persistence of hypoxia are influenced by meteorology (supply of oxygen; O'Donnell et al. [Chap. 3](#), in this volume) as well as by respiration and decay processes of organic materials (consumption of oxygen; Cuomo et al. [Chap. 4](#), in this volume), and decreases in N may not be the only factor influencing the extent and severity of hypoxia. Climate change and a hysteresis effect of the stack of sediment rich in organic matter may all influence the location and severity of LIS hypoxia.

Population and land development in the watershed have increased during the last few decades, adding nonpoint source loads of nutrients, as well as increasing wastewater volume. Much of the focus of research has been on N loading to LIS. Phosphorus loads from the major tributaries in Connecticut have generally declined from 1974 to 2008, but may be increasing in recent years. A coherent dataset to understand the trends in P loads from point sources in the LIS watershed is not available. The changing N/P and Si/N values have implications for changes in the composition of dominant phytoplankton in LIS. Further research is needed to understand the links among external and internal (from the sediment bed) sources of N, P, and Si, and hypoxia.

It is uncertain how climate change may affect nutrient loads from forested watersheds. Predictions of the water budget under a range of global emissions scenarios indicate likely increases in groundwater recharge and decrease in snowfall over the next century, especially over southern parts of the LIS watershed (Bjerklie et al. 2011). These changes will have implications for tree species shifts, deposition, and processing of N in forests, as well as possible changes in the timing and delivery of N to LIS.

The largest N sources for LIS are associated with the East River (Fig. 5.33) due to the sewage inputs of N from the New York City area. Currently, a delivery factor of 21 % has been used in N management from this zone, based on modeling done for the LIS TMDL (CTDEP and NYSDEC 2000). Studies to determine the net flux across this boundary would be essential to constrain the magnitude of this large source of N. In addition, limited information exists on the N losses in the tidal reaches of the major rivers. For example, the Connecticut, Housatonic, and Quinnipiac Rivers have extensive tidal marshes and brackish zones that may use substantial amounts of N. Knowledge of such estimates has implications for accurate equivalency factors used in N trading among municipalities in the LIS watershed.

Long Island Sound is fortunate to have been the focus of several large-scale environmental assessments by NOAA, USGS, and the USEPA, and state agencies, some of which such as NCA and the NS&T continue to provide data today. The extensive CTDEEP dataset on nutrient levels in LIS should be evaluated in detail, and variations in fluxes and riverine inputs should be assessed within the context of measured nutrient levels in LIS. Potential trends in pH of LIS waters are just beginning to be monitored in recent years by CTDEEP, changes in DIC over time are currently completely unknown, and studies are needed that focus on existing datasets and/or sediment proxies. Periodic detailed sampling and analyses of both metals and organic contaminants in sediments should be continued at multiple year (possibly five year) intervals, particularly in coastal embayments with high population density. The fate of legacy contaminants such as Hg, Cr, and Cu from the Housatonic River and several harbor areas should be monitored, especially after major hurricanes or other wet events. The main data available today on contaminant levels in biota come from NS&T's Mussel Watch dataset, a few studies on PCBs by the NYSDEC, and some recent work on metals in bivalves in Connecticut harbors. A useful option for expanding this work is to include species harvested for human consumption as well as key resource species of importance to aquatic food chains. Assessment of contaminant-related effects in indigenous biota is particularly lacking as is assessment of how global climate change may influence sources of contaminants to LIS, their cycling within LIS, particularly from sediment reservoirs into biota. Also lacking is an assessment of the combined impact of environmental factors such as hypoxia, lowered pH and nutrient, and toxic chemical additions on local organisms. Monitoring plans also need to include advective transport and internal cycling of emerging contaminants such as PBDEs, PFCs, pharmaceuticals, hormones, and personal care and cleaning products, particularly those that have a potential to act synergistically with other contaminants or influence disease susceptibility in indigenous organisms.

In conclusion, extensive water quality monitoring, studies on biota, and sediment samples have documented the plethora of environmental problems that LIS has faced and to some degree is still facing today. Legislation to limit these fluxes of a variety of contaminants has improved or stabilized the water quality in LIS, but lingering legacy pollutants and toxic sediment beds remain. Future research would benefit from a focus on the linkages among the different processes that impact the LIS system. Resource management should use an ecosystem-based approach that takes direct anthropogenic inputs, climate change, and changes in the watershed into account.

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