ORGANOCHLORINE PESTICIDES IN SEDIMENTS

FROM LONG ISLAND SOUND

by

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Abstract

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Surficial sediments and sediment cores were collected at various sites in Long Island Sound (LIS) previously surveyed by the National Oceanic and Atmospheric Administration (NOAA)'s National Status and Trends (NS&T) Program. Archived surficial sediments at selected sites were acquired from the NS&T Specimen Bank.

Concentrations of organochlorine pesticides (OCPs) in recently collected sediments and archived sediments from LIS were determined. OCPs are still widely present in current LIS surficial sediments two decades after the use of these pesticides in the U.S. was banned. Sediments in the western part of the Sound are more contaminated than in the eastern part and all the most contaminated sites are located in the west tip of the Sound, which is close to the high population density metropolitan area. OCPs concentrations in LIS surficial sediments (sediments from the western LIS sites in particular) exceeded several sediment quality guidelines.

The OCPs concentration profiles showed that OCPs were present in every depth of the sediment cores. Direct comparison of the ^{137}Cs and chlordane profiles in the sediment

core suggested that the maximum releases of chlordane to the Sound occurred close in time to the ^{137}Cs fallout maximum (1963). Model simulations of the chlordane profiles suggest continual input at western LIS long after the 1980s.

The fact that chlordane in agricultural soils near LIS was greatly non-racemic but chlordane in LIS sediment in the past 60 years was racemic or near racemic suggested that runoff from agricultural soils constitutes, at most, a minor fraction of the recent input into LIS and house foundation soils are likely the major source of chlordane input into the Sound, at least for more recent input. It is probably also true that the chlordane input to LIS prior to the 1980s was from house foundation soils near urban areas.

Both continued input and significant sediment mixing may have led to persistent chlordane concentrations (and persistent organic pollutant concentrations in general) in LIS surficial sediments, posing long-term threats to benthic organisms. The lack of enantioselective microbial degradation of chlordane in LIS sediments makes it even more persistent in the Sound.

Dedicated to those who made this thesis possible:

My wife, my family and my friends

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Chapter 1

Introduction

1. Long Island Sound (LIS)

Long Island Sound (LIS) is a major coastal estuarine system on the Atlantic coast near the New York metropolitan area. It lies between the coast of Connecticut to the north and Long Island, New York to the south (Figure 1.1). New York City is located at the western end of the Sound. LIS is a water body where salt water from the Atlantic Ocean mixes with fresh water from several major rivers inland, including the Connecticut River that empties into the Sound at Old Saybrook. LIS is unique in that it has two connections to the sea - the Race to the east and the East River to the west.

The Sound is 110 miles long and 21 miles wide at its widest point. It has an average depth of 65 feet, with the deepest point being 150 feet. The volume of water in the Sound is 18 trillion US gallons. Including all islands, the Long Island Sound has a shoreline of 548 miles. Fresh water from the Connecticut and other rivers makes it less salty than the open ocean. The average water temperature for LIS is around 34°F (1°C) in January; some of the shallow inlets freeze over during winter. In July the water temperature is typically around 65°F (19°C), and typically peaks around 75°F (24°C) in mid-August, which contributes to relatively mild summer temperatures for Long Island and coastal Connecticut (Long Island Sound Study).

Figure 1.1 Long Island Sound (Long Island Sound Study).

Several major cities are situated along the LIS, resulting in a total of more than 8 million people living within its watershed. As such, LIS ranked 4th in population and 10th in population destiny among U.S. estuarine drainage areas. Major Connecticut cities on the Sound include Bridgeport, New London, Stamford, Norwalk, and New Haven. New York cities on the Sound include Port Jefferson and New York City (the boroughs of Queens and the Bronx).

The Sound provides feeding, breeding, nesting, and nursery areas for a diversity of plant and animal life that support large commercial and recreational fisheries. There are more than 120 species of fishes, including 21 tropical species that stray here seasonally; at least 50 species spawn in the Sound. The Sound contributes an estimated $5.5 billion

per year to the regional economy from boating, commercial and sport fishing, swimming, and sightseeing (USEPA).

The Sound, however, has been contaminated with various pollutants, including organochlorine pesticides. The contamination and declining environmental quality directly threatens the regional fishing and shell-fishing industry. Sediments of the Sound are a sink for wastes and contaminants from various sources such as wastewater treatment plants, urban and agricultural runoff, and waste disposal. Information on the fate of a contaminant such as organochlorine pesticides in the sediments is, therefore, of direct practical importance.

2. Organochlorine pesticides in the environment

It is estimated that about 1 billion pounds of pesticides are used every year in the United States to control a lot of different types of weeds, insects and other pests in a wide variety of agricultural and nonagricultural applications (Nowell, Capel et al. 1999). The total quantity of pesticides used, and the number of different chemicals applied, increased substantially from the early 1960s when the first reliable records were established to around 1980, when the number appeared to decrease. Benefits like increased crop production, lower-cost maintenance, and control of public health hazard have been attributed to the increased use of pesticides. At the mean time, public concerns and awareness about the potential adverse effects of the pesticides on the environment and human health, however, also have grown.

The public concerns for pesticide contamination have been existing for a long time. Organochlorine insecticides (OCPs), which are typically composed of carbon, hydrogen and chlorine, are of the greatest concern. OCPs are characterized to have low water solubility (hydrophobic), high octanol-water partition coefficients (high K_{ow}), strong tendency to sorb to soil (high-to-moderate K_{oc}), high bioaccumulation and high persistence in environment (high bioconcentration factor and long half-life) (Nowell, Capel et al. 1999).

OCPs and their degradation products have many toxic effects on animals, birds, fishes, and human beings. After being absorbed via the digestive system, OCPs primarily accumulate in lipid-rich tissues, including brain, adipose tissue, liver, and human milk (Nowell, Capel et al. 1999). OCPs have adverse effects on neurological effects and the hepatic microsomal enzyme system (USEPA 1994; Klaassen, Amdur et al. 1996). Different types of OCPs, including dichlorodiphenylethane compounds (such as DDT), chlorinated cyclodiene compounds (such as dieldrin), and the chlorinated benzenes and cyclohexanes (such as hexachlorobenzene and lindane, respectively), have different mechanisms and sites of toxic interactions. For example, DDT inhibits several functions in peripheral neurons by reducing the nerve membrane repolarization rate following stimulation while pesticides in the other groups appear to affect the central nervous system, rather than the peripheral (sensory) neurons (Nowell, Capel et al. 1999).

Many OCPs have endocrine-disrupting effects in a variety of animals (Colborn and Clement 1992) and interfere directly or indirectly with fertility and reproduction (Klaassen, Amdur et al. 1996). OCPs found in aquatic biota in the monitoring studies have moderate to high chronic toxicity; they tend to be associated with developmental or

reproductive effects in animal studies; they are potent enzyme inducers; and most are probable human carcinogens (Nowell, Capel et al. 1999).

From the mid-1940s to the mid-1960s, OCPs were heavily used in agriculture, subterranean termite control, and malaria control programs. Due to their persistence, their tendency to accumulate in the soil, sediment, and biota, and their impacts on wildlife, the use of OCPs in the United States was restricted and eventually most of them was suspended during the 1970s and early 1980s (Nowell, Capel et al. 1999). Some of them, however, continue to be used elsewhere in the world, especially in developing countries in the South America and Africa.

In this research we focus on six OCPs including *trans*-chlordane, *cis*-chlordane, dieldrin, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT. The structures of the 6 OCPs studied are shown in Figure 1.2 and their physical and chemical properties are listed in Table 1.1.

TABLE 1.1 Physical and chemical properties of OCPs (ARS 2001).

Compound	Molecular weight (g/mol)	Water solubility (mg/L)	$logK_{ow}$	$logK_{oc}$	Henry's Law Constant ($Pa \cdot m^3/mol$)	BCF (bioconcentration factor)	Soil half-life (days)
chlordane	409.8	0.06(25°C)	6.00	4.78	9.51	14000	350-3500
dieldrin	380.9	0.14(20°C)	3.69-6.20	4.08	0.065	4670	1000
p,p'-DDD	320.0	0.05(25°C)	5.06-6.22	5.38	0.9	53600	730-5690
p,p'-DDE	318.0	0.065(24°C)	5.69-6.96	5.95	1.02	53600-180000	730-5690
p,p'-DDT	354.5	0.0077(20°C)	5.98	5.63	394	53600	110-5480

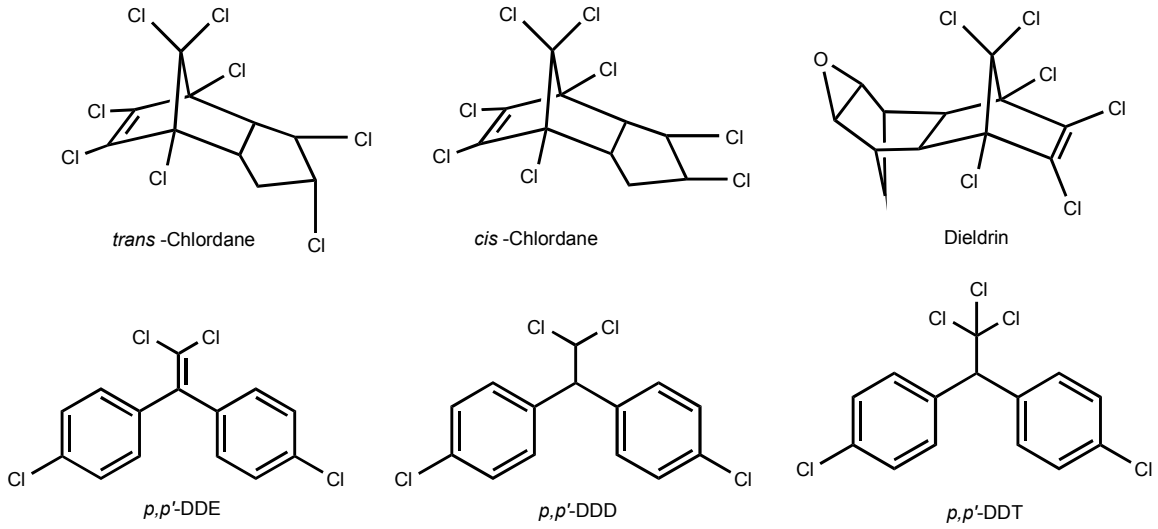

Figure 1.2 Structures of OCPs of concern.

2.1 Chlordane

Chlordane (octachloro-4,7-methanohydroindane) is derived from cyclopentadiene and hexachlorocyclopentadiene. Technical chlordane is a mixture of more than 140 components among which the major components are *cis*- and *trans*-chlordane. Technical chlordane is typically composed of about 24 percent *trans*-chlordane, 19 percent *cis*-chlordane, 10 percent heptachlor, 21.5 percent chlordane isomers, 7 percent nonachlor,

and 18.5 percent of other structurally related chlorinated compounds (USEPA 1980). In the United States, chlordane was widely used as an insecticide in agriculture field on corn, grapes, strawberries, and other crops; in home and garden for termite control (USEPA 1980). In 1978, all uses were cancelled except dipping of roots and tips of nonfood plants (which was also cancelled in 1987) and surface termite control (USEPA 1992). From 1983 to 1988, the only approved use was to control termites in homes and it was applied underground around the foundation of homes. After 1988, no commercial sale, distribution, or use was permitted (USEPA 1990; USEPA 1992). Water solubility of chlordane is low while its volatility is relatively high (moderately high Henry's law constant). Chlordane sorbs moderately to soil (moderate K_{oc}), and has strong tendency to bioaccumulate (high K_{ow} and BCF) (Table 1.1).

2.2 Dieldrin

Dieldrin (1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo,exo-1,4:5,8-dimethanonaphthalene), the epoxide of aldrin, was used to control insects in soil, public health insects, and termites (USEPA 1992). Dieldrin was used on corn and citrus and its usage decreased rapidly after 1966, primarily because of increased insect resistance and the development and availability of substitute chemicals (USEPA 1980). All uses of dieldrin were banned by 1972, except for subsurface termite control, dipping of nonfood rots and tops, and moth proofing (USEPA 1980); these remaining uses were also voluntarily cancelled by industry (USEPA 1992). Water solubility and volatility is very low for dieldrin and it has a strong tendency to sorb to soil and to bioaccumulate. Hydrolysis rate of dieldrin is very slow at neutral pH, with a half-life of about 10.5 years while its photo-degradation rate in water is faster, with a half-life of about 2 months.

(USEPA 1992). Microbial degradation of dieldrin in soil under aerobic or anaerobic conditions is very slow (USEPA 1992) and its field dissipation half-life is estimated at about 3 years (ARS 2001).

2.3 DDTs

DDT (1,1-*bis*-(4-chlorophenyl)-2,2,2-trichloroethane) is the first modern pesticide that was first synthesized in 1874 but its effectiveness as an insecticide was not discovered until 1939 (USEPA 1992). Since it is a wide spectrum pesticide that could be used to kill all kinds of insects, DDT was widely used in the United States on a variety of crops and for control of insect-borne diseases (USEPA 1992). Peak usage in the United States occurred at 80 million lb a.i. in 1959 and the usage then decreased steadily to less than 12 million lb a.i. by 1972 (USEPA 1975; USEPA 1980). Biodegradation of DDT in the environment is very slow with the rate and products of degradation depending on environmental conditions. The half-life of DDT in soil has been estimated at about 15 years (Mischke, Brunetti et al. 1985; ARS 2001). Its principle metabolites are DDE (1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethene) and DDD (1,1-*bis*-(4-chlorophenyl)-2,2-dichloroethane), which also are environmentally persistent. DDD was also applied as an insecticide for several years, but its agricultural use was only about 10 percent or less of that of DDT. USEPA cancelled all products containing DDD in 1971, and all remaining crop uses of DDT in 1972 (USEPA 1975; USEPA 1980). DDT is fairly volatile, has a very low water solubility, sorbs strongly to soil and has a strong tendency to bioaccumulate. The metabolites DDE and DDD are less volatile than DDT, but have comparably low water solubilities, strong tendencies to sorb to soil and to bioaccumulate, and long soil half-lives. DDT, DDD and DDE consist of *o,p'*- and *p,p'*- isomers.

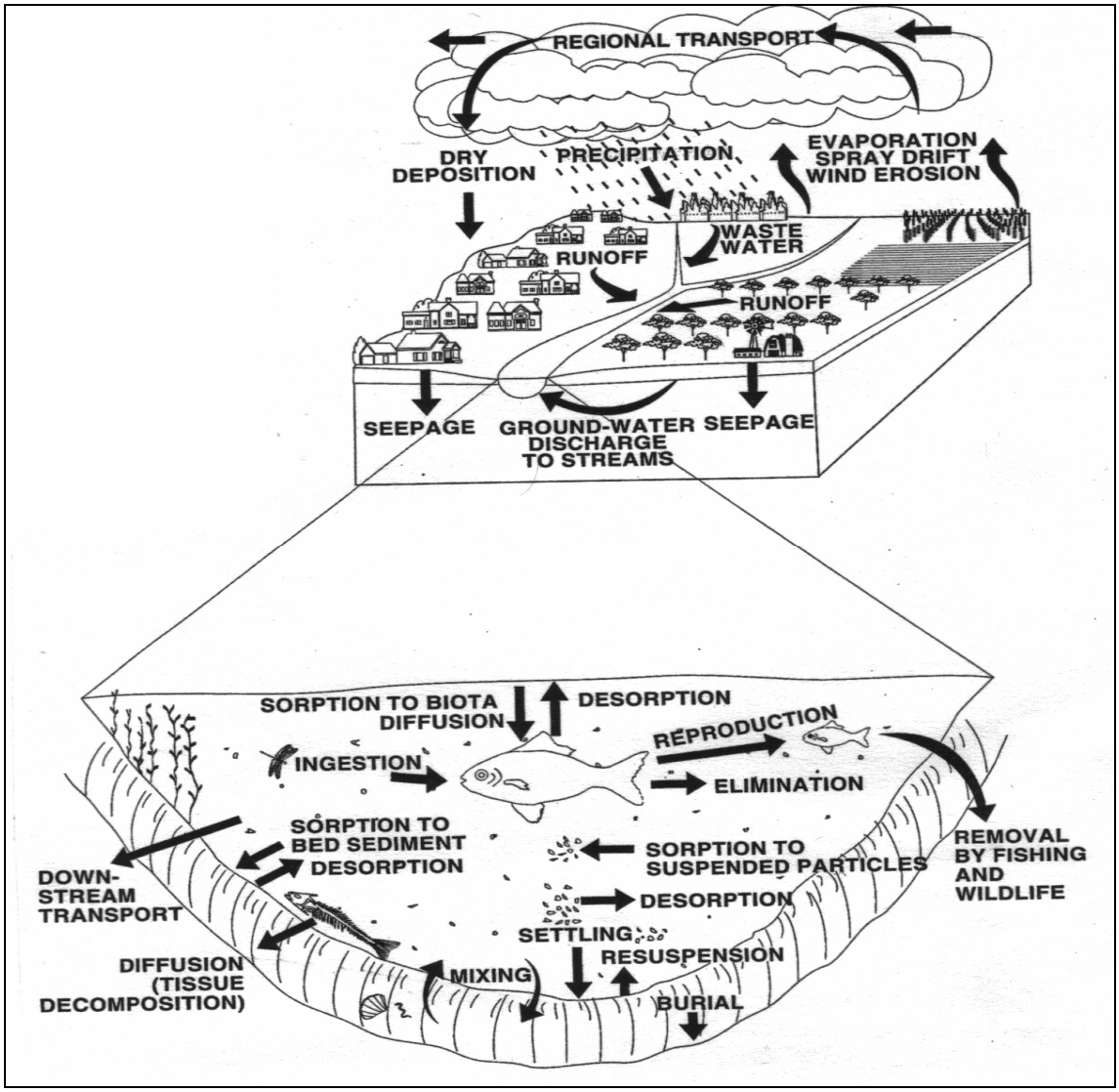

Figure 1.3 Pesticide movement in the hydrologic cycle (Majewski and Capel 1995).

Pesticides have the greatest potential of unintended adverse effects by contaminating the hydrologic system that supports aquatic life and related food chains and is used for recreation, drinking water, and many other purposes. Since water is one of the primary media in which pesticides are transported from targeted application sites to other parts of the environment, there is potential for pesticides to move into and through all components of the hydrologic cycle (Figure 1.3). For examples, pesticides have been frequently

detected in the United States in ground waters (USEPA 1990; Barbash and Resek 1996); freshwater lakes, reservoirs, rivers and streams (Gilliom, Alexander et al. 1985; Schmitt, Zajicek et al. 1990; Larson, Capel et al. 1997); marine and estuarine systems (NOAA 1987; NOAA 1988); and precipitation (Nations and Hallberg 1992; Majewski and Capel 1995). DDT and its transformation products in fish and mammals have been detected in samples from the Arctic (Cade, White et al. 1968; Addison and Smith 1974) and the Antarctic (Geoge and Frear 1966; Sladen, Menzie et al. 1966; Peterle 1969) which indicate the global distribution of pesticide.

Since OCPs are hydrophobic, their concentrations in the water column are very low levels and are commonly sorbed to suspended particles. Many OCPs also tend to be persistent because they are hard to be removed by abiotic or microbial degradation in water or sediment. Hydrophobic organochlorine insecticides may accumulate to substantial levels in bed sediment and aquatic biota via various phase-transfer and transport processes. Thus, these compounds may be detected in sediment or aquatic biota samples even though their concentrations in the water column are too low to be detected using traditional sampling and analytical methods. Therefore, when targeting hydrophobic OCPs, sediment and aquatic biota is frequently used as sampling media by many contaminant research and monitoring programs (Nowell, Capel et al. 1999).

Though the use of OCPs in the United States and Canada was restricted, these compounds continue to be detected in sediment and biological tissue samples recently collected throughout the United States. Several national monitoring programs have determined OCPs in aquatic biota and sediment. Many other smaller-scale studies have measured OCPs in bed sediment and aquatic biota. There are also many other studies that

focused on the processes by which OCPs are sorbed or bioaccumulated. Besides OCPs, structurally similar compounds, such as polychlorinated biphenyls (PCB), chlorinated dibenzo-*p*-dioxins, and chlorinated dibenzofurans, have also been studied by extensive research and monitoring programs.

3. Chiral pesticides

It is estimated that about 25% of all pesticides are chiral molecules that exist as two mirror images called enantiomers (Garrison 2006). Chiral compounds are generally produced as racemic mixtures that contain equal amount of (+) and (-) enantiomers. The enantiomer fraction (EF) or chiral signature is defined as:

$$EF = \frac{C_+}{C_+ + C_-} = \frac{C_+}{C} \qquad (1)$$

where C_+ and C_- are the concentrations of the (+) and (-) enantiomers, and C is the total concentration of the two enantiomers.

The phenomenon of enantiomer selectivity of chiral pesticides has been studied by environmental scientists for more than twenty years. Most of this research has been about the chirality of PCBs (19 of the 209 congeners are chiral) and OCPs such as *o*,*p*′-DDT, *o*,*p*′-DDD, α-HCH (hexachlorocyclohexane), and *cis*- and *trans*-chlordane (Garrison 2006). The chiral structures of *trans* - and *cis* –chlordane are showed in Figure 1.4.

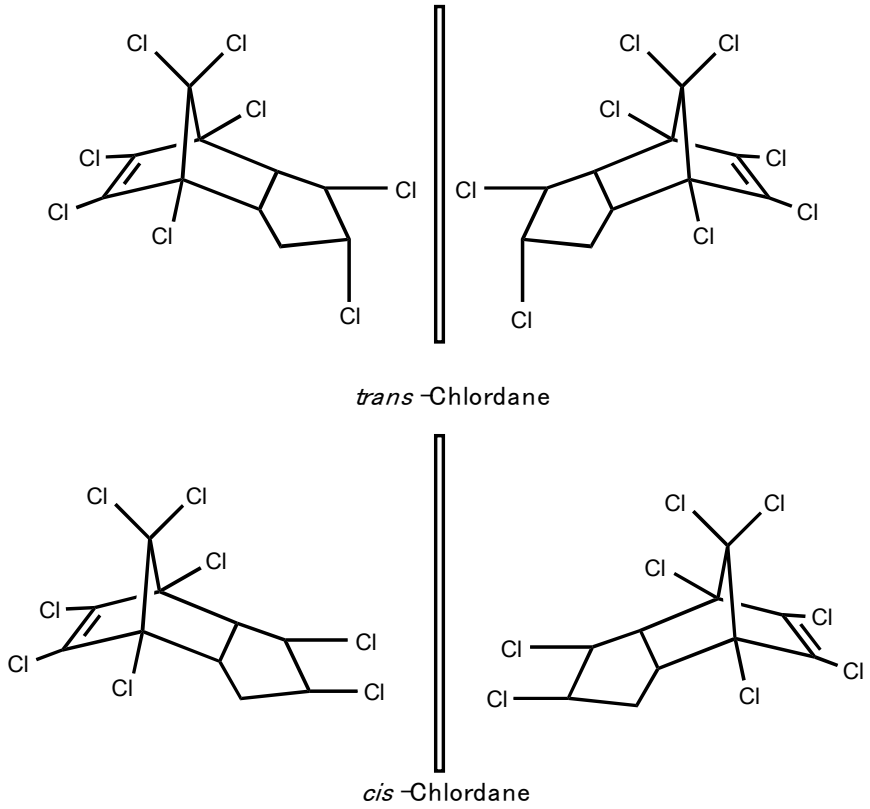

Figure 1.4. Chiral structures of trans- and cis- chlordane.

In either field applications or laboratory tests, selective microbial degradation of one of the enantiomers has often been observed when racemic pesticides are exposed to natural soils or water. Furthermore, pesticide enantiomers often exhibit differences on effect or toxicity: The "active" enantiomer of a chiral pesticide would have the desired effect on a target species, whereas the other enantiomer may not. Moreover, one or both enantiomers may have adverse effects on some nontarget species.

Besides pesticides and PCBs, there are many chiral environmental pollutants. For example, some chiral pharmaceutical, health-care, and cosmetic ingredients have been determined in the environment (Xia 2005). In addition, liver samples from whiting and bib fish caught in the Western Scheldt Estuary of the Netherlands were found to be

enriched in the (+)-enantiomer of α-hexabromocyclododecane, a chiral high-production-volume flame retardant (Janek 2005).

Some chiral PCBs are found to be nonracemic in lake and river sediments. This discovery may indicate that a biotransformation had occurred because abiotic reactions are not enantioselective (Wong, Garrison et al. 2001). Some of these same PCB are also found to be nonracemic in aquatic and riparian biota (Wong 2001). The (–) enantiomer of a chiral metabolite *o,p′*-DDD was found in fish tissue after exposure to DDT in another study. The enantiomer fractions for *o,p′*-DDD in two-thirds of these fish samples were between 0.29 and 0.44 (Garrison 1997).

Enantioselectivity in microbial degradation of α-HCH, the chlordanes, and the DDT analogs have been observed by other investigators (Vetter and Schurig 1997; Aigner, Leone et al. 1998; Hegeman and Laane 2002; Shen 2004). In general, the enantiomers of these chiral pesticides exist in nonracemic proportions in many environmental samples, such as biota (Lehmler 2003; Borga and Bidleman 2005; Janek 2005; Zegers 2005) and human tissues. These results indicate the existence of enantioselective metabolism, microbial transformation, or other biological processes. Enantiomer fractions have been used in several contamination studies. For example, fractions of chlordane enantiomers in air above chlordane-polluted soil were found to differ from those in the soil which indicates that the contamination source in the atmosphere is not from soil just under it but by the pesticide carried to the site via winds (Renner 1996).

In summary, physical processes (e.g., volatilization, leaching, and erosion) and chemical breakdown (e.g., hydrolysis and photolysis) do not change the racemic signature of chiral compounds (Buser and Mueller 1993; Mueller, Buser et al. 1997). In

contrast, microbial degradation and biological metabolism may be enantioselective and therefore change the enantiomer fraction (Falconer, Bidleman et al. 1997; Harner, Wiberg et al. 2000), as a result of the difference of interaction of enantiomers with enzymes or other naturally occurring chiral molecules (Hegeman and Laane 2002).

Therefore, examining the enantiomeric signature of the chlordane residues in the LIS sediments can shed light on the role of microbial degradation on chlordane removal. Moreover, when samples with different ages (e.g., archived samples or sediment cores) are available, temporal trends in enantiomer profiles may yield information on the relative rates of microbial degradation over time. Though, this research is only focused on the LIS sediment, the long-term goals are to determine the spatial distribution and severity of toxicity and to analyze the relationships between toxicity and chemical contamination in our Nation's estuarine and costal waters.

4. ^{137}Cs and ^{210}Pb as chronological tools

^{137}Cs and ^{210}Pb are two chronological tools commonly used to date recent sediments and to quantify both sedimentation and sediment mixing. ^{137}Cs has been distributed globally by atmospheric testing of nuclear weapons. Significant fallout commenced in 1952 and peaked in 1963. The first atmospheric testing of nuclear weapons by the United States was conducted in Nevada in 1951, and much larger-scale testings began in 1952 (Beck, Helfer et al. 1990). ^{137}Cs fallout in the United States peaked in 1958 due to the extensive testing in Nevada (Beck, Helfer et al. 1990). The atmospheric testing was resumed in 1961 and the largest tests were conducted in 1961-63. In the summer of 1963 Limited Test Ban Treaty was signed by the United States, Britain, and Soviet Union to

ban aboveground and ocean testing. Since ^{137}Cs is particle active, it sorbs to particles in the atmosphere and gets deposited onto the earth surface. Thus, ^{137}Cs nuclide is also found in sediments. The 1963 atmospheric fallout peak results in large peaks in ^{137}Cs activity in undisturbed sediment cores (Holmes 1998) and is assigned a date of 1964.0 (in decimal years). The 1958 peak is sometimes seen in cores with relatively high sedimentation rates in the western and central United States and can also be used as a date marker.

Besides ^{137}Cs, ^{210}Pb was also used as a primary age-dating tool. ^{210}Pb occurs naturally as the result of the decay of ^{222}Rn, a member of the ^{238}U decay series (Figure 1.5). Over geological time, the radionuclides in the ^{238}U decay series in rocks come to equilibrium. In shallow fresh and marine sediments, much of the ^{210}Pb results from decay of atmospheric ^{222}Rn. ^{210}Pb is also particle-reactive and quickly sorbs to settling particulate matter. The fallout of ^{210}Pb from atmospheric ^{222}Rn results in more ^{210}Pb in surficial sediments than can be accounted for by decay of ^{226}Ra in deep sediments. As surficial sediments are gradually buried, the excess ^{210}Pb (the amount above equilibrium) decays with a half-life of 22.3 yr. Thus, ^{210}Pb provides information about sediment ages, accumulation rates, and particle reworking over timescales of roughly 100-150 years (Robbins 1978; Appleby 2001).

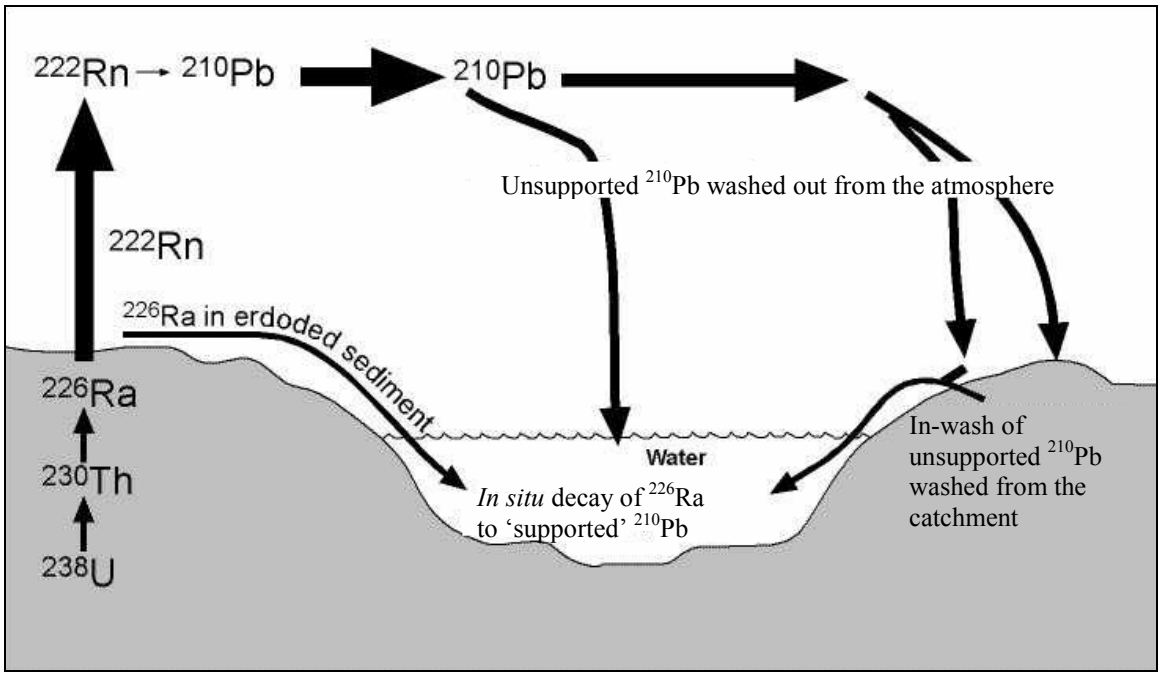

Figure 1.5 Pathways by which ^{210}Pb reaches aquatic sediments (Oldfield and Appleby 1984).

Two models were used for ^{210}Pb as an age-dating tool for sediment cores: the constant rate of supply (CRS) model and the constant flux, constant sedimentation rate (CF:CS) model (Appleby and Oldfield 1992). The CRS model assumes that the rate of supply of unsupported ^{210}Pb to the ocean is constant which implies that any change in mass accumulation rate (MAR) is caused by the removal or addition of sediment with no unsupported ^{210}Pb and, therefore, that the initial ^{210}Pb activity in surface sediment varies inversely with the MAR. However, this assumption rarely is met in practice because, for example, an increase in MAR caused by land disturbance associated with urban development transports additional surficial soils and sediments into the ocean. MAR is increased by this additional erosion, because at least part of the additional sediment is from the land surface which contains excess ^{210}Pb.

The assumption for the second model, the CF:CS model, is that both MAR and the flux of ^{210}Pb to the ocean are constant over time (Appleby and Oldfield 1992). It is similar to the constant input concentration (CIC) model, which assumes constant input concentration of unsupported ^{210}Pb; the simplest way for constant input to happen is for the assumption of CF:CS model to be met. Both models assume that the initial unsupported ^{210}Pb activity in newly deposited sediments is constant over time, which indicates an exponential decline in ^{210}Pb activity with depth in the core.

Chapter 2

Objectives

The main objective of this work is to determine the concentration, fate, source and removal mechanisms of the organochlorine pesticides in the sediment from Long Island Sound. This is achieved by using the following approaches: (1) determine organochlorine pesticides concentrations in sediments from LIS; (2) examine the chiral signature of chlordane residues in the LIS sediments to assess the significance of microbial degradation on chlordane removal. (3) Age date the samples in the sediment cores by measuring the activity of ^{210}Pb and ^{137}Cs; (4) measure the total organic carbon (TOC) and total nitrogen (TN) contents in the sediments; (5) determine the particle size distribution in the sediment samples.

The research is expected to elucidate the mechanisms that may have caused the pesticides concentration change in LIS sediments. Possible mechanisms to cause a concentration change of an organic contaminant in estuarine sediments may include: 1) burial of highly contaminated sediments with less contaminated solids; 2) erosion of highly contaminated surface sediments; 3) dissolution from sediments; and 4) microbial degradation. The first three mechanisms are closely related to the sedimentary environments and may be examined by inspecting concentration profiles in sediment cores. By measuring the EF values of chlordane in surficial sediments and sediment cores, the importance of microbial degradation in the pesticide removal can be elucidated. In addition, we expect our work to shed light on the possible sources of organochlorine pesticides contamination.

Chapter 3

Background

1. Previous investigations

The monitoring activities for pesticides in the United States began in the 1960s in response to a directive from President John F. Kennedy in 1963 to implement recommendations made by the President's Science Advisory Committee that federal agencies should develop a network to monitor pesticide residues in air, water, soil, fish, wildlife, and humans (Bennett 1967). From the late 1960s to the 1970s, several federal agencies carried out the following monitoring programs: (1) the U.S. Environmental Protection Agency (USEPA) analyzed pesticides in humans (adipose tissue, blood serum, and urine), soils (agricultural and urban), raw agricultural crops, surface water (including bed sediment), estuarine fish and shellfish, and ambient air in suburban areas; (2) the Food and Drug Administration (FDA) determined pesticides in processed, ready-to-eat foods, in raw foods, and in animal feeds; (3) the U.S. Department of Agriculture analyzed pesticides in meat and poultry; and (4) the U.S. Department of the Interior determined pesticides in water, sediment, fish, and migratory and nonmigratory birds (Carey and Kutz 1985). Many hundreds of state and local monitoring studies supplemented the national monitoring activities.

There are six major national programs that have monitored pesticides in bed sediment or aquatic biota throughout the United States. (1) FDA's National Monitoring Program for Food and Feed (NMPFF); (2) Bureau of Commercial Fisheries and USEPA's

National Pesticide Monitoring Program (NPMP); (3) U.S. Fish and Wildlife Service (USFWS)'s National Contaminant Biomonitoring Program; (4) U.S. Geological Survey (USGS) and USEPA's Pesticide Monitoring Network (PMN) (5) U.S. National Oceanic and Atmospheric Administration (NOAA)'s National Status and Trends Program (NS&T) – Mussel Watch and Benthic Surveillance Projects; (6) USEPA's National Study of Chemical Residues in Fish. Among all these six national programs, two analyzed pesticides in bed sediment: one in major rivers and one in coastal and estuarine areas. There are five national programs that monitored pesticides in aquatic biota: two targeted marine and estuarine biota, and two targeted primarily freshwater fish. The FDA's NMPFF did not report sources of fish and shellfish samples, but these sources probably included both freshwater and marine systems.

1.1 The FDA's National Monitoring Program for Food and Feed (NMPFF)

From 1963 to 1999, NMPFF analyzed samples of domestically produced and imported foods for hundreds of pesticides including currently used pesticides as well as organochlorine insecticides. However, as noted previously, it is not clear whether all types of food and feed samples were analyzed for all the target pesticide analytes. Fish and shellfish samples analyzed in this program represent products in interstate commerce in the United States, rather than the water resources in the United States. Generally the FDA data for all domestic fish and shellfish samples were combined. Furthermore, published FDA reports did not provide information on sampling location, tissue type, species of organism, or even type of hydrological system (lake, river, marine system) sampled. Therefore, FDA's results are useful to an evaluation of human exposure, but do not contribute much to our understanding of insecticides in the hydrologic system.

1.2 The BofCF -USEPA's National Pesticide Monitoring Program (NPMP)

During 1965 to 1977, the Bureau of Commercial Fisheries (BofCF), and later the USEPA, monitored residues of organochlorine pesticides and polychlorinated biphenyls (PCB) in estuarine biota to determine the extent of pesticide contamination of estuary areas in the United States. From 1965 to 1972, mollusks were monitored monthly at 180 sites (Butler 1973), and to determine trends again since the previous sampling at a subset of 87 sites in 1977 (Butler, Kennedy et al. 1978). Estuarine fish were targeted for sampling from 1972 to 1976 because fish were considered to store synthetic compounds longer than mollusks (Butler and Schutzmann 1978). Fish were sampled once or twice a year in 144 estuarine areas. The mollusk samples were analyzed for organochlorine pesticides in 1965-1972. Organophosphate insecticides was included as target analytes for the analysis of the 1972-1976 fish and 1977 mollusk samples.

The most frequently detected pesticide in mollusks and fish was total DDT during all sampling periods. Dieldrin, endrin, mirex, and toxaphene were detected in some frequencies in mollusks samples that were collected from 1965 to 1972 (Butler 1973). The only detectable residues in frequencies in mollusks appeared to decrease between the survey in 1965-1972 and the resampling in 1977. The highest total DDT residues (> 1000 μg/kg) in mollusks were collected from 1965 to 1972 in drainage basins with heavy agricultural development in California, Florida, and Texas (Butler 1973). Dieldrin, chlordane, toxaphene, heptachlor exporide, methyl parathion, ethion, carbophenothion, and parthion and total DDT were detected in estuarine fish samples (Butler and Schutzmann 1978). Total DDT levels in the fish samples from Delaware, Florida, and

New York (1,000-4,000 μg/kg) were found to be greater than those measured in mollusks collected from the same estuaries during 1965-1972.

1.3 The FWS's National Contaminant Biomonitoring Program (NCBP)

During 1967 to 1986, the FWS determined organochlorine compounds and trace elements in whole freshwater fish nationwide every 1-3 year as part of the NCBP, formerly part of the interagency National Pesticide Monitoring Program. The objective of the program was to record temporal and geographic trends in concentrations of environmental contaminants that may threaten fish and wildlife resources. Stations were selected to locate in major rivers system throughout the United States, including Alaska and Hawaii, and in the Great Lakes. Over time, the program was expanded from 50 sites to 112 sites nationwide. The whole-body residues in fish were measured since the NCBP program focus on potential threats to fish and wildlife resources, (Schmitt, Ludke et al. 1981).

Chlordane, dieldrin and total DDT were detected consistently at sites throughout the NCBP program. Every year, *cis*-Chlordane, *trans*-nonachlor, and dieldrin were detected at over 70 percent of sites, and total DDT was detected at over 97 percent of sites. Other organochlorine pesticides were detected at an intermediate number of sites: toxaphene (59-88 percent of sites in different years), α-HCH (47-90 percent), endrin (22-47 percent), heptachlor expoxide (38-55 percent), methoxychlor (32 percent), and lindane (8-31 percent). A wood preservative metabolite , pentachloroanisole, was detected at low levels at 24-30 percent of sites. The herbicide dacthal was detected at 28-45 percent of sites since 1978. Because the half-lives of α-HCH, lindane, methoxychlor, and

pentachloroanisole are shorter than most organochlorine insecticides, their detection in environmental samples might indicate recent inputs (Schmitt, Zajicek et al. 1985; Schmitt, Zajicek et al. 1990). There were a few sites that were polluted with unusually high residues of aldrin, endrin, or hexachlorobenzene (> 50 μg/kg), or an unusually high proportion of *o,p'*-DDT and homologues (>20 percent of total DDT); these residues were probably a result of contamination from chemical manufacturing, or chemical storage facilities (Schmitt, Ribick et al. 1983; Schmitt, Zajicek et al. 1990). Some sites at Great Lakes were among the most contaminated sites for many pesticidess, including total DDT, chlordane, dieldrin, α-HCH, total heptachlor, methoxychlor, mirex and toxaphene. High concentrations of selected pesticides were detected in fish from agricultural sites (Schmitt, Zajicek et al. 1990) including dachal (> 70 μg/kg, in the lower Rio Grande and lower Snake rivers), total DDT (> 1000 μg/kg, in the Yazoo, Colorado and Rio Grande rivers), dieldrin (> 200 μg/kg, in major rivers draining the Corn Belt), and toxaphene source of chlordane to aquatic ecosystems (Schmitt, Ribick et al. 1983; Schmitt, Zajicek et al. 1990). Atmospheric transport was attributed in part to the distributions of toxaphene and α-HCH (Schmitt, Ribick et al. 1983; Schmitt, Zajicek et al. 1985).

1.4 The USGS-USEPA's Pesticide Monitoring Network (PMN)

PMN was the first national effort to monitor insecticides in bed sediment, operated by the USGS and USEPA as part of the interagency National Pesticide Monitoring Program (Gilliom, Alexander et al. 1985). The USGS collected whole water and bed sediment samples at 160-180 sites on major rivers throughout the United States, and the USEPA analyzed them for pesticides. The objective was to evaluate levels of pesticide contaminations in runoff and bed sediment, and to identify areas with problems. Bed

sediment data for 1975 to 1980 were analyzed by Gilliom and others (Gilliom, Alexander et al. 1985). Surficial sediment samples were collected along a cross-section of the river and composited, then analyzed unsieved. Target analytes in bed sediment included organochlorine and organophosphate pesticide, and a few chlorophenoxy acid and triazine herbicides.

Organochlorine pesticides were detected at more sites and in a higher percentage of samples in bed sediment than in river water (Gilliom, Alexander et al. 1985). DDE was detected in bed sediment at the most sites. Detection frequencies for an individual organochlorine pesticide were found to relate with its degree of use on farms (by agriculture region), and its water solubility, environmental persistence and analytical detection limit.

1.5 The USEPA's National Study of Chemical Residues in Fish (NSCRF)

The USEPA carried out the National Dioxin Study, a 2-year nationwide investigation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) contamination in air, water, soil, sediment, and fish in 1983. As an outgrowth of this study, USEPA conducted a one-time nationwide survey of pollutant residues in fish, titled the NSCRF (formerly titled the National Bioaccumulation Study). The objectives of the survey were to analyze the prevalence of selected bioaccumulative chemicals in fish, to determine sources of these contaminants, and to evaluate human health risks. Fish samples were collected from 1986 to 1987 at about 400 sites nationwide of which most sites were on rivers and lakes and a few were estuarine or coastal sites. Around 80 percent of the total sites were near potential point and nonpoint contamination sources (called "targeted sites"), 10 percent

were in areas expected to have less or no contamination to provide background concentrations, and about 10 percent were collocated with a subset of USGS National Stream Quality Accounting Network (NASQAN) sites to provide geographic coverage. Two composite fish samples were collected from each site: a representative game fish, which was analyzed as a fillet (skin off), and a representative bottom-feeding fish, which was analyzed whole. Target analytes included chlorinated dibenzo-p-dixoins and dibenzofurans, PCBs, organochlorine pesticides, and selected other insecticides. The results from the NSCRF were published by U.S. Environmental Protection Agency (USEPA 1992; USEPA 1992).

p,p'-DDE was the most frequently detected contaminant in the NSCRF, which was detected in fish at 99 percent of sites. Other pesticides detected at over 50 percent of sites included *cis*- and *trans*- chlordane, dieldrin, α-HCH*, trans*-nonachlor, pentachloroanisole. About 25 to 50 percent of sites were detected to have hexachlorobenzene, lindane, mirex, oxychlordane, and chlopyrifos; heptachlor epoxide, endrin, and trifluralin were detected at 10-20 percent of sites; and dicofol, heptachlor, methoxychlor, isopropalin, and nitrofen at fewer than 8 percent of sites. Mean or median residues of *p,p'*-DDE, chlorpyrifos, trifluralin, and dicofol were the highest at agricultural sites while those of total chlordane, dieldrin, total nonachlor, hexachlorobenzene, HCH isomers, and isopropalin were the highest at Superfund sites, sites in industrial and urban areas, and sites near refineries, and other industry. The median concentrations of pentachloroanisole, a metabolite of the wood preservative pentachlorophenol, and 2,3,7,8-TCDD, a byproduct of paper and pulp mill bleaching processes that use chlorine, were the highest at sites near paper mills. Whole-body residues in bottom feeders were higher than residues in game fish fillets for

chlordane compounds and HCH isomers, but not DDE and dieldrin (USEPA 1992; USEPA 1992).

1.6 The NOAA's National Status and Trends Program (NS&T)

The NOAA's NS&T Program includes two projects: the National Mussel Watch Project and the National Benthic Surveillance Project. The National Mussel Watch Project has monitored bivalve mollusks and associated surficial sediment at about 150 coastal and estuarine sites in the United States since 1986. The National Benthic Surveillance Project has analyzed benthic fish and associated surficial sediment from about 50 coastal and estuarine sites around the United States since 1984. The main objectives of the program were to determine the current status and to detect trends in the environmental quality of the nation's coastal and estuarine areas (Lauenstein, Cantillo et al. 1993). Residues in sediment were used to determine geographic distributions of pollutants since their concentrations in biological tissues may vary with species, age, sex, size and other factors (NOAA 1989) while residues in fish and mollusks were used to analyze temporal trends in contamination because contaminant levels in biota change relatively rapidly in response to surrounding environments (NOAA 1988). The National Benthic Surveillance Project also analyzed the association of chemical contaminants with fish diseases.

The sites of NS&T were carefully selected to be representative of their surrounding environments, and to avoid small-scale areas of contamination and known point source discharge (NOAA 1989). Forty-five percent of the sites were around 20 km of population centers with more than 1000,000 people. All sites were subtidal (never exposed at lowest

tides). Organochlorine pesticides, PCBs, PAHs and trace elements were included in the target analyte list.

Sediment samples were collected from depositional areas as close as possible to the corresponding sampling sites for biota (Lauenstein, Cantillo et al. 1993). All sediment samples were taken from the top 1-3 cm of three grabs or cores. Sediment data were normalized by dividing the raw concentration of contaminant in a composite by the weight fraction of sediment particles that were less than 63 μm in diameter based on the assumption that no contaminants were associated with sand-sized particles, that the presence of sand merely diluted the concentration of contaminants (NOAA 1991). The pollutant concentrations in sediment were not normalized by total organic carbon (TOC) content (NOAA 1988; NOAA 1991) because TOC was high near urban areas just like trace contaminants, which suggested that TOC was influenced by human activity and was itself behaving as a contaminant. Sediment data from the National Mussel Watch Project and the National Benthic Surveillance Project were processed together and published in two NS&T progress reports of which the first (NOAA 1988) was superseded by the second (NOAA 1991), which presented sediment data from 1984 to 1989.

The data for mollusk and fish tissue were reported on a dry weight basis. Two species of mussels and two species of oysters were collected in the National Mussel Watch Project. Contaminant data for bivalve mollusks were published in two technical memorandums, of which the first (NOAA 1987) was superseded by the second (NOAA 1989), which covers mollusk data during 1986-1988. A series of regional reports were published about the estuarine fish contamination at National Benthic Surveillance Project sites. Seven fish species were collected at 31 sites on the Pacific coast (Veranasi, Chan et

al. 1988; Veranasi, Chan et al. 1989; Myers, Stehr. et al. 1993), five species at 20 sites on the Atlantic coast (Zadanowicz and Gadbois 1990; Johnson, Stehr. et al. 1992; Johnson, Stehr. et al. 1993) during 1984-1986 and two species from 16 sites on the Atlantic and Gulf coasts during1984-1985 (Hanson, Evans et al. 1989).

The most frequently detected pesticide in sediment was total DDT. Other pesticides detected in sediment included total chlordane, dieldrin, hexachlorobenzene, lindane, and mirex. Most contaminants occurred together and their concentrations (as well as TOC) were related to human population levels (NOAA 1991). An exception was total DDT, which was not correlated with human population levels on a national scale, but was highly associated with southern California. The concentration measured probably overestimated the extent of contamination in typical United States coastal sediment considering 45 percent of NS&T sites were near urban areas, but might also grossly underestimate concentrations found at hot spots, such as near point source discharges (NOAA 1991).

During 1986-1988, total DDT and total chlordane were detected in 98 percent of samples nationally in mollusks, followed by dieldrin (91 percent), lindane (70 percent), mirex (30 percent), and hexachlorobenzene (23 percent). In mollusks, the highest levels of total DDT, total chlordane, dieldrin, and lindane were found in urban areas (NOAA 1989; O'Connor 1992). During 1986-1988, the highest average total DDT levels in bivalves were detected at west coast sites had the, followed by east coast sites, while the lowest average levels were found at Gulf coast sites (Sericano, Atlas et al. 1990).

Total DDT, dieldrin, and total chlordane were the most commonly detected pollutants in estuarine fish livers. Again, organochlorine concentrations tended to be higher at urban sites than at rural sites (Hanson, Evans et al. 1989; Veranasi, Chan et al. 1989; Zadanowicz and Gadbois 1990). The incidence of certain fish diseases also was greater near urban areas (Hanson, Evans et al. 1989). Typically, concentrations of organic pollutants in the southeast were average to low comparing to other parts of the United States (Hanson, Evans et al. 1989).

The differences among the six national programs in their scope, objectives, and study design affect the study results and need to be considered in integrating the results of these studies into a comprehensive picture of pesticides in bed sediment and aquatic biota in the United States. Comparison of results within and among these programs is complicated because of the differences in site selection strategy, sampling season, year and duration of sampling, species collected, and type of tissue analyzed (fish fillet, liver, or whole body). Except the NMPFF, all other national programs share one common design feature: they targeted predominantly or exclusively hydrophobic, persistent pollutants that are expected to sorb to sediment and to bioaccumulate, such as the organochlorine pesticides.

Globally, the OCPs were detected in sediments from the world wide coastal zones and estuary systems. For example, total DDT concentrations ranged from 2.6 to 1629 ng/g in China (Mai, Fu et al. 2002), 0 to 364 ng/g in India (Pandit, Mohan Rao et al. 2001), 2.5 to 12 ng/g in Japan (Iwata, Tanabe et al. 1994), 0.01 to 135 ng/g in Korea (Hong, Yim et al. 2006), 2.2-11.9 ng/g in Singapore (Wurl and Obbard 2005), 6.2-10.4 ng/g in Vietnam

(Nhan, Am et al. 1999), 0.04-43.7 ng/g in Spain (Peris, Requena et al. 2005), and 1.9 to 6.9 ng/g in the Baltic Sea (Strandberg, van Bavel et al. 1998).

Besides sediment, OCPs have been detected in many matrixes in the hydrologic cycle. For example, concentrations of OCPs in 38 agricultural soils and two garden soils from U.S. Corn Belt were determined with geometric mean values of 9.6 ng/g for total DDT, 1.4 ng/g for total chlordane, 1.0 ng/g for dieldrin respectively (Aigner, Leone et al. 1998); the highest concentrations of OCPs in 36 Alabama agricultural soils were measured as 285±390 ng/g for toxaphene, 22.7±21.4 ng/g for *p,p′*-DDE, 24.6±30.5 ng/g for *p,p′*-DDT, 4.00±5.86 ng/g for *o,p′*-DDT, and 2.40±2.41 ng/g for *p,p′*-DDD (Harner, Wideman et al. 1999); atmosphere concentrations of chlordane compounds ranged from 6.1 to 481 pg/m^3 in 1997-1999 at three New Jersey locations (Offenberg, Nelson et al. 2004); outdoor air concentrations of six chlordane components (*trans*-chlordane, *cis*-chlordane, trans-nonachlor, cis-nonachlor, oxychlordane, and MC5) in 3 urban areas during June 1999-May 2000 ranged from 0.036-4.27 ng m^{-3} in Los Angeles County, from 0.008-11.00 ng m^{-3} in Elizabeth, and from 0.062-1.77 ng m^{-3} in Houston while the corresponding indoor total chlordane concentrations ranged from 0.037-112.0 ng m^{-3} in Los Angeles County, from 0.260-31.80 ng m^{-3} in Elizabeth, and from 0.410-38.90 ng m^{-3} in Houston study homes (Offenberg, Naumova et al. 2004); concentrations of OCPs in lake water from Siberia were measured with average values of 64 pg/L for toxaphene and 87 pg/L for total DDT (Kucklick, Bidleman et al. 1994). OCPs have even been detected in Great Lakes precipitation (Sun, Backus et al. 2006), Arctic air (Bidleman, Jantunen et al. 2002) and Arctic Ocean water (Jantunen and Bidleman 1998).

Besides concentrations, the enantiomeric fractions or chiral signatures of chiral OCPs have been measured as an indicator for transport, source and biodegradation of OCPs. The enantiomer fractions of *trans*- and *cis*-chlordane were found to be nonracemic in the Arctic air samples which indicate a long-range transport of chlordane-related compounds (Bidleman, Jantunen et al. 2002). The enantiomeric ratios (ER, the area of the (+) enantiomer divided by the area of the (-) enantiomer) of 59 air samples near the Great Lakes were determined and the overall ER was close to racemic for *cis*-chlordane (1.05±0.02) while the overall ER was significantly different than racemic for *trans*-chlordane (0.88±0.02) and *exo*-heptachlor epoxide (1.99±0.04) which suggests that *trans*- and *cis*-chlordane are metabolized differently in the environment and *exo*-heptachlor epoxide is an enzymatic degradation product (Ulrich and Hites 1998). Evidence of enantioselective degradation of OCPs was found in 30 soils from the U.S. Corn Belt with the (+) *trans*-chlordane, (-) *cis*-chlordane and (-) *exo*-heptachlor epoxide were in excess with nonracemic compositions (Aigner, Leone et al. 1998). The enantiomeric fractions of chlordanes and chlordane metabolites differed in general significantly from racemic in 35 Alabama soils samples (Wiberg, Harner et al. 2001). Chiral OCPs (α-HCH, o,p'-DDT, *trans*- and *cis*-chlordane) were found to be nonracemic in some arctic marine invertebrates which indicate strong enantioselective bioaccumulation (Borga and Bidleman 2005).

Chiral OCPs, however, were racemic in the samples from some studies. For example, *trans*- and *cis*-chlordane, however, were found to be racemic in the silt loam and muck soils from British Columbia of Canada (Falconer, Bidleman et al. 1997). In Connecticut,

chlordanes in the agricultural soils were found to be nonracemic while residential soils near home foundation were racemic (Eizer, Iannucci-Berger et al. 2003).

Globally, chiral signatures were investigated in 65 background soils collected from different locations across the world. The soils were taken from different ecosystems (e.g., grasslands, forests), and the EFs of chiral chlordanes, α-HCH, and *o,p'*-DDT were determined. Chlordanes in most of the soils showed the usual pattern of enantioselective degradation seen in agricultural soils, depletion of (+)-*trans*-chlordane (TC) and (-)-*cis*-chlordane (CC). However, some samples showed opposite enantiomer degradation patterns for TC and CC (Kurt-Karakus, Bidleman et al. 2005).

2. Background for this research

The LIS was selected as our study area for several reasons. First, LIS is an estuary of national significance, and the contamination and declining environmental quality directly threatens the regional fishing and shell-fishing industry. Information on the fate of organochlorine pesticides in the sediments is, therefore, of direct practical importance.

Furthermore, LIS has been under intensive study by NOAA (e.g., National Status and Trends (NS&T) Program), EPA (e.g., Long Island Sound Study Program), U.S. Geological Survey (e.g. Coastal and Marine Geology Program), and others. As a result, an extensive database exists for marine geology of the Sound as well as contaminant distribution in the sediments, water columns and organisms in the Sound. For example, the NS&T's Mussel Watch Project provides long-term (1986 to 1996) sediment and

tissue chemistry data that allow us to observe the change of some persistent pollutants over time.

Third, the NS&T Program maintains a specimen bank that has archived LIS sediments (at -150 °C) dating back to 1986 (Lauenstein, Cantillo et al. 1996). These archived sediment samples are available upon request, and the chiral signature of chlordane residues in the archived samples can be determined and compared to the chiral signature of fresh sediments to examine relative rates of microbial degradation over time.

Fourth, LIS is very close to our institutions for convenient access.

The loss of organochlorine pesticides in soils has been observed to follow pseudo-first order kinetics (Merjer, Halsall et al. 2001):

$$\ln C = \ln C_0 - kt \qquad (1)$$

where C_0 is the original concentration (around 1988 for chlordane), C is the concentration at time t, and k is the rate constant which has been determined by plotting natural logarithm of concentration against time and deriving the slope of the linear regression line (Merjer, Halsall et al. 2001). In order to obtain a meaningful slope, however, at least three data points are needed. Although there are 3-4 temporal data points for chlordane concentration in sediments from each of the Mussel Watch Project site in LIS, the pre-1988 data are generally not suitable for determining the rates of chlordane decline since any addition of chlordane to the sediments might alter the temporal trends.

Unfortunately, the investigations on LIS sediments carried out by NOAA, EPA and USGS were stopped in the 1980s to 1990s and there is no information available anymore

about the pesticides in LIS sediments for the last decade. To our knowledge, neither NOAA nor any other government agencies plans to conduct a new sediment survey in LIS in the near future.

Therefore, it is necessary to revisit the Mussel Watch Project sites in LIS and determine the sediment OCPs concentrations in order to derive reliable OCPs changing trends. This sampling event also allows us to collect sediment cores to examine possible mechanisms that have caused the OCPs decline, and to analyze the chiral signature of chlordane residues in the sediments to assess the significance of microbial degradation of chlordane.

Chapter 4

Experimental

1. Materials

1.1 Chemicals

All chemicals were used as received unless otherwise specified. Six certified reference solutions of *trans*-chlordane (100 μg/mL in methanol), *cis*-chlordane (100 μg/mL in methanol), *p,p'*-DDE (1000 μg/mL in methanol), *p,p'*-DDD (5000 μg/mL in methanol), *p,p'*-DDT (5000 μg/mL in methanol) and dieldrin (1000 μg/mL in methanol) were purchased from Ultrascientific (North Kingstown, RI). A certified reference composite solution (1000 μg/mL in hexane/toluene (1:1)) was purchased from Ultrascientific (North Kingstown, RI). This composite standard solution contains 20 organochlorine pesticides with a concentration of 1000 μg/mL for each component. Surrogate standard PCB 166 (2,3,4,4',5,6-hexachlorobiphenyl, 100 μg/mL in hexane) was purchased from Ultrascientific (North Kingstown, RI). D(+)-Glucose anhydrous and potassium nitrate were obtained from Acros (Morris Plains, NJ).

All organic solvents and reagents used were pesticide grade. Hexane, acetone, methanol, diethyl ether, sulfurous acid (8%), nitric acid (69.4%) and sodium sulfate anhydrous (10-60 mesh) were obtained from Fisher Scientific (Fair Lawn, NJ). dichloromethane was obtained from Acros (Morris Plains, NJ). Water used was deionized water (DW) (Milli-Q gradient system, Millipore, Bedford, MA). Florisil (PR 60-100 mesh) was obtained from Supelco (Bellefonte, PA). Granular copper and copper metal

shot (3-14 mesh) were purchased from Fisher Scientific (Rochester, NY). Helium (5.0 ultra high purity) and nitrogen (5.0 ultra high purity) were obtained from Welco-CGI (Newark, NJ). Mixture makeup gas (5.1% methane in argon) was obtained from Welco-CGI (Bethlehem, PA).

1.2 Preparation of calibration standards and surrogate spiking solution

Five standard calibration solutions with concentrations in the range of 1 - 100 ng/mL for each individual standard were prepared by diluting the respective stock standard solution with hexane in the volumetric flasks.

Five composite standard calibration solutions with concentrations in the range of 1 - 100 ng/mL were prepared by diluting the composite stock standard solution with hexane in the volumetric flasks.

A surrogate spiking solution with a concentration of 200 ng/mL was prepared by diluting this surrogate standard with acetone in a volumetric flask.

1.3 Preparation of activated copper

Oxides were removed by treating copper pellets with dilute nitric acid (about 7%), then rinsed with organic-free reagent water to remove all traces of acid, rinsed with acetone and dried under a stream of argon (USEPA 1996).

1.4 Preparation of sodium sulfate

Sodium sulfate was precleaned with methylene chloride and dried in oven at 60 °C. It was further purified by heating at 400°C for 4 hours in a muffle furnace. The sodium sulfate was cooled in a dessicator (USEPA 1996).

1.5 Preparation of Florisil cleanup column

Florisil was precleaned with acetone and then heated in an oven at 130°C overnight. The Florisil was cooled in a dessicator before use. 20 g activated Florisil was added to a 20 mm ID chromatographic column and settled by tapping the column. 20 g anhydrous sodium sulfate was added to the top of the Florisil. The column was pre-eluted with 60 mL of hexane and the eluate was discarded (USEPA 1996).

1.6 Preparation of aluminum holding block and aluminum cup

An aluminum holding block with a total of 50 holes of 7/16 inch diameter was made (Verardo, Froelich et al. 1990). A series of 2.3 cm diameter discs weighing approximately 15-18 mg each was cut out from a piece of aluminum foil. The aluminum cups were formed by molding the aluminum discs, one at a time, around the mandrel. The cups were molded to form a water-tight seal. The newly constructed sample cups were placed in a glass beaker filled with the distilled water. The beaker was then placed in a water bath and sonicated for 2 min. Excess water was decanted and each cup was carefully picked up with clean forceps and placed in a separate well in the clean aluminum holding block. The holding block with cups was then baked in a muffle furnace at 550 °C for 24 hours. The holding block was removed after the muffle furnace was cooled and placed in an air-tight container.

2. Methods

Sediment samples were taken in 2005 and 2006 and were kept frozen. Part of the sediment sample was used for total organic carbon and total nitrogen analysis, particle size analysis, isotope analysis and organochlorine pesticide analysis, respectively. Organochlorine pesticide contaminants were extracted from sediments by Soxhlet

extraction. The extracts were concentrated and cleaned by Florisil cleanup. The eluents were concentrated and analyzed by GC-ECD and GC-MS respectively (Figure 4.1).

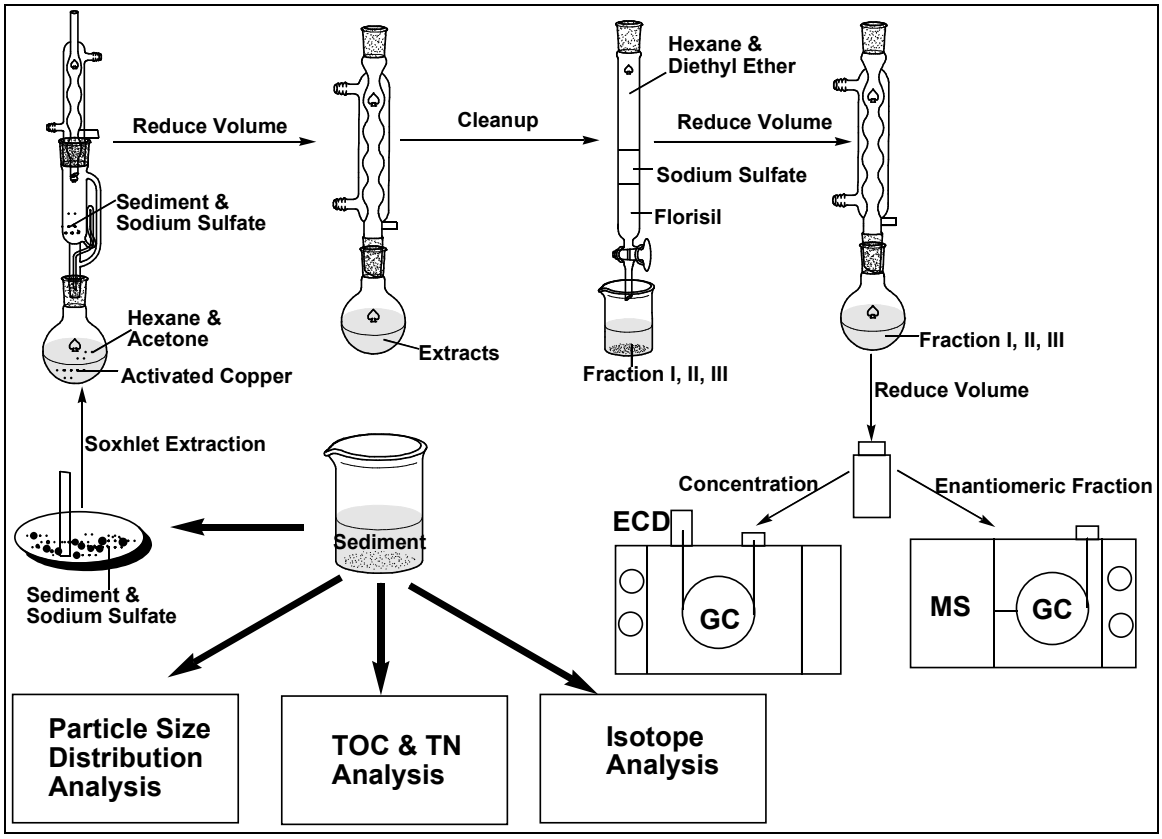

Figure 4.1 Experimental setup.

2.1 Sample collection and acquisition.

2.1.1 Recent collected samples.

Surficial sediments were collected in 2005 and 2006 at eight LIS sites (LICR, LIHR, LISI, LIMR, LITN, LIHH, LIHU, and LIPJ, Figure 4.1 & Table 4.1) that were previously surveyed (1986-1996) by the NS&T Program's Mussel Watch Project (Lauenstein, Cantillo et al. 1997). These sites were carefully selected by the NS&T Program to avoid point sources and to represent general contamination conditions in the Sound. Sediment samples were also collected at two additional sites, Little Neck Bay (LILN) and

Manhasset Bay (LIMB) (Figure 4.1), where very high chlordane concentrations (>21 ng/g dry weight) were detected during the 1991 sediment toxicity survey conducted by the NS&T Program (Wolfe, Bricher et al. 1994). Sample collection was performed using a Kynar-coated Van-Veen grab sampler (5-6 grabs per site). The top 1 cm sediments from different grabs at a site were collected using a stainless steel flat-bottom scoop. Foreign items like rocks, sticks, mussels etc. were removed from the sediment samples. Several scoops of sediments were mixed in a Teflon beaker.

The homogenized samples were frozen in the field by dry ice in a cooler. Sediment cores were collected at four sites that showed highest chlordane concentrations during past surveys (LITN, LIHH, LILN, and LIMB, Figure 4.2). Core collection followed the methodology established by the U.S. Geological Survey (USGS) (Buchholtz Ten Brink, Mecrey et al. 2001). Briefly, cores of 11-cm diameter and 41-56 cm in length were collected using polycarbonate tubes by scuba divers from the USGS. The lengths of the cores were approximately the depth of clay layers below the sediment surface at these sites. Care was taken to drain the overlying water (using a hand pump) without disturbing the core surfaces. The capped cores were frozen in the field in an insulated storage box with dry ice. The frozen cores were sectioned in the laboratory into slices approximately 1 cm thick using a custom made core extruder and a stainless steel spatula. The sliced core sediments and surficial sediments were stored in a freezer at -20 °C until analysis.

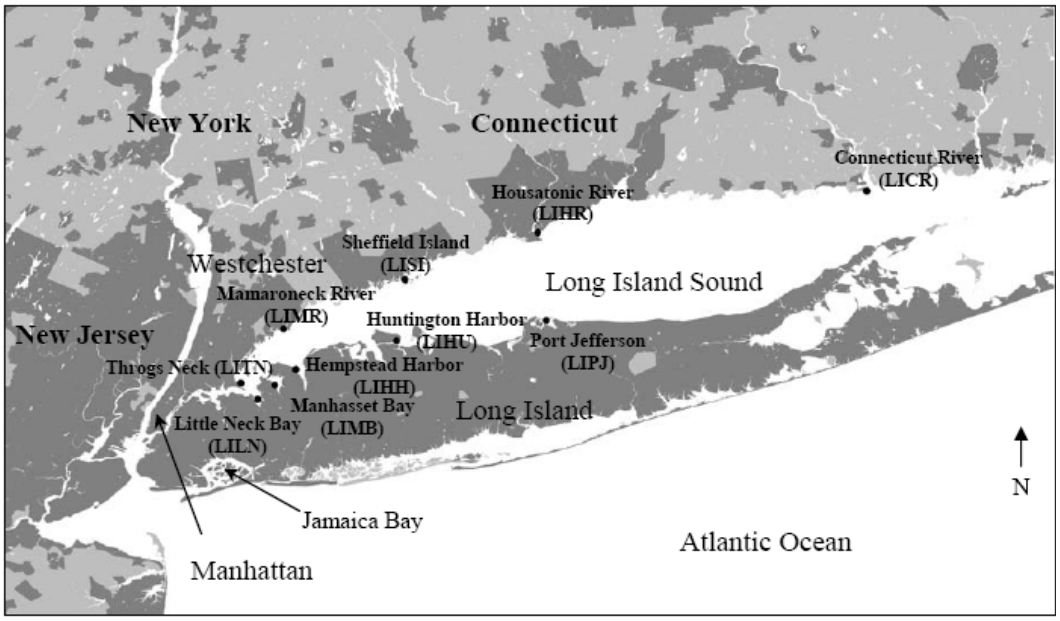

Figure 4.2 Sampling sites in Long Island Sound.

2.1.2 Archived samples

To examine the temporal trends of enantiomeric compositions of TC and CC in surficial sediments, aliquots of archived surficial sediments at five sites (LIHR, LIPJ, LICR, LITN, LIHH) collected by the NS&T Mussel Watch Project were requested from NS&T Specimen Bank (archived samples have abbreviation preceded by "A-"). These sites are geographically scattered around a large portion of the LIS (Figure 4.2).

Therefore, comparison of the enantiomeric compositions of TC and CC in archived and corresponding recent sediments is expected to reflect the overall temporal trend of enantiomeric compositions and concentrations of TC and CC in the Sound. Before they were acquired, the archived surficial sediments were stored in a liquid nitrogen freezer at approximately -150 °C at the specimen bank (Lauenstein, Cantillo et al. 1996; Lauenstein, Cantillo et al. 1997). The sample collection dates and longitudes/latitudes of the archived and recently collected surficial sediments are provided in Table 1. The size

of our sampling vessel prevented access to the exact locations of some archived samples (where water was too shallow for the vessel) (Table 4.1).

TABLE 4.1 Site names, codes, latitudes, longitudes, and collection dates of archived surficial sediments (collected prior to 1990) and recently collected sediments (collected in 2005 and 2006).

Site Code	Site Name	State	Collection Date	Latitude (N)	Longitude (W)
LICR	Connecticut River	CT	01-Apr-2006	41˚15.59'	72˚20.55'
A-LICR	Connecticut River	CT	11-Nov-1986	41°15.83'	72°20.50'
LINH	New Haven	CT	28-Nov-1989	41°15.40′	72°56.67′
LIHR	Housatonic River	CT	09-Apr-2005	41°10.12'	73˚06.42'
A-LIHR	Housatonic River	CT	11-Nov-1986	41˚10.47'	73˚07.23'
LISI	Sheffield Island	CT	09-Apr-2005	41° 03.40'	73° 24.71'
LIMR	Mamaroneck River	NY	09-Apr-2005	40° 56.48'	73° 42.03'
LITN	Throgs Neck	NY	09-Apr-2005	40˚49.15'	73˚48.01'
A-LITN	Throgs Neck	NY	12-Nov-1988	40˚49.17'	73˚48.07'
LIHH	Hempstead Harbor	NY	08-Apr-2005	40˚51.10'	73˚40.21'
A-LIHH	Hempstead Harbor	NY	7-Dec-1987	40°51.15'	73°40.17'
LIHU	Huntington Harbor	NY	25-Mar-2006	40° 55.07'	73° 25.82'
LIPJ	Port Jefferson	NY	01-Apr-2006	40˚57.58'	73˚05.31'
A-LIPJ	Port Jefferson	NY	1-Dec-1989	40˚57.42'	73˚04.96'
LILN	Little Neck Bay	NY	09-Apr-2005	40° 46.61'	73° 45.39'
LIMB	Manhasset Bay	NY	08-Apr-2005	40° 48.57'	73° 42.76'

2.2 Sample extraction and cleanup

The archived and recently collected sediment samples were extracted following EPA standard method 3540C (USEPA 1996). Briefly, the thawed sediment (approximately 10 g) was mixed with 0.5 mL of surrogate standards and ground with 50 g of anhydrous granular sodium sulfate using ceramic mortar and pestle; the mixtures were extracted with 250 mL acetone and hexane (1:1 v/v) using a Soxhlet system for 24 h (4 cycles per hour).

About 5 g of activated copper pellets were added to the flask to remove sulfur. The extracts were then reduced to 1-2 mL using a Turbovap 500 rotary evaporator (Zymark, Boston, MA). The extracts were cleaned by passing through columns (2.5 cm diameter) packed with 20 g of activated Florisil (Supelco, Bellefonte, PA) that was capped with 3-5 cm (about 20 g) of sodium sulfate. The columns were eluted with three fractions, each consisting of 200 mL diethyl ether/hexane of different volume ratios (sequentially, 6/94, 15/85, and 50/50, v/v). Each fraction was concentrated into 1 mL hexane, and fraction 1 was used for concentration and chiral signature analysis.

2.3 Concentration and chiral analysis

2.3.1 Concentration analysis

OCPs in sediments were analyzed using a Fisons GC 8000 gas chromatograph equipped with an AS 800 autosampler and a Fisons ECD-800 Nickel-63 electron capture detector (ECD) (Fisons Instruments SpA, Milan, Italy). A SLB-5ms capillary column of 60 m × 0.25 mm × 0.25 μm (silphenylene polymer virtually equivalent in polarity to poly(5% diphenyl/95% dimethyl siloxane) phase) (Supelco, Bellefonte, PA) was employed. The carrier gas was helium (99.999%) and the pressure was set to 240 kPa.

Samples (2 μL) were injected splitless (split opened 1 minute after injection) at an injector temperature of 280 °C. The oven temperature was held at 100 °C for 2 minutes, ramped to 160 °C at 10 °C/min, then ramped from 160 °C to 290 °C at 5 °C/min, and held at 290 °C for 5 minutes. The detector temperature was set to 300 °C. The makeup gas for the ECD detector was 5.2% methane in argon and the pressure was set at 130 kPa.

2.3.2 Chiral analysis

The enantiomeric compositions of TC and CC (fraction 1) were determined using a TRACE GC-DSQ (Thermo Electron Co., Madison, WI) gas chromatograph-mass spectrometer (GC-MS) operated in a negative ion mode (NIMS). A chiral Betadex-120 column (20% permethylated β-cyclodextrin in SPB-25, 30 m × 0.25 mm ID, 0.25 μm film thickness, Supelco) was used to separate the enantiomers. The instrument was operated in the selected ion monitoring mode at m/z 410 and 412. Samples (2 μL) were injected splitless (split opens after 1 min) at an oven temperature of 90 °C. After a 1-min hold, the oven temperature was ramped to 155 °C at 15 °C/min, to 188 °C at 0.4 °C/min, held for 1 min, ramped to 220 °C at 20 °C/min, and held for 10 min. The temperatures of the injector, the transfer line, and the ion source were set at 220, 220, and 150 °C, respectively. Each sample was injected for 6-9 times to derive the mean and standard deviation, which were used in the two-tailed Student t-test to determine whether two sample means were statistically different. Briefly, a non-negative t-statistic was computed from the observations, and the probability (p) of getting a higher absolute value of the t-statistic under the "same population means" assumption was calculated. A p value of greater than 0.05 was used to indicate that two means are not significantly different (Sachs 1982).

2.3.3 Quality control

OCPs concentrations were quantified using external standards (ranging from 1 ng/mL to 25 ng/mL) and were corrected by the recoveries (ranging from 41 to 57 %) of the surrogate, PCB 166. Each sample was injected three times and the relative standard deviation of three injections was typically within 2%. Analytical blanks, processed using the identical procedure for real samples, were included in every batch of five sediment samples. OCPs concentrations were below detection limit in the blanks. To check the reproducibility of extraction, four replicates of the LIMB surficial sediment were extracted and the relative standard deviation of the four replicates was 7%. To determine the completeness of extraction, the LIMB surficial sediment was extracted a second time immediately after the first extraction. All OCPs were below detection limit in the second extraction. Recoveries of OCPs were also determined by spiking randomly selected sediment samples with about two to five times the native amounts of OCPs. The spiked sediments were extracted, cleaned up and analyzed in the same way as real samples. The final OCPs concentrations corrected by the surrogate (PCB 166) recoveries were typically within ±15% of the final concentrations corrected by the recoveries of spiked OCPs, validating the concentration correction using surrogate recoveries for the rest of the samples. Blanks, prepared using the same procedure as for the real samples, were included for every five samples. No OCPs was found in the blanks.

The enantiomeric compositions of TC and CC are expressed as enantiomeric fractions (EFs), defined as $A_+/(A_+ + A_-)$, where A_+ and A_- are the peak areas of the (+) and (-) enantiomers, respectively. An EF = 0.5 indicates a racemic compound, whereas EFs < 0.5 or >0.5 indicates preferential depletion of the (+) or (-) enantiomers, respectively. The (+) enantiomers of TC and CC are eluting earlier relative to the (-) enantiomers on the

Betadex-120 column (Kurt-Karakus, Bidleman et al. 2005). The enantiomer peaks were automatically integrated using the batch reprocessing function of the software Xcalibur provided by the manufacturer of the GC-MS (Thermo Electron Co.). For the peaks (of a very small number of samples) that were not integrated properly under the batch reprocessing, manual integration was performed. Racemic standards (Ultra Scientific Inc., North Kingstown, RI) were injected at the beginning and the end of a sequence (typically consisting of 12 injections) to determine the reproducibility of the EF analysis. Mean EFs of the standards (10 pg/μL) were 0.501 ± 0.014 for TC (n = 74) and 0.502 ± 0.017 (n = 88) for CC. Monitoring endosulfan I (which interferes with the (-) CC enantiomer on Betadex column) using the m/z 404 ion indicated that this compound was not present in fraction 1 of any sample following florisil cleanup. The following criteria were set as a quality control protocol for acceptable EF values: EF values using each of the two monitored ions (m/z 410 and 412) agree within 5%; area ratios of the two monitored ions for samples and standards agree within 5%. Such criteria have been applied in previous studies (e.g., (Aigner, Leone et al. 1998)).

2.4 Total organic carbon and total nitrogen analysis

The total organic carbon (TOC) and total nitrogen (TN) contents of surficial sediments were determined using a Shimadzu TOC-V total organic carbon analyzer equipped with a Shimadzu nitrogen detector and a Shimadzu SSM-5000A solid sample module (Shimadzu, Columbia, MD). Sediments were dried, ground, and weighed (5-10 mg for each sample) into custom made aluminum sample cups for analysis. Inorganic carbon was removed before measurements by adding 8% sulfurous acid to the aluminum cups to acidify the sediments (Verardo, Froelich et al. 1990). The aluminum cup was put into a ceramic sample boat and covered with ceramic fibers (Shimadzu, Columbia, MD) for

analysis in the instrument's furnace. D(+) Glucose was used to prepare a series of standard solutions in the range of 40-700 mg carbon/100 mL for TOC measurement. Potassium nitrate was used to prepare a series of standard solutions in the range of 7-60 mg/ 100 mL for TN measurement. Air and oxygen (both at a flow rate of 150 mL/min) were used as the carrier gas for the TOC-V and the SSM-5000A, respectively. The combustion furnace temperature was 900 °C.

Aluminum holding block and aluminum cups were baked in a muffle furnace at 550 °C for 24 hours. Ceramic fibers and ceramic sample boats were baked in a muffle furnace at 900 °C for 20 minutes. Two blanks were analyzed every ten samples, no carbon nor nitrogen peak was observed in blanks. The relative standard deviation is typically within 5%.

2.5 Particle size analysis

Particle size analysis of sediments was performed following the pipette method described by Galehouse (Galehouse 1971). Briefly, sediments were dried and ground to break aggregates. Twenty grams of ground sediments were put into a glass bottle. After adding 20 mL of 30% hydrogen peroxide (by 5 mL increment), the mixture was boiled for 15-20 min using a water bath. The bottle was shaken overnight following addition of 20 mL of calgon solution (37.5 g/L sodium metahexaphosphate) to the bottle. The suspension was filtered using a mesh screen with 62.5 μm openings. Sand and gravel remained on the screen and were transferred into a beaker for drying in an oven. Filtrate (containing silt and clay) was held using a 1 L graduated cylinder which was filled to 1 L using Milli-Q water. The suspension in the cylinder was thoroughly mixed, before settling and time counting started. Twenty seconds after counting began (at a temperature

of 21 °C), 20 mL of the suspension was taken by dipping the tip of the pipette 10 cm below the liquid surface. This suspension (containing both silt and clay) was transferred into a beaker and dried in an oven. After 59.38 min, another 20 mL of suspension that contained only clay (size smaller than 3.9 micron) was taken, transferred to a beaker, and dried in an oven. Based on the mass of clay, total mass of clay and silt in 20 mL suspension, and the mass of gravel and sand, fraction of clay, silt, gravel and sand in the sediment were calculated. The mass recovery was above 91% for all samples, with an overwhelming majority over 96%. The final fractions of the three components were adjusted using the mass recovery to yield 100% mass balance.

2.6 ^{137}Cs and ^{210}Pb analysis

To infer the history of chlordane releases to LIS sediments, the sediments from the cores collected at LILN, LITN and LIMB were analyzed for ^{137}Cs and ^{210}Pb by gamma counting. Between 5 and 10 grams of dried, disaggregated sediment was sealed in counting vials and stored for at least 21 days to allow for the in-growth of ^{222}Ra and ^{214}Pb to approximate equilibrium values. Samples were counted for 2-5 d using a Princeton Gamma-Tech Ge well detector (Princeton, NJ), detecting the 46.3 keV ^{210}Pb peak and the 661.6 keV ^{137}Cs peak. Detector efficiencies were determined by counting standards filled to the same vial height as the samples. EPA standard pitchblend ore was used for ^{210}Pb and SLOSH III standard (Olsen 1979) and NIST SRM 4350b were used for ^{137}Cs. Supported ^{210}Pb activities were determined from the total ^{210}Pb activity at the base of the core, whereas excess ^{210}Pb was calculated by subtracting the supported ^{210}Pb from the total ^{210}Pb activity.

The nuclide fluxes from atmospheric fallout were estimated from the ^{90}Sr fallout record measured at New York City, assuming a $^{137}Cs/^{90}Sr$ ratio of 1.5 (http://www.eml.st.dhs.gov/databases/fallout/), and the ^{210}Pb fallout record measured at New Haven, CT (Benninger 1978). Note that there was no detectable ^{60}Co in any of the cores, which is consistent with an atmospheric fallout origin for the ^{137}Cs rather than releases from nuclear power plants in the LIS vicinity (Benoit, Rozan et al. 1999).

Chapter 5

Results and Discussion

1. OCPs in surficial sediments

1.1 Concentrations

Concentrations of *trans*-chlordane (TC) and *cis*-chlordane (CC), dieldrin, *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT in surficial sediments are summarized in Table 5.1. TC and CC concentrations are plotted in Figure 5.1 while concentrations of dieldrin and DDTs (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) are plotted in Figure 5.2.

The data show that organochlorine pesticides were still widely present in the recently collected surficial LIS sediments even after the use of these compounds in the U.S. has been banned for more than 20 years. All the six OCPs were detected in surficial sediments with concentrations ranged from 0.46 (LIHR) to 12.97 (LIMB) ng/g dry weight for TC, from 0.35 (LIHR) to 12.04 (LIMB) ng/g dry weight for CC, from 0.05 (LIHR) to 5.27 (LIMB) ng/g dry weight for dieldrin, from 0.16 (LIHR) to 14.79 (LIMB) ng/g dry weight for *p,p'*-DDE, from 1.60 (LIHR) to 13.35 (LILN) ng/g dry weight for *p,p'*-DDD, and from 0.31 (LIHR) to 6.02 ng/g dry weight (LILN) for *p,p'*-DDT. LILN, LIMB, LITN and LIHH were the most contaminated sites while LINH and LIHR were the least contaminated sites in terms of organochlorine compounds.

TABLE 5.1 Concentrations of organochlorine pesticides in surficial sediments from LIS in ng/g dry weight (mean ± sd, n=3). (Archived sample are labled with an "A")

Site	TC	CC	Dieldrin	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT
A-LINH	0.49±0.08	0.58±0.02	0.19±0.06	0.29±0.05	0.63±0.06	0.39±0.08
LIHR	0.46±0.02	0.35±0.01	0.05±0.03	0.16±0.00	1.60±0.03	0.31±0.05
A-LIHR	2.16±0.17	1.92±0.15	0.70±0.06	4.05±0.27	9.66±0.46	4.80±0.63
LIHU	1.12±0.03	1.10±0.02	0.72±0.04	1.88±0.08	1.61±0.04	1.52±0.72
LISI	1.20±0.05	1.33±0.06	0.23±0.09	2.57±0.06	2.87±0.06	1.33±0.07
LICR	1.48±0.29	1.47±0.04	0.57±0.01	2.78±0.06	1.87±0.03	1.38±0.12
A-LICR	1.64±0.01	1.28±0.04	0.25±0.06	2.13±0.04	2.04±0.04	0.82±0.17
LIPJ	1.69±0.06	1.72±0.04	0.48±0.10	4.00±0.51	2.24±0.08	1.52±0.81
A-LIPJ	1.59±0.18	1.31±0.14	0.26±0.08	2.65±0.43	1.48±0.12	1.43±0.05
LIMR	1.74±0.03	1.81±0.01	0.64±0.07	3.60±0.08	3.23±0.11	1.69±0.22
LITN	3.83±0.17	3.90±0.17	1.65±0.26	8.29±0.08	9.67±0.00	4.05±0.53
A-LITN	2.29±0.03	1.70±0.04	0.67±0.11	1.41±0.04	2.60±0.07	0.94±0.09
LIHH	4.33±0.31	3.55±0.12	1.09±0.31	6.03±0.14	5.80±0.11	2.71±0.25
A-LIHH	11.80±0.17	9.02±0.31	1.94±1.00	13.23±0.21	13.22±0.29	6.11±0.83
LILN	11.18±0.11	8.91±0.35	3.56±0.62	10.29±0.07	13.35±0.10	6.02±0.31
LIMB	12.97±0.23	12.04±0.22	5.27±0.04	14.79±0.20	12.93±0.17	5.46±0.57

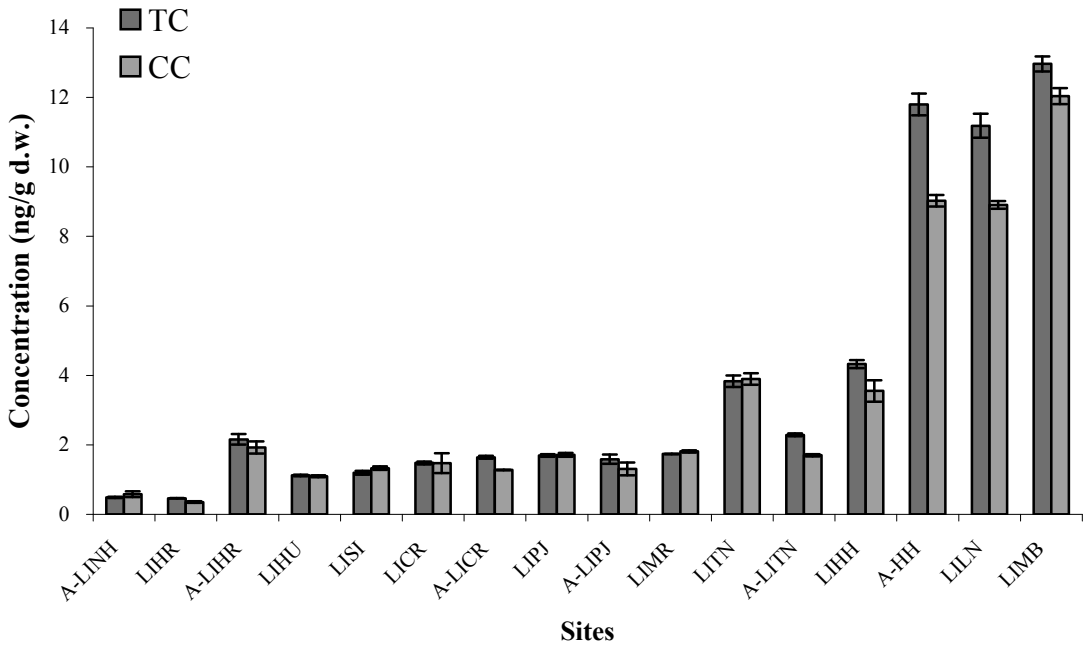

Figure 5.1 Concentrations of trans- and cis-chlordane in LIS surficial sediments.

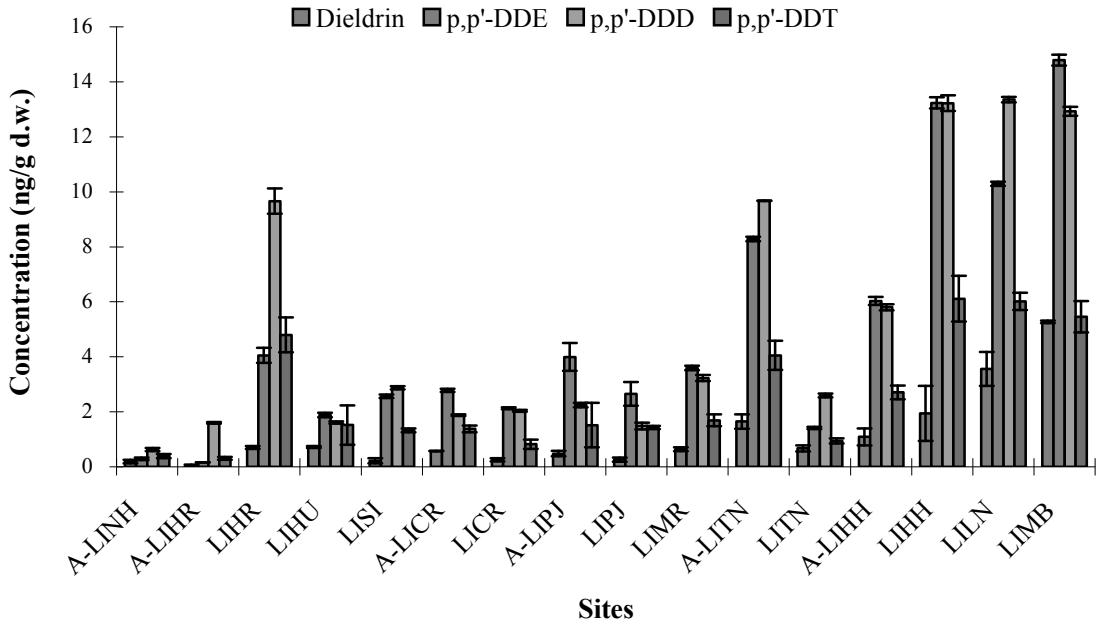

Figure 5.2 Concentrations of dieldrin and DDTs in LIS surficial sediments.

1.2 Geographic distribution

The concentration data showed that sediments in the western part of the Sound were more contaminated than in the eastern part and all three most contaminated sites, LITN, LIMB and LILN are located in the west tip of LIS. A similar trend was also observed in NOAA and USGS's studies (NOAA 2004). OCPs concentrations were the highest at western LIS sites (LITN, LIHH, LILN, and LIMB, Figure 5.1, Figure 5.2), as was observed in previous surveys (Wolfe, Bricher et al. 1994). Higher organochlorine contamination in estuaries near highly urbanized areas in this region (e.g., New York City and Newark) has also been observed by others (Phillips, Riva-Murray et al. 1997; Kennish and Ruppel 1998).

One possible cause for higher OCPs concentrations in western LIS is that OCPs input into western LIS were greater than to the rest of the Sound. The western LIS is close to high population density area like New York City, where more contaminants are expected from wastewater treatment plants, urban runoff, waste disposal, etc. For example, runoff from house foundation soils at western LIS is expected to carry more chlordane due to the greater population (house) density than those from other parts of the Sound.

Another possible reason is that OCPs input into eastern LIS (from riverine/agricultural sources through the Connecticut River and the Housatonic River) were transported to the western LIS by bottom water that flows west and southwest (Knebel, Signell et al. 1999). The OCPs may have then been deposited in the western LIS as a result of quiescent and eutrophic conditions in this sheltered part of the Sound that allow fine-grained, organic-rich material to accumulate. Near-bottom current simulations showed that the tidal currents, locally enhanced by estuarine circulation and wind events, control transport in

the deeper parts of the Sound and promote net westward sediment transport (USGS). Strong water currents remove fine-grained sediments, and the contaminants that are associated with them from sandy, reworked environments and concentrate them in the muddy sediments of the central and western basins of LIS. As a result, contaminant concentrations in western LIS sediment where clayey silt and silty clay are predominant are much higher than those of eastern LIS where gravelly and sandy sediments are dominant (Table 5.2, Figure 5.3).

Similar spatial distribution trends can be seen from TOC profiles and particle size distribution measured for these sediment samples. Indeed, the total organic carbon (TOC) content was highest in the western LIS (Table 5.3, Figure 5.4). Plotting total chlordane concentrations against TOC content yielded a coefficient of determination (R^2) value of 0.68 (Figure 5.5).

Table 5.2 Particle size distribution of surficial sediments.

	Gravel + Sand %	Silt %	Clay %	Silt+ Clay %
LIHR	96.3	0.8	2.9	3.7
A-LITN	91.1	4.4	4.4	8.8
A-LIHR	90.3	4.3	5.4	9.6
A-LIPJ	77.5	15.2	7.2	22.4
LICR	59.4	19.9	20.7	40.6
A-LICR	48.7	45.3	5.8	51.1
LIHU	40.5	21.6	37.9	59.5
LIMR	39.4	34.8	25.8	60.6
LIHH	27.2	31.5	41.4	72.9
LIPJ	24.0	24.0	51.9	75.9
LISI	16.0	44.0	40.0	84.0
LITN	13.4	20.9	65.7	86.6
LIMB	11.6	45.7	42.7	88.4
LILN	10.0	46.4	43.5	89.9
A-LIHH	7.6	58.6	36.0	94.6

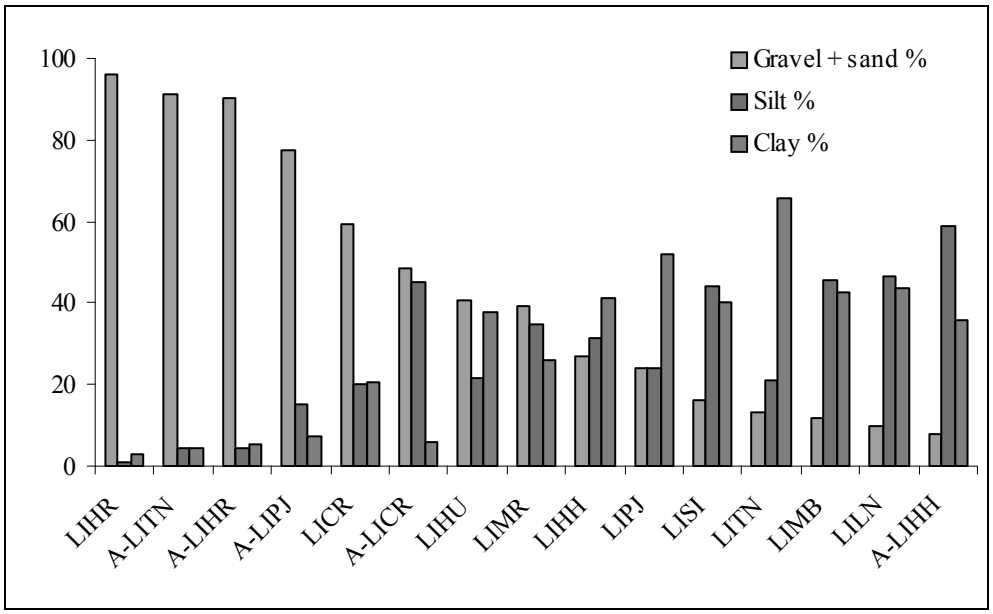

Figure 5.3 Particle size distribution in surficial sediments.

Table 5.3 TOC content in surficial sediments and sediment cores.

Site	TOC%	Site	TOC%
LIHH	2.76	A-LIPJ	1.08
LISI	1.88	LIHR	0.36
LIHR	0.08	A-LITN	0.41
LITN	2.58	A-LINH	0.26
LIMB	4.13	A-LICR	0.90
LILN	1.78	A-LIHH	3.16
LIHU	0.74	LILN	3.09
LICR	0.97	LIPJ	2.49

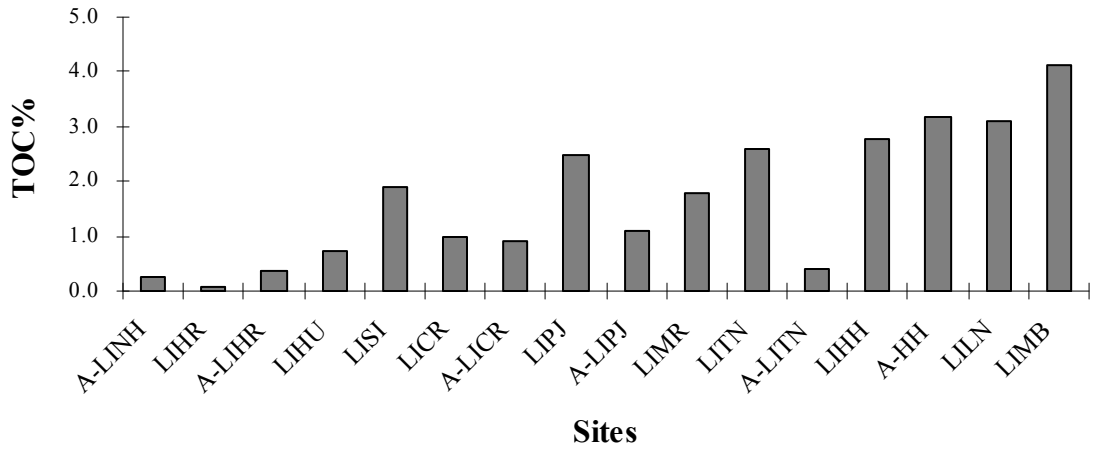

Figure 5.4 TOC content in surficial sediments.

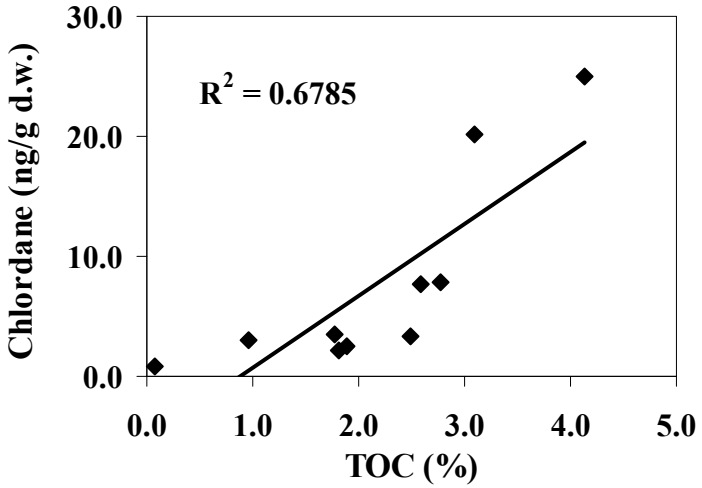

Figure 5.5 Relationship between total chlordane concentrations and TOC contents in surficial sediments in LIS.

1.3 Temporal trends

In order to determine the temporal trends of OCPs in LIS sediments, five archived surficial sediments (A-LIHR, A-LICR, A-LIPJ, A-LITN, A-LIHH) that were collected two decades ago were analyzed, and the data for chlordane concentrations, TOC content,

particle size distribution are summarized together with that for recently collected surficial sediments in Table 5.4 and plotted in Figure 5.1- Figure 5.4.

The observed chlordane concentrations have decreased appreciably at two out of the ten sites since the last survey in the 1990s (by a factor of about five at LIHR and a factor of two at LIMB), decreased slightly at LIMR and LILN, and increased somewhat at the remaining sites (Figure 5.6 and Table 5.4). Similar trends were observed for dieldrin and DDTs (*p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT). When compared to the archived sediments, the dieldrin and DDTs concentrations in recently collected sediments have decreased appreciably at one out of the five sites (by a factor of about four at LITN), decreased slightly at LICR and LIPJ, and increased at two sites (by a factor of five at LIHR and two at LIHH) (Figure 5.2 and Table 5.1).

These observations indicate that overall OCPs concentrations in surficial sediments did not decrease significantly in the past decade, consistent with the near-constant chlordane concentrations in mussel tissues in the past decade (Figure 5.7). OCPs concentration increases at some sites in the past decade may be due to spatial variations in OCPs concentrations (e.g., sampling locations were a few to a few hundred meters apart between this and previous surveys, Table 5.4). OCPs concentration increases may also be caused by the differences in sample extraction and analysis. Ratios of CC concentrations of archived sediments obtained in this study to the corresponding concentrations from NOAA ranged from about 0.6 (LITN) to 3.0 (LIPJ), indicating that different analytical procedures (e.g., NOAA's values were not corrected by surrogate) may indeed yield significantly different concentration values for the same sediment (Table 5.4).

Table 5.4 Sample locations, chlordane concentrations, total organic carbon (TOC) content, and particle size distribution of the surficial sediments.

Site Name	Site Code	Collection Date	Latitude (N)	Longitude (W)	CC (ng/g d.w.)	TC (ng/g d.w.)	TOC (%)	Particle Size Distribution		
								Gravel + Sand (%)	Silt (%)	Clay (%)
Housatonic River	LIHR	09-Apr-2005	41°10.12'	73°06.42'	0.35	0.46	0.08	96.3	0.8	2.9
	A-LIHR	11-Nov-1986	41°10.47'	73°07.23'	1.92 (2.56[a])	2.16	0.36 (0.37[a])	90.3	4.3	5.4
Throgs Neck	LITN	09-Apr-2005	40°49.15'	73°48.01'	3.90	3.83	2.58	13.4	20.9	65.7
	A-LITN	12-Nov-1988	40°49.17'	73°48.07'	1.70 (2.94[a])	2.29	0.41 (0.41[a])	91.1	4.4	4.4
Hempstead Harbor	LIHH	08-Apr-2005	40°51.10'	73°40.21'	3.55	4.33	2.77	27.2	31.5	41.4
	A-LIHH	7-Dec-1987	40°51.15'	73°40.17'	9.02 (4.87[a])	11.80	3.16 (3.63[a])	7.6	58.6	36.0
Port Jefferson	LIPJ	01-Apr-2006	40°57.58'	73°05.31'	1.72	1.69	2.49	24.0	24.0	51.9
	A-LIPJ	1-Dec-1989	40°57.42'	73°04.96'	1.31 (0.44[a])	1.59	1.08 (0.76[a])	77.5	15.2	7.2
Connecticut River	LICR	01-Apr-2006	41°15.59'	72°20.55'	1.28	1.64	0.97	59.4	19.9	20.7
	A-LICR	11-Nov-1986	41°15.83'	72°20.50'	1.47 (0.76[a])	1.48	0.90 (0.99[a])	48.7	45.3	5.8
Sheffield Island	LISI	09-Apr-2005	41° 03.40'	73° 24.71'	1.33	1.20	1.88	16.0	44.0	40.0
Mamaroneck River	LIMR	09-Apr-2005	40° 56.48'	73° 42.03'	1.81	1.74	1.78	39.4	34.8	25.8
Huntington Harbor	LIHU	25-Mar-2006	40° 55.07'	73° 25.82'	1.10	1.12	1.81	40.5	21.6	37.9
Little Neck Bay	LILN	09-Apr-2005	40° 46.61'	73° 45.39'	8.91	11.18	3.09	10.0	46.4	43.5
Manhasset Bay	LIMB	08-Apr-2005	40° 48.57'	73° 42.76'	12.04	12.97	4.13	11.6	45.7	42.7

[a]Values are taken from the website of NOAA's Mussel Watch Project (http://egisws01.nos.noaa.gov/website/nsandt/mw/viewer.htm). Other concentrations were obtained in this work.

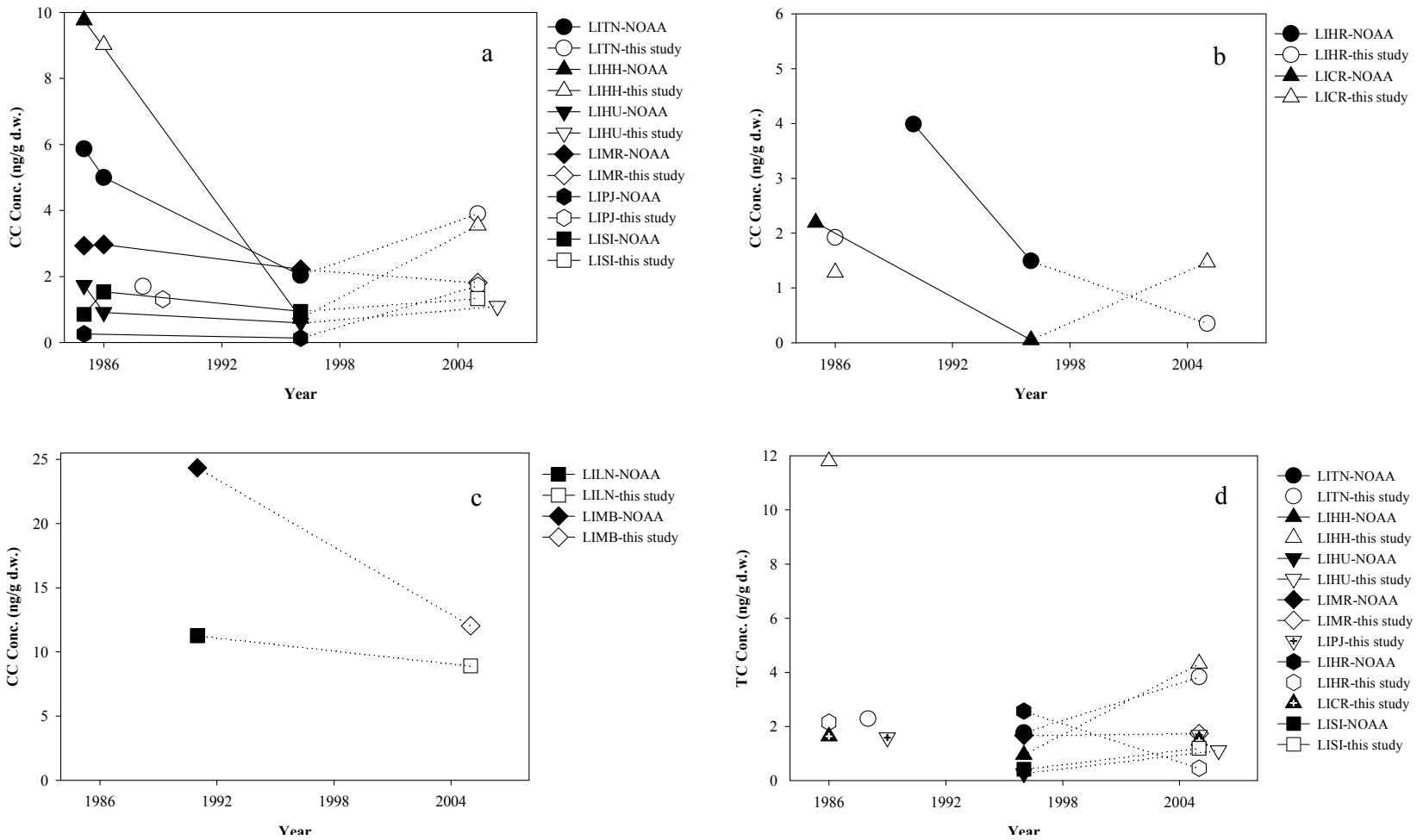

Figure 5.6 *cis*-Chlordane (a-c) and *trans*-chlordane (d) concentrations in surficial sediments from mid-1980s to 2006. Chlordane concentrations prior to 2005 were obtained from the website of NOAA's Mussel Watch Project (http://egisws01.nos.noaa.gov/website/nsandt/mw/viewer.htm), or when applicable, from the analysis of the archived sediment samples in this study (Table S1).

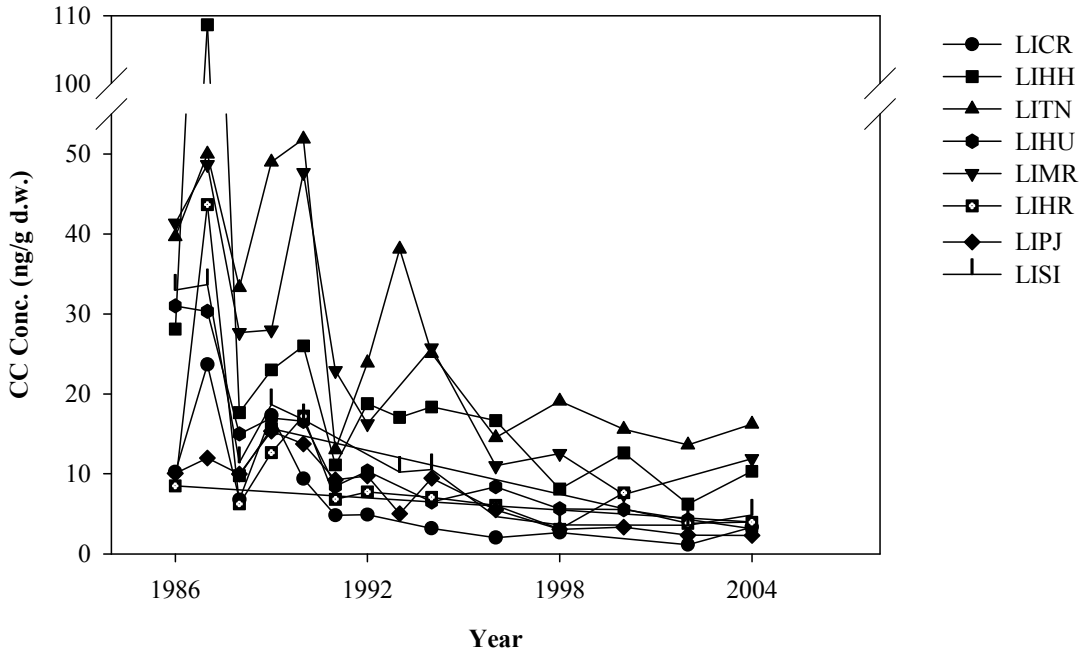

Figure 5.7 *cis*-Chlordane concentrations in bivalve (*Mytilus edulis*) tissues from the mid-1980s to 2004 at various LIS sites. The concentration values were adopted from the website of NOAA's Mussel Watch Project (http://egisws01.nos.noaa.gov/website/nsandt/mw/viewer.htm).

1.4 Sediment quality guidelines

Sediment quality issues are an important focus in the assessment, protection, and management of aquatic ecosystems. Because sediments influence the fate of many chemicals, concern exists about the potential impact on organisms that are exposed to sediments with elevated chemical concentrations. To address this concern, environmental managers require practical, scientific tools with which to evaluate the potential impacts of sediment-associated chemicals on various resource uses.

Numerical sediment quality guidelines (SQGs; including sediment quality criteria, sediment quality objectives, and sediment quality standards) have been developed by various federal, state, and provincial agencies in North America for both freshwater and

marine ecosystems. Guidelines for assessing sediment quality relative to the potential for adverse effects on sediment-dwelling organisms in freshwater systems have been derived using a combination of theoretical and empirical approaches, primarily including the equilibrium partitioning approach (EqPA) (Di Toro, Zarba et al. 1991; NYSDEC 1994; USEPA 1997), screening level concentration approach (SLCA) (Persaud, Jaagumagi et al. 1993), effects range approach (ERA) (Long and Morgan 1991; Ingersoll, Haverland et al. 1996), effects level approach (ELA) (Ingersoll, Haverland et al. 1996; Smith, MacDonald et al. 1996), and apparent effects threshold approach (AETA) (Cubbage, Batts et al. 1997). Application of these methods has resulted in the derivation of numerical SQGs for many chemicals of potential concern in freshwater sediments.

The previously published SQGs for the protection of sediment-dwelling organisms in freshwater ecosystems were grouped into two categories according to their original narrative intent, including TECs (threshold effect concentrations, below which adverse effects are not expected to occur) and PECs (probable effect concentrations, above which adverse effects are expected to occur more often than not). The TECs were intended to identify contaminant concentrations below which harmful effects on sediment dwelling organisms were not expected. TECs include threshold effect levels (TELs) (Smith, MacDonald et al. 1996; USEPA 1996), effect range low values (ERLs) (Long and Morgan 1991), lowest effect levels (LELs) (Persaud, Jaagumagi et al. 1993), minimal effect thresholds (METs) (EC and MENVIQ 1992), and sediment quality advisory levels (SQALs) (USEPA 1997). The PECs were intended to identify contaminant concentrations above which harmful effects on sediment-dwelling organisms were expected to occur frequently (MacDonald, Carr et al. 1996; Swartz 1999). PECs include

probable effect levels (PELs) (Smith, MacDonald et al. 1996; USEPA 1996), effect range median values (ERMs) (Long and Morgan 1991); severe effect levels (SELs) (Persaud, Jaagumagi et al. 1993), and toxic effect thresholds (TETs) (EC and MENVIQ 1992). Some TEC and PEC values for the 6 OCPs are summarized in Table 5.5.

Table 5.5 Sediment quality guidelines for the OCPs in ng/g d.w. (MacDonald, Carr et al. 1996; Smith, MacDonald et al. 1996; Wurl and Obbard 2005).

	TEL	ERL	PEL	ERM
p,p'-DDD	3.54	2	8.51	20
p,p'-DDE	1.42	2	6.75	15
p,p'-DDT	1.19	1	4.77	7
Dieldrin	2.85	0.02	6.67	8
Total Chlordane [a]	2.26	0.5	4.79	6

a: sum of *cis*-chlordane and *trans*-chlordane.

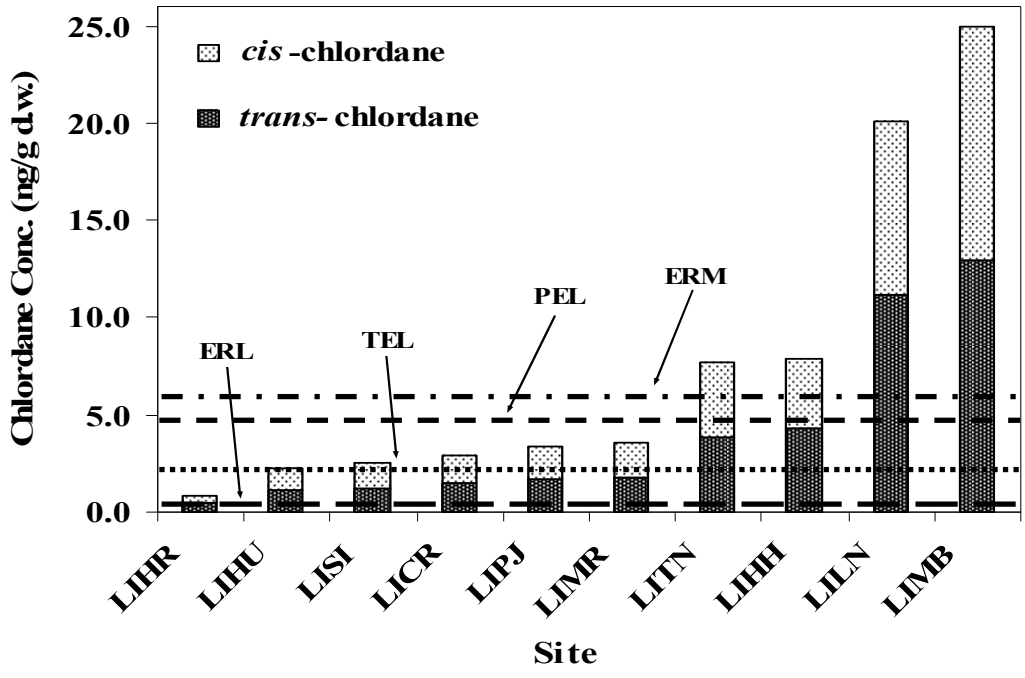

Figure 5.8 Concentrations of trans- and cis- chlordane and corresponding SQGs.

Chlordane concentrations exceeded the effect range-low (ERL) value at all ten sites, and exceeded the threshold effect level (TEL) at all sites except LIHR. Chlordane

concentrations at four most western LIS sites (LITN, LIHH, LILN, and LIMB) also exceeded the probable effect level (PEL) and the effect range-median (ERM) value (Figure 5.8). Dieldrin concentrations exceeded the effect range-low (ERL) value at all sites, and exceeded the threshold effect level (TEL) at two western LIS sites (LILN and LIMB). *p,p'*-DDE concentrations exceeded the effect range-low (ERL) value at all sites except LIHR and LIHU, and exceeded the threshold effect level (TEL) at all sites except LIHR. *p,p'*-DDE concentrations at two most western LIS sites (LITN and LIMB) also exceeded the probable effect level (PEL). *p,p'*-DDD concentrations exceeded the effect range-low (ERL) value at all sites except three sites (LIHR, LIHU and LICR), and exceeded the threshold effect level (TEL) at four most western sites (LITN, LIHH, LILN and LIMB). *p,p'*-DDD concentrations at three most western LIS sites (LITN, LILN and LIMB) also exceeded the probable effect level (PEL). *p,p'*-DDT concentrations exceeded both the effect range-low (ERL) value and the threshold effect level (TEL) at all sites except one site (LIHR). *p,p'*-DDT concentrations at two most western LIS sites (LILN and LIMB) also exceeded the probable effect level (PEL) (Figure A.1).

The ERL and TEL represent the chemical concentrations below which adverse effects would be rarely observed, whereas the PEL and ERM represent the contaminant concentrations above which adverse effects would frequently occur (MacDonald, Carr et al. 1996; Smith, MacDonald et al. 1996). Therefore, Figure 5.8 and Figure 5.9 clearly indicate that sediment toxicity by OCPs exists at all sites sampled and OCPs still poses significant threats to benthic organisms at the western LIS, even after the use of OCPs has been completely banned for nearly two decades in the U.S.

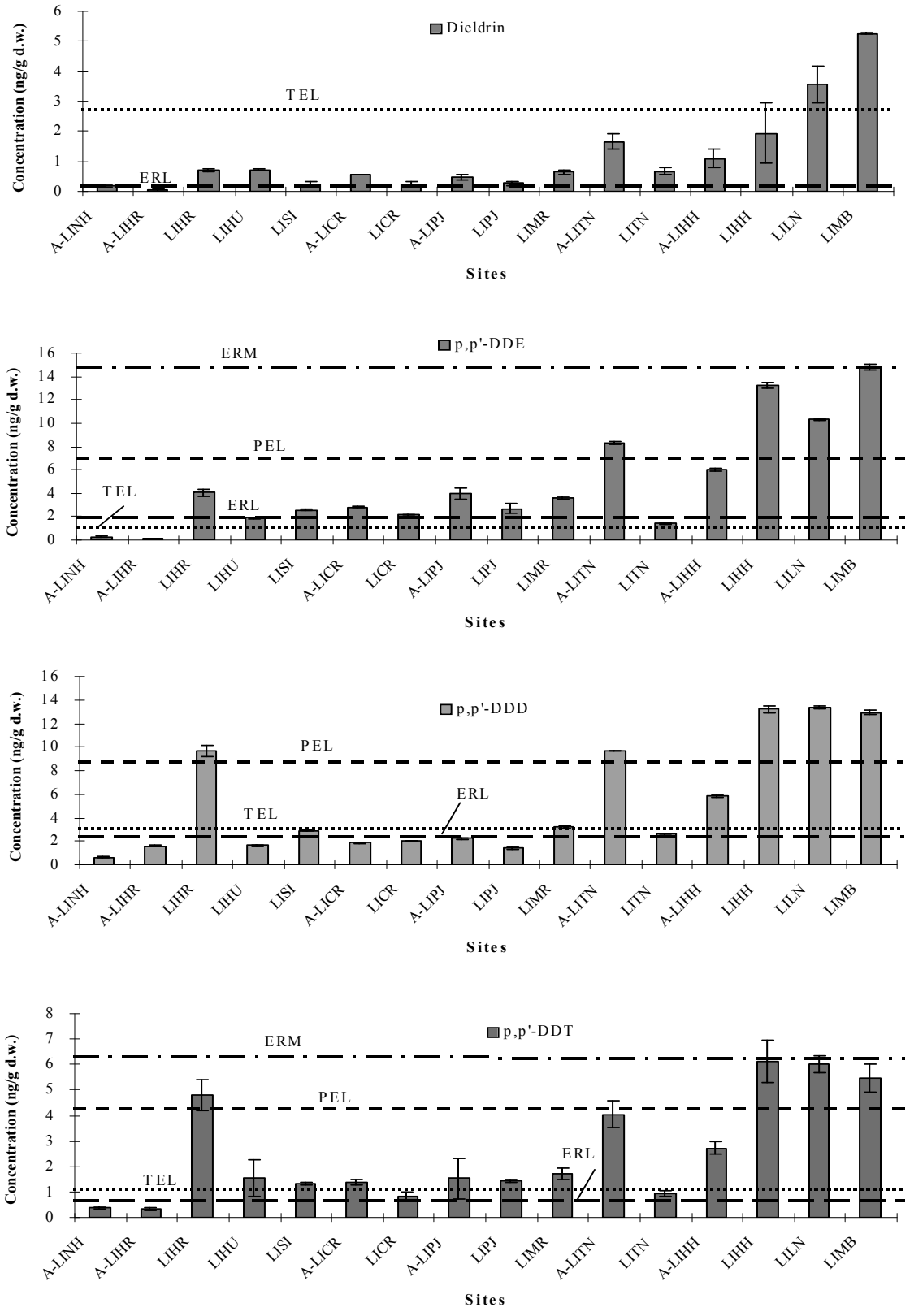

Figure 5.9 OCPs concentrations and corresponding SQGs

2. OCPs in sediment cores

2.1 Concentration profiles

The concentration-depth profiles of *trans*-chlordane and *cis*-chlordane are plotted in Figure 5.10. Both chlordanes follow similar trend in the four cores. In LIMB core, chlordane concentration increased from about 10 ng/g at the surface to a maximum value of about 15 ng/g at the depth of 30 cm, and then dropped to about 3 ng/g at a depth of about 50 cm. In LILN core, chlordane concentration maintained at a relatively constant level from the sediment surface down to a depth of about 50 cm and there were no clear peaks in the profiles. LIHH core followed similar trends as the LIMB core with the chlordane concentration increased from about 4 ng/g at the surface to a maximum value of about 8 ng/g at the depth close to 30 cm, and then dropped to about 4 ng/g at a depth close to 40 cm. In LITN core, chlordane concentration maintained at a relatively constant level from the sediment surface down to about 30 cm, and then dropped to near zero values at a depth close to 60 cm.

The concentration-depth profiles of dieldrin and DDTs are plotted in Figure 5.11. In LIMB core, the concentration profiles for dieldrin and *p,p'*-DDT were relatively constant, whereas the concentrations for *p,p'*-DDD and *p,p'*-DDE increased slowly from surface down to 40 cm and then decreased quickly afterwards. In LILN core, dieldrin concentration remained fairly constant across the depth, whereas the other three OCPs increased gradually down to about 30 cm, and then remained relatively constant. In LIHH core, the concentrations of the four OCPs increased gradually from surface down to 40 cm. In LITN core, the *p,p'*-DDD and *p,p'*-DDE concentration peaked at around 25 cm, and then dropped quickly after 40 cm. The profiles for dieldrin and *p,p'*-DDT were quite

constant from surface to 35 cm, and the concentrations decreased slowly afterwards. Regardless of these differences, the concentration profiles showed that OCPs were present in every depth of the four sediment cores, and indicated that significant sediment mixing may have occurred (i.e., no clear sharp contaminant peaks). The differences in the OCPs profiles at the four sites may be partly due to the variations in the magnitude of sediment mixing and sediment deposition at these sites.

Sediment mixing may be caused by bottom currents driven by tide, wind or wave. It also can be caused by storm events, sediment reworking, or spring turnover (Nowell, Capel et al. 1999). Bioturbation caused by small organisms living on the sea floor is another factor that contributes to the mixing of the sediment cores. Such sediment mixing was supported by ^{137}Cs and ^{210}Pb isotope data. Activities of ^{137}Cs and ^{210}Pb in sediment cores were determined and simulated by an advection-diffusion model. The modeling results indicated that both bioturbation (up to 19 cm) and sedimentation (0.7-0.9 cm yr^{-1}) were occurring at western LIS. Sediment mixing would bring highly contaminated sediment at depth to the surface, leading to persistent surficial contaminant concentrations even when there was no new source of input. The presence of sediment mixing, however, cannot rule out the possibility of new input of OCPs into the Sound. The new input of contaminants may include run off from urban and agricultural soils, seepage of old landfills, and/or atmospheric deposition.

TABLE 5.6 Concentrations of OCPs in ng/g dry weight (mean ± sd, n=3) of sediment cores from LIS.

Site	Depth / cm	TC	CC	Dieldrin	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT
LIMB	0.6	11.50±0.98	8.63±0.24	4.32±0.22	14.48±0.11	11.65±0.26	2.42±0.28
LIMB	6.1	11.64±0.56	10.60±0.61	11.71±0.49	22.83±0.56	19.69±1.40	11.10±0.04
LIMB	11.7	11.80±1.01	9.75±0.86	4.44±0.85	17.08±1.82	14.34±1.36	5.37±0.13
LIMB	17.2	14.99±0.40	12.33±0.29	5.24±0.29	20.59±0.31	17.41±0.10	7.47±0.68
LIMB	22.8	14.49±0.18	11.68±0.21	7.68±0.94	25.92±0.33	20.93±0.19	7.22±1.15
LIMB	28.3	17.68±0.68	12.96±0.47	6.14±0.14	27.72±0.27	20.86±0.27	7.18±0.89
LIMB	33.9	10.63±0.36	8.39±0.26	4.80±0.19	24.36±0.53	17.08±0.46	7.07±0.19
LIMB	39.4	8.09±0.70	6.81±0.42	5.69±0.94	35.24±0.98	22.80±0.89	8.32±0.69
LIMB	45.0	2.47±0.16	2.32±0.09	1.31±0.01	19.95±0.18	13.55±0.36	2.78±0.09
LIMB	49.4	3.08±0.08	2.60±0.13	2.56±0.11	10.03±0.09	9.59±0.32	2.63±0.36
LILN	0.6	10.79±1.03	10.11±0.29	4.99±0.37	17.26±1.46	19.15±1.27	7.17±0.57
LILN	3.9	13.35±0.77	9.29±0.46	3.66±0.25	10.65±0.24	16.69±1.55	2.55±0.23
LILN	6.1	14.04±0.95	9.66±0.24	5.59±0.96	12.80±0.64	19.50±0.90	13.50±0.81
LILN	11.7	12.33±0.40	8.28±0.06	5.51±0.34	11.45±0.07	17.79±0.22	5.02±0.05
LILN	17.2	13.47±0.69	8.99±0.16	5.66±0.29	13.38±0.44	20.30±0.63	6.14±0.69
LILN	22.8	15.09±0.98	9.33±0.24	5.77±0.46	15.92±0.15	25.07±0.95	8.94±1.27
LILN	28.3	14.47±0.66	10.63±0.39	5.28±0.29	17.37±0.68	25.00±1.18	10.90±0.80
LILN	32.7	14.73±0.31	11.80±0.20	3.86±0.12	15.48±0.33	20.97±1.02	4.29±0.51
LILN	33.9	12.89±0.41	10.33±0.50	4.55±0.09	15.66±0.07	20.22±0.76	5.69±0.31
LILN	35.0	16.52±0.44	13.51±0.14	4.32±0.17	16.41±0.55	23.90±1.31	5.31±0.43
LILN	39.4	14.84±1.03	12.00±0.88	6.64±0.69	17.19±0.74	23.90±0.87	6.74±0.49
LILN	43.8	13.18±0.28	11.43±0.59	3.38±0.11	15.99±0.42	20.36±0.92	4.19±0.54
LILN	45.0	12.27±0.79	10.57±0.37	5.29±0.45	16.67±0.63	23.66±0.99	14.08±1.48
LILN	46.1	13.38±0.11	11.82±1.00	3.54±0.10	14.94±0.38	20.19±0.95	4.55±0.44
LILN	50.5	14.82±0.31	10.25±0.13	4.89±0.10	17.78±0.29	24.57±0.53	8.39±0.66

LIHH	0.6	4.10±0.05	3.90±0.04	1.81±0.08	6.03±0.21	5.55±0.05	2.73±0.06
LIHH	5.3	3.25±0.24	3.57±0.28	1.30±0.18	6.92±0.12	6.57±0.22	2.65±0.35
LIHH	11.1	4.12±0.28	4.07±0.31	1.90±0.13	10.70±0.11	7.51±0.25	3.17±0.33
LIHH	17.0	4.94±0.27	4.65±0.27	3.13±0.09	11.70±0.39	9.45±0.03	4.10±0.10
LIHH	22.8	5.17±0.26	4.97±0.20	2.77±0.11	12.93±0.24	9.34±0.37	4.16±0.55
LIHH	27.2	8.20±0.57	7.56±0.56	3.96±0.10	17.74±0.32	12.36±0.11	5.56±0.53
LIHH	32.8	3.09±0.27	2.49±0.27	1.92±0.04	8.74±0.12	5.20±0.07	2.82±0.26
LIHH	38.3	3.71±0.29	3.35±0.45	5.44±0.10	26.56±0.54	15.28±0.67	8.50±0.71
LITN	1.8	4.55±0.36	4.14±0.41	1.84±0.15	9.43±0.42	8.28±0.54	4.85±0.39
LITN	6.4	4.41±0.38	3.84±0.16	1.82±0.39	10.05±0.33	9.48±0.38	5.38±0.49
LITN	13.5	4.18±0.51	3.38±0.46	2.07±0.20	11.87±0.50	9.74±1.25	5.14±1.05
LITN	18.1	5.27±0.11	4.39±0.05	1.06±0.08	15.97±0.09	13.38±1.41	5.00±0.65
LITN	24.0	4.17±0.57	3.86±0.54	1.97±0.16	12.31±0.72	11.94±0.97	4.62±0.72
LITN	29.8	4.32±0.19	3.77±0.56	1.93±0.03	11.11±0.30	10.20±0.93	4.96±0.26
LITN	35.7	5.85±0.18	3.91±0.01	1.65±0.05	10.66±0.29	9.62±1.31	1.97±0.07
LITN	41.5	1.39±0.70	1.09±0.13	0.05±0.04	2.79±0.33	1.30±0.39	1.44±0.42
LITN	47.4	0.42±0.01	0.37±0.02	0.12±0.07	0.71±0.02	0.70±0.54	0.42±0.08
LITN	52.1	0.19±0.02	0.26±0.01	0.06±0.03	0.52±0.02	0.49±0.67	0.10±0.04
LITN	55.6	0.11±0.01	0.16±0.01	0.10±0.03	0.34±0.04	0.69±0.62	0.08±0.01

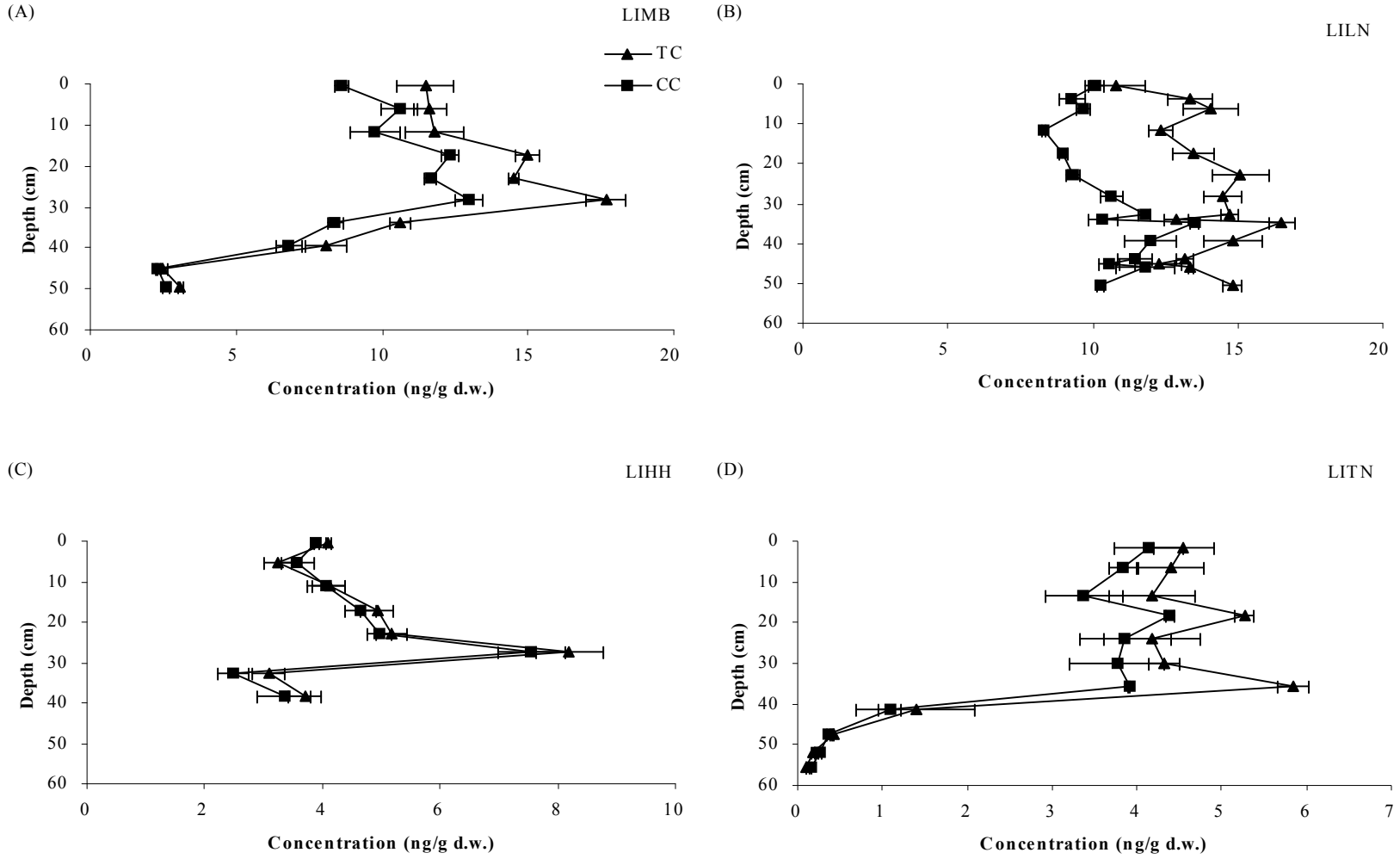

Figure 5.10 Concentration profiles of trans-chlordane (TC) and cis-chlordane (CC) in sediment cores.

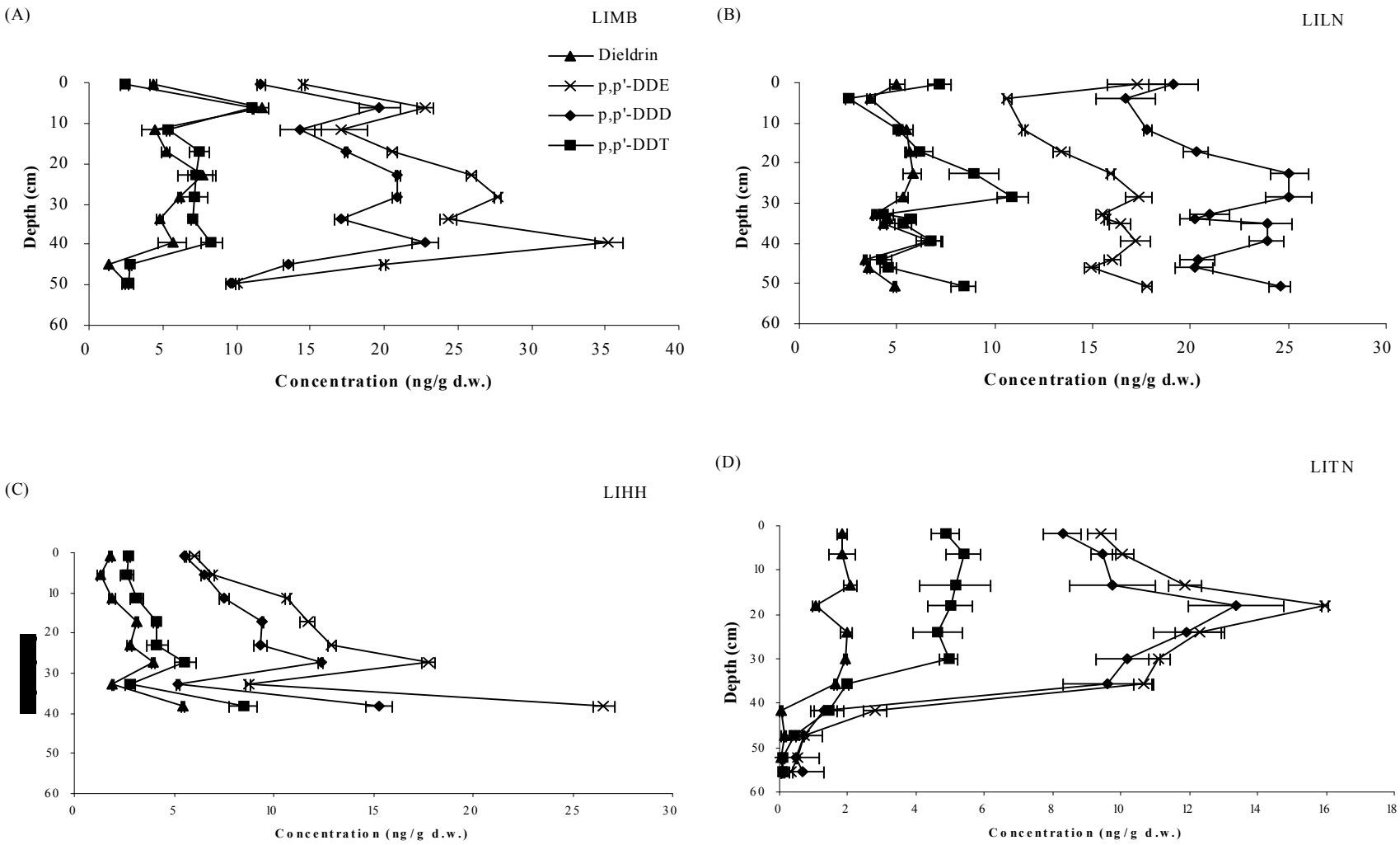

Figure 5.11 Concentration profiles of dieldrin and DDTs in sediment cores.

2.2 Total organic carbon (TOC) and total nitrogen (TN) profiles

Total organic carbon (TOC) content in two sediment cores (LIMB and LITN) and total nitrogen content in one sediment core (LITN) are summarized in Table 5.7 and plotted in Figure 5.12.

TN profiles are similar to the TOC profiles and they all show a gradual decrease with depth. Unlike the surficial sediments, there was no clear relationship between chlordane concentrations and TOC content in the cores.

TABLE 5.7 TOC and TN content in sediment cores.

LIMB		LITN		
Depth/cm	TOC%	Depth/cm	TOC%	TN%
0.6	4.27	0.6	3.00	0.29
6.1	3.90	7.6	2.45	0.30
11.7	3.90	21.7	2.91	0.29
17.2	3.78	25.2	2.64	0.28
22.8	3.47	28.7	2.42	0.26
28.3	3.55	32.2	1.91	0.18
33.9	3.47	39.2	1.19	0.18
39.4	2.61	42.7	1.33	0.18
45.0	2.84	46.2	0.79	0.15
49.4	3.34	49.7	1.05	0.18
		53.2	0.47	0.10
		55.6	0.37	0.08

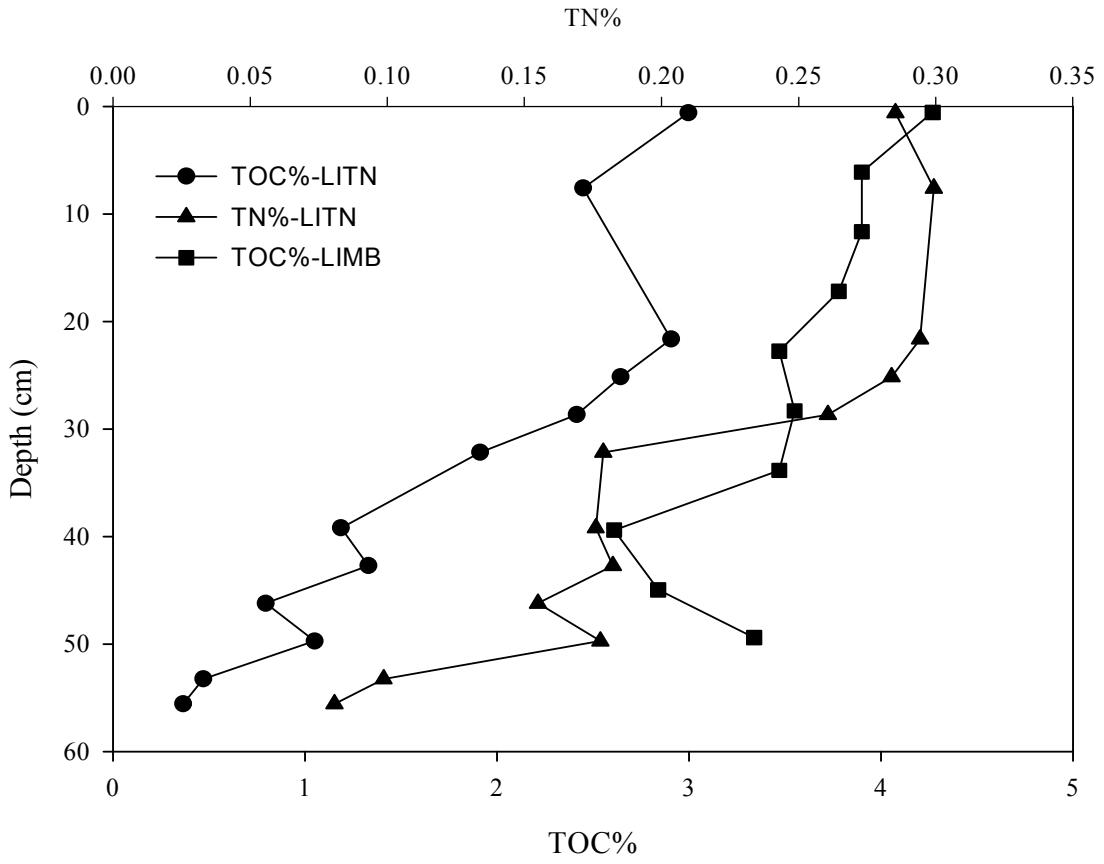

Figure 5.12 TOC and TN profiles in sediment cores at site LITN and LIMB.

2.3 Composition of DDTs

DDT persists in the environment with a half-life of 20-30 years. DDE and DDD are two stable and toxic degradation metabolites of DDT. The rate of degradation depends on several factors including sediment type, temperature and organic carbon content (Hitch and Day 1992). The composition of total DDT residues detected in bed sediment or aquatic biota from a given hydrologic system may provide information on the likely source of the residues and the length of time the residues have been in that system. Because DDT is expected to degrade to its fairly stable products DDD and DDE in soil, the DDT/total DDTs ratio has been used as an indicator of the length of time that the

DDT residues have been in the environment (White and Krynitsky 1986). In general, a small value of DDT: ΣDDTs ratio is indicative of aged DDT and a value close to one indicates fresh application (Hitch and Day 1992).

The values of ΣDDTs (the sum of *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT) and the ratio of DDT: ΣDDTs in surficial sediments and sediment cores from LIS are listed in Table 1. The ratios ranged from 0.16 to 0.30 for surficial sediments and from 0.07 to 0.26 for core sediments. Since the use of DDT in the United States has been limited to emergency situations since 1973, it is no surprise to see such small ratios in LIS sediments. In comparison ratios in the range of 0.31 to 0.52 are reported in Alabama soils (Harner, Wideman et al. 1999). However, there was no obvious decreasing trend of the ratios from top to bottom of the sediment cores, which might indicate the existence of some sediment mixing.

From the National Contaminant Biomonitoring Program database, *p,p'*-DDD/*p,p'*-DDE ratio can be calculated for a large number of samples of which 80% of the ratio is lower than one (Schmitt, Zajicek et al. 1990). This ratio was below one in three sediment cores (LIMB, LIHH and LITN), but was higher than one in all depths at the LILN site. In addition to being a DDT metabolite, *p,p'*-DDD was formulated and applied as a pesticide in the United States, sold under the names of "Rothane" or TDE (ATSDR). Therefore, it is possible that *p,p'*-DDD could have been applied near site LILN, resulting in higher *p,p'*-DDD concentration.

TABLE 5.8 The values of ΣDDTs (the sum of *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT) and the ratio of *p,p'*-DDT: ΣDDTs in surficial sediments and sediment cores from LIS.

Site	Depth / cm	ΣDDTs	*p,p'*-DDT/ ΣDDTs	Site	Depth / cm	ΣDDTs	*p,p'*-DDT/ ΣDDTs
LIHR	Surficial	1.53	0.20	LILN	22.8	49.93	0.18
A-HR	Surficial	18.51	0.26	LILN	28.3	53.28	0.20
LIHU	Surficial	5.02	0.30	LILN	32.8	40.73	0.11
LISI	Surficial	6.77	0.20	LILN	33.9	41.57	0.14
LICR	Surficial	6.03	0.23	LILN	35.0	45.62	0.12
A-CR	Surficial	4.99	0.16	LILN	39.4	47.84	0.14
LIPJ	Surficial	7.76	0.20	LILN	43.9	40.54	0.10
A-PJ	Surficial	5.57	0.26	LILN	46.1	39.67	0.11
LIMR	Surficial	8.52	0.20	LILN	50.5	50.75	0.17
LITN	Surficial	22.01	0.18	LIHH	0.6	14.31	0.19
A-TN	Surficial	4.95	0.19	LIHH	5.3	16.14	0.16
LIHH	Surficial	14.54	0.19	LIHH	11.1	21.37	0.15
A-HH	Surficial	32.57	0.19	LIHH	17.0	25.24	0.16
LILN	Surficial	29.66	0.20	LIHH	22.8	26.43	0.16
LIMB	Surficial	33.18	0.16	LIHH	27.2	35.66	0.16
LIMB	0.6	28.55	0.08	LIHH	32.8	16.75	0.17
LIMB	6.1	53.62	0.21	LIHH	38.3	50.34	0.17
LIMB	11.7	36.79	0.15	LITN	1.8	22.57	0.22
LIMB	17.2	48.91	0.22	LITN	6.4	24.91	0.22
LIMB	22.8	54.07	0.13	LITN	13.5	26.76	0.19
LIMB	28.3	55.75	0.13	LITN	18.1	34.35	0.15
LIMB	33.9	48.51	0.15	LITN	24.0	28.88	0.16
LIMB	39.4	66.36	0.13	LITN	29.8	26.27	0.19
LIMB	45.0	36.28	0.08	LITN	35.7	22.25	0.09
LIMB	49.4	22.25	0.12	LITN	41.5	5.53	0.26
LILN	0.6	43.58	0.16	LITN	47.4	1.82	0.23
LILN	3.9	29.89	0.09	LITN	52.1	1.11	0.09
LILN	11.7	34.26	0.15	LITN	55.6	1.11	0.07
LILN	17.2	39.83	0.15				

Comparing to other US coastal and estuarine areas, sediments from LIS are highly polluted, especially in the western part of the Sound. According to the Coastal Sediment Database (COSED), which contains data from 13500 US coastal sediment samples, the 'high' concentration for total DDTs is 22 ng/g (Daskalakis and O'Connor 1995). In this study, the total DDTs concentrations in LIS surficial sediments ranged from 1.53 to 33.18 ng/g (Table 5.8), with a geometric mean of 9.6 ng/g. The concentrations of 5 out of 15 surficial sediment samples were above the 'high' level. The total DDTs concentrations in LIS sediment cores ranged from 1.11 to 66.36 ng/g (Table 5.8), with a geometric mean of 26.13 ng/g. The concentrations of 35 out of 42 sediment core samples are above the 'high' level. Nation wide, based on NOAA's National Status and Trends' Benthic Surveillance Program and Mussel Watch Program, about 20% of US coastal and estuarine areas have concentrations above 'high'. Only 2% of US coastal and estuarine areas have concentrations exceeding the '5×high' (five times 'high', 110 ng/g for total DDTs) (Daskalakis and O'Connor 1995), of which 40% are located in the New York Bight and 20% are located in the San Francisco Bay. The total DDTs concentration from worldwide coastal zones ranged from 2.6 to 1629 ng/g in China (Mai, Fu et al. 2002), 0 to 364 ng/g in India (Pandit, Mohan Rao et al. 2001), 2.5 to 12 ng/g in Japan (Iwata, Tanabe et al. 1994), 0.01 to 135 ng/g in Korea (Hong, Yim et al. 2006), 2.2-11.9 ng/g in Singapore (Wurl and Obbard 2005), 6.2-10.4 ng/g in Vietnam (Nhan, Am et al. 1999) and 1.9 to 6.9 ng/g in the Baltic Sea (Strandberg, van Bavel et al. 1998).

2.3 ^{137}Cs and ^{210}Pb profiles in sediment cores

TC and CC concentrations followed similar trends with depth at all sites where sediment cores were collected. Total chlordane (TC+CC) profiles (Figure 5.13) were very similar to ^{137}Cs profiles (Figure 5.14-5.16). In the LIMB core, the excess ^{210}Pb decreased from the maximum value of 7 dpm g^{-1} at the sediment surface to values below 1 dpm g^{-1} at a depth of ~33 cm (Figure 5.14, supported ^{210}Pb activity was 2.2 dpm g^{-1}). The ^{137}Cs activity and chlordane concentration maintained intermediate levels at the sediment surface, reached a maximum at a depth near 28 cm, and decreased to near-zero values at a depth close to ~50 cm (Figures 5.13a and Figure 5.14).

Chlordane profiles in the LIHH core were similar to those in the LIMB core albeit the concentrations were lower (Figure 5.13a). In the LITN core, the excess ^{210}Pb decreased from a maximum of ~8 dpm g^{-1} at the sediment surface to less than 1 dpm g^{-1} at a depth of ~40 cm (Figure 5.15). The ^{137}Cs activity and chlordane concentration maintained at relatively constant levels from the sediment surface down to ~30 cm, and then dropped to near zero values at a depth of ~40 cm (Figures 5.13b, Figure 5.15). In the LILN core, the ^{210}Pb activities generally decreased from ~5 dpm g^{-1} at the sediment surface to ~2 dpm g^{-1} at a depth of ~50 cm (Figure 5.16). The ^{137}Cs activitiy and chlordane concentration were variable in the core and showed no clear peaks, although there was a hint of a possible ^{137}Cs maximum at a depth of ~25-30 cm (Figure 5.13b and Figure A.1).

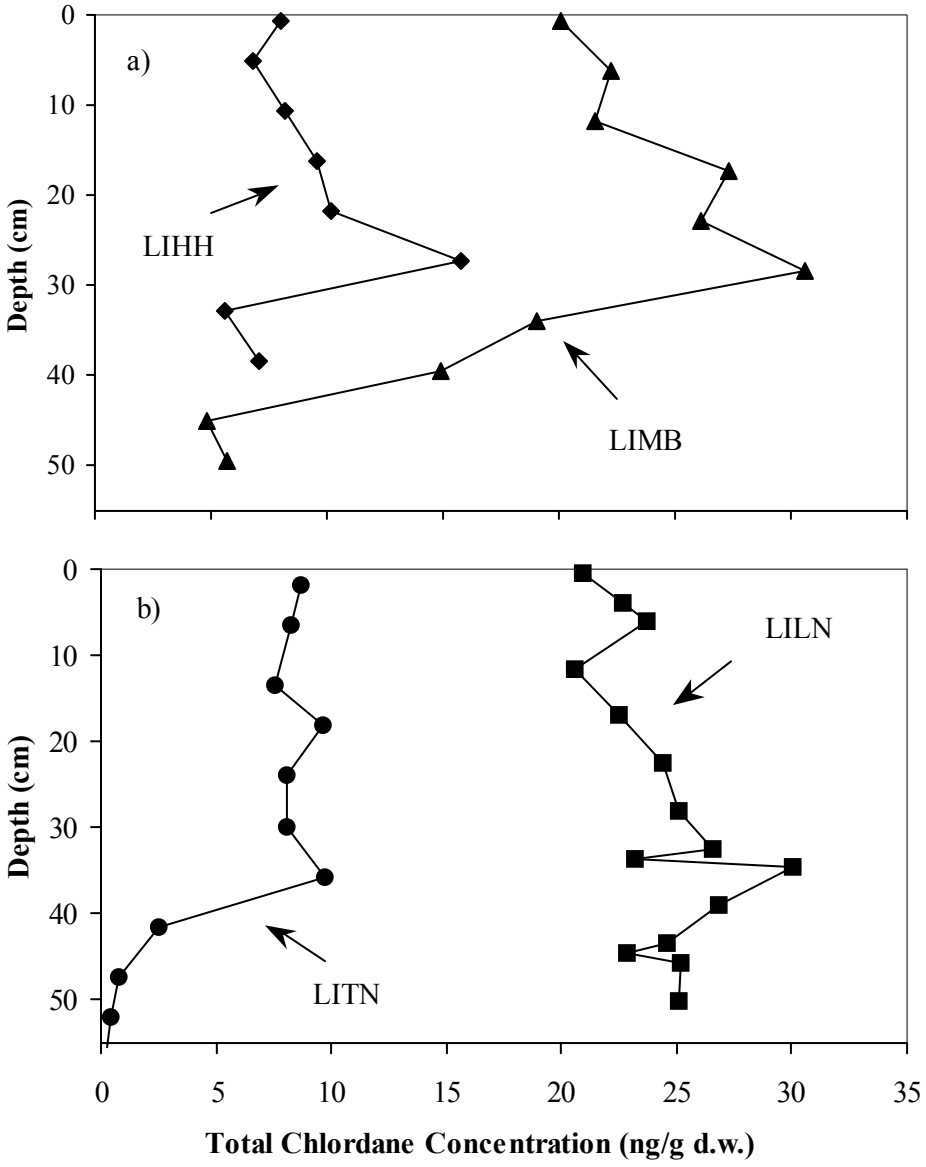

Figure 5.13 *Concentration profiles of total chlordane (sum of trans- and cis-chlordane) in sediment cores collected at LIMB, LIHH, LILN, and LITN.*

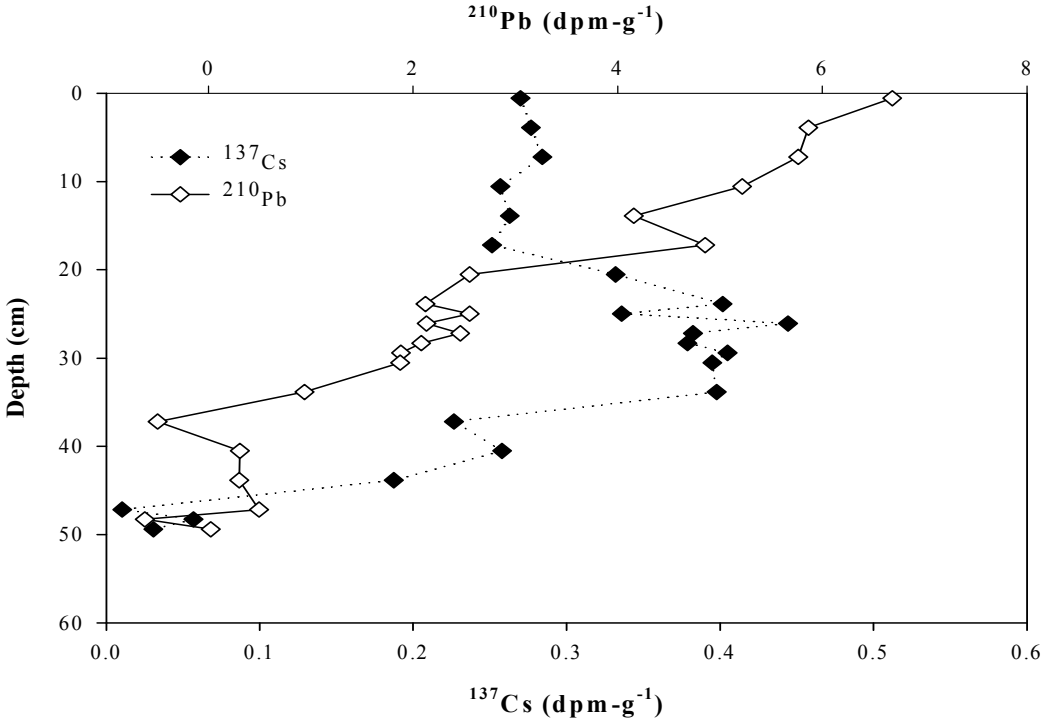

Figure 5.14 ^{137}Cs and excess ^{210}Pb concentrations in the LIMB core sediments.

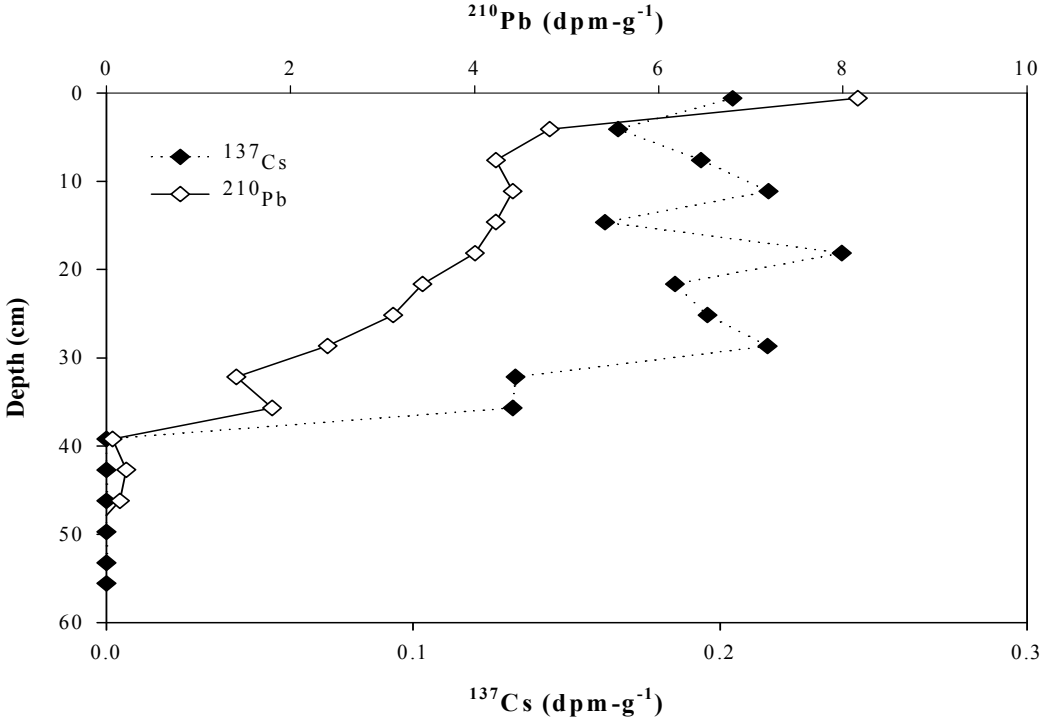

Figure 5.15 ^{137}Cs and excess ^{210}Pb concentrations in the LITN core sediments.

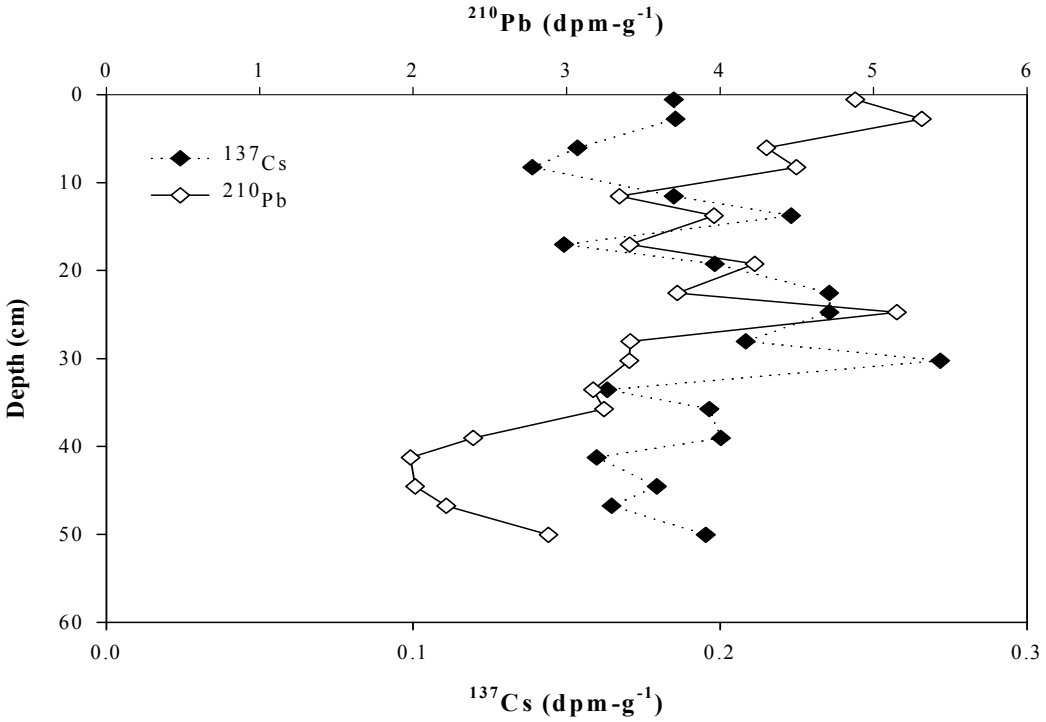

Figure 5.16 ^{137}Cs and excess ^{210}Pb concentrations in the LILN core sediments.

Because the LIMB core has both a well-defined onset of ^{137}Cs activity in the core and a well-defined ^{137}Cs peak, some simple sediment accumulation rate estimates can be made. In the other cores the radionuclide data are more complex and will be interpreted later with the aid of a sediment-mixing model. Based on a simple interpretation that the depth of maximum ^{137}Cs activity (~30 cm) at LIMB corresponds to 1963, a sedimentation rate of 0.7 cm yr^{-1} was estimated. This rate is very similar to the estimate of 0.8 cm yr^{-1} assuming that the initial detection of ^{137}Cs (at ~44 cm) corresponds to 1952, and that the first detection of significant chlordane (~49 cm) corresponds to its first use in the U.S. around 1948 (ATSDR 1994). These sedimentation rates translate to mass accumulation rates of ~0.3 g cm^{-2} yr^{-1}, assuming an average determined porosity of 0.84.

^{137}Cs, ^{210}Pb and chlordane can be transported downwards by sedimentation, bioturbation, and possibly diffusion (e.g., desorption and/or diagenetic mobility (the

process by which certain particle-bound substances are released into solution by a variety of reactions in the sediment)). Desorption and/or diagenetic mobility of ^{137}Cs have been observed in various locations (Patel, Patel et al. 1978; Crusius and Anderson 1995). The fact that the ^{137}Cs inventories in the cores range from 30-60% of that expected from atmospheric fallout, while the ^{210}Pb inventories range from 170% to 210% of the value expected from fallout (Table A.1), is consistent with similar low ^{137}Cs inventories in other estuarine environments attributed to mobility of ^{137}Cs under high-salinity conditions (Olsen, Simpson et al. 1981), and enhancement of the ^{210}Pb inventory due to sediment focusing (the resuspension and movement of sediment from shallow to deep parts of the basin by water currents) (Davis 1968). As noted above, however, the depths at which chlordane concentrations and ^{137}Cs activities first increase significantly were very similar (Figures 5.14, 5.15). Since chlordane was first introduced into the environment around 1948 (ATSDR 1994) and the first significant weapons fallout began in 1952, it is concluded that diagenetic mobility has had little effect on the penetration of ^{137}Cs into the sediment. The alternative possibility that ^{137}Cs and chlordane have diffused downward in the sediments comparable distances is unlikely, given the different conditions required for mobility of the two contaminants (Patel, Patel et al. 1978; Johnson-Logan, Broshears et al. 1992).

2.4 Sediment mixing model

A simple sediment mixing model was used in this work to simulate ^{137}Cs, ^{210}Pb and chlordane profiles. In this model sedimentation was treated as a process of advection while sediment mixing was treated as a process of diffusion, as described in the following equation:

$$\frac{\partial \rho A}{\partial t} = \frac{\partial}{\partial z}\left[\frac{D_b \partial \rho A}{\partial z}\right] - s\frac{\partial \rho A}{\partial z} - \lambda \rho A$$

where ρ is the density of the solid phase (assumed to be 2.5 cm^3 g^{-1}), A the nuclide activity (dpm g^{-1}) or chlordane concentration (ng/g), t the time (yr), z the depth (cm), Db the diffusive mixing rate (cm^2 yr^{-1}), s the sedimentation rate (cm yr^{-1}), and λ the decay constant (0.0311 yr^{-1} for ^{210}Pb, 0.0230 yr^{-1} for ^{137}Cs, and 0 for chlordane).

Sediment mixing in estuaries can be caused by bioturbation, bottom currents, storm events, etc. Bioturbation refers to the enhanced transport of particles, solutes, and sorbed species in bed sediment by the activities of benthic organisms, such as feeding, burrowing, excavation, tube construction and irrigation (Warren, Allan et al. 2003). Bioturbation can redistribute sediments (and the associated contaminants) from their original stratigraphic position and may penetrate to depths of tens of centimeters (Crusius, Bothner et al. 2004). This simple treatment of diffusive sediment mixing provided a reasonable description of the available radionuclide data in our study area, and allowed quantifying the time-averaged impact of mixing processes using just two parameters, the diffusive mixing coefficient (Db, cm^2 yr^{-1}) (Goldberg and Koide 1962; Guinasso and Schink 1975), and the sediment mixed layer depth. The model used a finite difference approximation of the above equation whose origin dates to Santschi et al.

(Santschi, Li et al. 1980) but has been subsequently modified (Crusius, Bothner et al. 2004).

The sediment mixing model was used to evaluate whether the ^{137}Cs, ^{210}Pb, and chlordane data at each site could be explained by a common set of sediment accumulation and bioturbation rate estimates. The numerical model simulation results for sediment cores were shown in Figure A.1-A.3 in the appendix. The parameters used in the numerical model were summarized in Table A.1-A.2.

While the ^{210}Pb profile at LIMB could be simulated well assuming bioturbation with no sedimentation (Figure A.2a), the ^{137}Cs profile could not (Figure A.2b), indicating that downward transport of ^{210}Pb and ^{137}Cs was not solely due to bioturbation. Likewise, the radionuclide data were inconsistent with downward transport by sedimentation only, because the ^{137}Cs profile from such a model run maintained a maximum that is far sharper than is apparent in the data (Figure 18c, d).

For the LIMB core, the ^{210}Pb profile could be reproduced by a combination of sedimentation (0.8 cm yr^{-1}) and mixing to 19 cm (Figure A.1a). A diffusive mixing rate of 28 cm^2 yr^{-1} to 19 cm yielded a fair fit of the ^{137}Cs profile (Figure A.1b). This fit is not perfect in the sense that the constant ^{137}Cs activity in the top ~19 cm of core and the slope immediately above the peak (~19 cm-~25 cm) were not reproduced. The constant ^{137}Cs activities in the top ~19 cm of the core, despite a clear slope in the ^{210}Pb profile over this depth range, could only be reproduced if there was continued ^{137}Cs input to the sediments over and above that predicted from fallout. Possible sources include sediments (e.g., via sediment focusing, defined as the resuspension and movement of sediment from shallow to deep parts of the basin by water currents (Davis 1968)) or material from the terrestrial

watershed (e.g., via weathering) (Olsen, Larsen et al. 1993). Hence, a ^{137}Cs flux over and above that expected from fallout was included. The best fit to both the ^{210}Pb and ^{137}Cs profiles, assuming such ^{137}Cs input over and above fallout, resulted from a sedimentation rate of 0.8 cm yr^{-1} (mass accumulation rate of 0.27 g cm^{-2} yr^{-1}) and a diffusive mixing rate of 3.4 cm^2 yr^{-1} (Figure A.1d, e). For the LITN core, the best fit to both the ^{210}Pb and ^{137}Cs profiles was achieved with a sedimentation rate of 0.6 cm yr^{-1} and a diffusive mixing rate of 60 cm^2 yr^{-1} (Figure A.3a, b). Because the ^{137}Cs data from the LILN core do not show a clear maximum, nor do they decrease to near-zero values at the bottom of the core (Figure 5.16), sedimentation and bioturbation rates could not be estimated with confidence. The sedimentation and sediment mixing rates determined in this study are near or within the ranges previously determined in LIS sediments (~0.06 - ~0.6 cm yr^{-1} and ~6 - ~60 cm^2 yr^{-1}, respectively) (Tromp, Van Cappellen et al. 1995).

Total chlordane (TC+CC) profiles were also simulated with the numerical model (using the sedimentation rate and mixing rate derived from the best-fit of radionuclide data) to examine the possibility of continued input after the 1980s. Annual chlordane input to surface waters was assumed proportional to records of chlordane sales in the U.S. (Table 5.9, Figure 5.17), adjusted to match the observed total sediment inventory. Based on these data, the chlordane input increased gradually from 1944 to 1964, peaked in 1971, and decreased to very low values by 1979. For the LIMB core, using the model parameters obtained from the best fits of the ^{210}Pb and ^{137}Cs data (Table A.2), the onset of chlordane in the sediments and the depth of the chlordane maximum were fit reasonably well (Figure A.1). However, the modeled surface sediments contained much less chlordane than observed, suggesting that there was significant chlordane input to LIS

after the early 1980s. The data from the other cores do not help to constrain post-1980 chlordane inputs due to very high sediment mixing, discussed below.

Table 5.9 Sales and usages of chlordane in the U.S. (USEPA 1975; USEPA 1976; Ayrus, Ayrus et al. 1988).

Year	1944	1964	1966	1971	1974	1978	1979
Total sales (tons)	0	5118	5107	9318	5500	200	100
Non-agricultural usage (tons)	0	4885	4490	6583	3900	140	70
Hudson-Raritan Basin usage (tons)	0	192	179	326	193	7	4

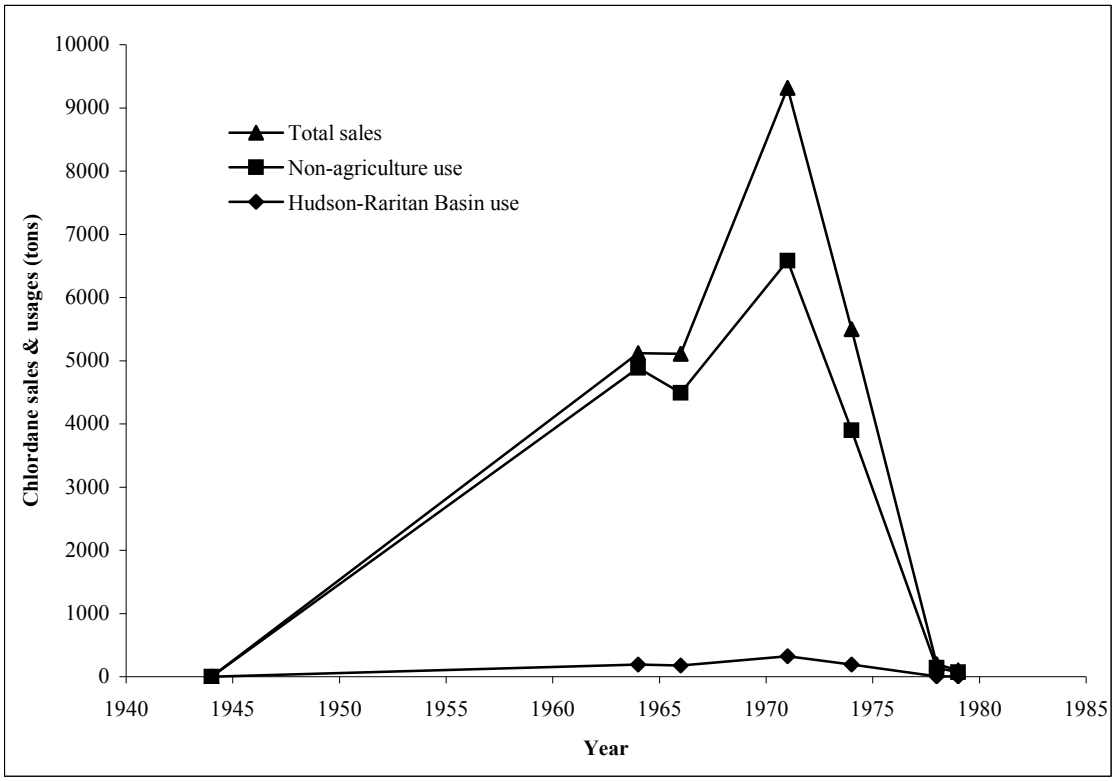

Figure 5.17 Chlordane sales and usages in the U.S.

Modeling of the radionuclide profiles from all three sediment cores indicated that both sedimentation and sediment mixing were occurring at all three sites where such data were generated (Table A.2). The lack of a well-defined peak in both chlordane and ^{137}Cs in the

LITN and LILN cores can readily be explained in light of the inferred rates of sedimentation and sediment mixing. The relative influence of sedimentation and sediment mixing in transport of particulate materials in the sediment mixed layer can be assessed using the dimensionless Peclet number (*Pe*)

$$Pe = sz_b / D_b$$

where z_b is the mixed layer depth (Boudreau 1986; Tromp, Van Cappellen et al. 1995). Large values of *Pe* imply sedimentation dominates the vertical transport of sediments, whereas small values (<1) indicate dominance of sediment mixing. The *Pe* values (estimated from the best-fit sediment-mixing model runs) for the LIMB, LITN and LILN cores were 3.3, 0.15 and 0.1-0.4 (depending on possible model fits), respectively (Table A.2). These values clearly indicate the dominance of sediment mixing at LITN and LILN and the dominance of sedimentation at LIMB (the only one with a well-defined ^{137}Cs and chlordane concentration maximum among the three cores).

2.5 Implications from chlordane, ^{210}Pb and ^{137}Cs profiles

Direct comparison of the ^{137}Cs and chlordane profiles (both peaked at ~30 cm, Figure 5.14b, c) in the LIMB core suggested that the maximum releases of chlordane to the Sound occurred close in time to the ^{137}Cs fallout maximum (1963). This interpretation would be reasonably consistent with previous work suggesting maximum chlordane releases in the early 1970s to the nearby Jamaica Bay (see Figure 4.2 for location) (Bopp, Simpson et al. 1993), and maximum chlordane sales in the same period (Table A.1). Model simulations of the chlordane profiles suggest continual input at western LIS long after the 1980s although the extent of such input could not be easily quantified. Possible

sources of continual chlordane inputs include sediment focusing, runoff from house foundation and agricultural soils, and volatilization of chlordanes from the soils followed by atmospheric deposition into the Sound.

Both continued input and significant sediment mixing may have led to persistent chlordane concentrations (and persistent organic pollutant concentrations in general) in LIS surficial sediments, posing long-term threats to benthic organisms (e.g., constant chlordane concentrations in blue mussel tissues). The lack of enantioselective microbial degradation of chlordane in LIS sediments (discussed below) makes it even more persistent in the Sound.

3. Enantiomeric fractions of chlordane in sediments

3.1 EFs in surficial sediments.

The enantiomeric fractions of TC and CC in the recently collected surficial sediments were between 0.482 and 0.513, with the vast majority between 0.489 and 0.506 (Table 5.10, Figure 5.19). A typical chromatogram of the chiral separation was shown in Figure 5.18. Two tailed t-test indicated that the mean EFs of CC in none of the recent surficial sediments were statistically different from the mean EF of the standard ($p_1 > 0.05$ in all cases, Table 5.10, Figure 5.19b). The mean EF of TC was statistically different from the mean EF of the standard only in one recent surficial sediment (LIPJ, $p_1 < 0.05$, Table 5.10, Figure 5.19a).

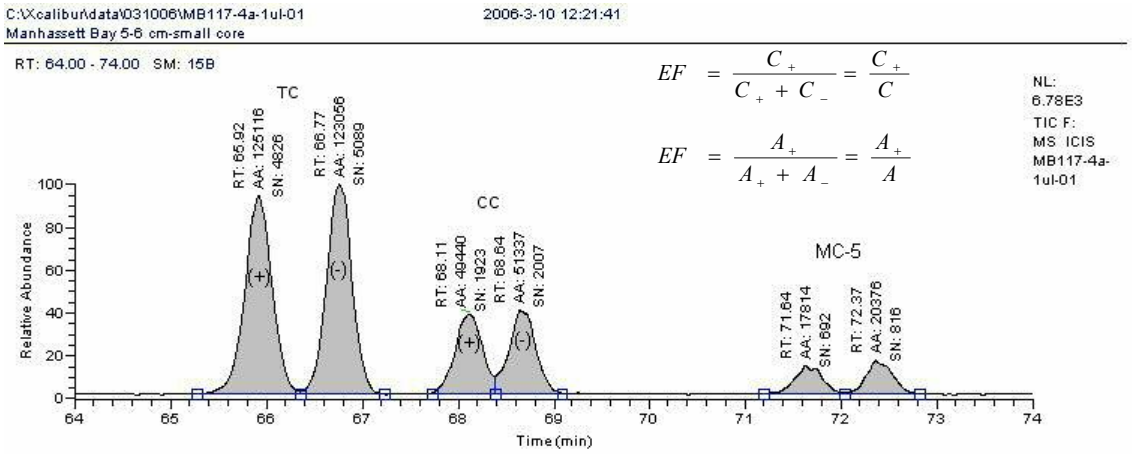

Figure 5.18 GC-MS chromatogram and enantiomer fraction of chiral molecules.

The mean EFs of TC and CC in the archived sediments were close to 0.500, with the overwhelming majority lying between 0.491 and 0.500 (Table 5.10, Figure 5.19). The only outlier was the EF of CC in archived LICR sediment (0.475) and this was the only EF that was statistically different from racemic signature (p_1<0.05, Table A.2, Figure 5.19). The t-test also revealed that the mean EFs of TC and CC in recently collected surficial sediments were not statistically different from the corresponding EFs of the archived sediments at all sites where such comparison could be made (p_2 > 0.05, Table 5.10, Figure 5.19). This observation clearly demonstrated that EFs of TC and CC in the surficial sediments did not change significantly in the past two decades in LIS.

Table 5.10 Mean enantiomeric fractions (EFs) and standard deviations (SD) of archived and recently collected surficial sediments. p_1 represents the probability (associated with the two-tailed t-test) between the mean EFs of the sediment samples and the standard, whereas p_2 represents the probability between the mean EFs of archived sediments and those of the recently collected surficial sediments. A p value greater than 0.05 indicates that the two means are not significantly different.

	TC				CC			
Site	EF	SD	p_1	p_2	EF	SD	p_1	p_2
LIHR	0.502	0.007	0.81	0.40	0.493	0.011	0.41	0.64
	*0.491**	*0.020*	*0.43*		*0.498*	*0.024*	*0.54*	
LIHH	0.495	0.020	0.43	0.73	0.506	0.024	0.71	0.34
	0.498	*0.008*	*0.39*		*0.495*	*0.016*	*0.31*	
LITN	0.491	0.009	0.14	0.20	0.498	0.022	0.29	0.47
	0.500	*0.014*	*0.85*		*0.489*	*0.021*	*0.22*	
LICR	0.485	0.031	0.21	0.45	0.490	0.022	0.33	0.34
	0.495	*0.014*	*0.35*		*0.475*	*0.021*	***0.04***	
LIPJ	0.482	0.016	**0.03**	0.13	0.498	0.020	0.57	0.99
	0.497	*0.014*	*0.48*		*0.498*	*0.016*	*0.58*	
LISI	0.503	0.025	0.86		0.489	0.012	0.08	
LIMR	0.483	0.028	0.22		0.499	0.017	0.63	
LIHU	0.497	0.014	0.53		0.501	0.008	0.78	
LILN	0.493	0.017	0.28		0.513	0.019	0.30	
LIMB	0.491	0.014	0.14		0.490	0.015	0.10	

* Values in the second row (*Italic*) of a site are for the archived sample of that site.

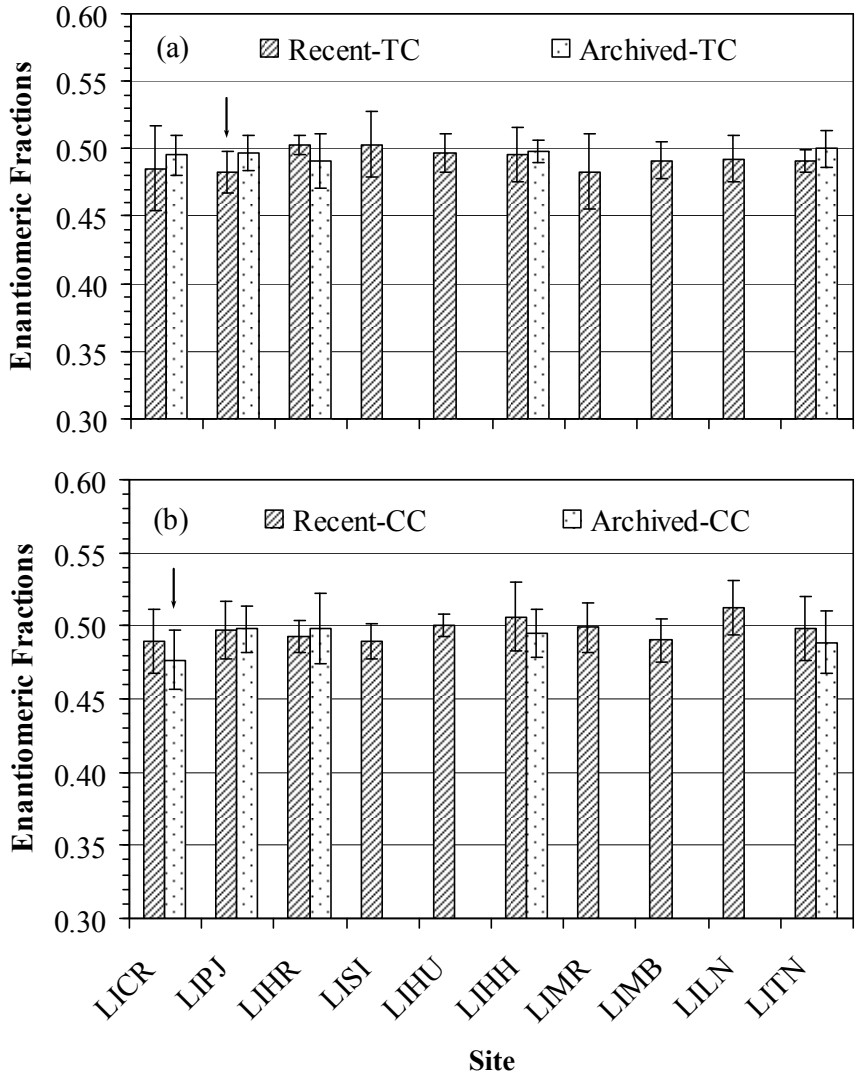

Figure 5.19 Enantiomeric fractions (EFs) of (a) TC and (b) CC in archived and recently collected surficial sediments. Arrow indicates that the EF of the sample is statistically different from the mean EF of the corresponding racemic standard.

3.2 EFs in core sediments.

The sediment cores were sectioned into slices approximately 1.1 cm thick and the interval between two adjacent extracted slices was approximately 4.4 cm since every fifth core slice was extracted and analyzed to determine EFs of TC and CC. The total lengths of the cores were 41, 51, 51, and 56 cm at LIHH, LILN, LIMB, and LITN, respectively. For the LITN core slices with depths greater than 36 cm, TC and CC concentrations were too low to allow reliable determination of EF values. The EFs of TC and CC are presented in Figure 5.20 and Tables 5.13-5.16. Note that the EFs of the surface slice (~1.1 cm thick) are not exactly the same as the EFs of the surficial sediments at the same site (Tables 5.12-5.16), since the surficial sediments and the sediment cores were collected separately (a few to a few tens of meters apart). A student t-test indicates that the EFs of the surface slice were not statistically different from those of the surficial sediments.

Table 5.11 Enantiomeric fractions (EFs) and standard deviations (SD) of the core sediments at LILN. p_1 represents the probability (associated with the two-tailed t-test) between the EFs of core slices and the EF of the standard, p_2 represents the probability between the EFs of the core slices and the EF of the middle slice, and p_3 represents the probability between the EFs of various slices with the EF of the surface slice. Same notation also applies to Tables 5.13-5.15.

Depth	TC					CC				
(cm)	EF	SD	p_1	p_2	p_3	EF	SD	p_1	p_2	p_3
0.6	0.491	0.018	0.235	0.528	1.000	0.505	0.013	0.701	0.917	1.000
6.1	0.495	0.010	0.211	0.764	0.681	0.505	0.012	0.659	0.936	0.980
11.6	0.491	0.011	0.090	0.359	1.000	0.500	0.016	0.774	0.531	0.622
17.2	0.493	0.018	0.328	0.692	0.855	0.514	0.021	0.244	0.388	0.380
22.7	0.504	0.012	0.619	0.198	0.183	0.505	0.007	0.496	0.905	0.985
28.3	0.497	0.005	0.118	1.000	0.528	0.505	0.009	0.506	1.000	0.917
33.8	0.494	0.013	0.171	0.592	0.818	0.508	0.010	0.286	0.687	0.663
39.4	0.498	0.011	0.561	0.718	0.436	0.501	0.016	0.845	0.584	0.675
44.9	0.489	0.015	0.103	0.289	0.790	0.497	0.018	0.527	0.360	0.437
50.4	0.498	0.013	0.476	0.791	0.468	0.511	0.011	0.226	0.449	0.446

Table 5.12 Enantiomeric fractions (EFs) and standard deviations (SD) of the core sediments at LIHH.

Depth (cm)	TC					CC				
	EF	SD	p_1	p_2	p_3	EF	SD	p_1	p_2	p_3
0.6	0.497	0.017	0.429	0.550	1.000	0.504	0.019	0.859	0.449	1.000
5.0	0.487	0.011	**0.009**	0.096	0.139	0.500	0.016	0.785	0.667	0.734
10.5	0.491	0.028	0.400	0.417	0.658	0.495	0.023	0.473	0.969	0.468
16.1	0.506	0.021	0.602	0.769	0.374	0.498	0.020	0.649	0.802	0.624
21.6	0.503	0.020	0.879	1.000	0.550	0.496	0.018	0.443	1.000	0.449
27.1	0.490	0.020	0.230	0.302	0.529	0.503	0.010	0.901	0.441	0.941
32.7	0.492	0.005	**0.003**	0.238	0.417	0.509	0.009	0.179	0.181	0.487
39.3	0.493	0.009	**0.036**	0.302	0.572	0.491	0.018	0.185	0.684	0.220

Table 5.13 Enantiomeric fractions (EFs) and standard deviations (SD) of the core sediments at LITN. The length of the sampled core was 56 cm. However, below the depth of 35.6 cm, TC and CC concentrations were too low to allow reliable determination of EFs.

Depth (cm)	TC					CC				
	EF	SD	p_1	p_2	p_3	EF	SD	p_1	p_2	p_3
1.8	0.490	0.010	**0.031**	0.503	1.000	0.494	0.011	0.163	0.944	1.000
6.4	0.487	0.008	**0.003**	0.280	0.544	0.502	0.014	0.940	0.524	0.386
12.3	0.493	0.011	0.157	0.836	0.560	0.490	0.014	0.077	0.636	0.585
18.1	0.495	0.016	0.402	1.000	0.503	0.495	0.020	0.401	1.000	0.944
23.9	0.492	0.019	0.284	0.766	0.796	0.501	0.013	0.869	0.531	0.367
29.8	0.495	0.010	0.163	0.955	0.394	0.501	0.018	0.893	0.565	0.433
35.6	0.493	0.007	**0.032**	0.811	0.468	0.501	0.014	0.781	0.568	0.397

Table 5.14 Enantiomeric fractions (EFs) and standard deviations (SD) of the core sediments at LIMB.

Depth (cm)	TC					CC				
	EF	SD	p_1	p_2	p_3	EF	SD	p_1	p_2	p_3
0.6	0.491	0.017	0.191	0.704	1.000	0.499	0.013	0.528	0.814	1.000
6.1	0.496	0.008	0.123	0.394	0.557	0.500	0.020	0.738	0.663	0.924
11.6	0.497	0.006	0.200	**0.018**	0.400	0.494	0.013	0.151	0.328	0.513
17.2	0.486	0.010	**0.004**	0.672	0.554	0.503	0.013	0.937	0.692	0.582
22.7	0.485	0.010	**0.000**	0.425	0.439	0.501	0.014	0.807	0.889	0.737
28.3	0.488	0.006	**0.001**	1.000	0.704	0.500	0.009	0.625	1.000	0.814
33.8	0.491	0.003	**0.000**	0.312	0.986	0.504	0.007	0.700	0.479	0.421
39.4	0.493	0.009	**0.030**	0.178	0.752	0.488	0.007	**0.000**	**0.020**	0.095
44.9	0.489	0.013	**0.026**	0.848	0.821	0.501	0.015	0.872	0.886	0.751
50.4	0.494	0.025	0.515	0.582	0.832	0.492	0.039	0.578	0.658	0.720

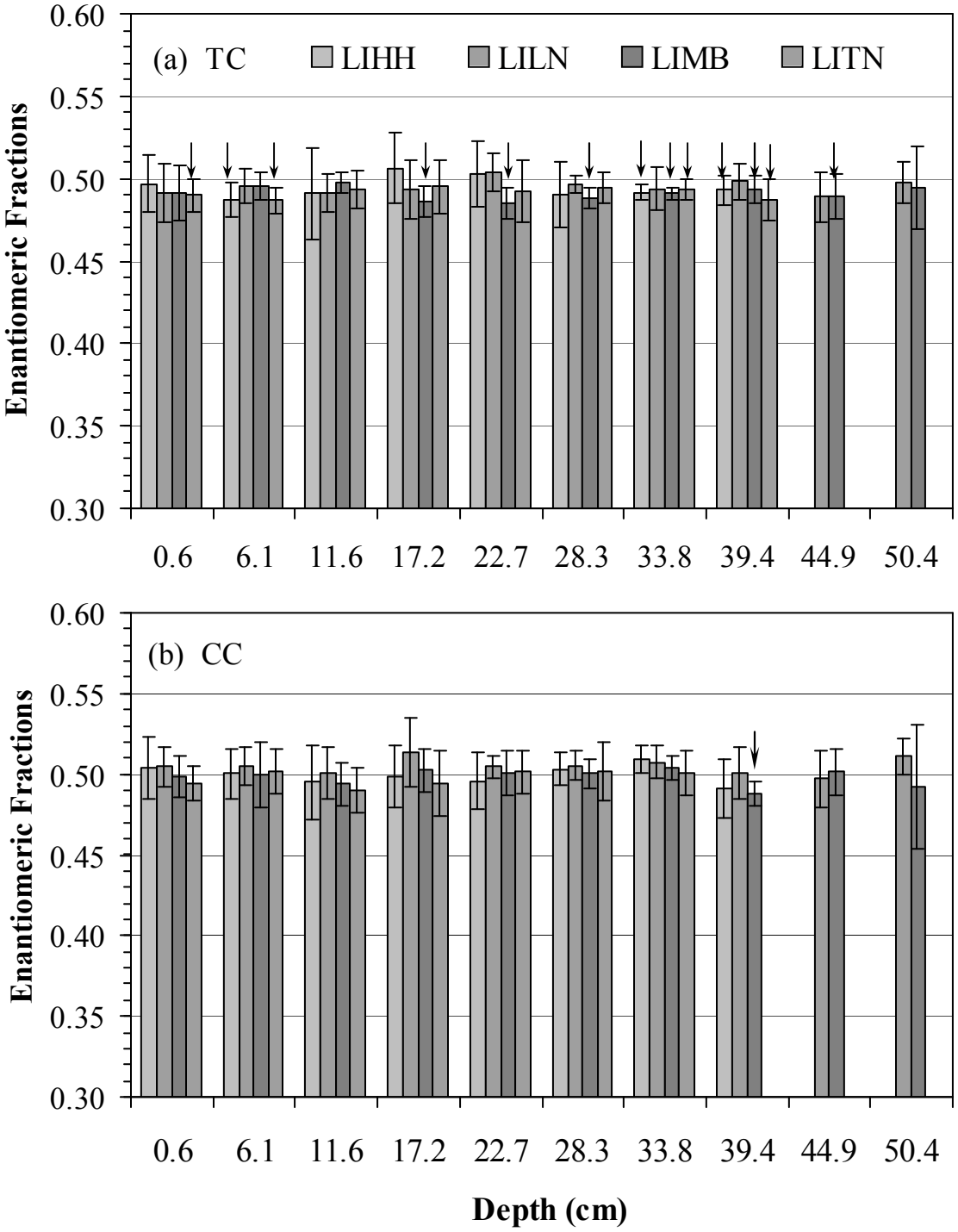

Figure 5.20 Enantiomeric fractions (EFs) of (a) TC and (b) CC in core sediments collected at LIHH, LILN, LIMB, and LITN. Arrow indicates that the EF of the sample is statistically different from the mean EF of the corresponding racemic standard.

3.2.1 cis-Chlordane

The averages of the mean EFs of CC across the core lengths were 0.500 (0.017), 0.505 (0.014), 0.498 (0.017), and 0.498 (0.015) for LIHH, LILN, LIMB, and LITN, respectively. Except at one sediment slice (depth 39.4 cm) of LIMB, the mean EFs of CC were not statistically different from the mean EF of the standard ($p_1 > 0.05$, Figure 5.20b, Table 5.14). To examine whether EF values of CC varied significantly across the core lengths, a t-test was performed to compare the EFs of the sediment slices. For illustration purposes, the probabilities associated with the two-tailed t-tests between each slice and the middle slice (p_2) and between each slice and the surface slice (p_3) are presented here (Tables 5.13-5.16). The middle slice depths were 21.6, 28.3, 28.3, and 18.1 cm for LIHH, LILN, LIMB, and LITN, respectively. Statistically different EF of a particular slice from the EFs at the two reference slices occurred only at one slice in one core (39.4 cm, LIMB) (Tables 5.13-5.16). Even for this slice, the mean EF value (0.488) differed from the average EF of the entire core (0.498) by only 0.010, indicating that EFs of CC were virtually invariant with depth in all the sediment cores.

3.2.2 trans-Chlordane

The averages of the mean TC EFs across the core lengths were 0.495 (0.017), 0.495 (0.013), 0.491 (0.012), and 0.492 (0.011) for LIHH, LILN, LIMB, and LITN, respectively. Mean EFs of TC were not statistically different from the mean EF of the racemic standard across the LILN core ($p_1 > 0.05$, Figure 5.20a, Table 5.12). Statistically different EFs from the EF of the racemic standard were found at three slices (5.0, 32.7, and 39.3 cm) for the LIHH core (Figure 5.20a, Table 5.11), six slices (17.2-44.9 cm) for the LIMB core (Figure 5.20a, Table 5.13), and three slices (1.8, 6.4, and 35.6 cm) for the

LITN core (Figure 5.20a, Table 5.14). Except at one slice of the LIMB core (depth 11.6 cm), mean TC EFs were not statistically different from the EFs at the surface and middle slices in any cores (Tables 5.13-5.16). At this depth of the LIMB core, the EF value (0.497) differed from the average EF across the core length (0.491) only by 0.006, indicating that EFs of TC were also virtually invariant across the depth in all the sediment cores.

3.3 Lack of enantioselective biodegradation in LIS sediment

In a previous study that examined TC EFs in sediment cores (Bidleman, Wong et al. 2004; Stern, Braekevelt et al. 2005), enantiomeric degradation was inferred by comparing the EFs in the air samples and those in the core layers of the same ages. This approach was feasible because the sampling site was in the Arctic (where atmospheric deposition was the sole input of TC) and the sediment cores were annually laminated (which allowed accurate age-dating using radionuclides ^{210}Pb and ^{137}Cs). Such an approach could not be adopted in this work, even though EFs of TC and CC in the atmosphere nearby are available in the literature (Eizer, Iannucci-Berger et al. 2003) and ^{210}Pb and ^{137}Cs isotope analysis was performed. One reason is that there may be multiple sources of chlordane to LIS, including atmospheric deposition, runoff from urban and agricultural applications, etc. The other reason is that temporal resolution of EFs across the cores may well be obscured due to sediment mixing in estuaries caused by bioturbation and/or storm events. Bioturbation refers to the enhanced transport processes of particles, solutes, sorbed species in bed sediment by daily activities of benthic organisms, such as feeding, burrowing, excavation, tube construction, and irrigation (Warren, Allan et al. 2003). Bioturbation can transport newly deposited material and conceivably the associated

contaminants to depths of tens of centimeters (Crusius, Bothner et al. 2004). ^{210}Pb and ^{137}Cs data from the LILN core indicate that significant sediment mixing did occur at this site, as evidenced by the lack of a sharp peak on the ^{137}Cs concentration-depth profile (Figure 5.16). ^{210}Pb and ^{137}Cs data from the LIMB core also indicated sediment mixing, albeit at a lesser degree.

Sediment mixing can potentially lead to constant contaminant parameters (such as EFs of chlordanes) at different depths of sediment cores. Therefore, the observed depth invariant EFs alone do not necessarily ensure the lack of enantioselective biodegradation of chlordanes. Likewise, temporally invariant EFs in surficial sediments alone do not guarantee the lack of enantioselective biodegradation either, because without sediment mixing, surficial sediments (in depositional environments) are deposited recently, and EFs in these sediments would largely reflect the EFs of the source which could be temporally constant. However, our findings that EFs were virtually invariant both temporally in surficial sediments and across the lengths of core sediments and that chlordane in the vast majority (>95%) of the sediment samples were racemic or nearly racemic (EFs between 0.49 and 0.51) clearly demonstrate the lack of enantioselective biodegradation of chlordane in LIS sediment.

3.4 Implications

Upon entry into the atmosphere, chiral pesticides such as chlordane only undergo abiotic processes (e.g., photolysis, atmospheric deposition) and their distinctive chiral signatures are preserved. For this reason, enantiomers of pesticides have been proposed to trace the soil-air and water-air exchange processes and to identify the sources of pesticides in the atmosphere (Bidleman, Jantunen et al. 1998; Bidleman and Falconer

1999). For example, racemic or nearly racemic chlordane in the ambient air of northern Alabama indicates that little airborne chlordane in this region comes from volatilization of chlordane in agricultural soils, which contain nonracemic chlordane (Bidleman, Jantunen et al. 1998; Wiberg, Harner et al. 2001). Since chiral signatures of chlordanes were also preserved in LIS sediments (due to the lack of enantioselective biodegradation), chiral signatures in LIS sediments can also help to provide insights into the sources of chlordane. Chlordanes in agricultural soils near LIS have been demonstrated to be greatly nonracemic (EF = 0.464 for TC and 0.538 for CC) in at least one study (Eizer, Iannucci-Berger et al. 2003). The observed racemic or nearly racemic signature in surficial sediments at most sampling sites in this study suggests that runoff from agricultural soils constitutes, at most, a minor fraction of the recent input into LIS. Since chlordanes in house foundation soils remain racemic, racemic or nearly racemic chlordanes in LIS sediment suggest that house foundation soils are likely the major source of chlordane input into the Sound, at least for more recent input. It is estimated that 24 million homes were treated with chlordanes for termite control (ATSDR 1994). It is conceivable that a tremendous amount of chlordanes has been used as a termiticide in the heavily populated area around LIS. It is probably also true that the chlordane input to LIS prior to the 1980s was from house foundation soils near urban areas since about 60% of the chlordane use in the northeast in early 1970s was for industrial/commercial purposes (USEPA 1975) and the use of chlordane in the nearby Hudson-Raritan Basin (including most of New York City) was almost exclusively for the control of termites and other insects in suburban and urban areas (Rod 1989).

Possible pathways of chlordane transport into LIS include runoff from house foundation soils and volatilization of chlordanes from the soils followed by atmospheric deposition into the Sound.

Since biodegradation is the sole possible enantioselective removal mechanism of chlordane, racemic or nearly racemic chlordane signatures may indicate that biodegradation is inhibited in LIS sediment. The lack of enantioselective biodegradation suggests that chlordane might be more persistent in LIS sediment than in agricultural soils where biodegradation occurs. An important distinction between soil and sediment is that the former is aerobic and the latter is anaerobic. The lack of biodegradation in sediments but not in soils indicates that biodegradation of chlordane may be inhibited under anaerobic conditions. This is consistent with the previous observation that chlordane does not degrade in the anaerobic conditions in flooded soils (Sethunathan 1973). Alternatively, lack of enantioselective removal of chlordanes may suggest that biodegradation of chlordanes in LIS sediment is non-enantioselective. Hence, the observation of enantioselective degradation of TC in the Canadian Arctic (Stern, Braekevelt et al. 2005) and the lack of enantioselective degradation of chlordanes in LIS may indicate that enantioselectivity of biodegradation of chlordane (and presumably other organochlorine compounds) is site specific.

Chapter 6

Conclusions

OCPs are still widely present in current LIS surficial sediments two decades after the use of these pesticides in the U.S. was banned. Sediments in the western part of the Sound are more contaminated than in the eastern part and all the most contaminated sites are located in the west tip of the Sound, which is close to the high population density metropolitan area.

OCPs concentrations in LIS surficial sediments (sediments from the western LIS sites in particular) exceeded several sediment quality guidelines (SQGs) including the effect range-low (ERL), the threshold effect level (TEL), the probable effect level (PEL) and/or the effect range-median (ERM). Therefore, sediment toxicity by OCPs still exists at most sites sampled and OCPs still pose significant threats to benthic organisms in the western LIS, even after the use of OCPs has been completely banned for nearly two decades in the U.S.

The concentration data from this research and previous surveys indicate that overall OCPs concentrations in surficial sediments did not decrease significantly in the past decade.

The OCPs concentration profiles showed that OCPs were present in every depth of the sediment cores. Direct comparison of the ^{137}Cs and chlordane profiles in the sediment core suggested that the maximum releases of chlordane to the Sound occurred close in time to the ^{137}Cs fallout maximum (1963). Model simulations of the chlordane profiles

suggest continual input at western LIS long after the 1980s. Possible sources of continual chlordane inputs include sediment focusing, runoff from house foundation and agricultural soils, and volatilization of chlordanes from the soils followed by atmospheric deposition into the Sound. However, it is difficult to discriminate contamination sources among burial of pollutants, erosion of contaminated sediment surface or dissolution from sediments due to the significant sediment mixing.

The fact that chlordane in agricultural soils near LIS was greatly non-racemic but chlordane in LIS sediment in the past 60 years was racemic or near racemic suggested that runoff from agricultural soils constitutes, at most, a minor fraction of the recent input into LIS and house foundation soils are likely the major source of chlordane input into the Sound, at least for more recent input. It is probably also true that the chlordane input to LIS prior to the 1980s was from house foundation soils near urban areas since about 60% of the chlordane use in the northeast in early 1970s was for industrial/commercial purposes and the use of chlordane in the nearby Hudson-Raritan Basin (including most of New York City) was almost exclusively for the control of termites and other insects in suburban and urban areas.

Since biodegradation is the sole possible enantioselective removal mechanism of chlordane, racemic or nearly racemic chlordane signatures may indicate that biodegradation is inhibited in LIS sediment. The lack of biodegradation suggests that chlordane might be more persistent in LIS sediment than in agricultural soils where biodegradation occurs. The lack of biodegradation in sediments but not in soils indicates that biodegradation of chlordane may be inhibited under anaerobic conditions.

Alternatively, lack of enantioselective removal of chlordanes may suggest that biodegradation of chlordanes in LIS sediment is non-enantioselective.

Both continued input and significant sediment mixing may have led to persistent chlordane concentrations (and persistent organic pollutant concentrations in general) in LIS surficial sediments, posing long-term threats to benthic organisms (e.g., constant chlordane concentrations in blue mussel tissues). The lack of enantioselective microbial degradation of chlordane in LIS sediments makes it even more persistent in the Sound.

Chapter 7

Impact and Environmental Significance

The results of this research provide the most recent concentration data on organochlorinated pesticides including chlordane, dieldrin, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT in LIS sediments. When these concentration data were combined with existing data from previous surveys, no significant decrease of OCPs concentrations in LIS sediments is observed. Note that the last sediment survey in LIS was conducted by NOAA almost a decade ago, and neither NOAA nor any other government agency plans to conduct another sediment survey in LIS in the near future. Therefore, the concentration data resulted from this study might be the only information available for the assessment of current status of pesticide contamination in LIS sediments.

The research results help us better understand the fate, the contaminant source and the major removal mechanisms of OCPs in the estuary sediments. The results indicate that biodegradation is not the major removal mechanism for chlordane under the anaerobic condition in the sediment; both continued input and significant sediment mixing may have led to persistent organic pollutant concentrations in LIS surficial sediments, posing long-term threats to benthic organisms. The lack of enantioselective microbial degradation of chlordane in LIS sediments makes it even more persistent in the Sound.

Understanding the concentrations, fate, contaminant source and removal mechanisms of persistent pollutants from estuarine sediments is essential to the development of management strategies to sustain/improve the environmental quality of our nation's estuarine and costal areas.

Appendix

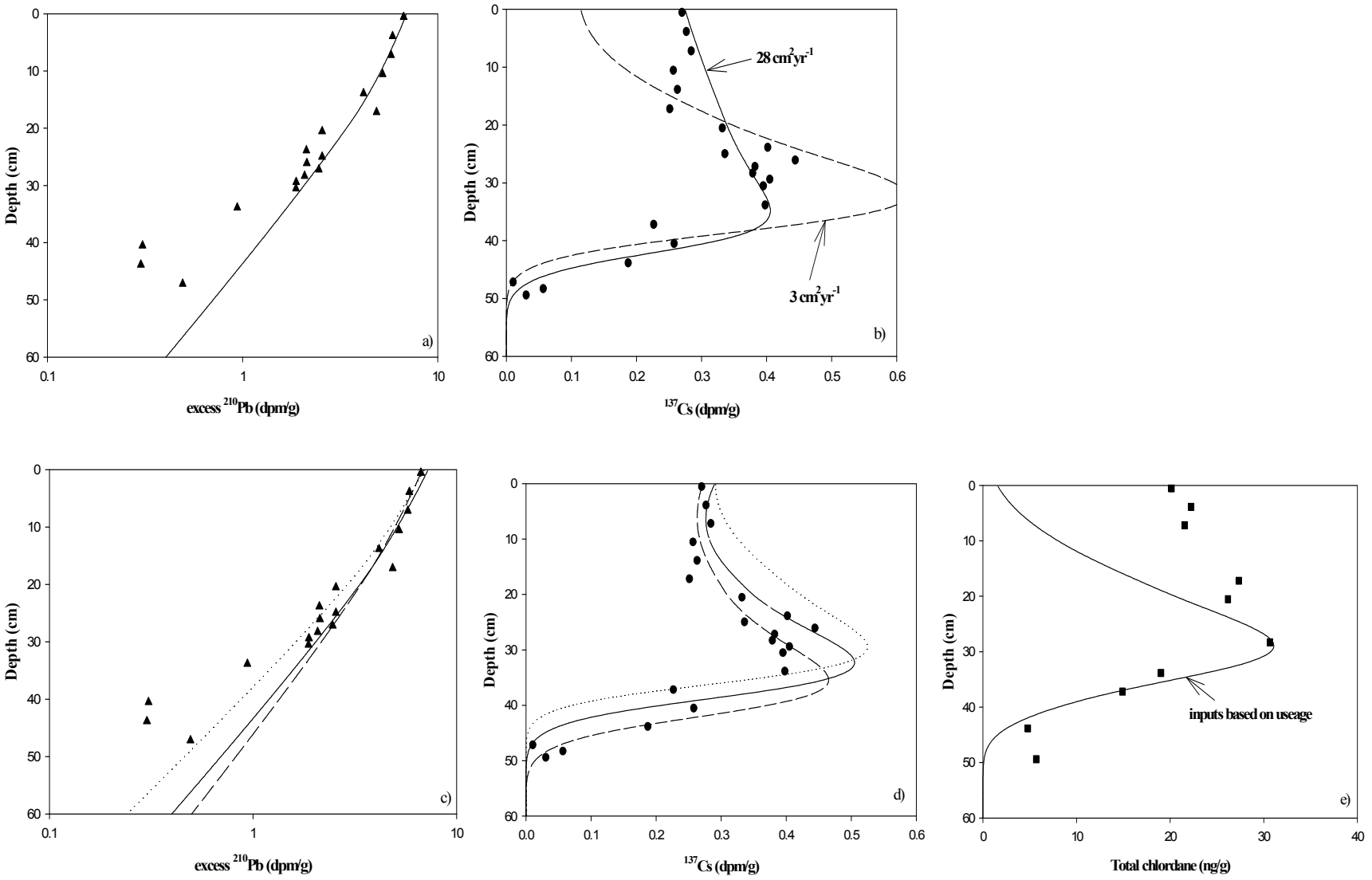
Depth (cm)
excess ^{210}Pb (dpm/g)
a)
^{137}Cs (dpm/g)
28 cm^{2}yr^{-1}
3 cm^{2}yr^{-1}
b)
c)
d)
inputs based on useage
e)
Total chlordane (ng/g)

Figure A.1 ^{210}Pb (triangles), ^{137}Cs (circles) and total chlordane (TC+CC, squares) profiles from the LIMB core, and sediment-mixing model simulations (lines), assuming a constant flux of ^{210}Pb and a time-varying ^{137}Cs flux to surface-waters (assuming input from fallout only in b). The complete list of model inputs is provided in Table A.1. Brief model simulation descriptions include: a, b) mass accumulation rate = 0.27 g cm^{-2} yr^{-1} (sedimentation rate ≈ 0.7 cm yr^{-1}) with bioturbation to 19 cm averaging 28 cm^2yr^{-1} (solid line), and 3 cm^2yr^{-1} (dashed line); c, d, e) mass accumulation rates of 0.23 g cm^{-2} yr^{-1} (dotted line), 0.27 g cm^{-2} yr^{-1} (solid line) 0.30 cm^{-2} yr^{-1} (dashed line) (sedimentation rates = 0.57, 0.68 and 0.74 cm yr^{-1}), with bioturbation to 19 cm averaging 5 cm^2 yr^{-1}(dotted line), 3.4 cm^2 yr^{-1}(solid line) and 5 cm^2 yr^{-1}(dashed line). ^{137}Cs input includes a flux over and above that expected from fallout in d), as discussed in text; e) mass accumulation = 0.27 g cm^{-2} yr^{-1} and bioturbation to 19 cm averaging 3.4 cm^2 yr^{-1}, with a peak in chlordane delivery to surface waters in 1971 (line), based on usage records (see text).

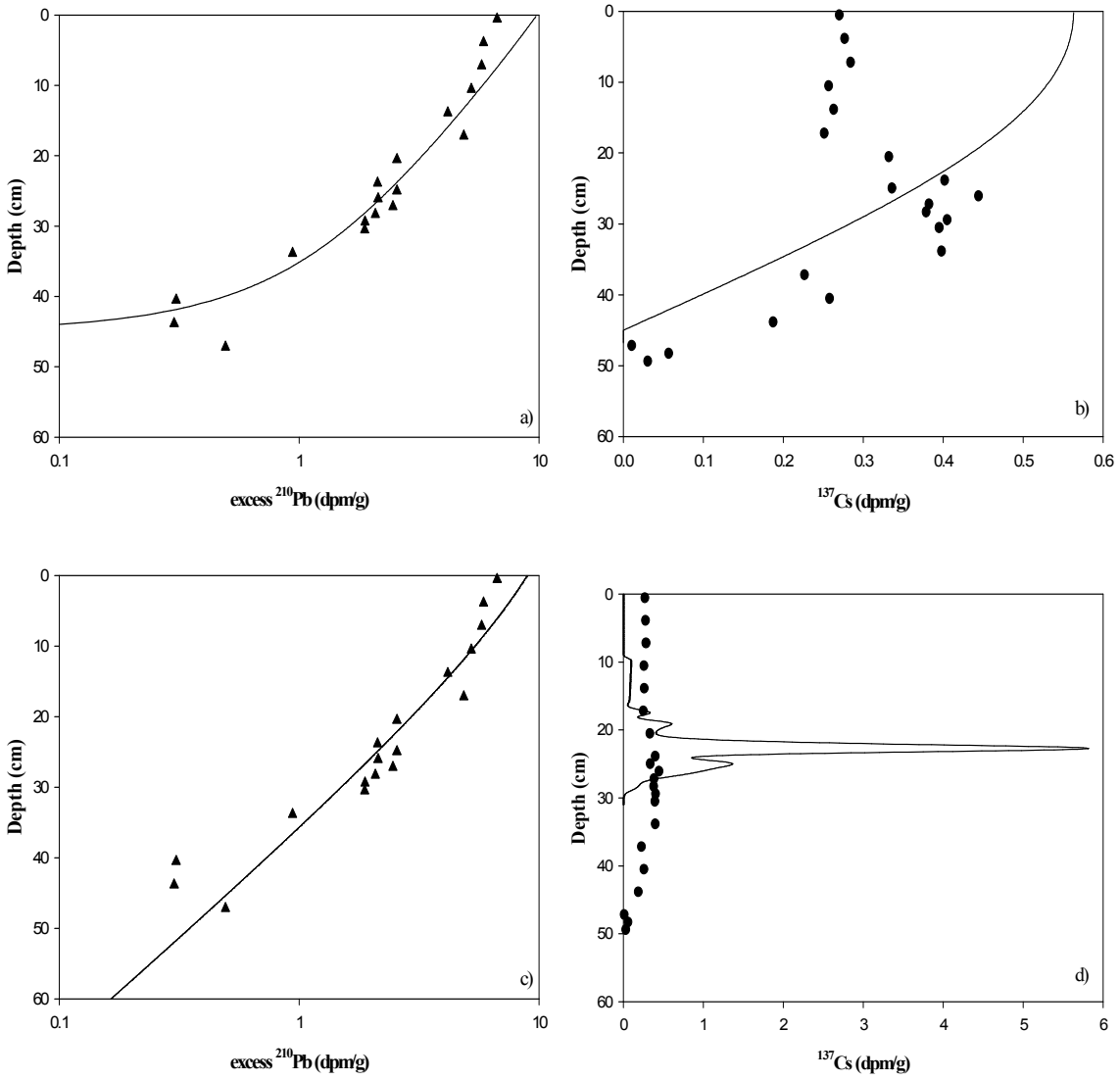

Figure A.2 ^{210}Pb (triangles) and ^{137}Cs (circles) profiles from the LIMB, and sediment-mixing model simulations (lines), assuming a constant flux of ^{210}Pb and a time-varying ^{137}Cs flux to surface-waters. Brief model simulation descriptions include: a, b) diffusive bioturbation to 45 cm, averaging 11 $cm^2\ yr^{-1}$ (no sedimentation); c, d) sedimentation only (no mixing), with mass accumulation = 0.2 $g\ cm^{-2}\ yr^{-1}$ (sedimentation rate=0.5 $cm\ yr^{-1}$). Note different scale for d.

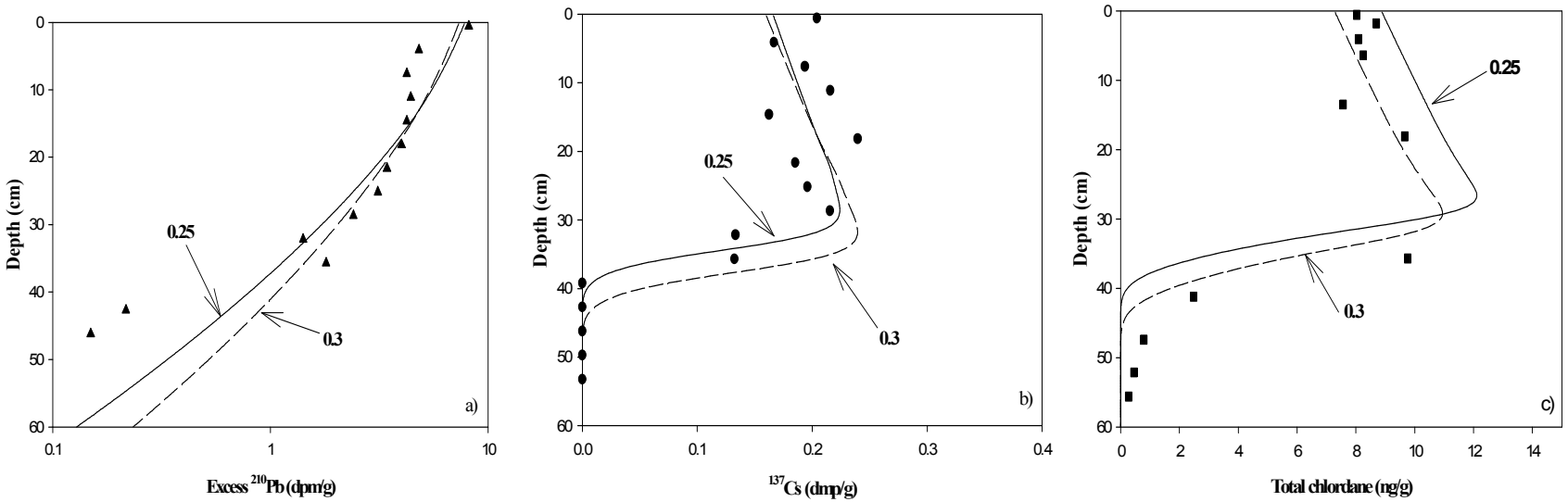

Figure A.3 Excess ^{210}Pb (a), ^{137}Cs (b) and total chlordane data (c) from the LITN core, as well as model simulations assuming mass accumulation rates of 0.25 g cm^{-2} yr^{-1} (solid line) and 0.30 g cm^{-2} yr^{-1} (dashed line). The chlordane input in c) peaks in 1971 based on usage records (see text).

Table A.1 A brief description of each model parameter and parameter values used in the numerical model runs presented in Figures 5.14, 5.15. For a more thorough description of model parameters see ref (Santschi, Li et al. 1980; Crusius 1992; Crusius, Bothner et al. 2004). Porosities were fit to measured porosities.

		LIMB	**LIMB**	**LIMB**	**LIMB**	**LITN**
		Fig. A.1a,b	**Fig. A.1c,d,e**	**Fig. A.2a,b**	**Fig. A.2c,d**	**Fig. A.3**
z1	Bottom depth of top mixed layer (cm)	19	19	45	19	15
z3	Bottom depth of modeled profile (cm)	120	120	120	120	130
r1	Surficial sediment mixing parameter (g cm^{-2} yr^{-1}) that affects D_b, $D_b(z)$ = r1*mz/((1-p(z))*rs), for 0 < z < z1	50 (solid) 6(dashed)	5 (dotted) 6 (solid) 9 (dashed)	23	0.001	100
pinf	Porosity at infinite depth (cm^3 water cm^{-3} total sediment)	0.80	0.80	0.80	0.80	0.4
p0	Porosity increment	0.09	0.09	0.09	0.09	0.5
a	Attenuation constant of porosity with depth, in overall porosity expression of p(z) = pinf+p0*exp(-a*z).	0.05	0.05	0.05	0.05	0.01
mz	Model depth step (cm)	0.2	0.2	0.2	0.2	0.2
rs	Sediment dry density (g cm^{-3})	2.5	2.5	2.5	2.5	2.5
MAR	Mass accumulation rate (g cm^{-2} yr^{-1})	0.27	0.23 (dotted) 0.27 (solid) 0.30 (dashed)	0.0001	0.2	0.25 (solid) 0.30 (dashed)
alr	Decay constant (yr^{-1})	0.0311, 0.023	0.0311, 0.023	0.0311, 0.023	0.0311, 0.023	0.0311, 0.023

Table A.2 Parameter values derived from the best-fit simulations of the radionuclide data and inventories of ^{210}Pb, ^{137}Cs and chlordane.

Parameter	LIMB	LITN	LILN
	Fig. A.1c,d,e	**Fig. A.3**	**No Fig.**
Z_b, Mixed layer depth (cm)	19	15	50
D_b, Bioturbation rate (cm^2 yr^{-1})[a]	3.4 (solid)	60	80
Porosity range[b]	0.80-0.89	0.73-0.90	0.85
MAR, Mass accumulation rate (g cm^{-2} yr^{-1})	0.27 (solid)	0.3 (dashed)	0.26
s, Sedimentation rate (cm yr^{-1})[c]	0.68 (solid)	0.6 (dashed)	0.7
P_e, Peclet number	3.8	0.15	0.4[e]
^{210}Pb (dpm cm^{-2})	54.8	67.8	54.5
^{137}Cs (dpm cm^{-2})	6.13	3.58	2.89
Chlordane (ng cm^{-2})	417	449	159

[a] Average for entire mixed layer (decreases with decreasing porosity).
[b]The porosity data were fit with an exponential function, with highest porosities at the sediment-water interface.
[c]The mass accumulation rate is assumed constant in this model, but the sedimentation rate is dependent on the porosity, which decreases with depth in most sediment cores. For this estimate of sedimentation rate, the average porosity for the excess ^{210}Pb and ^{137}Cs-containing sediments has been used.
[d]Not estimated with confidence.
[e]Highest of all estimates (could be as low as 0.1).

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