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Relations Between Land Use and Organochlorine Pesticides, PCBs, and Semi-Volatile Organic Compounds in Streambed Sediment and Fish on the Island of Oahu, Hawaii

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Abstract. Bed-sediment and/or fish samples were collected from 27 sites around the island of Oahu (representing urban, agricultural, mixed, and forested land use) to determine the occurrence and distribution of hydrophobic organic compounds including organochlorine pesticides, polychlorinated biphenyls (PCBs), and semi-volatile organic compounds (SVOCs). Of the 28 organochlorine compounds analyzed in the fish, 14 were detected during this study. Nineteen of the 31 organochlorine compounds and 40 of the 65 SVOCs were detected in the sediment. Urban sites had the highest number of detections and tended to have the highest concentrations of pesticides. Chlordane compounds were the most frequently detected constituents at urban sites, followed by dieldrin, polycyclic aromatic hydrocarbons (PAHs), and DDT compounds. PAHs were the most frequently detected constituents in watersheds with mixed (urban and agricultural) land use. The only pesticides detected at agricultural sites were DDT and its degradation products, DDD and DDE. No pesticides or PCBs were detected at the forested sites, but a few ubiquitous SVOCs were found in sediments at some forested sites. In general, concentrations of the most frequently detected pesticides were higher in fish than in sediment. Following a trend that has been observed elsewhere in the nation, concentrations of most organochlorine pesticides and PCBs are decreasing in Hawaii.

Although production or use of many organochlorine compounds, including pesticides and polychlorinated biphenyls (PCBs), has been banned in the United States for more than 25 years, they continue to be detected in streambed sediment and fish across the nation (Nowell *et al.* 1999; Smith *et al.* 1988). These compounds can occur at levels that exceed criteria for the protection of fish and invertebrates that live in streams, and of the wildlife that consume them (Black *et al.* 2000; Lopes and Furlong 2001). Other, semi-volatile, organic compounds (SVOCs) such as phenols, phthalates, and polycyclic aromatic hydrocarbons (PAHs) continue to have widespread usage today (Lopes and Furlong 2001; Van Metre *et al.* 2000). The persistence of these compounds, their tendency to accumulate in sediment and biota, and their potentially harmful effects have made them a substantial management concern.

The presence of persistent organic compounds in the environment has been shown to be related to both past and present land use in a watershed (Nowell *et al.* 1999). Following the first applications of DDT in 1939, organochlorine pesticides were heavily used in agricultural settings and to control urban pests such as termites and mosquitoes (Wong *et al.* 2000). Use of these pesticides was largely banned in the United States in the 1970s and 1980s. Other types of organic compounds including PCBs and SVOCs typically have industrial applications and are primarily associated with urban land use (Lopes and Furlong 2001). PCBs and chlorinated insecticides have been described as the most persistent anthropogenic organic compounds introduced into the environment since the lead and arsenic pesticides of the early 1900s (Smith *et al.* 1988). PCBs were primarily used to insulate electrical equipment such as high-voltage transformers, and also in the manufacture of a variety of materials including hydraulic fuels, paints and dyes, adhesives, wood preservatives, and in pesticide preparations. Production of PCBs ceased in the 1970s, but they still exist today in more than 2 million transformers and capacitors in the United States (Smith *et al.* 1988). SVOCs are so commonly used and in such a wide variety of functions that they are nearly ubiquitous in the environment. SVOCs include phthalates used in plastics, phenols used in disinfectants and in manufacturing chemicals, and polycyclic aromatic hydrocarbons (PAHs). PAHs are produced during incomplete combustion, for example from vehicle exhaust and waste incinerators (Lopes and Furlong 2001), and concentrations appear to be increasing over the past three decades in urban areas (Van Metre *et al.* 2000).

Organic compounds can enter the aquatic environment from a variety of sources including the atmosphere, industrial and municipal effluents, and agricultural and urban nonpoint-source runoff. Organochlorine pesticides, PCBs, and SVOCs typically have low solubility, are associated with particulates,

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and are often transported through soil erosion and surface runoff. They are commonly associated with bottom sediments and are transported through the food chain via benthic algae and invertebrates, which can then be eaten by fish and birds. Many contaminants have been linked to detrimental effects on stream biota, ranging from acute exposure, leading directly to mortality, to chronic and indirect effects. Many organochlorine pesticides are known animal carcinogens and are potential human carcinogens (Nowell *et al.* 1999). The adverse effects of DDT on reproduction in birds has been well documented (Faber and Hickey 1973), and other organochlorine pesticides have been linked to a range of sublethal effects including biochemical and physiological changes, behavioral changes, suppressed immune system responses, reduced fecundity, morphological deformations, and endocrine disruption (Murty 1986; Madhun and Freed 1990). Endocrine disruption in particular has been the focus of an increasing number of scientific investigations in recent years (Goodbred *et al.* 1996; Kavlock *et al.* 1996; Colborn and Thayer 2000).

The presence and persistence of organic compounds have been well documented in the temperate continental United States, with a growing interest in the spatial and temporal patterns of these compounds (Schmitt *et al.* 1990; Nowell *et al.* 1999; Van Metre *et al.* 2000; Wong *et al.* 2000). Less is known of their fate in tropical island systems, but previous studies in Hawaii have shown concentrations of certain compounds such as chlordane and dieldrin to be among the highest in the nation (Bevenue *et al.* 1972; Tanita *et al.* 1976; Schmitt *et al.* 1981, 1985, 1990; Hunter *et al.* 1995; Brasher and Anthony 2000).

Large-scale organochlorine pesticide application has been utilized in urban Oahu areas to control termites and mosquitoes. Over 100 million dollars is spent annually to prevent and control infestations of the Formosan subterranean termite (*Coptotermes formosanus*) and to repair the damage they cause to buildings (Yates and Tamashiro 1990). The organochlorine pesticides chlordane, aldrin, dieldrin, and heptachlor have been used for termite control. In 1977, 125,600 pounds of chlordane, 24,000 pounds of heptachlor, and 9,000 pounds of aldrin were used for pest control in Hawaii (Pesticide Hazard Assessment Project 1982).

The Hawaiian island of Oahu was one of 51 study units established as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) program to assess the status and trends of the nation's surface and groundwater resources, and to link status and trends with an understanding of the natural and human factors that affect water quality (Gilliom *et al.* 1995). As part of the NAWQA program, streambed sediment and/or fish were collected from 27 stream sites in 16 watersheds around the island of Oahu. Sites were selected to represent the major land uses on Oahu. The objectives of this study were 1) to determine the occurrence and distribution of organochlorine pesticides, PCBs, and SVOCs in streams on the island of Oahu, 2) to assess their relation to land use, and 3) to assess temporal and geographical trends in the concentrations of these compounds.

Description of Study Area

The island of Oahu is the third largest and most populous island in the State of Hawaii. Current land-use patterns on Oahu reflect increases in population and decreases in large-scale agriculture during the 20th century (Klasner and Mikami 2003). The last two sugar cane plantations on Oahu closed in the mid-1990s, and most of the land that was once used for sugar cane has been or is now being converted to diversified agriculture, or is being developed for urban use (Oki and Brasher 2003). Accompanying this transition from plantation-style agriculture to developed urban areas, the resident population of Oahu increased from 58,500 people in 1900 to more than 876,000 in 2000 (State of Hawaii 2000). Honolulu, which is the capital city located on the island of Oahu, is one of the 25 largest cities in the nation and is now considered the most densely populated city in the nation (Fulton *et al.* 2001). As of 1998, about 26% of the land on Oahu was classified as urban, 16% as agricultural, and 58% was classified as other (primarily forested) (Klasner and Mikami 2003).

Streams on Oahu originate in the steep mountainous interiors of the island and generally flow less than 16 km before reaching the coast. The upper portions of all watersheds on Oahu are forested, with agriculture and urban development occurring closest to the coast (Oki and Brasher 2003). Both intermittent and perennial streams on Oahu may gain water along some reaches and lose water along other reaches depending on local geohydrologic conditions. Streams on Oahu flow perennially mainly because of ground-water discharge, with rainfall and runoff primarily contributing to high flows and flood events (Oki and Brasher 2003). Consequently, both ground water and surface water runoff can contribute contaminants to stream systems in Hawaii.

Materials and Methods

Sites were selected to represent the major land uses on Oahu: urban (residential and commercial-industrial), agricultural, and forested reference (Fig. 1). Because the upper reaches of all sites on Oahu are forested, a certain percentage of land cover upstream in the watershed at every site is forest. For this study, sites were assigned land-use designations (urban, mixed urban and agriculture, agriculture, or forested) based on dominant mapped land-use (Klasner and Mikami 2003) and personal observation of the surrounding area. Eight sites were designated urban, 10 sites were mixed, 3 sites were agricultural, and 6 sites were forested (Table 1).

Fish samples were analyzed for organochlorine pesticides and PCBs. Sediment samples were analyzed for organochlorine pesticides, PCBs, and SVOCs. A complete list of analytes and minimum reporting levels (mrl's) are available in Lopes and Furlong (2001) and Wong *et al.* (2000). Briefly, mrl's for fish were 5 μg/kg wet weight for all compounds except total PCBs (50 μg/kg) and toxaphene (200 μg/kg). For sediment, mrl's (dry weight) were 1 or 2 μg/kg for most organochlorine compounds; 5 μg/kg for chlorneb, DCPA, methoxychlor and permethrin; 100 μg/kg for total PCBs; and 200 μg/kg for toxaphene. The mrl for all SVOCs in sediment was 50 μg/kg (dry weight).

Sample Collection

Streambed sediment samples were collected during low flow conditions in 1998 and 2000 at 17 sites on Oahu. Samples were collected following standard NAWQA protocols (Shelton and Capel 1994). Clean techniques were used throughout sample collection and processing. Bed-sediment samples were collected by using stainless steel spoons and were deposited in a glass bowl. Prior to sampling, equip-

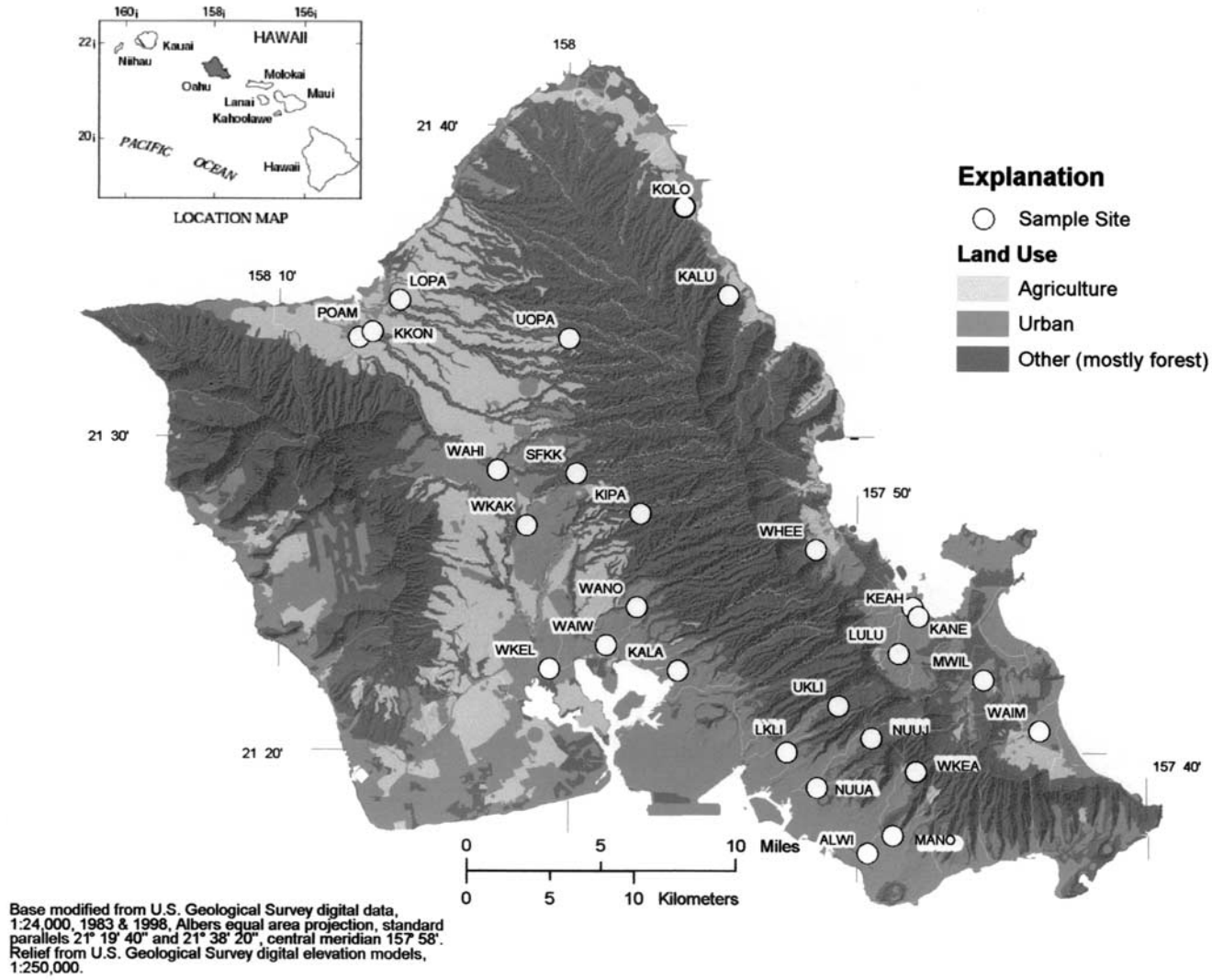

Fig. 1. Sampling sites on the island of Oahu. Land use modified from Klasner and Mikami (2003). See Table 1 for site names corresponding to four-letter code

ment was washed in a dilute solution of a phosphate-free detergent, then rinsed in tap water, deionized water, and finally methanol. Equipment was allowed to air dry and was then wrapped in aluminum foil.

At wadeable sites, fine sediment was obtained from the surficial 2 cm at various undisturbed depositional areas along each 100-m stream reach. At non-wadeable sites, a stainless-steel corer with a Teflon® sleeve was used to collect samples. The upper 2 cm of the core was used as the sample, with five to ten cores taken at each site. Sediment was composited into a glass bowl until an adequate amount (around 1.5 L) was obtained for processing. The composite samples were well mixed and then put through a 2.0-mm stainless steel sieve and collected in 500-ml precleaned glass containers. Samples were then placed on ice and shipped to the U.S. Geological Survey's National Water Quality Laboratory in Denver, Colorado for analysis.

Fish were collected and processed following standard NAWQA protocols (Crawford and Luoma 1993; Meador *et al.* 1993). Sampling was conducted during low flow conditions in 1998, 2000, and 2001. Fish were collected from all available habitat types within a 100-m reach at each site by using a battery-powered backpack electrofisher. Clean techniques were used throughout sample collection and processing. Individual fish were sorted by species, sexed, weighed, and measured. Composite samples of approximately 100 g of whole fish of the same species were obtained from each site. For smaller species (Poeciliidae), composites consisted of approximately 100 individuals per sample; for larger species, five to eight individuals were composited. The composite samples were wrapped in aluminum foil, placed in plastic bags, then frozen on dry ice and shipped to the National Water Quality Laboratory for analysis.

Laboratory Analysis

Bed-sediment and fish samples were analyzed for organochlorine pesticides and breakdown products, total PCBs, and semi-volatile organic compounds (sediment only) at the U.S. Geological Survey National Water Quality Laboratory. Methods are described in detail in Foreman *et al.* (1995) for sediment and in Leiker *et al.* (1995) for fish. Briefly, bed-sediment composite samples were centrifuged and homogenized. An aliquot of approximately 2 g was placed on a drying balance for determination of dry weight. Another sub-sample equivalent to 25 g of sediment on a dry-weight basis was taken, treated to

Table 1. Sampling sites, site acronyms, fish species collected, and land use (total percentage land use may not be exactly 100, due to rounding)

		Fish		Sediment		Land-use categories (percent)				
Site	Code	1998	2000/ 2001	1998	2000	Urban Residential	Urban Industrial	Agriculture	Forest	Land-use designation
Ala Wai Canal	ALWI	TILP				43	3	2	52	urban
Kalauao Stream	KALA		SPHE		x	12	1	0	87	urban
Kalihi Stream (Lower)	LKLI		XIPH		x	20	4	0	77	
			SPHE							urban
Kalihi Stream (Upper)	UKLI		ANCI		x	2	3	0	95	urban
Kaluanui Stream	KALU		XIPH			0	0	0	100	forest
Kaneohe Stream	KANE	SPHE	SPHE	x		51	11	3	36	
		GAMB								urban
Kaukonahua Stream	KKON		TILP			11	5	11	74	mixed
Keaahala Stream	KEAH		SPHE			77	9	0	15	
			GAMB							urban
Kipapa Stream	KIPA		ANCI		x	0	0	0	100	forest
Koloa Gulch	KOLO		TILP			0	0	4	96	agriculture
Luluku Stream	LULU		XIPH		x	2	11	17	70	mixed
Manoa Stream	MANO	XIPH	SPHE	x		37	1	1	61	
		GAMB	ANCI							urban
Maunawili Stream	MWIL		HEMI		x	13	0	3	83	mixed
Nuuanu Stream (Lower)	NUUA	SPHE	SPHE	x		19	1	0	80	
			ELEO							urban
Nuuanu Stream (Upper)	NUUJ		DOLO			4	1	0	95	forest
Opaeula Stream (Lower)	LOPA		HEMI			0	0	19	81	agriculture
Opaeula Stream (Upper)	UOPA		XIPH			0	0	0	100	forest
Poamoho Stream	POAM	HEMI		x		3	4	55	38	agriculture
SF Kaukonahua Stream	SFKK		DOLO			0	0	0	100	mixed
Wahiawa Reservoir	WAHI		TILP			16	3	1	80	mixed
Waiakeakua Stream	WKEA		XIPH		x	0	0	4	96	mixed
Waiawa Stream	WAIW		SPHE		x	9	2	16	73	mixed
Waihee Stream	WHEE	XIPH	XIPH	x		1	0	0	99	forest
Waikakalaua Stream	WKAK		XIPH		x	35	5	7	52	mixed
Waikele Stream	WKEL	XIPH		x		18	10	26	46	mixed
Waimanalo Stream	WAIM		SPHE		x	10	0	19	71	mixed
Waimano Stream	WANO		XIPH		x	4	0	0	96	forest

Fish acronyms: *Ancistrus* sp. (ANCI), *Eleotris sandwicensis* (ELEO), *Gambusia affinis* (GAMB), *Hemichromis elongatus* (HEMI), *Micropterus dolomieu* (DOLO), *Poecilia sphenops* (SPHE), *Tilapia melanotheron* (TILP), *Xiphophorus helleri* (XIPH)

remove residual water, and four to six surrogate compounds (α-d6-hexachlorocyclohexane, 3,5-dichlorobiphenyl, octachlorobiphenyl, terphenyl-d14, 2-fluorobiphenyl, and nitrobenzene) were added. Whole-fish samples were homogenized, by using a meat grinder, to form a single composite sample. A 10-g aliquot was then treated to remove residual water, and two surrogates (α-d6-hexachlorocyclohexane and 3,5-dichlorobiphenyl) were added. Both the bed-sediment and fish samples were Soxhlet extracted in methylene chloride overnight. For fish samples, the extract was then concentrated to a volume of 5 ml, and a 1-ml aliquot was removed for determination of lipid content.

Analytes of interest were isolated by gel permeation chromatography. Alumina/silica adsorption chromatography was used to fractionate the extract, and each fraction was then analyzed by dual capillary-column gas chromatography (GC) with electron-capture detection. Compound identification in a sample was based on comparison of GC retention times on both capillary columns with those obtained with external standard mixtures. Compound quantitation was based on calibration curves derived from external standard mixtures. Reported concentrations are from the lower of the two responses observed on the two GC columns, except where recognized compound coelutions or interferences result in a single-column quantitation only (Foreman *et al.* 1995; Leiker *et al.* 1995). Quality assurance procedures performed by the laboratory included blanks, surrogate spikes, and reagent spikes, and standard reference material for tissue. No adjustments for recovery efficiency were made in the data analysis. Surrogate and reagent recoveries were within acceptable levels according to methods performance standards outlined in reports by Leiker *et al.* (1995) and Foreman *et al.* (1995). A split of each bed-sediment sample was sent to the U.S. Geological Survey's Cascades Volcano Laboratory in Vancouver, Washington for determination of percentage particle-size distribution.

Data Analysis

Data presented in this report from Oahu are available on the web at http://hi.water.usgs.gov/nawqa/bst.html. National NAWQA data, a list of target analytes, and analytical reporting levels are available at http://ca.water.usgs.gov/pnsp/. In calculating detection frequencies, all samples reported by the laboratory as detected were counted. This includes samples with estimated concentrations. In these cases, the compound being measured has been conclusively identified as present, but quantification is approximate. Five SVOCs (bis 2-ethylhexylphtha-

late, butylbenzylphthalate, di-*n*-butylphthalate, diethylphthalate, and phenol) showed contamination in 5% or more of the laboratory blank samples; data for these compounds were censored for concentrations below the 95th percentile blank (L. Nowell, U.S. Geological Survey, personal communication).

Although lipid concentration varied between species, and within the same species in different samples, from a low of 1.2% at two sites to a high of 14% at one site (mean 4.72 ± 2.80), normalizing for lipid concentration to standardize the data did not provide consistent results. No correlation was found between percentage lipid content and concentration of the most frequently detected compounds in fish. The fish data presented here were, therefore, not normalized for lipid content.

To evaluate the absorption potential of sediment from different streams, samples were analyzed for total organic carbon (TOC) and percentage particle-size distribution less than 63 μm (silt). TOC concentrations ranged from 9 to 81 g/kg (mean 43 ± 26) and percent silt from 5 to 100 (mean 49 ± 26). However, no correlation was found between either TOC or particle size and concentration of the most frequently detected compounds in sediment; therefore, the data presented here were not corrected for TOC or particle size.

Concentrations measured in the sediment were compared with the Canadian Sediment Quality Guidelines (CSQG) for aquatic life (Canadian Council of Ministers of the Environment 1999). Two assessment values have been calculated for the CSQG. The lower value or threshold effect level (TEL) represents concentrations below which adverse effects to aquatic biota are rarely expected to occur. The upper value or probable effect level (PEL) defines the level above which adverse effects to biota are expected to occur frequently. These guidelines are based on chronic (long-term) effects of contaminants on aquatic organisms.

Contaminant levels found in fish were compared with the New York State Department of Environmental Conservation (NYSDEC) guidelines for the protection of mammals and birds that consume fish (Newell *et al.* 1987), currently the most comprehensive guidelines available for fish. As a screening tool only, concentrations in fish that could potentially be consumed by humans were compared with the U.S. Environmental Protection Agency (USEPA) screening criteria for edible fish for the protection of human health (USEPA 2000).

Principal components analysis (PCA) was performed on the bed sediment SVOC contaminant data (Kovach 1998). PCA is a multivariate technique that can reduce the individual effects of multiple variables into principal components that are linear combinations of the original variables. Redundant variables can be eliminated from subsequent analysis by an iterative process until surrogate variables are identified that best represent each portion of the variance within the group of correlated variables. Spearman rank correlations (a nonparametric technique; SAS Institute 1993) were performed to identify correlated variables that contributed redundant information. These two techniques were used to reduce the SVOC data set from 40 variables to 9 proxy variables. Patterns among the variables were used to identify associations between land use and organic compounds.

Table 2. Number of organic compounds detected (including estimated concentrations) in whole fish and bed sediment (<2 mm size fraction). Site and fish acronyms in Table 1

Land use designation	Site	Fish	Number of compounds detected in fish (maximum 28)	Number of compounds detected in sediment (maximum 96)
Urban	ALWI	TILP	9	[a]
	KALA	SPHE	10	39
	KANE	SPHE	10	33
		SPHE	9	
		GAMB	7	
	KEAH	SPHE	11	[a]
		GAMB	9	
	LKLI	SPHE	11	35
		XIPH	11	
	MANO	SPHE	10	45
		XIPH	10	
		GAMB	8	
		ANCI	11	
	NUUA	ELEO	8	33
		SPHE	11	
		SPHE	11	
	UKLI	ANCI	2	9
Mixed	KKON	TILP	8	[a]
	LULU	XIPH	2	10
	MWIL	HEMI	4	33
	SFKK	DOLO	11	[a]
	WAHI	TILP	5	[a]
	WAIM	SPHE	5	17
	WAIW	SPHE	6	38
	WKAK	XIPH	11	32
	WKEA	XIPH	4	13
	WKEL	XIPH	3	41
Agriculture	KOLO	TILP	1	[a]
	LOPA	HEMI	1	[a]
	POAM	HEMI	3	5
Forest	KALU	XIPH	0	[a]
	KIPA	ANCI	0	0
	NUUJ	DOLO	0	[a]
	UOPA	XIPH	0	[a]
	WANO	XIPH	0	4
	WHEE	XIPH	0	3
		XIPH	0	

[a] Sediment not sampled at site.

Results and Discussion

Of the 96 organochlorine compounds analyzed in sediment, no more than five were detected at any given forested or agricultural site (Table 2). No organochlorine compounds were detected in fish at the forested sites. Only one compound (of 28) was detected in fish at two of the agricultural sites, and only three compounds were detected at the third agricultural site. In general, urban and mixed land-use sites that had a low number of detections (such as UKLI) tended to have a relatively high percentage of forested land in the watershed.

Chlordane compounds (*cis*-chlordane, *trans*-chlordane, heptachlor epoxide, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane) were the most frequently detected constituents at urban sites and were detected in nearly every fish and sediment sample from urban sites (Table 3). Chlordane and aldrin (the parent compound of dieldrin, the second most frequently detected constituent at urban sites) were widely used in Hawaii for termite control (Pesticide Hazard Assessment Project 1982). Chlordane compounds and dieldrin were also commonly detected in fish at mixed land-use sites, but never at agricultural or forested sites.

The insecticide DDT was viewed as highly beneficial to crop production and was used extensively in Hawaii to control agricultural pests (Honolulu Star Bulletin 1944). There was also widespread aerial spraying of DDT for mosquito control to

Table 3. Number of detections of organochlorine pesticides and PCBs in whole fish and bed sediment at urban, mixed, agriculture, and forest land-use settings (including estimated concentrations)

	Urban		Mixed		Agriculture		Forest	
Compound	Fish (n = 8)	Sediment (n = 6)	Fish (n = 10)	Sediment (n = 7)	Fish (n = 3)	Sediment (n = 1)	Fish (n = 6)	Sediment (n = 3)
Aldrin	0	4	0	1	0	0	0	0
cis-Chlordane	8	6	6	6	0	0	0	0
trans-Chlordane	7	6	1	6	0	0	0	0
o,p′-DDD	0	0	0	1	0	0	0	0
p,p′-DDD	5	5	3	2	1	1	0	0
o,p′-DDE	0	0	0	1	0	0	0	0
p,p′-DDE	6	5	8	4	3	1	0	0
o,p′-DDT	1	0	0	1	0	1	0	0
p,p′-DDT	5	4	3	3	1	1	0	0
Dieldrin	7	5	7	5	0	0	0	0
Endrin	0	1	0	0	0	0	0	0
Heptachlor	0	5	0	0	0	0	0	0
Heptachlor epoxide	6	4	5	0	0	0	0	0
Hexachlorobenzene	6	2	2	4	0	0	0	0
cis-Nonachlor	7	5	8	5	0	0	0	0
trans-Nonachlor	8	6	9	6	0	0	0	0
Oxychlordane	7	2	4	0	0	0	0	0
PCB	1	3	2	3	0	0	0	0
Pentachloroanisole	0	0	1	0	0	0	0	0
cis-Permethrin	[a]	1	[a]	0	[a]	0	[a]	0
trans-Permethrin	[a]	1	[a]	0	[a]	0	[a]	0

Sites grouped by land use.
[a] Not measured in fish.

prevent the transmission of human diseases in urban areas (R. Boesch, Hawaii Department of Agriculture, personal communication). The only compounds detected in fish at the agricultural sites were DDT and its degradation products DDE and DDD (Table 3). DDD and DDT were detected in fish at 63% of the urban sites and at 30% of the mixed land-use sites. DDE was detected in fish in at least 75% of the urban and mixed land-use sites. At least one metabolite of DDT, or DDT itself, was detected in sediment at 83% of the urban sites, 57% of the mixed land-use sites, and at the one agricultural site where sediment was collected.

Hexachlorobenzene, which has been used as a fungicide and in the production of rubber, dyes, wood preservatives, and fireworks, was frequently detected in both fish (75% and 20%) and sediment (33% and 57%) at the urban and mixed land-use sites, respectively. Total PCB concentration was calculated at the laboratory as the sum of Aroclors 1242, 1254, and 1260. PCBs were detected only at urban and mixed land-use sites and were more common in the sediment than in the fish.

Of the compounds analyzed in both fish and sediment, five compounds were detected only in sediment and not in fish, and the compound pentachloroanisole was detected only once, in a fish sample (Table 3). Aldrin, which is quickly metabolized to dieldrin in the environment, and heptachlor, which is quickly degraded to heptachlor epoxide, were found only in the sediment. The metabolites dieldrin and heptachlor epoxide were found in both fish and sediment. Concentrations of the most frequently detected pesticides (chlordane compounds, dieldrin, hexachlorobenzene, and DDT compounds) tended to be much higher in fish (wet weight) than in sediment (dry weight). Concentrations were not adjusted for moisture content, which would amplify this pattern. However, at four sites, *trans*-chlordane concentrations in sediment exceeded those in fish, and at two sites *p,p′*-DDT in sediment exceeded that in fish.

The most frequently detected SVOCs were PAHs (Table 4). Phthalates were also commonly detected. Least commonly detected were chloro-aromatics, nitro-aromatics, and chloro-ethers. Urban and mixed land-use sites had the highest number of SVOCs detected; as many as 30 of the 65 compounds analyzed were detected at such sites. Only one SVOC was detected at the agricultural site, and between zero and four at the forested sites.

A principal components analysis (PCA) of nine SVOC proxy variables resulted in two principal components explaining 82% of the variance in the dataset. The first principal component accounted for 60% of the variance and was primarily associated with PAHs and azaarenes, compounds associated with incomplete combustion. The second principal component accounted for an additional 22% of the variance. This component was primarily associated with phthalates and cresol (a phenol). The PCA resulted in three distinct groupings of sites based on the SVOCs (Fig. 2). The first group was associated with phthalates and cresol, compounds used in textiles, paint, construction materials, wood preservation and disinfectants. In addition, phthalates are used as plasticizers in an endless variety of household items including appliances, furnishings, apparel, and food containers and wrapping (Smith *et al.* 1988). These sites were in dense urban residential settings, typically close to the stream mouth, with a high proportion of land use categorized as urban, and population densities of approximately 2000 or more people per square mile. The second group were sites with mixed urban and agricultural land uses, with the urban land tending to be

Table 4. Number of detections of semi-volatile organic compounds in bed sediment at urban, mixed, agriculture, and forest land-use settings (including estimated concentrations)

Compound	Class	Urban (n = 6)	Mixed (n = 7)	Agriculture (n = 1)	Forest (n = 3)
1,6-Dimethylnaphthalene	Alkyl-PAH	1	2	0	0
1-Methyl-9H-fluorene	Alkyl-PAH	0	1	0	0
1-Methylphenanthrene	Alkyl-PAH	4	4	0	0
1-Methylpyrene	Alkyl-PAH	4	4	0	0
2,3,6-Trimethylnaphthalene	Alkyl-PAH	1	0	0	0
2,6-Dimethylnaphthalene	Alkyl-PAH	5	6	0	0
2-Methylanthracene	Alkyl-PAH	2	2	0	0
4-HCY Penphenanthrene	Alkyl-PAH	5	3	0	0
2,2′-Biquinoline	Azaarene	0	1	0	0
Acridine	Azaarene	2	3	0	0
Carbazole	Azaarene	3	2	0	0
Isoquinoline	Azaarene	0	1	0	0
Phenanthridine	Azaarene	2	2	0	0
Hexachlorobenzene	Chloro-aromatic	2	4	0	0
Isophorone	Cyclic ketone	0	1	0	0
9H-Fluorene	PAH	2	3	0	0
Acenaphthene	PAH	1	2	0	0
Acenaphthylene	PAH	1	2	0	0
Anthracene	PAH	6	6	0	0
Benzo(a)anthracene	PAH	6	6	0	0
Benzo(a)pyrene	PAH	5	6	0	0
Benzo(b)fluoranthene	PAH	5	6	0	0
Benzo(g,h,I)perylene	PAH	5	4	0	1
Benzo(k)fluoranthene	PAH	5	5	0	0
Chrysene	PAH	6	5	0	0
Dibenzo(a,h)anthracene	PAH	2	4	0	0
Fluoranthene	PAH	6	7	0	0
Indeno(1,2,3-cd) pyrene	PAH	5	5	0	0
Phenanthrene	PAH	6	5	0	0
Pyrene	PAH	6	7	0	0
p-Cresol	Phenol	5	6	0	1
Phenol	Phenol	3	2	1	0
bis(2-Ethylhexyl) phthalate	Phthalate	5	7	0	2
Butylbenzyl phthalate	Phthalate	5	5	0	1
Diethyl phthalate	Phthalate	0	0	0	1
Dimethyl phthalate	Phthalate	0	2	0	0
Di-*n*-butyl phthalate	Phthalate	3	2	0	1
Di-*n*-octyl phthalate	Phthalate	3	1	0	1
9,10-Anthraquinone	Quinone	5	3	0	0
Dibenzothiophene	Sulfurous-PAH	3	2	0	0

Sites grouped by land use. Only compounds detected at least once are included in the table.

dominated by commercial and industrial activities. The SVOCs typifying these sites included PAHs and azaarenes. In addition to being combustion by-products, PAHs are also used in manufacturing processes to produce moth balls, pesticides, dyes, synthetic resins, solvents, and lubricants. The third group of sites were those with mainly agricultural or forested land use. Few SVOCs were associated with these sites.

Half of the 28 organochlorine compounds analyzed in fish were not detected during this study. Twelve of the 31 organochlorine compounds and 25 of the 65 SVOCs analyzed in sediment were not detected. Many of the compounds that were not detected (such as toxaphene, chloroneb, pentachloronitrobenzene, lindane, and HCH (hexachlorocyclohexane)-isomers are typically used on corn, cotton, or soybeans, which are not grown extensively in Hawaii (R. Boesch, Hawaii State Department of Agriculture, personal communication). One example is the insecticide toxaphene, which was extensively used on cotton following the ban on DDT in 1972. Toxaphene residues in fish from cotton-growing regions of the continental United States were described as virtually ubiquitous during sampling from 1976 to 1979 (Schmitt *et al.* 1983). However, toxaphene was not detected in fish or sediment samples from Oahu during our study.

To assess potential impacts on stream biota and wildlife on Oahu, concentrations of the most frequently detected compounds in bed sediment and fish were compared with published guidelines for the protection of invertebrates in sediment, and wildlife that consume fish (Figs. 3 and 4). At present, few guidelines exist for SVOCs, but comparisons were made where possible. Concentrations of dieldrin and total chlordane (sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane) in sediment at the urban sites greatly

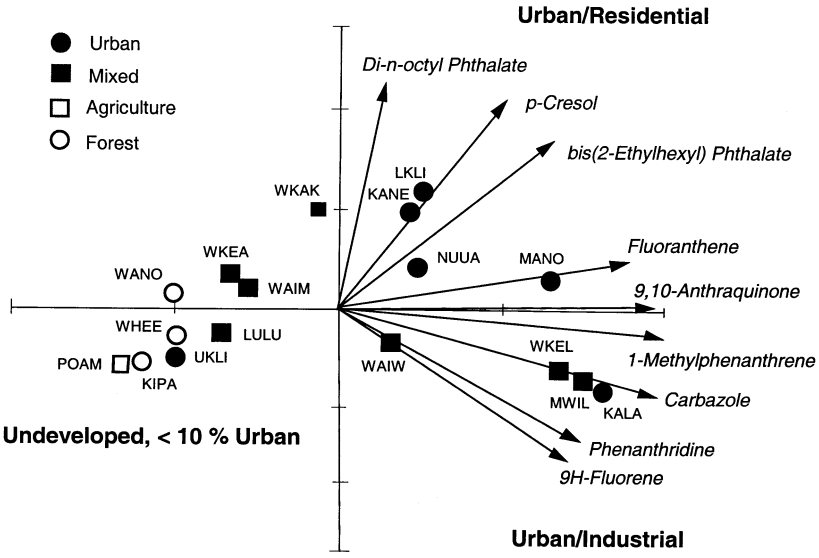

Fig. 2. Principal components analysis using nine proxy variables to represent semi-volatile organic compounds in sediment. Concentrations log 10 transformed. See Table 1 for site names corresponding to four-letter code

exceeded the PEL (above which deleterious effects are likely) of the Canadian Sediment Quality Guidelines (Canadian Council of Ministers of the Environment 1999). Concentrations of dieldrin in sediment ranged from 71 to 300 μg/kg at the urban sites ($n = 4$), concentrations of *cis*-chlordane from 31 to 120 μg/kg, and *trans*-nonachlor from 28 to 87 μg/kg. PCBs in sediment at the urban and mixed land-use site exceeded the TEL (below which adverse effects are unlikely), and at one urban site (NUUA) exceeded the PEL. DDE in sediment exceeded the PEL at the agricultural site, several of the mixed land-use sites, and one urban site. At sites where it was detected, concentrations of *p,p′*-DDE in the sediment ranged from 1 to 34 μg/kg. The PAHs benzo(a)anthracene, phenanthrene, pyrene, and chrysene consistently exceeded the TEL at both urban and mixed land-use sites. Concentrations of these SVOCs in sediment at one urban (KALA) and at least one mixed land-use (WKEL and MWIL) site also exceeded the PEL (except for chrysene at the mixed land-use sites).

Concentrations of dieldrin and total chlordane (sum of *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, and oxychlordane) in fish at the urban sites greatly exceeded the New York State Department of Environmental Conservation (NYSDEC) guidelines for the protection of birds and mammals that consume fish (Newell et al 1987). Concentrations of dieldrin in fish ($n = 16$) ranged from 50 to 1700 μg/kg at the urban sites. Only three samples were less than 400 μg/kg, and nine of the samples were greater than 700 μg/kg. Concentrations of *cis*-chlordane ranged from 17 to 460 μg/kg and *trans*-nonachlor from 36 to 640 μg/kg in fish at urban sites. Total DDT (*o,p′* and *p,p′* isomers of DDT, DDD, and DDE) in fish exceeded the guidelines at one mixed and one agricultural site. At sites where it was detected, concentrations of *p,p′*-DDE ranged from 4 to 180 μg/kg. Total PCBs in fish exceeded the NYSDEC guidelines at the three sites (one urban and two mixed land use) where they were detected. Although frequently detected at both urban and mixed land-use sites, hexachlorobenzene did not exceed the NYSDEC of 300 μg/kg.

Fish that could potentially be consumed by humans, tilapia (*Tilapia melanotheron*) or smallmouth bass (*Micropterus dolomieu*), were collected at six sites. Whole fish, rather than fillets, were analyzed. Consequently, human health guidelines (which are based on fillets) are not appropriate for direct comparison, but can be useful as a screening tool for indicating potential areas of concern (Nowell and Resek 1994) and may be useful in determining whether additional sampling of edible fish is warranted. At the urban and mixed land-use sites, between 5 and 11 organochlorine compounds were detected in the edible fish. At three sites (ALWI, SFKK, WAHI), concentrations in the whole-fish samples were higher than the USEPA screening criteria (USEPA 2000) for recreational fishers of edible fish, 20 μg/kg for total PCBs, and 2.5 μg/kg for dieldrin, suggesting additional analysis of fillets may be warranted. No samples exceeded the criteria of 117 μg/kg for total DDT or 114 μg/kg for total chlordane. No organochlorine compounds were detected in the edible fish from the forested site (NUUJ), and only a trace amount of *p,p′*-DDE was detected in the edible fish from the agricultural site (KOLO).

For chlordane-related compounds, there has been a general trend across the continental United States for the proportional composition of the chlordane mixture to change. Relative concentrations of *cis*-chlordane are increasing, while relative concentrations of *trans*-nonachlor, the most stable of the chlordane compounds, are decreasing (Schmitt *et al.* 1990; Nowell *et al.* 1999). However, this is not the case on Oahu, where concentrations of *cis*-chlordane and *trans*-nonachlor were nearly identical in fish. This has also been noted in a study by Tate and Heiny (1996) and may be an indication of more recent introductions into the aquatic system. Oxychlordane was detected in 88% of the fish samples and in only 33% of the sediment samples at urban sites, and in 40% of the fish samples but none of the sediment samples at mixed land-use sites. The relative abundance of oxychlordane in fish compared with sediment suggests that it is being produced by fish as a transformation product of chlordane, since oxychlordane is not expected to preferentially bioaccumulate in fish (Wong *et al.* 2000).

Technical DDT is made up primarily of *p,p′*-isomers, which were the predominant form found in both fish and sediment during this study. Ortho-isomers are found only as impurities in

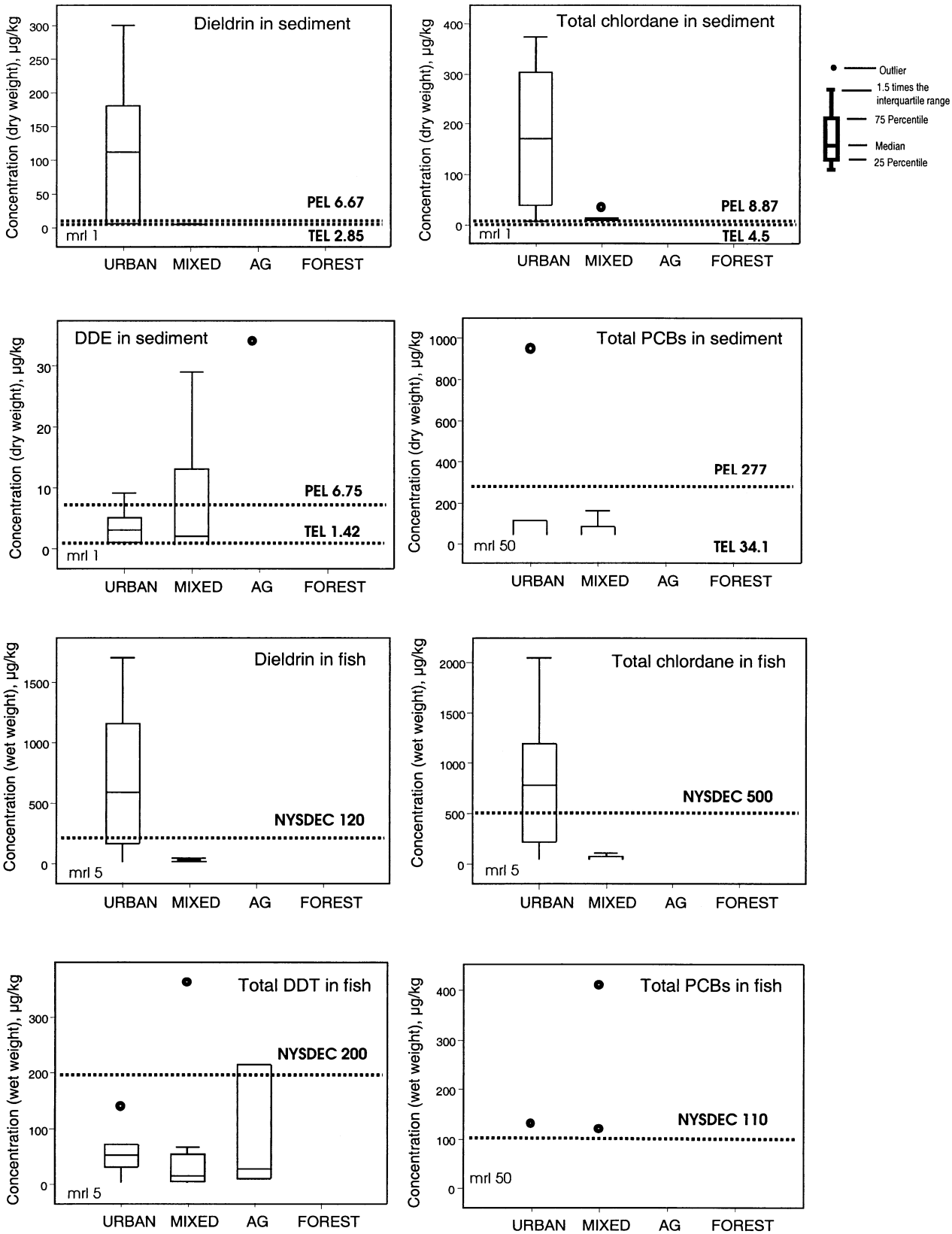

Fig. 3. Distribution of organic compound concentrations in fish and sediment samples from urban, mixed, agriculture (ag), and forested land-use sites. New York State Department of Environmental Conservation (NYSDEC) guidelines for fish. Canadian environmental quality guidelines for sediment; PEL, probable effect level; TEL, threshold effect level; mrl, minimum reporting level. Box plots are truncated at the lowest level of detection (minimum reporting level); the y-axis varies for different constituents

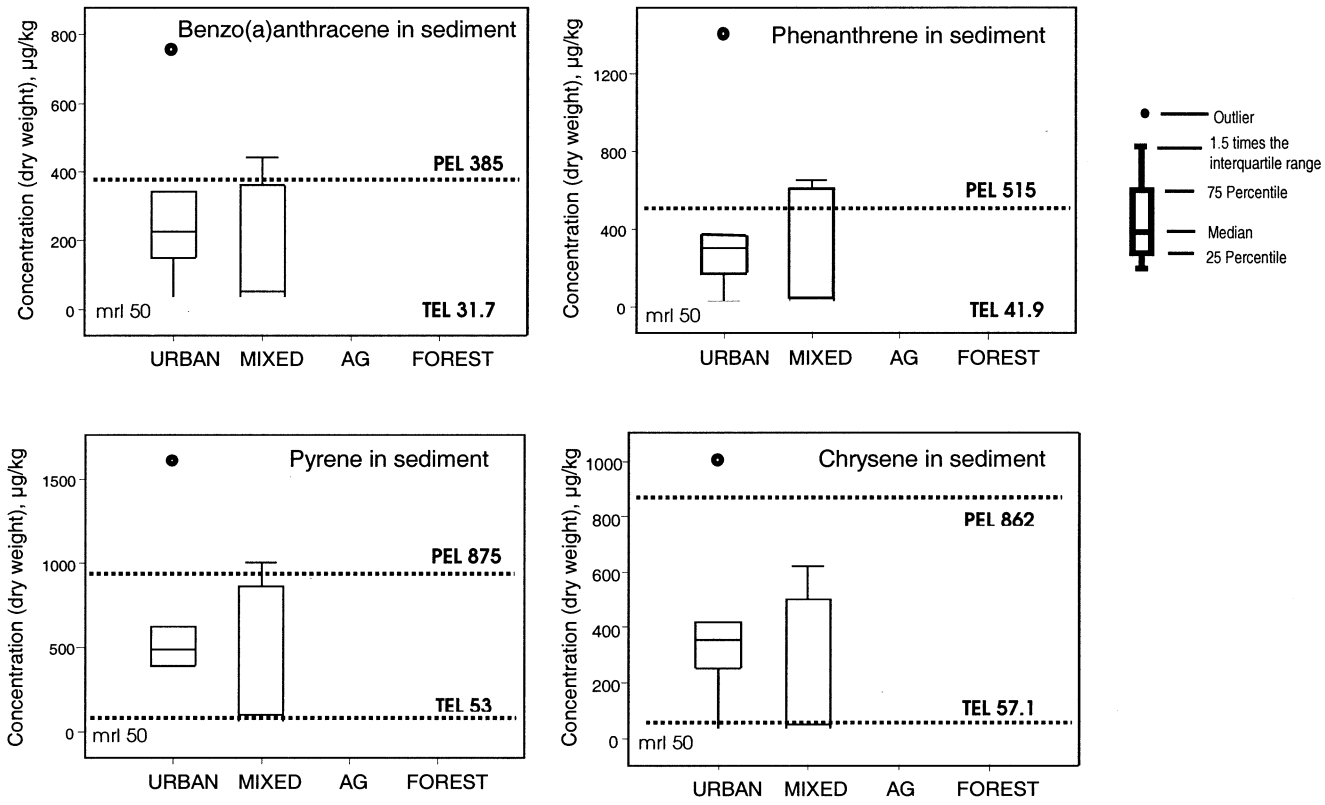

Fig. 4. Distribution of semi-volatile organic compound concentrations in sediment samples from urban, mixed, agriculture (ag), and forested land-use sites. Canadian environmental quality guidelines for sediment; PEL, probable effect level; TEL, threshold effect level; mrl, minimum reporting level. TEL falls below mrl for benzo(a)anthracene and phenanthrene, so is not plotted. Box plots are truncated at the lowest level of detection (minimum reporting level). The y-axis varies for different constituents

technical DDT and are usually not found in the environment. However, the compounds *o,p′*-DDT, DDE, and DDD were each detected once in the sediment at a mixed land-use site, and *o,p′*-DDT was also detected once in fish at an urban site and in the sediment at all three agricultural sites. Nationally, the ratio of *p,p′*-isomers of DDT:DDE:DDD in fish (~10:70:20) changed little from 1976 to 1981 (Schmitt *et al.* 1990), although more recent studies are showing a relatively higher fraction of DDE (Wong *et al.* 2000), with DDE making up 78% in 1984 (Schmitt *et al.* 1990) and 74% in 1986 (Schmitt *et al.* 1999), perhaps reflecting the reduced influx and continued weathering of *p,p′*-DDT in the environment (Schmitt 2002). While *p,p′*-DDE was the most predominant DDT compound in the Oahu samples, the relative fraction of DDE was lower (64 in fish, 43 in sediment) than recent national results (84.5 in fish, 55.9 in sediment) (Wong *et al.* 2000), and DDT accounted for 15% in fish and 31% in sediment. The relatively high percentage of DDT in the Oahu samples probably indicates residues that entered the system recently owing to soil erosion, where DDT may be more stable than in the aquatic environment.

Urban sites tended to have a higher frequency of detection of DDD relative to the other land-use types. However, the ratio of DDT:DDE:DDD was highly variable between sites. At seven of the eleven agricultural or mixed land-use sites, DDE accounted for 100% of the DDT-related compounds in fish. At one mixed land-use site (WKAK), DDD accounted for 78%, possibly an indication that the compound DDD was used as an insecticide in this area (Nowell *et al.* 1999; Schmitt *et al.* 1990).

A comparison of Oahu samples with national NAWQA data from 1994 to 2001 indicates that concentrations of pesticides used for termite control in Hawaii (chlordane and dieldrin/aldrin) remain the highest in the nation. Concentrations of total chlordane and dieldrin at urban sites on Oahu are in the top 5% nationally (Fig. 5), and the maximum concentrations of these compounds measured in both fish and sediment nationally were each measured from a site on Oahu. Concentration of total DDT in sediment at the one agricultural site on Oahu where sediment was analyzed (the only organochlorine pesticide detected at that site) and at two of the mixed land-use sites was also in the highest 5% nationally. Total PCBs in the sediment were in the highest 15th percentile at five sites (three urban and two mixed), but were not detected at any other sites. Total PAHs were in the highest 25th percentile nationally at eight Oahu sites. At the two forested reference sites, total organochlorine pesticides, PCBs, and PAHs in sediment were in the lowest percentile nationally.

As part of the National Pesticide Monitoring Program (later called the National Contaminant Biomonitoring Program), the U.S. Fish and Wildlife Service (USFWS) periodically analyzed organochlorine pesticides and PCBs in fish from more than 100 sites around the country between 1970 and 1986 (data available on the web at www.cerc.usgs.gov/data/ncbp/fish.htm), includ-

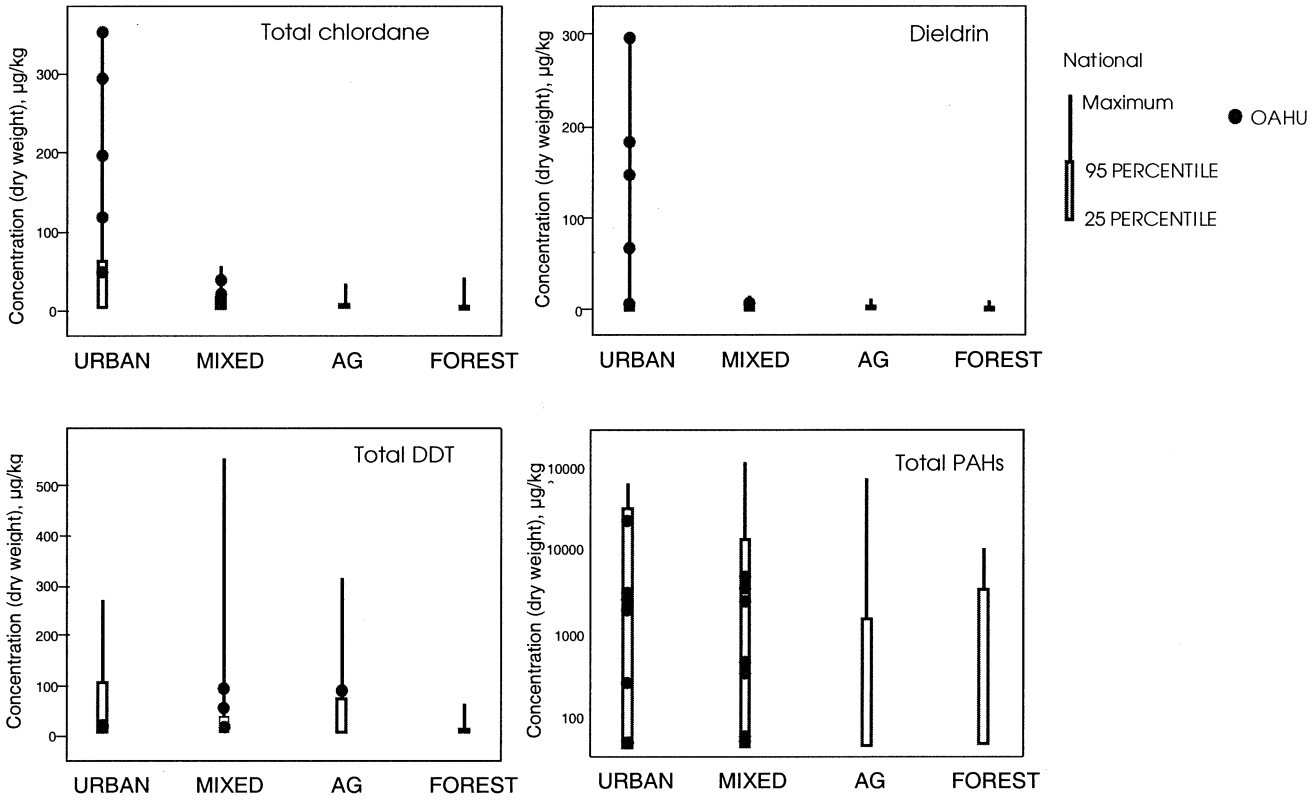

Fig. 5. Range of selected organic compound concentrations in sediment from urban, mixed, agriculture (ag), and forested land-use sites, collected by NAWQA study units across the continental United States in 1992–2001 and from Oahu NAWQA sites in 1998–2001. Data shown do not include non-detections, or those concentrations that fall below the minimum reporting level. The y-axis varies for different constituents. The y-axis for total PAHs is a log scale

ing two streams, Waikele (WKEL) and Manoa (MANO), in Hawaii (Schmitt *et al.* 1981, 1985, 1990, 1999). Although collection sites and target species may not have been identical, and the methods of sample analysis may have changed over time, a general comparison can track the persistence of compounds in the environment after their use was banned. For this analysis, only Poeciliidae fish were used from each study. Following a trend that has been observed across the country (Schmitt *et al.* 1990, 1999; Nowell *et al.* 1999; Wong *et al.* 2000), concentrations of organochlorine compounds are generally decreasing in Hawaii (Fig. 6). This was true for dieldrin, PCBs, total DDT, and total chlordane, in fish at Waikele. Although PCBs were present in fish samples from the 1970s and 1980s, no PCBs were detected in fish at Waikele in 1998. At Manoa, total DDT in fish has decreased over time, while dieldrin is still present at levels similar to those measured in the 1980s. Total chlordane appears to have decreased very slightly. As at Waikele, PCBs were detected in earlier samples, but were not found in fish at Manoa in 1998 or 2000.

Traditionally, water quality monitoring activities have focused on surface-water sampling. However, there are compelling reasons to also analyze for contaminants in streambed sediment and fish. Different types of compounds are likely to be present in tissue and sediment (hydrophobic) than in water (hydrophilic), and fish and sediment can provide an integrated picture of these contaminants over time. Interestingly, in some instances more organochlorine compounds have been detected in fish, while at other sites more organochlorine compounds were detected in sediment (Tate and Heiny 1996; Brown 1997; Munn and Gruber 1997; Wong *et al.* 2000), indicating that a single target may not adequately represent the organochlorine compounds present at a given site. In addition, many regulatory agencies are interested in bioaccumulation of compounds in biota and associated health risks to humans and wildlife that consume contaminated biota (Brown 1997).

Sediment serves as both a source and a removal mechanism for contaminants to and from the stream, and as a means of contaminant transport downstream. Because streams can potentially transport significant amounts of contaminated sediment to the near shore areas, this is a major concern in island ecosystems. On Oahu, elevated concentrations of dieldrin and chlordane were found in oyster tissues in Kaneohe Bay (Hunter *et al.* 1995), the receiving waters for several urban streams (including KANE and KEEA in this study).

Summary

Of the 28 organochlorine compounds analyzed in the fish, 14 were detected during this study. Nineteen of the 31 organochlorine compounds and 40 of the 65 SVOCs were detected in the sediment. Urban sites had the highest number of detections and tended to have the highest concentrations of organochlo-

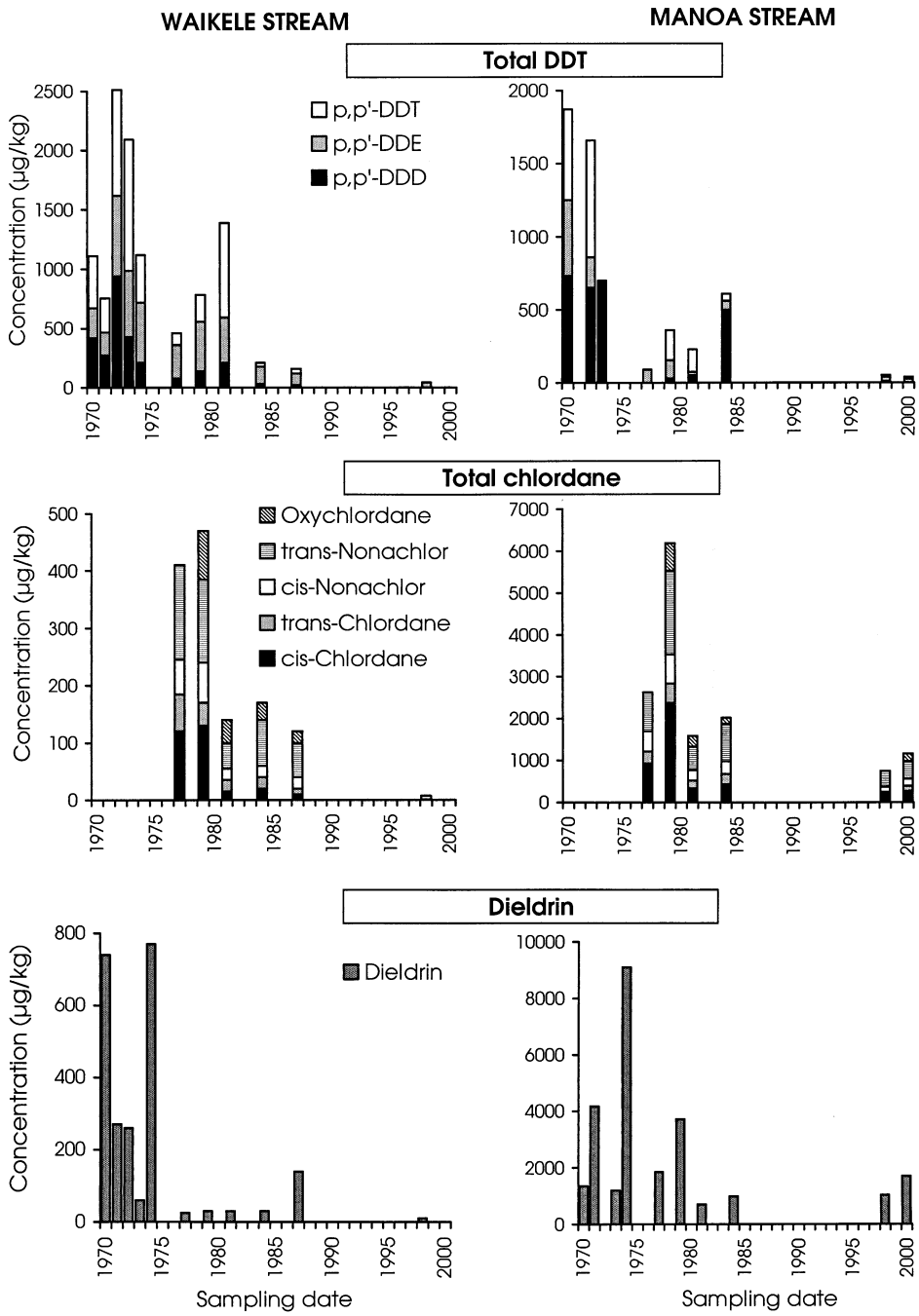

Fig. 6. Selected organochlorine compounds (wet weight) detected in whole fish (Poeciliidae) composite samples over time at Manoa and Waikele Streams on Oahu. Sampling dates 1970–1986 are data from the National Contaminants Biomonitoring Program; sampling dates 1998 and 2000 are from the U.S. Geological Survey NAWQA program. Data shown from 1971, 1977, 1979, and 1981 at Waikele and from 1998 at Manoa are the means of two samples. The y-axis varies for different constituents

rine pesticides. Chlordane compounds were the most frequently detected constituents at urban sites, followed by dieldrin, polycyclic aromatic hydrocarbons (PAHs), and DDT compounds. Chlordane compounds and aldrin (the parent compound of dieldrin) were widely applied in residential areas for termite control and continue to occur in bed sediment and fish at levels that greatly exceed criteria for the protection of invertebrates and fish-eating birds and wildlife.

PAHs were the most frequently detected constituents at mixed land-use sites. PAHs and phthalates were detected in sediment at nearly every urban and mixed land-use site. Phthalates tended to be most associated with residential land use, while PAHs were frequently associated with industrial land use. Although concentrations of most SVOCs did not exceed the PEL, they often exceeded the TEL (below which negative effects are not expected) and consequently can be considered a

potential concern. In addition, even when concentrations are low, contaminants that occur together in the environment can have additive toxic effects (Lopes and Furlong 2001).

The only organochlorine pesticides detected at agricultural sites were DDT and its degradates DDD and DDE. No pesticides or PCBs were detected at the forested sites, but a few ubiquitous SVOCs were found in bed sediment at two forested sites. In general, concentrations of the most commonly detected compounds were higher in fish than in bed sediment.

Together, sediment and fish comprise dual lines of evidence for contamination of a hydrologic system. An integrated approach of sampling water, streambed sediment, and fish will provide the most comprehensive picture of water quality, and the most information for management decisions. In addition to concerns about direct toxicity, exposure to these compounds may cause a variety of sublethal effects, and a number are known to be endocrine disruptors. Understanding how land use is associated with contaminants allows the development of management strategies that can reduce the loading of these contaminants to surface water. For example, although little can be done about present concentrations in soils, controlling soil erosion (especially during clearing of land and construction in newly developed areas) could reduce the quantities of contaminated sediment entering the streams and, ultimately, estuaries and nearshore marine environments.

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