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SURVEY OF PESTICIDES IN SEDIMENTS IN THE VICINITY OF SHOALWATER BAY TRIBAL LANDS

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ABSTRACT

In 1978 and 1979, persistent pesticides were found in water and sediments in streams that emptied into Willapa Bay tideflats adjacent to Shoalwater Bay Indian tribal lands. This study reports analyses of sediments collected during 1989 in the same area. No chlorinated pesticides, PCB's or organophosphorus pesticides were detected in four sediment samples or one composite shellfish sample taken from tribal tideflats. Bioassays (Microtox(R) and *Hyallela azteca*) found the sediments non-toxic. One explanation for the decreased values is pesticide contamination has decreased in the area over 10 years.

BACKGROUND

A study conducted in 1978 and 1979 by the USGS in cooperation with the Shoalwater Bay Indian Tribe found several pesticides in water and sediments in streams that emptied into Willapa Bay tideflats adjacent to tribal lands (Lum, 1984). Pesticides found included DDT and metabolites DDE and DDD. Water quality criteria for DDT were exceeded. The tribe intends to culture shellfish in its tidelands and is concerned about this apparent contamination (Bruce Pederson, Shoalwater Bay Tribal biologist, personal communication).

The primary source of agricultural chemicals within the drainage is cranberry culture. The U.S. Environmental Protection Agency (EPA) produced a study of agricultural chemicals that ranked them by overall "concern" based on persistence, toxicity, ubiquity, and amount (Tetra Tech, 1988). Of the agricultural chemicals applied by cranberry growers, chlorpyrifos is listed as a "Primary Concern" in sediments and biological tissue.

To determine current concentrations of agricultural chemicals near the Shoalwater Bay Indian Reservation area, four sediment samples and one shellfish sample were collected at sites that were sampled in 1978 and 1979. These samples were analyzed for chlorinated and organo-phosphorus pesticides and PCB's. One sediment sample was tested for potential biological impacts through bioassay. This work was requested and partially funded by U.S. EPA, Region 10.

METHODS

Field and Lab Methods

Four sediment samples and one shellfish sample were collected in the locations shown in Figure 1. Sample Site #4 (Pacific Country Drainage Ditch #1) is where the U.S. Geological Survey (USGS) collected sediment in 1978-79. For this study, samples were collected later in the year (August 16, 1989) than the USGS study (April 26, 1978; March 28, 1979). All samples were analyzed for chlorinated pesticides and PCB's (EPA method 8080), organo-phosphorus pesticides (EPA method 8140), and for sediments grain size, percent total organic carbon, and percent solids. The shellfish sample was analyzed for percent lipids.

Sediments were collected at locations within a site with stainless steel spoons into stainless steel beakers, homogenized, and a subsample taken for analysis. Sediment from Site #4 (Pacific County Drainage Ditch # 1) was taken by dragging a two quart stainless steel beaker along the ditch bottom. Japanese littleneck clams (Tapes japonica) were collected over a 200 meter square area (Site 5) and allowed to depurate for 24 hours in seawater. Forty-two clams (mean length = 36 mm) were shucked and homogenized in a Waring blender. All samples were frozen within 26 hours of collection except sediment taken for bioassays.

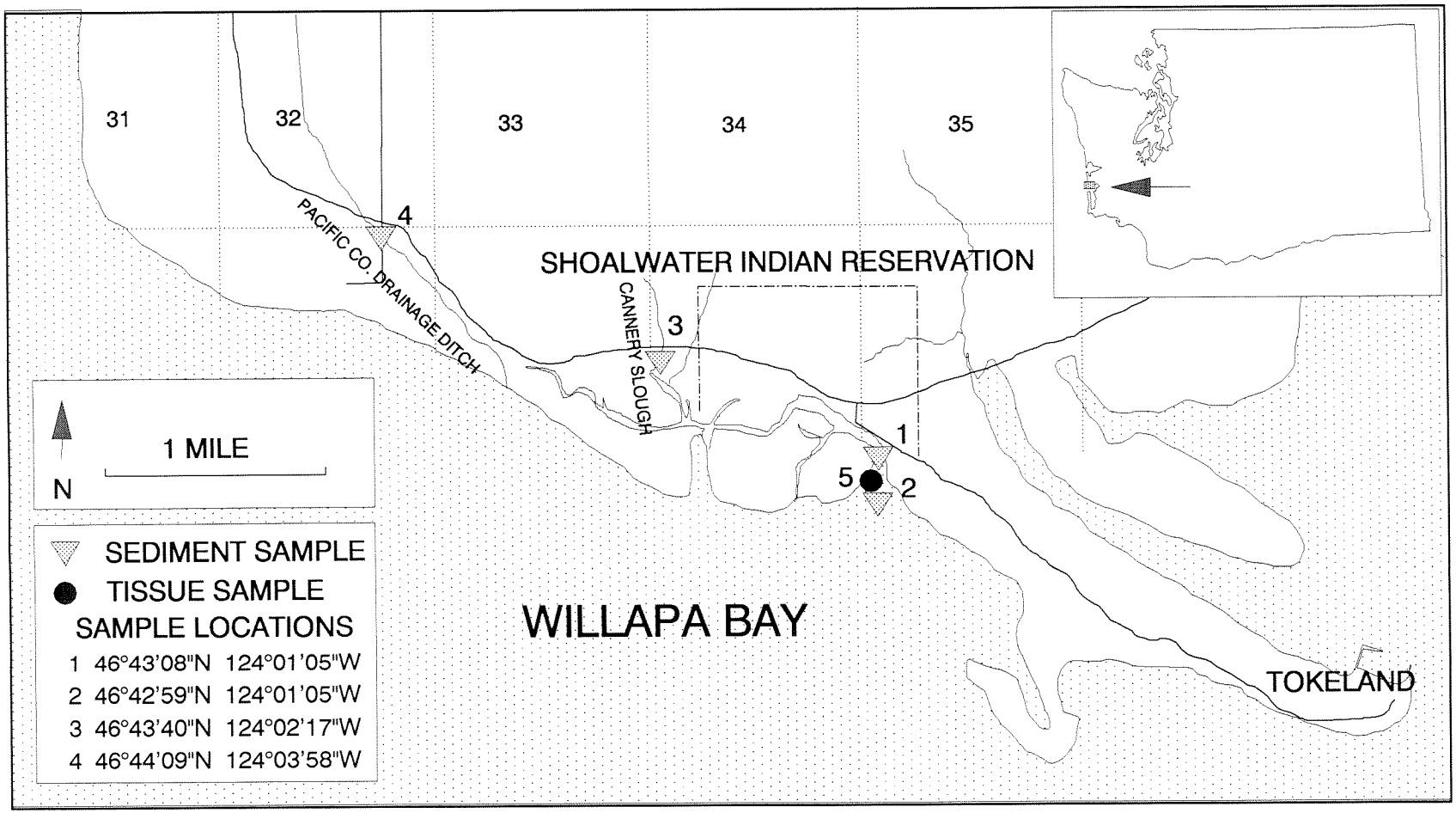

Figure 1. Study area with vicinity map of Washington State.

All sampling gear (beakers, spoons, knives) were cleaned with detergent, rinsed in 10% nitric acid, distilled water, and acetone. Collection jars were supplied by ICHEM (300 series) and are certified priority pollutant clean. To assess precision and to some extent accuracy, a matrix spike (MS) and a duplicate matrix spike (MSD) analysis were performed on the sediment and tissue samples. Measures of grain size and total organic carbon were duplicated. All pollutant analyses were performed at the EPA/Department of Ecology Laboratory at Manchester. Percent TOC was determined by ARI laboratory (Seattle) and grain size by AM-Test laboratory (Seattle).

Bioassays of the Pacific County Drainage Ditch sediment (Site 4) were conducted on Microtox(R) bacteria and freshwater amphipods (Hyallela azteca). Microtox(R) analyses were conducted as described in the Puget Sound Protocols (Tetra Tech 1986). Hyallela were tested as described in Nebeker et al. (1984). The sediment was collected from freshwater and the salinity was adjusted to 2% NaCl for the Microtox(R) test as directed in Puget Sound Protocols.

Quality Assurance

Table 1 shows percent recovery of 0.8 to 2 ug of representative chemicals spiked into 30 gms of sample before extraction (27 to 67 ug/kg). A duplicate extraction and analysis was run and forms the matrix spike (MS) and matrix spike duplicate (MSD). For most pesticides spiked, recovery was good and the relative percent difference (RPD) between the MS and MSD was low, indicating good precision. The exceptions were endrin aldehyde and the sole organophosphorus pesticide chlorpyrifos. Both had poor recoveries on the duplicate analysis. Guidelines from EPA contract laboratory program (CLP) for matrix spike recovery also are shown in Table 1. All six pesticides that are listed by the CLP were within the guidelines.

The bioassay tests relied on controls and reference toxicants for quality assurance checks. The Microtox(R) test had an median sublethal effect concentration (EC50) of 0.121 mg/L phenol, a result similar to the typically reported value from Manchester Laboratory. Both replicates obtained the same result. In the Hyallela bioassay three replicate tests of reference toxicant cadmium chloride showed a median lethal concentration (LC50) of 8 ug/L. Five replicate bioassays were conducted on 10 animals each for the test sediment and the laboratory reference sediment.

RESULTS

Table 2 shows results of all pesticide analyses in sediment and tissue. No pesticides were found in any of the samples. Table 3 shows other physical characteristics of the sediments and tissue. The values reported in Table 2 are the limits of detection for the method and the matrix. No PCB's, chlorinated or organophosphorus pesticides were detected at or above these limits.

Table 1. Recovery of selected pesticides spiked in sediment at 27 to 67 ug/kg.

	Sediment				Tissue		
Compound	Recovery %[1]		RPD[2]	CLP Recov[3]	Recovery %		RPD
PESTICIDE/PCB's							
4,4'-DDT	83	85	2	23-134	89	85	5
gamma-BHC	71	63	12	46-127	92	87	6
Dieldrin	81	79	3	31-134	92	85	8
Endrin	79	78	1	42-139	86	92	7
Methoxychlor	87	87	0		91	77	17
4,4'-DDE	80	81	1		82	79	4
4,4'-DDD	-	-	-		88	85	3
Heptachlor	65	45	36	35-130	81	74	9
Aldrin	69	63	9	34-132	87	85	2
alpha-BHC	66	58	13		89	87	2
beta-BHC	79	74	7		87	80	8
delta-BHC	72	65	10		81	69	16
alpha-Endosulfan	78	70	11		83	82	1
beta-Endosulfan	81	82	1		84	84	0
Heptachlor epoxide	77	71	8		90	86	5
Endosulfan sulfate	82	84	2		91	81	12
Endrin aldehyde	35	6	141		85	31	93
ORGANOPHOSPHORUS PESTICIDE							
Chlorpyrifos	91	39	80		62	27	79

[1]Percent recovery of matrix spike and matrix spike duplicate.

[2]RPD = Relative percent difference (range of duplicates as percent of the mean) = x-y/(x+y)/2 * 100 where x and y are values from replicate analyses.

[3]Recovery limits listed in EPA contract lab program (CLP) for selected compounds.

Table 2a. Concentrations of chlorinated pesticide/PCB's found in samples (sediments reported in ug/kg dry weight, tissue in ug/kg wet weight).

Compound	Site#[1] =	Sediment 1	Sediment 2	Sediment 3	Sediment 4	Tissue 5
4,4'-DDT		2 U[2]	2 U	3 U	2 U	1 U
4,4'-DDD		2 U	2 U	3 U	2 U	1 U
4,4'-DDE		2 U	2 U	3 U	2 U	1 U
Chlordane		5 U	5 U	7 U	5 U	3 U
Dieldrin		2 U	2 U	3 U	2 U	1 U
Endrin		2 U	2 U	3 U	2 U	1 U
Endrin aldehyde		2 U	2 U	3 U	2 U	1 U
Methoxychlor		5 U	5 U	7 U	5 U	13 U
Heptachlor		2 U	2 U	3 U	2 U	1 U
Heptachlor epoxide		2 U	2 U	3 U	2 U	1 U
Aldrin		2 U	2 U	3 U	2 U	1 U
alpha-BHC		2 U	2 U	3 U	2 U	1 U
beta-BHC		2 U	2 U	3 U	2 U	1 U
delta-BHC		2 U	2 U	3 U	2 U	1 U
gamma-BHC		2 U	2 U	3 U	2 U	1 U
alpha-Endosulfan		2 U	2 U	3 U	2 U	1 U
beta-Endosulfan		2 U	2 U	3 U	2 U	1 U
Endosulfan sulfate		2 U	2 U	3 U	2 U	1 U
Toxaphene		60 U	60 U	90 U	60 U	39 U
PCB-1260		20 U	20 U	30 U	20 U	13 U
PCB-1254		20 U	20 U	30 U	20 U	13 U
PCB-1248		20 U	20 U	30 U	20 U	13 U
PCB-1242		20 U	20 U	30 U	20 U	13 U
PCB-1232		20 U	20 U	30 U	20 U	13 U
PCB-1221		20 U	20 U	30 U	20 U	13 U
PCB-1016		20 U	20 U	30 U	20 U	13 U

[1] Site # refer to Figure 1.

[2] U = Detection limit. No compounds found at or above this concentration.

Table 2b. Concentrations of organophosphorus pesticides found in samples (sediments reported in ug/kg dry weight, tissue in ug/kg wet weight).

Compound	Sediment 1	Sediment 2	Sediment 3	Sediment 4	Tissue 6
Fenthion	2 U[1]	2 U	2 U	2 U	5 U
Parathion	2 U	2 U	2 U	2 U	5 U
Coumaphos	2 U	2 U	2 U	2 U	5 U
Dimethoate	2 U	2 U	2 U	2 U	5 U
Dichlorvos (DDVP)	2 U	2 U	2 U	2 U	5 U
Dioxathion	2 U	2 U	2 U	2 U	5 U
DEF	2 U	2 U	2 U	2 U	5 U
Azinphos (Guthion)	2 U	2 U	2 U	2 U	5 U
Malathion	2 U	2 U	2 U	2 U	5 U
Folex	2 U	2 U	2 U	2 U	5 U
Methyl parathion	2 U	2 U	2 U	2 U	5 U
Phorate	2 U	2 U	2 U	2 U	5 U
Disulfoton	2 U	2 U	2 U	2 U	5 U
Ronnel	2 U	2 U	2 U	2 U	5 U
Diazinon	2 U	2 U	2 U	2 U	5 U
Ethion	2 U	2 U	2 U	2 U	5 U
Imidan	2 U	2 U	2 U	2 U	5 U
Carbophenothion	2 U	2 U	2 U	2 U	5 U
EPN	2 U	2 U	2 U	2 U	5 U
Phebcapton	2 U	2 U	2 U	2 U	5 U
Ethyl azinphos	2 U	2 U	2 U	2 U	5 U
Chlorpyrifos	2 U	2 U	2 U	2 U	5 U
Monocrotophos	2 U	2 U	2 U	2 U	5 U
Mevinphos	2 U	2 U	2 U	2 U	5 U

[1] U = Detection limit. No compounds found at or above this concentration.

Table 3. Measures of solids, total organic carbon, grain size in sediments, and solids and lipids in tissues.

Measure	Sediment 1	Sediment 2	Sediment 3	Sediment 4	Tissue 6
Percent solids	69	65	41	75	12
Percent total organic carbon	1.3	3.2	27.5	1.3	--
Percent fines (< 64 um grain)	3.6	14.3	6.2	1.0	--
Percent lipids	--	--	--	--	.32

Sediments from Site 4 (Pacific County Drainage Ditch) were non-toxic to Microtox(R) and Hyallela azteca. Estimated EC50 for Microtox(R) was greater than 100% concentration of sediment extract for two duplicate analyses of sediment from Site 4. Survival of Hyallela azteca was 92% in the sediment. The reference sediment survival was 96% and was not significantly different from the test sediment (Dunnett's test).

DISCUSSION

Lum (1984) analyzed water and sediments in the Pacific County Drainage Ditch # 1 taken in 1978 and 1979 and reported up to 42 ug/kg DDE in sediments (dry weight). He also found DDD, DDT, and diazinon above the detection limits reported here. Aldrin and dieldrin were found at 0.4 ug/kg, both are values below the limits of detection achieved in this study. Dichlobenil (casoron) was also found at a low concentration (0.45 ug/kg) but was not looked for in this study.

The sediments were low in percent fines and in total organic carbon except for Site 3 (Cannery Slough) which was high in total organic carbon. These measures reflect total surface area of the particles of sediments and are often correlated with organic contaminant concentrations (reviewed in PTI and Tetra Tech 1988). Thus, low total organic carbon is associated with relatively lowered concentrations of contaminants. Presumably, Lum (1984) sampled sediments that had the same low percentage of total organic carbon and fines (high percentage of sand) as found in this study for the area and thus comparisons between studies are not confounded by variation in these measurements.

The lack of contamination found in this study compared to the 1978-1979 results probably reflects a reduction in contamination in the area. There is no evidence of a contemporary contamination problem on Shoalwater Tribal Lands. Furthermore, though USGS topographic map shows the Pacific South Drainage Ditch #1 draining into west side of the bay where the Shoalwater Bay Tribe intends to grow shellfish, the ditch now drains directly into Willapa Bay, well west of the proposed shellfish area (Sites 1 and 2) and thus even if pesticides were found in the Drainage Ditch sediments, they would probably not directly affect concentrations at the shellfish area.

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