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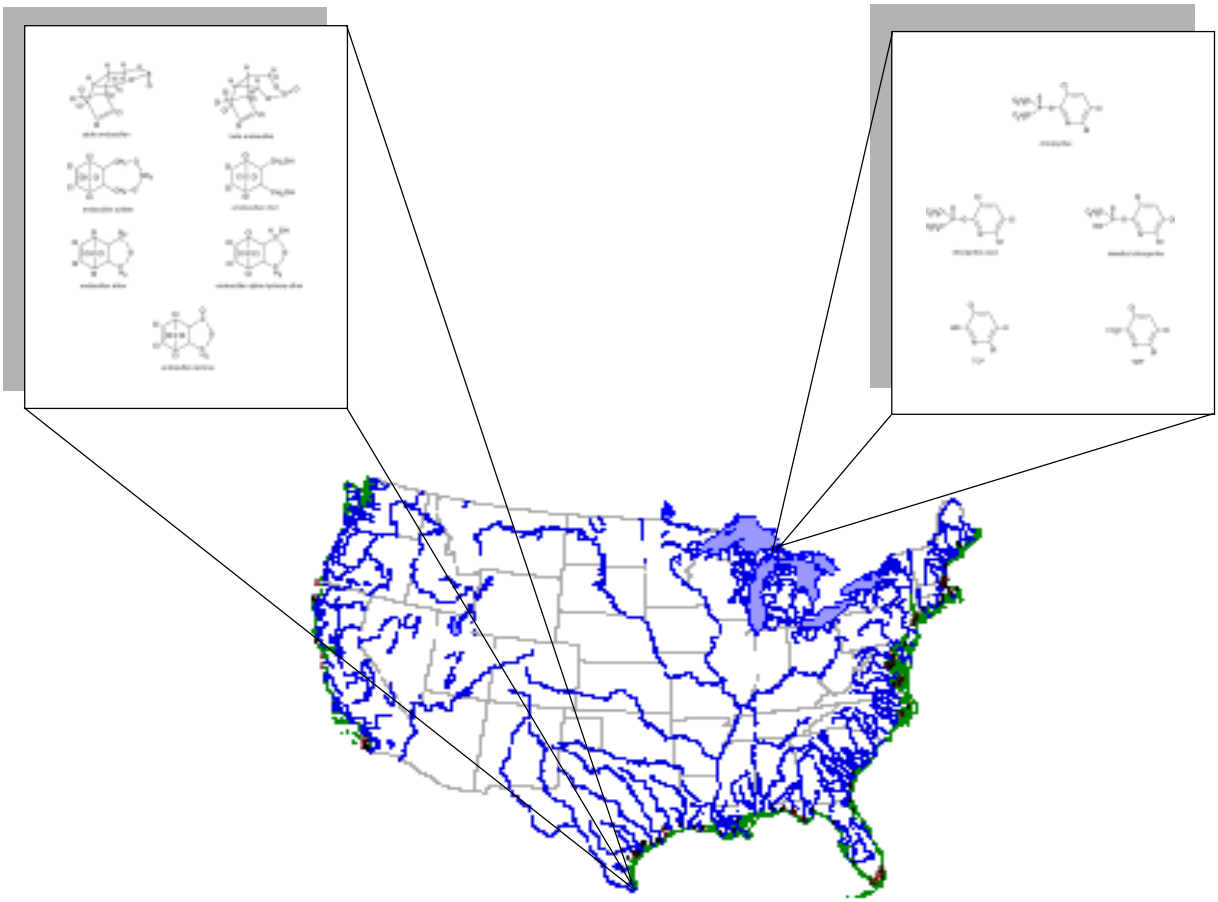
National Status and Trends Program
for Marine Environmental Quality

Spatial Distribution of Chlorpyrifos and Endosulfan in USA Coastal Waters and the Great Lakes



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December 1999

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Notice

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Spatial Distribution of Chlorpyrifos and Endosulfan in USA Coastal Waters and the Great Lakes

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Abstract

Between 1994 and 1997, 258 tissue and 178 sediment samples were analyzed for chlorpyrifos throughout the coastal United States and the Great Lakes. Subsequently, 95 of the 1997 tissue samples were reanalyzed for endosulfan. Tissue chlorpyrifos concentrations, which exceeded the 90th percentile, were found in coastal regions known to have high agricultural use rates but also strongly correlated with sites near high population. The highest concentrations of endosulfans in contrast, were generally limited to agricultural regions of the country. Detections of chlorpyrifos at several Alaskan sites suggest an atmospheric transport mechanism. Many Great Lakes sites had chlorpyrifos tissue concentrations above the 90th percentile which decreased with increasing distance from the Corn Belt region (Iowa, Indiana, Illinois, and Wisconsin) where most agriculturally applied chlorpyrifos is used. Correlation analysis suggests that fluvial discharge is the primary transport pathway on the Atlantic and Gulf of Mexico coasts for chlorpyrifos but not necessarily for endosulfans.

Introduction

While synthetic organic pesticides are often implicated for their potential to adversely affect the health of coastal ecosystems, evidence to support this is primarily limited to the organochlorine insecticides that were banned in the 1970s and 1980s. In contrast, evidence of aquatic ecosystem impact from contemporary pesticides is scarce and limited to site specific contamination during isolated storm and runoff events (Pait et al., 1992; Johnson et al., 1994).

The National Oceanic and Atmospheric Administration (NOAA) through its National Status and Trends (NS&T) Program, Mussel Watch Project, monitors chemical contamination in coastal waters of the United States, and the Great Lakes. The goal of the project is to assess the status and trends of chemical contamination through the collection and analysis of bivalve tissues at over 280 sites biennially and sediments on a less frequent basis. Among the more than 80 chemicals monitored are many of the banned organochlorine insecticides (Table 1). Except for gamma hexachlorocyclohexane (lindane), no contemporary pesticides were monitored in the MW Project prior to 1993 at which time two contemporary pesticides, chlorpyrifos and endosulfan, were added to the list of compounds.

We report here the results four years of chlorpyrifos monitoring (1994 to 1997) in bivalve tissue and sediment, and one year (1997) of endosulfan monitoring in bivalve tissue. The spatial distribution of these two compounds and the mechanisms by which they are transported to coastal environments are evaluated. Concentrations of these compounds are compared with respect to their proximity to human population, freshwater discharges from fluvial and estuarine drainage areas, and pesticide and land use characteristics. Analysis of the temporal tends in concentrations will be determined after at least six years of monitoring has been completed.

Table 1. Pesticides monitored in the NS&T Program since 1986 are all banned insecticides or used only minimally in the United States and Canada.

Pesticide	Status
DDT and its metabolites	Banned
Aldrin	Banned
Dieldrin	Banned
Chlordanes	Banned
Heptachlor	Banned
Heptachlor epoxide	Banned
Lindane (gamma hexachlorocyclohexane)	RUP[a]
Alpha hexachlorocyclohexane	Banned
Hexachlorobenzenes	Banned
Tetrachlorobenzenes	Banned
Mirex	Banned
Endrin	Banned

[a] Restricted Use Pesticide, purchase and use by certified applicators or designees only.

Background

Pesticides, unlike most compounds monitored in the NS&T Program, are intentionally released into the environment to control plant and animal pests. Once released they may transform into other compounds of equal, greater or lesser toxicity and they may leave the site of application by different pathways including surface runoff to streams and rivers, leaching to groundwater and subsequent discharge to surface waters, and volatilization followed by short or long-range transport in the atmosphere and deposition. The chemical and physical properties of chlorpyrifos and endosulfan, and estimates of their usage (the amount of pesticide applied to control plant or animal pests) and loadings (the amount of pesticide delivered down stream or down wind, through fluvial or atmospheric transport, respectively) are discussed below.

Chlorpyrifos. The broad-spectrum organophosphate insecticide, chlorpyrifos (Fig. 1) is moderately persistent in soils with a half-life usually between 60 and 120 days, but that can range from 2 weeks to over 1 year, depending on the soil type, climate, and other conditions (Howard, 1991; Wauchope et al., 1992). When applied to moist soils, the volatility half-life of chlorpyrifos is short with 62 to 89 percent of the applied chlorpyrifos remaining on the soil after 36 hours (Racke, 1992). The principal transformation product, 3,5,6-trichloro-2-pyridinol (TCP) (Fig. 1), absorbs weakly to soil particles and appears to be moderately mobile and persistent in soils (Racke and Robbins, 1991). TCP is also a transformation product of the herbicide triclopyr (Racke and Robbins, 1991). The organophosphate insecticides including chlorpyrifos are transformed to their respective oxons (Fig. 1) by photolytic processes. The oxons have been measured in fog (Glotfelty et al., 1987; Schomburg et al., 1991) at concentrations 20 times the parent compound. Volatilization is also the primary route of loss of chlorpyrifos from water. Volatility half-lives of 3.5 and 20 days have been estimated for pond water (Racke, 1992). In general, pesticides with organic carbon partitioning coefficients (K_{OC}) less than 500 tend to remain dissolved while those

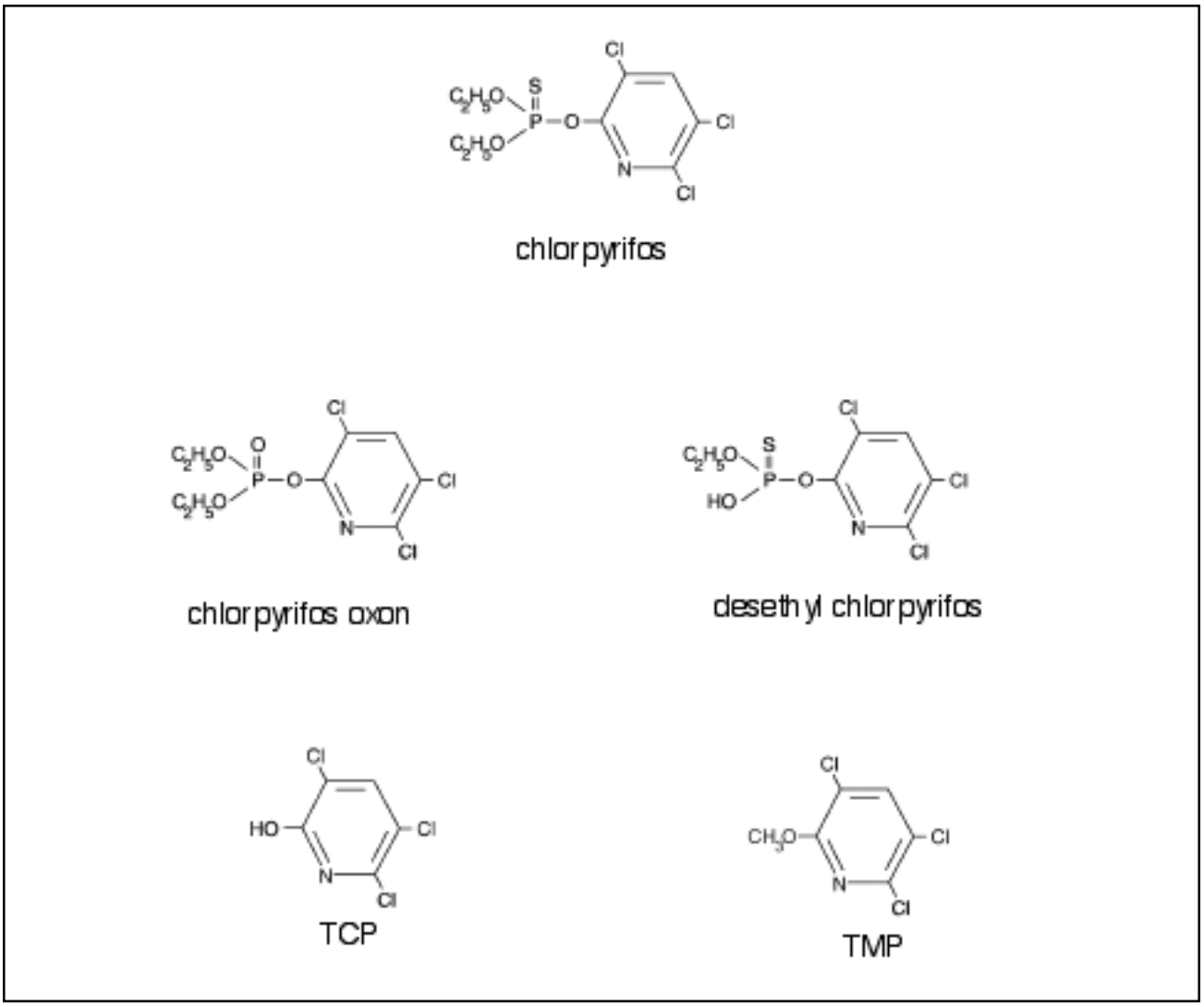

Figure 1. Chlorpyrifos and some of its transformation products.

with K_{OC} values of more than 1,000 are primarily on suspended-sediment particles. The K_{OC} of chlorpyrifos (9,930) is not remarkable relative to endosulfan, nor is its water solubility (1.18 mg/l) suggestive of mobility via surface runoff.

Endosulfan. Endosulfan (Fig. 2) is a chlorinated hydrocarbon insecticide and acaricide of the cyclodiene subgroup. It is a contact poison to a wide variety of insects and mites. Although it may also be used as a wood preservative, it is used primarily on a wide variety of food crops including tea, coffee, fruits, and vegetables, as well as on rice, cereals, maize, sorghum, and other grains. Endosulfan has a high K_{OC} of 12,400 (USDA ARS Pesticide Properties Database) and like chlorpyrifos, adsorbs to particles in surface runoff. Technical endosulfan is made up of a 70/30 isomeric mixture of alpha and beta isomers (endosulfan I and endosulfan II, respectively). Alpha endosulfan is the more volatile and predominates in air, whereas both alpha- and beta-endosulfan are found in water. Endosulfan isomers have different degradation times in soil. The alpha and beta isomers have 35 and 150 day half-lives, respectively, under neutral conditions and persist longer under more acidic conditions (Kidd and James, 1991). In addition alpha endosulfan is actually two enanti-

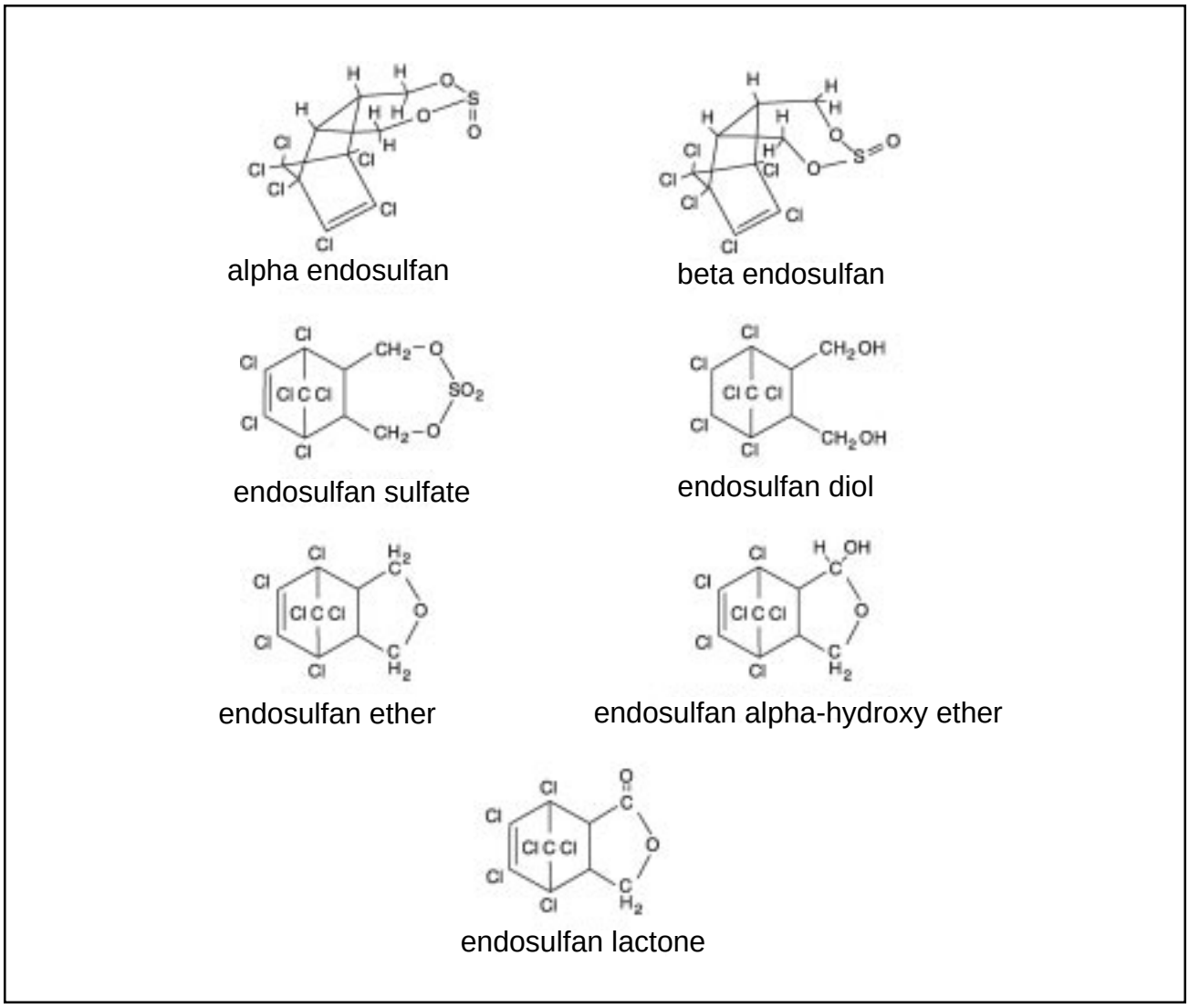

Figure 2. Endosulfan and its primary transformation products.

omers (Schmidt, et al., 1997). Transformation products of endosulfan include endosulfan sulfate, endosulfan diol, endosulfan ether, endosulfan alpha-hydroxy ether, and endosulfan lactone. The primary transformation products found in surface waters are endosulfan sulfate and endosulfan diol (NRCC, 1975).

Endosulfan and its sulfate are highly toxic to aquatic organisms (Day, 1991). In two aquatic invertebrates, the reported 96-hour LC50 values were, respectively, 5.8 mg/l and 3.3 mg/l (Johnson and Finley, 1980). Bioaccumulation of endosulfan by the mussel (*Mytilus edulis*) is reported to be 600 times the ambient water concentration (USNLM, 1995).

Usage and Loadings. The exact amounts of pesticides used are unknown. State and federal agencies using various methods and geographic scales estimate pesticide use. The US Department of Agriculture (USDA), US Environmental Protection Agency (EPA), and US Geological Survey (USGS) estimate agricultural pesticide use from data on crop type, crop acreage, pesticide application rates, and sales data (USEPA, 1992) and report usage on a national, regional, state, and sometimes county scale by crop. Individual states generally

estimate usage with random surveys of farmers and/or certified pesticide applicators and often report usage at the county scale. NOAA's estimates have aggregated 1987 pesticide use (Gianessi and Puffer, 1990) by estuarine drainage areas and portions of their corresponding fluvial drainages (Pait et al., 1992) (Table 2).

Table 2. Chlorpyrifos and endosulfan use estimates by coast in pounds of active ingredient. Adapted from Pait et al., 1992.

Coast	Year	Chlorpyrifos	Endosulfan
Atlantic Coast	87	545,718	147,384
Gulf of Mexico	87	297,743	135,869
Pacific Coast	87	55,944	33,020

Chlorpyrifos was the most widely used insecticide in 1995 with an estimated 6.3 million pounds applied to field crops (corn, cotton, and wheat) (USDA, 1996) and 0.237 million pounds on vegetable crops (USDA, 1997). In four of the Great Lakes states (Wisconsin, Illinois, Indiana, and Michigan) chlorpyrifos use is primarily on corn and in those states represented over 32 percent (1.456 million pounds) of all chlorpyrifos use on field crops in 1996. In contrast, endosulfan is primarily used on vegetable crops and only about 0.202 million pounds were used in 1996 (USDA, 1997). Endosulfan use is concentrated in Florida, California and Texas with 26.6, 15.6, and 10.6 percent, of the national usage respectively (USDA, 1997).

Other suspected major releases are from nonagricultural pesticide use for home and garden, golf courses, and for state and federal programs to control nonagricultural plant and insect pests. Quantitative information on the amounts of home and garden pesticide use are not available at this time and estimates of nonagricultural pesticide use, particularly private use, are difficult to make. Based on a national survey in 1990 there were about 41.9 million pounds of chlorpyrifos used in outdoor home applications and 0.561 million pounds of endosulfan used in the same way (Whitmore et al. 1992). Endosulfan is not a restricted use pesticide (RUP) but commercial products are marketed almost entirely for agricultural use and its use in the urban environment is limited.

Agricultural pesticide use is seasonal and the duration of application decreases with increasing latitude. After application, chlorpyrifos and endosulfan may leave the site of application in surface runoff to streams and rivers (Wauchope, 1978; Leonard, 1990), volatilize to the atmosphere (Taylor, 1995), be deposited downwind (Majewski and Capel, 1995; Glotfelty, et al., 1990), or undergo biotic and abiotic transformation (Racke and Robbins, 1991; Racke, 1992).

Surface runoff is of greatest importance with respect to pesticide loading to the coastal environment, because rivers and streams can carry large amounts of dissolved and sediment-bound pesticides downstream directly to sensitive estuarine ecosystems. River loadings of pesticides from fluvial drainage areas (FDA) into estuarine drainage areas (EDA) have been estimated for selected rivers and for specific compounds including some pesticides. In the mid-Atlantic region, Foster and Lippa (1993) measured dissolved and particulate loads of selected pesticides discharged by the Susquehanna, Potomac, and James Rivers. Although they did not analyze for chlorpyrifos or endosulfan, cumulative

dissolved and particulate loads for the organochlorine pesticides were about 35 kg, and about 15 kg, respectively for a 7-month period in 1992. Cumulative loads of herbicides were considerably higher, on the order of 4 to 5 metric tons (dissolved phase) for the same 7-month period. Loads are directly related to river flow and in high flow years these estimates could easily double. On the pacific coast, Pereira et al. (1996) measured chlorpyrifos concentrations of <1 ng/l, in water, and <0.5 ng/l, in sediment, from the San Joaquin River.

Pesticide loads in rivers, which discharge to the Gulf of Mexico, have also been measured. In the Mississippi River below its confluence with the Ohio River, a chlorpyrifos load of 65-kg was measured between April 1991 and March 1992 (Goolsby and Pereira, 1995). Over the same time period the discharge of four major herbicides directly to the Gulf of Mexico ranged from 365,700 kg for atrazine and its transformation products to 33,700 kg for alachlor (Goolsby and Pereira, 1995). Water concentrations of several pesticides including chlorpyrifos were monitored in several river basins (Ocmulgee, Flint, and Apalachicola) discharging into Apalachicola Bay and the Gulf of Mexico following flooding from tropical storm Alberto in July of 1994. Chlorpyrifos concentrations were below detection limits in the larger rivers however, diazinon (an organophosphate insecticide related to chlorpyrifos) had cumulative loads ranging from 11 kg to 18 kg during the storm event (Hippie et al., 1994).

In the Great Lakes region, maximum reported chlorpyrifos concentrations ranged from 0.161mg/l to 3.836 mg/l between 1983 to 1991 in unfiltered water samples of Lake Erie tributaries, (Richards and Baker, 1993). Estimated annual herbicide loads in Lake Erie tributaries, ranged from 500-20,000 kg/yr and 600-14,000 kg/yr for atrazine and metolachlor, respectively (Richards et al., 1996). Muir and Grift (1995) using literature values, estimated the loading of endosulfan to Lake Erie to be approximately 156 kg/yr with 8 percent entering from the Detroit River, 70 percent from other tributaries, and 22 percent from wet and dry atmospheric deposition. Other studies have concluded that the vast majority of loadings of contaminants to Saginaw Bay (Michigan) occur during a small number of climatic events which mobilize soils from surface runoff and resuspend in-stream sediments from upstream (Moll et al. 1995; Verbrugge et al. 1995). Resuspension of sediment is the primary mechanism of PCB export to lower Green Bay (Wisconsin) (Velleux and Endicott, 1994) and we speculate this mechanism maybe important in the transport of chlorpyrifos and endosulfan as well.

Atmospheric loadings of pesticides result from wet and dry deposition and direct gas exchange. Organophosphate insecticides and several herbicides have been measure in air, fog and rain and can be transport over long distances (Seiber et al., 1989; Glotfelty et al., 1987; McConnell et al., 1998; Rice and Chernyak, 1997). Air and water samples collected from the Chesapeake Bay to estimate depositional fluxes suggest that chlorpyrifos enters the Bay primarily in rivers during the spring months, and from the atmosphere in mid and late summer due to increased air concentrations (McConnell et al., 1998).

Methods

The NS&T sampling site locations and characteristics have been described by Lauenstein et al. (1997), as have the sampling and analytical methods (Lauenstein and Cantillo, 1998). Chlorpyrifos analyses were performed by the Geochemical and Environmental Research

Group at Texas A & M University, College Station, Texas, and a selected set of tissue samples were re-extracted and analyzed by the Environment Chemistry Laboratory of the Beltsville Agricultural Research Center, U.S. Department of Agriculture, Beltsville, Maryland for endosulfan concentrations. NS&T site locations with detections of chlorpyrifos and endosulfan were plotted using ARC/View GIS software (Environmental Systems Research Institute, Redlands, CA). Data manipulation and analysis were done with Statistical Analysis Systems (SAS) from SAS Institute, Inc., Cary, North Carolina.

Results and Discussion

Between 1994 and 1997, the Mussel Watch Project collected and analyzed 258 and 178 tissue and sediment samples for chlorpyrifos. Subsequently, 95 of the 1997 tissue samples were reanalyzed for endosulfan. Summary statistics for chlorpyrifos for the combined years (1994-1997) and endosulfan for 1997 are shown in Table 3. Tissue chlorpyrifos concentrations exceeded sediment chlorpyrifos concentrations by nearly one order of magnitude. The dry weight method detection limits (MDLs) for the compounds reported in this study were chlorpyrifos (0.25 ng/g), alpha endosulfan (0.68 ng/g) beta endosulfan (0.88 ng/g) and endosulfan sulfate (0.68 ng/g). The percentage of samples below MDLs ranged from 31.4 percent to 100 percent depending on the compound and the matrix. All NS&T concentrations in this report are in ng/g dry wt.

Table 3. Summary statistics: chlorpyrifos and endosulfan residues in sediment and tissue. Mean, median, maximum, percentiles, and MDLs are in ng/g dry wt.

Variable	Chlorpyrifos		Alpha Endosulfan	Beta Endosulfan	Endosulfan Sulfate
	Sediment	Tissue	Tissue	Tissue	Tissue
N observations	178	258	95	95	95
Mean	0.269	1.952	0.854	0.709	1.44
Median	0.040	0.782	0.477	0.362	0.898
Maximum	5.68	52.92	7.88	6.28	8.176
Percentiles:					
99^{th}	4.16	22.4	7.88	6.278	8.176
95^{th}	1.22	7.15	3.02	2.64	5.003
90^{th}	0.84	4.19	1.66	1.55	3.162
10			0.093	0.098	0.189
MDL[a]	0.13	0.50	0.68	0.88	0.68
% obs. <MDL	68.0	31.4	62.1	80.0	38.9

[a] Method detection limit.

The NS&T sampling site locations for five tissue concentrations of chlorpyrifos and endosulfans are plotted in Figures 3-6. NS&T sites with concentrations exceeding the 90^{th} percentile are shown in Tables 4-7. The NS&T sampling site locations for sediment concentrations of chlorpyrifos are plotted in Fig. 7 and sites exceeding the 90^{th} percentile are shown in Table 8. At present there are no FDA or EPA guidance levels for either chlorpyrifos or endosulfan in fish and fishery products for human consumption. For comparison, guid-

ance levels for the organochlorine insecticides range from 100 ng/g for Mirex to 5,000 ng/g for DDT and its metabolites (wet wt). Approximately 80 percent of bivalve tissue is water, therefore multiplying wet concentrations by 5 gives the equivalent dry wt range of 500 ng/g dry wt to 25,000. Peak tissue concentrations measure at NS&T sites fell well below this range.

Table 4. NS&T site locations with chlorpyrifos concentrations in tissue greater than the 90th percentile (ng/g dry wt).

Site Code	General Location	Specific Location	State	Chlorpyrifos
BRFS	Brazos River	Freeport Surfside	TX	52.92
LMHB	Lake Michigan	Holland Breakwater	MI	28.54
LMMB	Lake Michigan	Milwaukee Bay	WI	22.44
LMMU	Lake Michigan	Muskegon Breakwater	MI	20.31
LMNC	Lake Michigan	North Chicago	IL	15.97
MDSJ	Marina Del Rey	South Jetty	CA	13.30
BRCL	Brazos River	Cedar Lakes	TX	11.69
HRUB	Hudson/Raritan Estuary	Upper Bay	NY	10.91
HRLB	Hudson/Raritan Estuary	Lower Bay	NY	10.14
HRJB	Hudson/Raritan Estuary	Jamaica Bay	NY	8.07
MBHI	Mobile Bay	Hollingers Is. Chan.	AL	7.96
SBSR	Saginaw Bay	Saginaw River	MI	7.52
SFSM	San Francisco Bay	San Mateo Bridge	CA	7.15
NYSH	New York Bight	Sandy Hook	NJ	6.28
LEOW	Lake Erie	Old Woman Creek	OH	6.02
CBBL	Choctawhatchee Bay	Bens Lake	Fl	5.66
GBDP	Great Bay	Dover Point	NH	5.62
HRRB	Hudson/Raritan Estuary	Raritan Bay	NJ	5.53
TBOT	Tampa Bay	Old Tampa Bay	FL	5.33
LESP	Lake Erie	Stony Point	MI	4.90
LBBW	Long Beach	Breakwater	CA	4.62
HHKB	Hawaii	Kaneohe Bay	HI	4.42
SFEM	San Francisco Bay	Emeryville	CA	4.42
TBKA	Tampa Bay	Peter O. Knight Airport	FL	4.40
CBTP	Commencement Bay	Tahlequah Point	WA	4.35
NBNB	Naples Bay	Naples Bay	FL	4.18

Table 5. NS&T site locations with alpha endosulfan concentrations in tissue greater than the 90th percentile (ng/g dry wt).

Site	General Location	Specific Location	State	alpha Endosulfan
BBGC	Biscayne Bay	Goulds Canal	FL	7.883
LJLJ	La Jolla	Point La Jolla	CA	4.969
SHFP	Salem Harbor	Folger Point	MA	4.817
BBCC	Buzzards Bay	Cape Cod Canal	MA	4.392
FBJB	Florida Bay	Joe Bay	FL	3.022
SAWB	St. Andrews Bay	Watson Bayou	FL	2.581
GBOB	Galveston Bay	Offatts Bayou	TX	2.153
NMML	North Miami	Maule Lake	FL	2.152
SFSM	San Francisco Bay	San Mateo Bridge	CA	2.055
NYSH	New York Bight	Sandy Hook	NJ	1.655

Table 6. NS&T site locations with beta endosulfan concentrations in tissue greater than the 90th percentile (ng/g dry wt).

Site	General Location	Specific Location	State	beta Endosulfan
SHFP	Salem Harbor	Folger Point	MA	6.280
BBCC	Buzzards Bay	Cape Cod Canal	MA	5.312
LJLJ	La Jolla	Point La Jolla	CA	3.807
BBGC	Biscayne Bay	Goulds Canal	FL	3.468
CBDP	Chesapeake Bay	Dandy Point	VA	2.639
BIBI	Block Island Sound	Block Island	RI	2.305
CCNH	Cape Cod	Nauset Harbor	MA	2.131
EUSB	Eureka	Samoa Bridge	CA	1.794
CAGH	Cape Ann	Gap Head	MA	1.637
ARWI	Altamaha River	Wolfe Island	GA	1.550

Table 7. NS&T site locations with endosulfan sulfate concentrations in tissue greater than the 90th percentile (ng/g dry wt).

Site	General Location	Specific Location	State	Endosulfan Sulfate
BRCL	Brazos River	Cedar Lakes	TX	8.176
BBGC	Biscayne Bay	Goulds Canal	FL	8.071
SHFP	Salem Harbor	Folger Point	MA	6.834
CBDP	Chesapeake Bay	Dandy Point	VA	5.151
BBCC	Buzzards Bay	Cape Cod Canal	MA	5.003
CBHG	Chesapeake Bay	Hog Point	MD	4.155
CBBO	Chesapeake Bay	Bodkin Point	MD	4.073
CBHP	Chesapeake Bay	Hackett Point Bar	MD	3.742
FBJB	Florida Bay	Joe Bay	FL	3.496
BRFS	Brazos River	Freeport Surfside	TX	3.162

The highest tissue chlorpyrifos concentration (52.92 ng/g) was measured at Freeport Surfside, Texas and the seventh highest (11.69 ng/g) was measured at Cedar Lakes, Texas both sites are near the mouth of the Brazos River. Four of the five highest tissue chlorpyrifos concentrations were in the Great Lakes (Table 4). Chlorpyrifos use in both of these geographic regions is large. In the Brazos River watershed the combined 1992 estimate of chlorpyrifos use in the fluvial and estuarine drainage areas was 283,294 lbs, nearly 14 percent of the total chlorpyrifos application in Gulf of Mexico drainages (CA&Ds, 1999). In addition, the Brazos River watershed ranked second in chlorpyrifos use within all Gulf of Mexico river dominated drainages. In four of the Great Lakes states (Wisconsin, Illinois, Indiana, and Michigan) chlorpyrifos use is primarily on corn and represents over 32 percent (1.456 million pounds) of all 1996 chlorpyrifos usage on field crops in the United States. Another reason for the high concentrations in the Great Lakes region may have to do with the season in which samples are collected. Unlike the other NS&T sites, which are sampled between November and early April, the Great Lakes are sampled in August when the waters are warmer and before ice forms. Chlorpyrifos is applied in the Great Lakes

region usually during the months of June and July close to the time of sampling. Less chlorpyrifos is likely to have degraded than would be the case for samples collected in winter.

Chlorpyrifos levels in five of six NS&T sites within the Hudson/Raritan estuary and the New York Bight were above the 90th percentile and 3 of these were above the 95th percentile. These results were surprising for a heavily populated region with limited agricultural land use and may indicate high nonagricultural use of chlorpyrifos. Other urban areas with chlorpyrifos levels above the 90th percentile include Tampa Bay, Florida, and San Francisco Bay, California, but the watersheds of these estuaries contain heavy agricultural land use.

Low tissue concentrations of chlorpyrifos were detected at eight sites in Alaska (Fig. 3) where it has limited use. Runoff from agriculture or urban use is an unlikely source which suggests that atmospheric transport from Canada, the lower US or possibly Russia (Sergei Chernyak, Biological Resources Division, US Geological Survey, Ann Arbor, MI, personal communication, 1999).

Sediment levels of chlorpyrifos were poorly correlated with tissue levels. Only 3 of the 18 sites above the sediment 90th percentile were also above the corresponding tissue 90th percentile. These included two sites in Tampa Bay and Choctawhatchee Bay, Florida (Table 8).

Table 8. NS&T site locations with chlorpyrifos concentrations in sediment greater than the 90th percentile (ng/g dry wt).

Site Code	General Location	Specific Location	State	Chlorpyrifos
TBKA	Tampa Bay	Peter O. Knight Airport	FL	5.68
EUSB	Eureka	Samoa Bridge	CA	4.16
CBPP	Choctawhatchee Bay	Postil Point	FL	3.94
PVRP	Palos Verdes	Royal Palms State Park	CA	2.16
PCMP	Panama City	Municipal Pier	FL	1.74
MBNR	Massachusetts Bay	North River	MA	1.62
LIHR	Long Island Sound	Housatonic River	CT	1.46
CBBL	Choctawhatchee Bay	Bens Lake	Fl	1.24
BBSM	Bellingham Bay	Squalicum Marina Jetty	WA	1.22
BBRH	Buzzards Bay	Round Hill	MA	1.15
EVFU	Everglades	Faka Union Bay	FL	1.12
PRBJ	Puerto Rico	Bahia De Jobos	PR	1.08
CCBH	Corpus Christi	Boat Harbor	TX	1.07
TBMK	Tampa Bay	Mullet Key Bayou	FL	0.96
TBNP	Tampa Bay	Navarez Park	FL	0.94
CBBO	Chesapeake Bay	Bodkin Point	MD	0.89
MBES	Monterey Bay	Elkhorn Slough	CA	0.89
TBOT	Tampa Bay	Old Tampa Bay	FL	0.84

One or more of the three endosulfans (alpha, beta or sulfate) exceeded its tissue 90th percentile at 21 of 95 sites characterized in nine of the conterminous states. Three of these sites

exceeded the 90th percentile for all three endosulfans, i.e., sites in Buzzards Bay and Salem Harbor, Massachusetts, and Biscayne Bay, Florida. Two sites exceeded the 90th percentile for two endosulfans, i.e., La Jolla, California and Joe Bay, Florida. In contrast to chlorpyrifos, endosulfan residues in tissue were found less frequently in urban areas. The highest endosulfan concentrations were observed for endosulfan sulfate followed by alpha then beta endosulfan, with 38.9, 62.1 and 80.0 percent of samples, respectively falling below method detection limits.

Chlorpyrifos and endosulfan concentrations were compared with several watershed characteristics (Table 9) including estuarine drainage area, fluvial drainage area, chlorpyrifos and endosulfan use (as lbs of active ingredient); acres treated with chlorpyrifos and endosulfan, and average daily river discharge (Pait et al., 1992) by coast line. The estuarine drainage area, defined as that portion of the watershed that most directly affects the estuary, is defined by the U.S. Geological Survey Hydrologic Cataloging Units (watershed boundaries) and by the head of tide. It was further divided into land and surface water portions of the drainage basin. The fluvial drainage basin, which lies upstream from the head of tide, was similarly divided into land and surface water portions.

On a national basis, chlorpyrifos concentrations were positively correlated with land estuarine drainage area, and negatively correlated with water fluvial drainage area ($p<0.0001$) (Table 9). By coast, chlorpyrifos was positively correlated with river discharge on the Atlantic and Gulf coasts ($p<0.03$). Alpha and beta endosulfan concentrations were positively correlated with average daily freshwater discharge to Pacific and Atlantic estuaries, respectively ($p<0.04$) (Table 9). Significant correlations with river discharge to the Great Lakes were not found.

Correlations were tested between pesticide concentration and human population within 5 to 50 km of NS&T site locations. All correlations were positive, and significant at the $p<0.0001$ level for chlorpyrifos in both sediment and tissue (Table 10). In contrast, only beta endosulfan was positively correlated ($p<0.03$) with human population within 50 km of the sampling site (Table 10) and may reflect the limited use of endosulfan in urban environments.

Correlations were also tested between the pesticide concentration, and latitude and longitude of NS&T sampling sites. Tissue chlorpyrifos concentrations were positively correlated with East Coast latitude ($p<0.05$) and negatively correlated with West Coast latitude ($p<0.001$) (Table 10). Sediment chlorpyrifos was correlated with longitude ($p<0.04$; increasing from east to west). In contrast, none of the endosulfans were correlated ($p<0.05$) with latitude (East or West Coast) however, beta endosulfan and endosulfan sulfate were correlated with longitude (increasing west to east) (Table 10).

The mean and median alpha to beta endosulfan ratio in tissue based on 90 sites was 1.6 and 1.1, respectively. Similarly, the alpha/beta ratio for the four sites above the 90th percentile (Tables 5 and 6) ranged from 0.77 to 2.27 (mean = 1.30) or about half of the ratio in the applied formulated product (2.33). If the alpha isomer is more prevalent in the atmosphere as suggested by Schmidt, et al. (1997) and endosulfan usage is more prevalent in areas of vegetable production in the mid to lower latitudes, then it seems reasonable to expect a

Table 9. Spearman correlations of chlorpyrifos and endosulfan tissue concentrations and watershed characteristics. Values in () equal the Prob > | R | under Ho: Rho=0.

Variable	No. obs.	Chlorpyrifos	No. obs.	alpha endosulfan	beta endosulfan	Endosulfan sulfate
Land estuarine drainage area	177	0.195 (0.0092)	54	-0.132 (0.3410)	-0.250 (0.0688)	-0.115 (0.4088)
Land fluvial drainage area	94	-0.126 (0.2253)	35	0.066 (0.7076)	-0.120 (0.4941)	-0.140 (0.4219)
Water estuarine drainage area	177	-0.004 (0.9601)	54	0.035 (0.8012)	-0.240 (0.0803)	-0.207 (0.1323)
Water fluvial drainage area	22	-0.908 (0.0001)	1			
1992 chlorpyrifos use (lbs)	173	0.084 (0.2708)	53	-0.020 (0.8862)	-0.219 (0.1151)	-0.159 (0.2541)
1992 endosulfan use (lbs)	171	0.103 (0.1814)	53	0.018 (0.8998)	-0.188 (0.1784)	-0.101 (0.4733)
1992 chlorpyrifos AT	173	0.049 (0.5255)	53	-0.047 (0.7368)	-0.236 (0.0895)	-0.173 (0.2142)
1992 endosulfan AT	171	0.070 (0.3597)	53	-0.014 (0.9212)	-0.195 (0.1610)	-0.093 (0.5097)
Avg. Daily River Discharge:						
Atlantic Coast (exclud. FL)	34	0.376 (0.0284)	25	0.323 (0.1156)	0.531 (0.0063)	0.381 (0.0599)
Gulf Coast (exclud. FL)	34	0.376 (0.0284)	17	0.053 (0.8405)	-0.096 (0.7152)	-0.180 (0.4898)
Pacific Coast (exclud. AK)	26	0.192 (0.3469)	6	0.841 (0.0361)	0.261 (0.6175)	0.0290 (0.9565)

higher alpha to beta ratios with increasing latitude. This theory is weakly supported by the Spearman Rank correlation between the alpha to beta ratio and latitude ($p<0.08$, $n=90$).

Conclusions

Chlorpyrifos was detected in 32% of sediment and 68% of tissue samples collected throughout the Atlantic, Pacific and Gulf coasts of the United States and the Great Lakes including, tissue samples from all eight sites in Alaska, 1 in Hawaii and in Puerto Rico. Tissue chlorpyrifos concentrations, which exceeded the 90th percentile, were found in coastal regions known to have high rates agricultural use. Both sediment and tissue chlorpyrifos concentrations were strongly correlated with NS&T sites near large urban population centers which is consistent with estimates of large nonagricultural use in urban environments.

The detection of chlorpyrifos in Alaska supports reports that this compound can be transported atmospherically. Nearly all of the Great Lakes sites had chlorpyrifos tissue concentrations above the 90th percentile. These concentrations decreased from west to east corresponding to increased distance from the Corn Belt region (Iowa, Indiana, Illinois, and Wisconsin) where most chlorpyrifos is applied.

Correlation analysis suggests that fluvial discharge is the primary transportation pathway for chlorpyrifos on the Atlantic and Gulf of Mexico coasts. Sediment and tissue chlorpyrifos concentrations were strongly correlated with NS&T sites near large population centers, which is consistent with usage estimates of chlorpyrifos in urban areas. In contrast, the importance of fluvial discharge of endosulfans is less clear due to the lack of consistent correlations among the different endosulfan compounds and because endosulfan use is less uniform then chlorpyrifos and limited mostly to agricultural applications. Endosulfan levels were not correlated with urban population centers but were most commonly found in areas near agricultural watersheds.

Water quality studies of rivers and lakes throughout the United States and Canada have reported no or low levels of endosulfan and chlorpyrifos in the dissolved phase. However, the results reported here confirm that these compounds are leaving the site of application and are transported to the coastal environment where they are accumulated in sediment and tissue. Clearly the detection of these compounds in sediment and tissue from coastal waters demonstrates the importance of monitoring. Further monitoring of these compounds should continue on temporal and spatial scales consistent with their seasonal use and with low method detection limits for more accurate determinations of fluvial loadings.

Table 10. Spearman correlations between compound-matrix combination and human population within a given radius and with latitude and longitude (as negative decimal degrees).

Spearman Correlations :	Chlorpyrifos Sediment	Chlorpyrifos Tissue	alpha endo. Tissue	beta endo. Tissue	endo. sulfate Tissue
Population radius:					
5 Km	0.454 (0.0001)	0.403 (0.0001)	0.153 (0.1409)	0.102 (0.3270)	-0.035 (0.7364)
10 Km	0.486 (0.0001)	0.397 (0.0001)	0.191 (0.0656)	0.104 (0.3195)	0.029 (0.7799)
15 Km	0.517 (0.0001)	0.420 (0.0001)	0.191 (0.0647)	0.138 (0.1850)	0.015 (0.8854)
20 Km	0.476 (0.0001)	0.418 (0.0001)	0.186 (0.0707)	0.161 (0.1192)	0.058 (0.5766)
25 Km	0.526 (0.0001)	0.435 (0.0001)	0.176 (0.0900)	0.163 (0.1163)	0.048 (0.6479)
50 Km	0.456 (0.0001)	0.339 (0.0001)	0.182 (0.0790)	0.220 (0.0335)	0.102 (0.3295)
All coasts - Longitude	0.147 (0.0431)	0.0380(0.4446)	-0.095 (0.3555)	-0.246 (0.0168)	-0.328 (0.0011)
Atlantic– Latitude	0.178 (0.1725)	0.162 (0.0457)	-0.066 (0.6231)	0.137 (0.3055)	0.197 (0.1384)
Pacific (exclud. AK) - Lat.	-0.08370(0.6488)	-0.353 (0.0010)	0.298 (0.2799)	0.043 (0.8794)	0.198 (0.4784)

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