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Distribution of Organophosphorus Pesticides in some Estuarine Environments in Korea

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To study the distribution of organophosphorus pesticides which are extensively used for agriculture in Korea. Sea water samples were taken from 4 coastal areas during May and August of 1997 and sediment samples were collected from two coastal areas in August of 1997. These samples were analyzed using a Gas Chromatography/Nitrogen Phosphorus Detector (GC/NPD). In August the most commonly found organophosphorus pesticides in the surface waters of Kunsan area were IBP < *S*-Benzyl *O,O*-di-isopropyl phosphorothioate > (m=432.5 ng L^{-1}) and EDDP < *O*-ethyl *S,S*-diphenyl phosphorodithioate > (m=37.4 ng L^{-1}) which are largely used between June and September to prevent rice blast disease. In Danghang Bay, dry fields located near the mouth of the estuary seemed to affect the concentrations of certain organophosphorus pesticides in the surface waters. Since organophosphorus pesticides applied in the watershed are rapidly decomposed while being transported along freshwater streams, watershed size is not proportional to the concentrations of these pesticides in the coastal waters. Pesticides concentrations measured in August were compared with those in May. IBP concentrations in coastal waters were about an order of magnitude higher in August than in May. Temporal and geographical distribution of individual organophosphorus pesticides is likely to be affected by types of agricultural practices in the watershed. Chloropyrifos was the most important of the organophosphorus pesticides in the sediments of the study area because of its persistent nature and high affinity to particulates.

Introduction

Pesticides, because of their widespread distribution and toxic nature, have become an important class of aquatic pollutants. This fact has stimulated research into the nature, behavior, and fate of these compounds and their metabolites in the environment. Pesticides applied to agricultural crops, forests, or recreational areas are transported to rivers and oceans. Pesticides may also be directly applied to water to control aquatic pests (Ferrando et al., 1992). In many countries, restrictions have been imposed on the use of organochlorine pesticides. This has shifted the use patterns away from organochlorines toward organophosphorus and carbamate pesticides.

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Most organophosphorus and carbamate pestcides are regarded as being non-persistent, but some reports have indicated that residues of some organophosphorus pesticides are persisting for extended periods in organic soils and in surrounding drainage systems (Harris and Miles, 1975). Factors controlling the distribution of organophosphorus pesticides discharged to marine environment are the degree of natural degradation and the extent of adsorption onto particulate matter while moving toward the offshore area (Stoker and Seager, 1976). pH, temperature, contributions from microorganisms and levels of suspended solids in seawater are also important (Paris et al., 1975). Many authors have studied the persistence of organophosphorus pesticides in soil and waters. Decomposition of malathion, endosulfan, fenvalerate was studied in the microcosm of seawater and the seawater/sediment interface (Cotham and Bidleman, 1989).

Many organophosphorus pesticides are toxic to aquatic life. Many authors (Goodman et al., 1979; Hale 1989) have studied the toxicity of organophosphorus pesticides in marine organisms. Acute effects on marine crustaceans have been reported at concentrations of 1 g L^{-1} for several organophosphorus pesticides (Schimmel et al., 1983).

Organophosphorus pesticides are widely used in agricultural industries Korean with a period of extensive application to rice paddy fields during August. Organophosphorus pesticides in the Korean estuarine environments were studied in Suncheon Bay (Jeon and Yang, 1990) and in Kwangyang Bay (Park, 1995). We studied four Korean coastal areas for temporal variation and distribution patterns employing a relatively inexpensive GC/NPD analytical technique.

Materials and Methods

Samples were collected during May and August, 1997 from four estuarine areas (Fig. 1). Kunsan area (Kum River estuary) is located on the western coast of Korea. For the purpose of irrigation to rice paddy fields, a big freshwater reservoir was formed at the mouth of the Kum River by constructing the dike. Danghang Bay is a small inlet located on the southeastern coast of Korea. Small streams influenced by agricultural activities join this almost enclosed bay. Sachon Bay is a small bay influenced by agricultural wastes from surrounding agricultural area. Kwangyang Bay is a semi-enclosed bay with a surface area of 240 km^2. Main freshwater inflow to this bay is from the Somjin and Sueochon Rivers which drain an area of predominantly agricultural land-use. Somjin River is one of the five major river systems in Korea together with Kum River (Kunsan area).

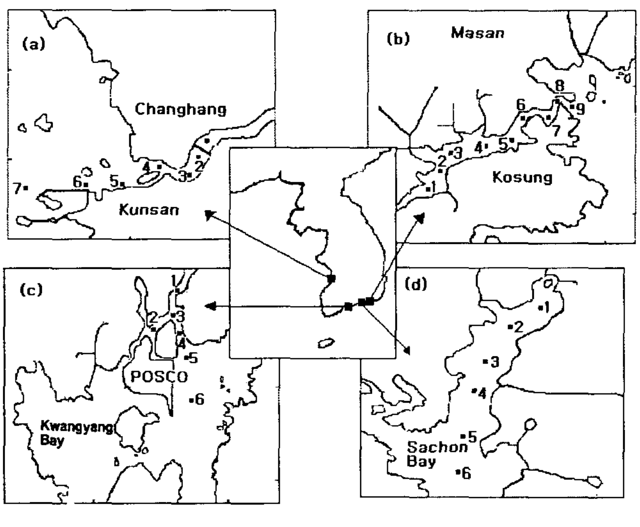

Fig. 1. Sampling stations of Kunsan area (a), Danghang Bay (b), Kwangyang Bay (c) and Sachon Bay (d).

Our analytical methods for organophosphorus pesticides were based on the method described by Tolosa et al. (1996). Surface seawater samples were taken at 0.5 m depth to avoid surface slicks and were kept frozen in amber bottles until analyzed. All samples were analyzed within one week following the sampling. Seawater samples were filtered through glass microfiber filters (0.45 μm) prior to extraction. Sixty milliliters of dichloromethane (CH_2Cl_2, Fisher Scientific, Fair Lawn, NJ, USA) was added to 1 liter of seawater in separatory funnel. The funnel was shaken vigorously and the organic phase was filtered onto column filled with 1~2 cm of anhydrous sodium sulfate. Two more extraction steps were repeated with 60 mL of dichloromethan. And mixed extracts were concentrated to 3~5 mL using rotary evaporator. Extracts were transferred to 10 mL test tube and evaporated to near dryness with nitrogen gas. Volume of the extracts was adjusted to 1 mL using hexane: acetone (9:1) and chlorthion was added as an internal standard. Gas chromatography/Nitrogen Phosphorus Detector (GC/NPD) was used for the analysis of organophosphorus pesticides (Hewllet-Packard 5890 Series II plus/nitrogen phophorus detector). By this method detection limit was measured to be 1.80 ng L^{-1} for IBP, 0.58 ng L^{-1} for DDVP (IUPAC name: 2,2-dichlorovinyl dimethyl phosphate) and 1.06 ng L^{-1} for chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl).

Three sediment samples from Danghang Bay and 5 samples from Sachon Bay were analyzed for organophosphorus pesticides in the sediments. Sediment samples were taken at the mouth of Danghang Bay (St. 7, 8 and 9) and Sachon Bay (St. 1 through 5) in August of 1997. Sediment samples were kept frozen and freeze-dried upon arrival at laboratory. Our analytical method of organophosphorus pesticide in sediment was based on that of

Readman et al. (1992) with some modifications. About 2~3 g of freezedried sediment was placed into a precleaned extraction thimble in a Soxhlet apparatus. Internal standard (about 100~200 ng chlorthion in acetone solvent) was added. Ethyl acetate:acetone (50:50) was added at about twice the volume of the Soxhlet apparatus and the sediment was extracted for 8 hours. The extracts were then concentrated on a rotary evaporator to about 10 mL. Other procedures were the same as described for the seawater sample. Recovery of organophosphorus pesticides by this method was over 86%.

Results and Discussion

Organophosphorus pesticides in the surface waters

In May of 1997, ethoprofos, diazinon, IBP and parathion methyl were measured in the surface waters of the Kunsan area (Table 1). As shown in Fig. 2, organophosphorus pesticide contents decreased with increasing distance from the Kum River mouth.

In August 1997, 356,289,000 tons of freshwater water were discharged through Kum River Dike to control the level of reservoir water one day before the sampling. Salinities in the surface waters of St. 1 through 4 were lower than 0.2 psu and those of St. 5 and 6 were about 8 psu. For this reason organophosphorus pesticide concentration showed little geographic variation along this salt wedge type estuary.

Table 1. Distribution of organophosphorus pesticides in Korean coastal waters in May 1997 (ng L^{-1})

Pesticides	Kunsan		Danghang		Sachon	
	Range	Mean	Range	Mean	Range	Mean
DDVP	ND	ND	ND	ND	ND	ND
Ethoprofos	ND−15.8	9.2	ND−9.8	1.1	ND	ND
Disulfoton	ND	ND	ND	ND	ND	ND
Diazinon	13.0−75.1	42.9	ND−6.7	1.4	ND−18.5	11.4
IBP	ND−72.2	40.1	ND−13.2	1.5	ND−33.3	20.1
P. Methyl	ND−16.2	4.3	ND−15.8	1.8	ND	ND
Fenchlorphos	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND−11.9	2.4	ND−14.4	6.4
Prothiophos	ND	ND	ND	ND	ND	ND
EDDP	ND	ND	ND	ND	ND	ND

ND: not detected (<0.1 ng).
DDVP: 2,2-dichlorovinyl dimethyl phosphate.
IBP: *S*-Benzyl *O,O*-di-isopropyl phosphorothioate.
EDDP: *O*-ethyl *S,S*-diphenyl phosphorodithioate.
P. Methyl: Parathion Methyl.

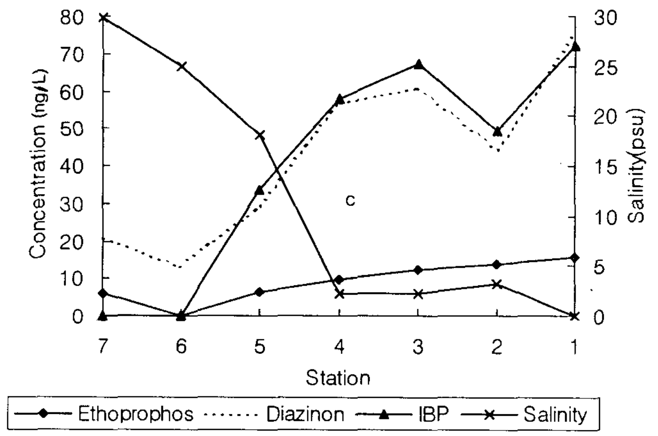

Fig. 2. Pesticides contents and salinity in Kunsan area in May 1997.

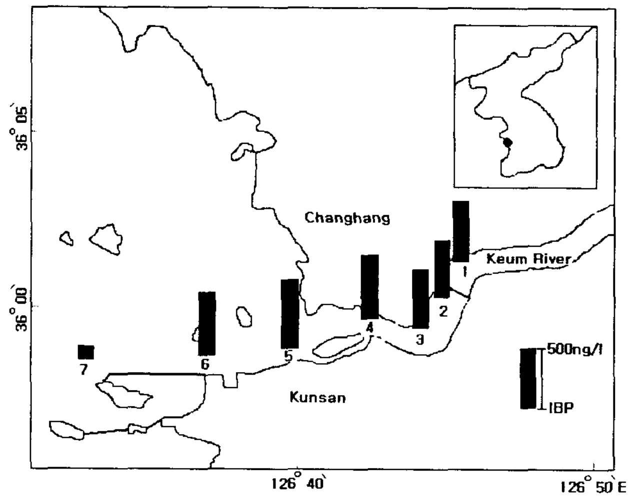

Fig. 3. IBP content in Kunsan area in August 1997.

The most commonly found organophosphorus pesticides in Kunsan area in August were IBP (m= 432.5 ng L^{-1}) and EDDP (m=37.4 ng L^{-1}). These compounds are largely used between June and September for rice blast disease (Table 2). The highest values of diazinon and chlorpyrifos were found in the freshwater reservoir (St. 1, 29.6 and 45.5 ng L^{-1}, respectively).

In Danghang Bay only small amount of pesticide could be measured in the surface waters in May (Table 1). IBP could be measured only at the head of the estuary (13.2 ng L^{-1}) and more than 10 ng L^{-1}

Table 2. Distribution of organophosphorus pesticides in Korean coastal waters in August 1997 (ng L^{-1})

Pesticides	Kunsan		Danghang		Sachon		Kwangyang	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
DDVP	4.6−26.5	12.7	3.5−20.7	6.6	ND−3.2	0.5	ND−6.9	2.5
Ethoprofos	1.5−5.3	4.5	1.2−1.6	1.4	ND−0.8	0.1	ND−1.3	0.9
Disulfoton	ND	ND	ND−7.1	2.1	ND	ND	ND	ND
Diazinon	11.1−29.6	24.4	1.6−8.1	5.4	4.7−6.5	5.3	1.8−396.3	78.2
IBP	101.0−528.0	432.5	68.6−172.6	118.1	48.2−75.4	56.3	42.1−105.3	59.2
P. Methyl	1.4−3.0	2.3	ND−4.2	0.5	ND	ND	ND	ND
Fenchlorphos	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	11.6−45.5	18.9	8.0−12.3	9.6	9.4−10.7	9.9	8.3−11.1	10.1
Prothiofos	ND	ND	ND−3.9	0.4	ND	ND	ND	ND
EDDP	3.6−58.9	37.3	1.3−4.3	1.8	2.1−3.3	2.8	ND−5.1	1.9

ND: not detected.
DDVP: 2,2-dichlorovinyl dimethyl phosphate.
IBP: *S*-Benzyl *O,O*-di-isopropyl phosphorothioate.
EDDP: *O*-ethyl *S,S*-diphenyl phosphorodithioate.
P. Methyl: Parathion Methyl.

of chlorpyrifos could be detected in the mid-estuary. In August, salinities ranged 19.78 to 25.38 psu in the surface waters of Danghang Bay. IBP, which was the most abundant organophosphorus pesticides, ranged from 68.6 to 172.6 ng L^{-1} showing its maximum in the headwaters of the estuary (Table 2). IBP content and salinity showed a negative relationship suggesting progressive dilution of this pesticide in the estuary (r^2=0.9224, Fig. 4). DDVP and diazinon concentrations were the highest at a station located in the lower estuary (20.7, 8.1 ng L^{-1}). The concentrations of these two pesticides were relatively low in the headwaters which are directly affected by runoff from rice paddy fields. This may be due to the predominance of dry fields over rice paddy fields around the lower estuary since DDVP and diazinon are preferentially used for dry fields.

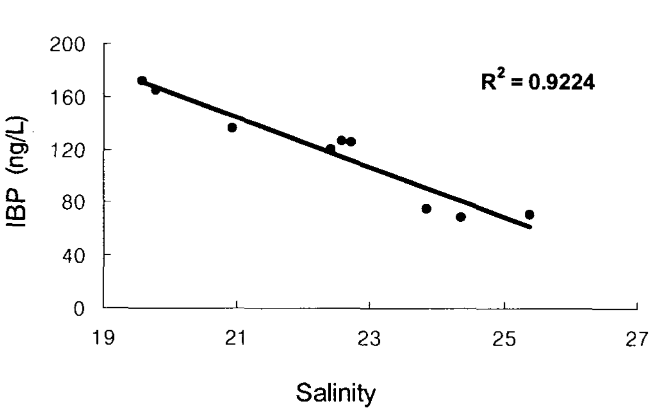

Fig. 4. Correlation between IBP content in Danghang Bay in August 1997.

In May up to 33.3 ng L^{-1} of IBP was measured (m=20.1 ng L^{-1}) and diazinon was also widely found (m=11.4 ng L^{-1}) in Sachon Bay. In August when salinities ranged from 29.47 to 29.79 psu, IBP content was relatively high in the headwaters of Sachon Bay and it tended to decrease with increasing distance from the head of the estuary (Fig. 5). IBP was also widely found in Kwangyang Bay in August (Fig. 6). The average IBP value for three stations in the headwaters was 59.2 ng L^{-1}. Park (1995) reported that in this bay IBP ranged 24.0~46.2 ng L^{-1} during the summer of 1994 which was comparable to our results.

Pesticides concentrations measured in August of 1997 were compared with those measured in May of 1997. Seasonal and geographical distributions of individual organophosphorus pesticides may be dependent upon the types of agricultural practices and preferentially used pesticide products in each region. Rice production is an important agricultural practice in Korea. The use of pesticides in Korea is almost year round, however, extensive use occurs after a monsoon period which normally ends by late July. Large amounts of pesticides are applied to prevent rice blast disease during hot and sunny August. IBP content was about an order of magnitude higher in August compared with that in May in all areas since it is the most commonly used pesticide for rice blast disease. EDDP was not

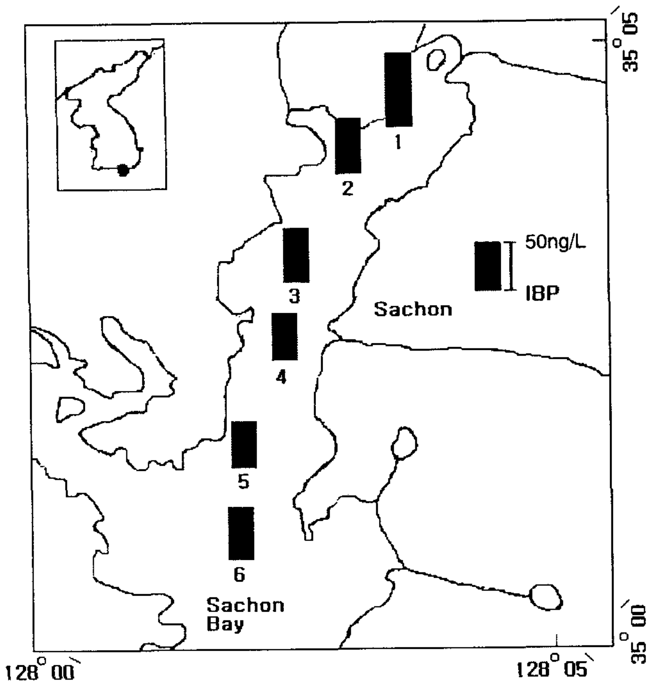

Fig. 5. IBP content in Sachon Bay in August 1997.

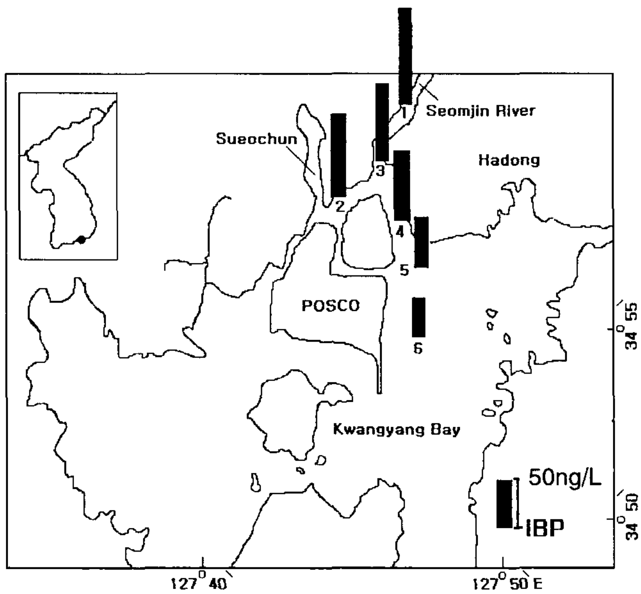

Fig. 6. IBP content in Kwangyang Bay in August 1997.

found in any study areas in May since it is mostly applied to prevent rice blast disease in August. Ethoprophos which is used for the culture of tobacco, red pepper, mulberry, garlic and potato was higher in May than in August. DDVP which is known to be used for the culture of apple, mulberry, cabbage and peach could only be measured in August in all areas since its use is usually limited from June to August. Small amounts of chlorpyrifos could be measured in May in Danghang and Sachon Bay, however, it was found in all areas in August. Chlorpyrifos is known to be used both for dry fields and rice paddy fields to prevent diverse aquatic pests.

In our study area relatively low concentrations of organophosphorus pesticides found in estuaries suggest its rapid decomposition before reaching saline waters. Since most organophosphorus pesticides are rapidly decomposed while being transported toward downstream, size of catchment area is not proportional to the amount of organophosphorus pesticides reaching estuarine area. Watershed size of Kum River (Kunsan area) and Somjin River (Kwangyang Bay) is reported to be 9,886 and 2,143 km^2, respectively while freshwater outflow from less than 100 km^2 of watershed affects Danghang Bay. However, a considerable amount of organophosphorus pesticides was found in Danghang Bay which may have resulted from the short travel time of agricultural wastewaters arriving at this bay. The type of estuary may also be an important factor regulating the distribution of organophosphorus pesticides by affecting the residence time of these pesticides in the estuary. Pesticides entered into Danghang Bay may not be easily dispersed because of its limited water exchange.

Flooding or immense freshwater outflow after heavy rainfall that can transport high amounts of organophosphorus pesticides could considerably increase their concentrations in coastal area and may significantly affect marine organisms due to their high acute toxicity. However the high IBP content occurred in Kunsan area in August may not be serious since IBP is not highly toxic. The LC_{50} of IBP for carp is 5.1 mg L^{-1} (Worthing 1979). The LC_{50} of organophosphorus compounds are usually lower than those of organochlorine pesticides (Stoker and Seager, 1976). For the case of chlorpyrifos, the 96 hour LC_{50} of Mysidacea (*Mysidopsis bahia*) was reported to be 0.035 $\mu g\ L^{-1}$ (Schimmel et al., 1983). The 96 hour LC_{50} of DDVP on arkshell (*Anadara granosa*) was measured to be 1.79 $\mu g\ L^{-1}$ (Bharath, 1994).

In our study chlorpyrifos content in the surface water in August was 8.0~12.3 ng L^{-1} (m=9.6 ng L^{-1}) in Danghang Bay and 9.4~10.7 ng L^{-1} (m=10.1 ng L^{-1}) in Sachon Bay. Chloropyrifos is considered to be extremely toxic. The 96 hour LC_{50} for a sensitive species of tropical shrimp has been reported as 10 ng L^{-1} (National Research Council of Canada, 1978). Thus, chlorpyrifos content in the study area might adversely affect the marine ecosystem.

Organophosphorus pesticides in the sediments

The distribution of organophosphorus pesticides in sediments is shown in Table 3. Chlorpyrifos appeared to be the most significant organophosphorus pesticide found in the sediments. Its mean value was 2.4 ng g^{-1} dry wt. in Danghang Bay and 1.7 ng g^{-1} dry wt. in Sachon Bay. The chlorpyrifos concentrations averaged to be 10 ng L^{-1} in the overlying water column of these areas.

Table 3. Organophosphorus pesticides in sediments (ng g^{-1} dry wt.)

Pesticides	Danghang	Sachon
DDVP	0.3	0.1
Ethoprofos	0.4	0.2
Diazinon	0.5	0.4
IBP	0.6	0.6
P. Methyl	0.6	0.4
Chlorpyrifos	2.4	1.7
Prothiophos	0.5	0.3

DDVP: 2,2-dichlorovinyl dimethyl phosphate.
IBP: *S*-Benzyl *O,O*-di-isopropyl phosphorothioate.
EDDP: *O*-ethyl *S,S*-diphenyl phosphorodithioate.
P. Methyl: Parathion Methyl.

Readman et al. (1992) reported that only a few of the pesticides are sufficiently persistent to reach marine sediments. Readman's investigations only identify chlorpyrifos and parathion as comparatively persistent. The physical chemistry of chlorpyrifos differs to that of most other organophosphorus pesticides and would enhance partitioning of chloropyrifos onto sediments compared to most other pesticides (Chiou et al., 1977). Schimmel et al. (1983) and Readman et al. (1992) reported that chlorpyrifos is known to be more adsorbed onto particulates than other pesticides. It appears that once organophosphorus pesticides compounds are sorbed onto sediments they are less easily degraded (Carvalho et al., 1992). Chlorpyrifos has been commonly encountered in sediments of tropical region, concentrations of up to 34 ng g^{-1} dry wt. were recorded, with highest levels in areas receiving agricultural runoff (Readman et al., 1992).

During this study chloropyrifos was indicated to be the most important organophosphorus pesticide in the sediments of the study area because of its persistent nature and high affinity to particulates. Possible impacts of this pesticide on the coastal ecosystem of the study area will be subjected to further detailed investigation.

To understand the behavior and fate of organophosphorus pesticides, mechanisms of its transport, including adsorption capacity onto different types of sediment particles, should be carefully studied in the future. More studies on bioavailability and toxicity are needed to predict adverse impacts of organophosphorus pesticides on marine ecosystems. Regular and systematic monitoring of organophosphorus pesticides in marine environment will provide a basis for understanding their geochemical cycles and adverse impacts on biota. Bioconcentration and excretion of organophosphorous pesticides have been studied in freshwater organisms (Tsuda et al., 1997). This kind of information on marine organisms would be essential to understand the bioeffects of organophosphorous pesticides.

Many organophosphorus chemicals exhibit high acute toxicity towards non-target species by interfering with the enzyme acetylcolinesterase which is essential for correct functioning of sensory and neuromuscular systems (De Bruijn and Hermens, 1993). Variation of AChE activities in muscle and brain of fish appeared to be a good indicator of bioeffects caused by organophosphorous pesticides (Galgani and Bocquene, 1989). The biomarker studies using acetylcolinesterase (AChE) activities combined with in situ organophosphorus pesticides distribution will greatly enhance capability for effective monitoring of this harmful substances in the marine environ-ment since measurements of such biomarker may provide early warning of impending environmental damage.

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