

## 아산만 해역의 유기인계농약 분포특성

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## Distribution characteristics of organophosphorous pesticides in Asan Bay, Korea

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### 요 약

아산만 해역의 유기인계농약 분포특성을 2004년 6월부터 2005년 8월까지 조사하였다. 조사 기간 동안 28가지의 유기인계 농약이 아산만에서 검출되었다. IBP는 표층수에서 가장 빈번하게 다량으로 검출되었다(최대 6,343.7 ng l<sup>-1</sup>). DDVP, diazidon, ethoprophos, methidathion도 비교적 높은 농도로 표층수에서 검출되었으며 최대 검출 농도는 조사기간 중 매달 100 ng l<sup>-1</sup> 이상이었다. Malathion, mevinphos, phorate, chlorfenvinphos도 비교적 높은 농도로 검출되었다. 많은 유기인계 농약들이 여름에 많이 사용되어지기 때문에 해양환경에서 겨울보다 여름에 더 빈번히 검출되었다. 해수 중 유기인계 농약의 농도는 만 입구에서 외만으로 갈수록 감소하여 이 농약들이 해양환경 중에서 분해, 희석되는 것으로 판단되었다. 아산만에서 측정된 diazidon 농도는 해양수질 환경기준인 20,000 ng l<sup>-1</sup>을 넘지 않았다. 표층수에서 검출된 malathion, parathion의 농도는 각각 해양수질 환경기준인 250,000 ng l<sup>-1</sup>과 60,000 ng l<sup>-1</sup>를 넘지 않았다. DDVP, phorate, stirofos, EPN, azinphos-methyl, IBP는 다른 유기인계 농약보다 부유입자에 잘 흡착되는 것으로 나타났다. 아산만에서 채취한 시료에서 계산된 유기인계 농약의 부유입자에 대한 흡착계수(K<sub>d</sub>-particle)는 보고되어진 토양에의 흡착계수(K<sub>d</sub>-soil)와 밀접한 관계가 있는 것으로 나타났다.

**Abstract** – Distribution characteristics of organophosphorous pesticides (OPs) in water and suspended particles were studied in Asan Bay, Korea, from June 2004 to October 2005. 28 organophosphorous pesticides could be detected in Asan Bay during this study. The most commonly and abundantly measured OPs in the surface waters were IBP (max=6343.7 ng l<sup>-1</sup>). DDVP, diazidon, ethoprophos and methidathion were also observed at relatively high concentrations. Their maximum concentrations exceeded 100 ng l<sup>-1</sup> in almost every month. Malathion, mevinphos, phorate and chlorfenvinphos were also detected at relatively high concentrations. Many OPs more frequently appeared in summer than in winter due to the intensive application of pesticides in summer months. The concentration of OPs generally decreased with increasing distance from the mouth of Asan Bay. This result implies progressive dilution of these pesticides in the marine environment. Measured concentrations of diazidon were well below 20,000 ng l<sup>-1</sup> which is a limit set by the seawater quality standard of Korea. The concentrations of malathion and parathion in the surface waters of Asan Bay did not exceed the seawater quality standard of Korea (250,000 and 60,000 ng l<sup>-1</sup> respectively). OPs adsorbed on suspended particles were also studied. DDVP, phorate, stirofos, EPN, azinphos-methyl and IBP had higher adsorption capacity onto suspended particles than other pesticides. Calculated pesticide-particle adsorption coefficient (K<sub>d</sub>-particle) for samples collected in Asan Bay were closely related to the reported pesticides-soil adsorption coefficient (K<sub>d</sub>-soil).

**Keywords:** Organophosphorous pesticides(유기인계농약), IBP(아이비피), Asan Bay(아산만), K<sub>d</sub>-particle(부유 입자에의 흡착계수)

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## 1. INTRODUCTION

Pesticides, due to their widespread distribution and toxic nature, have become an important class of aquatic pollutants. They are applied to agricultural crops, forest and recreational areas and transported to rivers and oceans. Pesticides also enter the environment from accidental spills during transport and leaks from storage containers. This fact has stimulated research into the nature, behavior and fate of these compounds and their metabolites in the environment. Pesticides include organochlorine pesticides and organophosphorous pesticides (OPs). However, because of strong persistence and bioaccumulation of organochlorine pesticides, restrictions have been imposed on the use of organochlorine pesticides in many countries. This has shifted the use patterns away from organochlorines and toward OPs. Today, OPs are general pesticides, primarily used for crop protection in agriculture, but they also have important use in urban and forestry sectors. Although OPs in general are acutely toxic, their tendency towards short persistence favors their application over their organochlorine counterparts. More than 100 OPs, including malathion, parathion, diazinon, chlorpyrifos, demeton and azinphosmethyl are used worldwide (World Health Organization [1986]; Tse *et al.* [2004]).

OPs are relatively soluble in water and have significant potential for entering aquatic environments through surface runoff, sprays and soil leachate (Ware [1986]). There is a great concern on the movement of the pollutants in the aquatic system, and several papers appeared in recent years on the distribution (Fries *et al.* [2004]; Isobe *et al.* [2001]). Although half-lives in soil are typically one to three weeks (ASTDR [2000]), residence time of in aquatic environments is variable with some factors, including adsorption onto suspended particulate (Stoker *et al.* [1976]), pH, temperature, contributions from microorganisms and levels of suspended solids in seawater which also is of importance (Paris *et al.* [1975]). Pesticides that are not persistent in the soil environment generally show the largest increases in detection frequency between the pre- and post-plant periods. After sprayed, organophosphorous agricultural chemicals's degradation and distribution are influenced by various environmental processes such as adsorption onto particle (Stoker *et al.* [1976]), pH, influence by microbe (Paris *et al.* [1975]), intensity of illumination, temperature and salinity.

OPs are known to inhibit cholinesterases, by binding to the active site and phosphorylating the enzyme (U.S. Public Health Service [1991]). Acetylcholinesterase (AChE) preferentially hydrolyze acetylcholine and their persistent inhibition causes neurotoxic effects

(O'Brien [1960]). The range of doses that results in toxic effects varies widely with formulation and with the individual species being exposed. There is a concern that OPs can affect non-target organisms, even though the bio-accumulation is not considered as an environmental factor (Ware [1986]). Eventually, OPs can cause severe, long-lasting population effects on aquatic non-target species, particularly on invertebrates (Schulz *et al.* [1999]). There is an increasing evidence that some synthetic chemicals in our environment may disrupt the endocrine system in several ways. They can mimic or block chemicals naturally found in the body and affect functions that these hormones control. Chemicals suspected to be endocrine disrupting can be found among insecticides, herbicides and fungicides. Most endocrine disrupting chemicals are fat-soluble and do not get rapidly flushed out of the body. The Japanese Ministry of Health, Labour and Welfare (<http://www.mhlw.go.jp>) considers among OPs, DDVP, demeton, parathion and parathion-methyl as the endocrine disrupting chemicals (EDC). Parathion and malathion are classified as endocrine disrupting chemicals by the World Wild Life Fund (WWF) (<http://www.worldwildlife.org>).

OPs are widely used in Korean agricultural industries with a period of extensive application to rice paddy fields. During the last 14 years, approximately 250 tons of pesticides were used each year in Korea, in which OPs account for about 60% (Agricultural Chemicals Industrial Association, 2001). Asan Bay is one of the largest bays located on the western coast of Korea. For the purpose of the irrigation of rice paddy fields, two artificial freshwater reservoirs were formed around the inner Asan Bay by constructing a dike. Asan Bay is a relatively large bay influenced by agricultural wastes from surrounding agricultural area. The surface area of Asan Bay is approximately to be 240 km<sup>2</sup>. Asan Bays was made by the construction of a dike having 2,564 km length. It is 2.2 km wide in width and its capacity is 1,420,000 t. After construction of Asan Bay, the farmland surrounding Asan Lake was expanded to 4,674 ha. Asan Bay is not only important agricultural area but also a tourist resort, in Korea.

Although OPs receive more and more attention as environmental contaminants, studies of those are dated or limited to a few compounds in some areas. In Korea, OPs in surface water and sediment have been studied in Suncheon Bay (Jeon *et al.* [1990]), Kwangyang Bay (Park [1995]), Asan Bay and Kyungki Bay (Yu *et al.* [2001]). Although there exists some studies on dissolved OPs in seawater, OPs adsorbed onto suspended particle and sediment are poorly understood in Korea (Yu *et al.* [2002]). In this study, distribution characteristics of organophosphorous pesticides (OPs) were studied in Asan Bay, Korea, from

June 2004 to August 2005. OPs adsorbed on suspended particles was also studied.

## 2. MATERIALS AND METHODS

Organophosphorous pesticides (OPs) widely used in Korea were selected for this study. OPs measured in this study are DDVP, mevinphos, ethoprophos, phorate, sulfotep, dyfonate, disulfoton, diazinon, demeton, IBP, parathion-methyl, fenitrothion, pirimiphos-methyl, malathion, parathion, trichloronate, fenthion, chlorfenvinfos, methidathion, tokuthion, merphos, fenamifos, stirofos, ethion, fensulfotthion, carbophenothion, EPN, azinphos-methyl and azinphos-ethyl. These OPs are chosen among the endocrine disrupting chemicals classified by the World Wild Life Fund (WWF) and Japanese Ministry of Health, Labour and Welfare.

### 2.1 Sampling and Extraction

Sampling locations are shown in Fig. 1. Samples were collected from June 2004 to August 2005, from Asan Bay, Korea. During the sampling period, surface water samples were taken once a month at each of stations in Asan Bay, Korea. Freshwater samples were taken both at Asan and Sapkyo Lake. Surface seawater samples were taken at 0.5 m depth to avoid surface slicks and were kept refrigerated below 10 °C in amber bottles until analysis. All samples were analyzed within one week following the sampling.

Our analytical methods for organophosphorus pesticides (OPs) were based on the method described by Tolosa *et al.* [1996].

Seawater samples were filtered through a glass micro-fiber filter (0.45  $\mu$ m, Whatman) prior to extraction. 60 ml of dichloromethane ( $\text{CH}_2\text{Cl}_2$ , Merck, Germany) was added to 1 liter of seawater sample in separatory funnel. 250 ng (in methanol solvent) of triphenylphosphate was added as a surrogate standard. The funnel was shaken vigorously for 5 minutes. The funnel was allowed to equilibrate before the solvent was separated from the sample. The organic phase was collected in round flask. Two more extraction steps were repeated with 60 ml of dichloromethane. Collected solvent was passed through a funnel filled with 1~2 cm of anhydrous sodium sulfate. Extracts were concentrated to 3~5 ml using rotary evaporator and then substituted for hexane. Extracts were transferred to 8 ml test tube and evaporated to near dryness with nitrogen gas. Volume of the extracts was finally adjusted to 250  $\mu$ l using hexane for GC analysis.

Suspended particles were separated from the water sample using a glass micro fiber filter (0.45  $\mu$ m Whatman GF/C). Filter papers were kept frozen and thawed prior to analysis. 30 ml of DCM ( $\text{CH}_2\text{Cl}_2$ , Merck, Germany) was added to a filter paper in a 50 ml test tube. 250 ng (in methanol solvent) of triphenylphosphate was added as a surrogate. OPs were extracted using sonicator (Powersonic 420, HWASHIN) for 20 minutes followed by handshaking (300-times). Extracts were drained into a flat bottom flask and filter papers were extracted three more times. Extracts were then passed successively through a funnel filled with 5 mg Florisil® (60-100 mesh, Ridel Co.), pre-cleaned sodium-sulphate and glass micro-fiber filters (0.45  $\mu$ m, Whatman). Extracts were concentrated to 250  $\mu$ l under nitrogen jet for GC analysis.

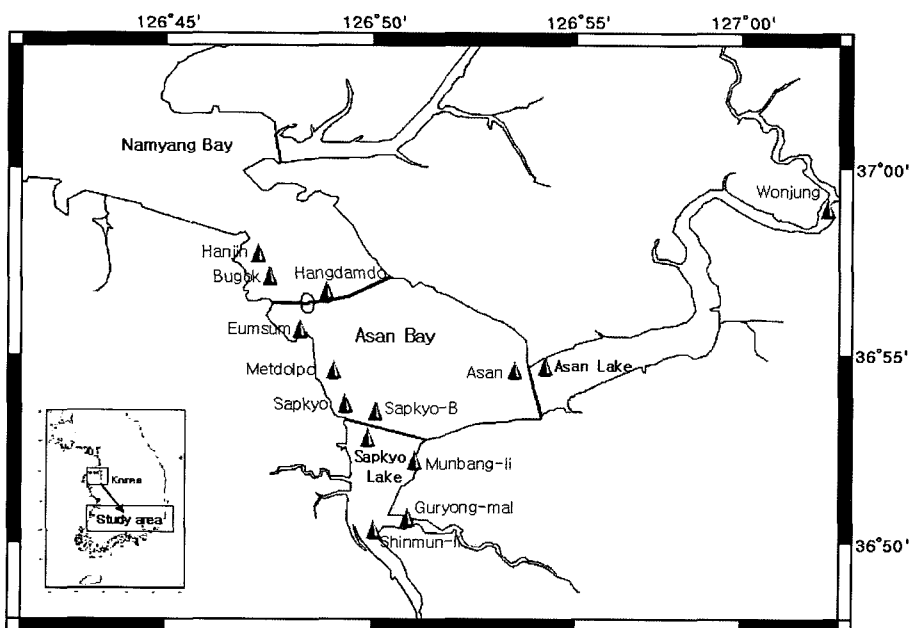
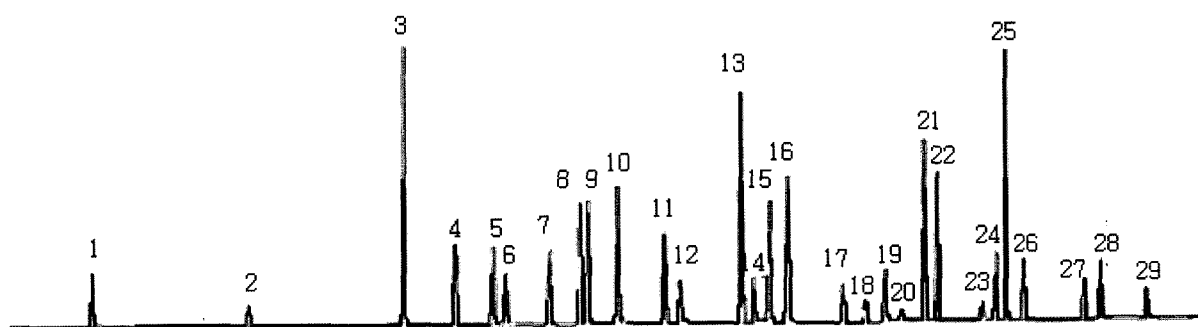


Fig. 1. Sampling stations in Asan Bay, Korea.

**Table 1.** GC/NPD condition used for analysis of organophosphorous pesticide residue

Instrument	Hewlet-Packard HP 5890 Series II Gaschromatograph
Feature	Split / Splitless mode
Inlet	
Detector	Nitrogen Phosphorous Detector (NPD)
Column	HP5 (Crosslinked, 5% PH ME Siloxane) 30 m × 0.32 mm × 0.25 μm
Carrier Gases	He - 30 ml/min Air - 115 ml/min H <sub>2</sub> - 34 ml/min
Injection Temp.	250 °C
Detector Temp	300 °C
Temperature Program	70 °C for 3 min.; 3 °C/min. to 150 °C; hold 5 min.; 2 °C/min to 180 °C; hold 2 min.; 5 °C/min to 280 °C; hold 2 min.
Other	Automatic Liquid Sampler (HP 6890 Series Injector) vol. 2 μl
Calibration	Three Point Calibration



**Fig. 2.** Chromatogram of standard organophosphorous pesticide standard. 1. DDVP, 2. mevinphos, 3. ethoprophos, 4. phorate, 5. demeton, 6. sulfotep, 7. dyfonate, 8. disulfoton, 9. diazinon, 10. IBP, 11. parathion-methyl, 12. fenitrothion, 13. pirimiphos-methyl, 14. malathion, 15. parathion, 16. trichloronate, 17. fenthion, 18. chlorfenvinphos, 19. methidathion, 20. tokuthion, 21. merphos, 22. fenamiphos, 23. stirofos, 24. ethion, 25. fensulfothion, 26. carbofenthion, 27. EPN, 28. azinphos-methyl, 29. azinphos-ethyl

## 2.2 GC-NPD analysis

A Gas Chromatography / Nitrogen Phosphorus Detector (GC/NPD) was used for the analysis of organophosphorous pesticides (Hewlet-Packard 5890 Series II plus / nitrogen phosphorous detector). GC conditions are shown in Table 1. Collected samples were analyzed for 29 organophosphorous pesticides. The chromatogram of pesticides analyzed in this study are shown in Fig. 2.

## 2.3 QA/QC

To determine accuracy of this experimental method, recovery yield of 16 OPs was tested. Organophosphorous pesticides mixture (OPP-8140JM, ChemService) was spiked into artificial seawater. Recovery of organophosphorous pesticides was evaluated by five replicate samples using our experimental method. Recovery of DDVP, mevinphos, diazinon, parathion-methyl, disulfoton and azinphos-methyl were respectively 88.68, 78.36, 98.36, 104.77, 91.92 and 86.31%. Detection limit was measured to be 1.80 ng l<sup>-1</sup> for IBP, 0.58 ng l<sup>-1</sup> for DDVP (IUPAC name: 2,2-dichlorovinyl dimethyl phosphate) and 1.06 ng l<sup>-1</sup> for chlorpyrifos (IUPAC name: *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl)).

## 3. RESULTS AND DISCUSSION

### 3.1 Organophosphorous pesticides in the surface waters

During the sampling period 28 organophosphorous pesticides (OPs) could be detected in the surface waters of Asan Bay. The most frequently and abundantly detected OPs were IBP. DDVP, diazinon, ethoprophos and methidathion were observed at relatively high concentration above 100 ng l<sup>-1</sup> in almost every month. Malathion, mevinphos, phorate and chlorfenvinfos were also detected at relatively high concentrations. The maximum concentration and detection frequency of organophosphorous pesticides measured in this study are summarized in Table 2.

#### 3.1.1 IBP

IBP is commonly called as Kitazin P, Iprobenfos and its chemical name (IUPAC) is dipropan-2-yloxyphosphorylsulfanylmethylbenzene. IBP is widely used in Korea as Fungicide for agricultural use. During the study period, the most commonly found organophosphorous pesticides in Asan Bay was IBP. The concentrations of IBP in the surface waters ranged from N.D. to 6,343.7 ng l<sup>-1</sup> during the sampling period throughout the study area. The concentrations of IBP were relatively high in the surface

**Table 2.** Maximum concentrations and frequency of detection of organophosphorous pesticides measured in Asan Bay

Pesticides Common name	Chemical name (IUPAC)	Maximum concentration (ng l <sup>-1</sup> )	Frequency of detection (among 78 samples)
azinthos-methyl	9-(dimethoxyphosphinothioylsulfanylmethyl)-7,8,9-triazabicyclo[4.4.0]deca-1,3,5,7-tetraen-10-one	171.2	41
azinthos-ethyl	9-(diethoxyphosphinothioylsulfanylmethyl)-7,8,9-triazabicyclo[4.4.0]deca-1,3,5,7-tetraen-10-one	177.0	29
carbophenothion	(4-chlorophenyl)sulfanylmethylsulfanyl-diethoxy-sulfanylidene-phosphorane	27.0	13
chlorfenvinphos	2,4-dichloro-1-(2-chloro-1-diethoxyphosphoryloxy-ethenyl)-benzene	163.5	21
DDVP	1,1-dichloro-2-dimethoxyphosphoryloxy-ethene	1265.4	56
demeton	diethoxy-(2-ethylsulfanylethoxy)-sulfanylidene-phosphoran; 1-(ethoxy-(2-ethylsulfanylethylsulfanyl)phosphoryl)oxyethane	-	0
diazinon	diethoxy-(6-methyl-2-propan-2-yl-pyrimidin-4-yl)oxy-sulfanylidene-phosphorane	209.5	43
disulfoton	diethoxy-(2-ethylsulfanylethylsulfanyl)-sulfanylidene-phosphorane	50	14
dyfonate	ethoxy-ethyl-phenylsulfanyl-sulfanylidene-phosphorane	20.2	16
EPN	ethoxy-(4-nitrophenoxy)-phenyl-sulfanylidene-phosphorane	7.3	14
ethion	diethoxyphosphinothioylsulfanylmethylsulfanyl-diethoxy-sulfanylidene-phosphorane	24.1	11
ethoprophos	1-(ethoxy-propylsulfanyl-phosphoryl)sulfanylpropane	124.4	52
fenamiphos	N-[ethoxy-(3-methyl-4-methylsulfanyl-phenoxy)-phosphoryl]propan-2-amine	5.3	3
fenthion	dimethoxy-(3-methyl-4-methylsulfanyl-phenoxy)-sulfanylidene-phosphorane	19.8	3
fenitrothion	dimethoxy-(3-methyl-4-nitro-phenoxy)-sulfanylidene-phosphorane	54.8	22
fensulfothion	diethoxy-(4-methylsulfanylphenoxy)-sulfanylidene-phosphorane	7.2	6
IBP	dipropan-2-yloxyphosphorylsulfanylmethylbenzene	6343.7	68
malathion	diethyl 2-dimethoxyphosphinothioylsulfanylbutanedioate	371.4	7
merphos	tris(butylsulfanyl)phosphane	56.7	34
methidathion	3-(dimethoxyphosphinothioylsulfanylmethyl)-5-methoxy-1,3,4-thiadiazol-2-one	84.6	29
mevinphos	methyl 3-dimethoxyphosphoryloxybut-2-enoate	157.3	14
phorate	diethoxy-(ethylsulfanylmethylsulfanyl)-sulfanylidene-phosphorane	142.6	17
parathion	diethoxy-(4-nitrophenoxy)-sulfanylidene-phosphorane	23.6	9
parathion-methyl	dimethoxy-(4-nitrophenoxy)-sulfanylidene-phosphorane	29.5	26
pirimiphos-methyl	4-dimethoxyphosphinothioxyloxy-N,N-diethyl-6-methyl-pyrimidin-2-amine	12.9	3
stirofos	1,2,4-trichloro-5-(2-chloro-1-dimethoxyphosphoryloxy-ethenyl)-benzene	52.2	18
sulfotep	diethoxyphosphinothioxyloxy-diethoxy-sulfanylidene-phosphorane	14.5	6
tokuthion	(2,4-dichlorophenoxy)-ethoxy-propylsulfanyl-sulfanylidene-phosphorane	157.2	11
trichloronate	ethoxy-ethyl-sulfanylidene-(2,4,5-trichlorophenoxy)-phosphorane	8.0	12

waters of Asan Lake and Sapkyo Lake receiving rural runoff from the watershed. In August 2004, the highest IBP concentration was found at Munbangli (6,343.7 ng l<sup>-1</sup>) located in the watershed of Lake Sapkyo (Fig. 3). IBP concentrations in the seawater of Metdolpo, Eumsum and Bugok at the same period were 3,300.0, 2,083.5 and 1,029.2 ng l<sup>-1</sup> respectively. IBP concentrations in the surface waters showed a gradual decrease from the mouth of Asan Bay to the outer bay (Table 3). As Shown in Fig. 4, IBP concentrations in Asan Bay decreased with increasing salinity in July 2004. This result implies the progressive dilution of this pesticide in the coastal environment. Yu *et al.* [2001] reported that IBP content and salinity showed a negative relationship in the estuary of Danghang Bay, Korea.

The concentrations of IBP in the surface waters showed a distinct seasonal variation. IBP concentrations in the surface

waters of Sapkyo were 1,127.9 and 2,122.6 ng l<sup>-1</sup> respectively in July 2004 and August 2005. The reason for this high concentration of IBP in summer could be the extensive use of this pesticide between July and September for rice blast disease. Not many pesticides are used throughout the year. The pattern of pesticide use follows the seasonal change. The main reasons for the pesticide use are pest control, extermination vermin and preventing mold on crops. In Korea, the rainy season between June and September is the time of appearance of noxious insects and mold. Similarly, many OPs appear more frequently in summer than in winter due to the intensive application of these pesticides in summer months. Inter-annual variability of IBP concentration could also be observed since the usage of the fungicide becomes extensive when the rainy season lasts longer. Yu *et al.* [2001] reported that IBP was the most commonly found organo-

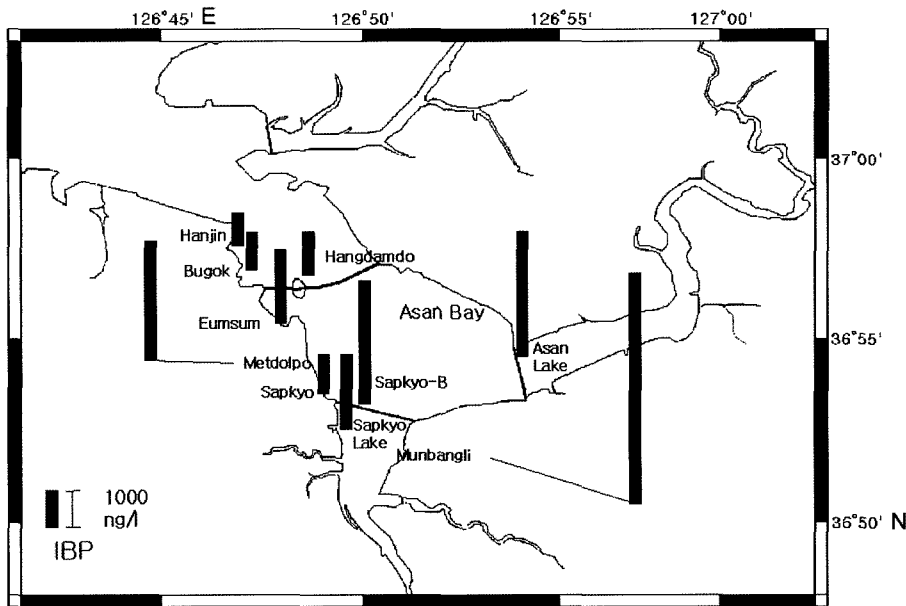


Fig. 3. Distribution of IBP in the surface waters of Asan Bay in August 2004.

Table 3. The concentrations of IBP in the surface waters of Asan Bay (ng l<sup>-1</sup>)

site	Sapkyo Lake	Sapkyo	Metdoltpo	Eumsum	Bugok	Hanjin	Asan	Asan Lake	Munbangli	
2004	June	226.3	340.1	579.0	249.2	255.9	270.8	445.9	1380.7	-
	July	1484.5	1127.9	915.3	648.4	611.6	516.5	2105.2	1469.8	2698.2
	August	2097.7	1058.6	3300.9	2033.5	1029.2	916.5	-	3448.6	6343.7
	October	2000.9	1431.9	1108.1	N.D.	1018.4	N.D.	N.D.	1346.3	-
2005	January	942.0	75.8	37.6	2671.9	79.2	N.D.	125.3	2671.8	-
	February	543.8	1327.9	N.D.	N.D.	12.2	N.D.	-	-	-
	March	1142.4	3.5	266.9	248.7	46.5	-	-	1023.7	-
	May	-	7.7	-	-	-	-	-	33.0	-
	June	104.5	732.8	21.1	634.9	35.6	13.6	1179.8	1400.8	-
	July	N.D.	-	200.1	-	-	-	-	2885.3	-
	August	2816.9	2122.6	1167.1	783.7	672.0	630.7	1555.0	1555.0	-

N.D.: Not detected -: Not analyzed

phosphorous pesticides in Kunsan area (101.0~528.0 ng l<sup>-1</sup>) in August, 1997. IBP found in Asan Bay would not have deleterious effects on the habitats of Asan Bay. The concentrations of IBP were well below 8,000 ng l<sup>-1</sup> which is a limit set by Japanese seawater quality guideline for the aquacultural purpose (<http://www.mhlw.go.jp>).

3.1.2 DDVP

DDVP (1,1-dichloro-2-dimethoxyphosphoryloxy-ethene) is known to degrade primarily by hydrolysis, with a half-life of approximately 4 days in lakes and rivers (U.S. Public Health Service [1991]). The concentrations of DDVP were much higher in the freshwater reservoir than in seawater. DDVP concentrations in the surface waters of Asan Lake and Asan were 250.7 ng l<sup>-1</sup> and 28.8 ng l<sup>-1</sup> respectively in June 2005 (Fig. 5). The concentrations of DDVP in the surface waters generally decreased from the

inner bay to the outer bay. During the sampling period, relatively high concentration of DDVP was observed in July 2005 (N.D.~1265.4 ng l<sup>-1</sup>). Generally maximum DDVP concentrations and frequency of detections follow pesticide application to fields in the summer. DDVP is commonly used from June to August for an apple field and from July to September for a peach field. Yu *et al.* [2001] reported that in August, 1997, DDVP concentration ranged from 4.6 to 26.5 ng l<sup>-1</sup> in Kunsan from 3.5 to 20.7 ng l<sup>-1</sup> in Danghang Bay, Korea.

3.1.3 Diazinon

The concentration of diazinon in seawater is regulated by the seawater quality standard of Korea because of its acute toxicity. Diazinon is highly toxic to fish. In rainbow trout, LC<sub>50</sub> of diazinon is reported to be 2.6~3.2 mg l<sup>-1</sup> (Kidd *et al.* [1991]). Diazinon concentration varied considerably both spatially and

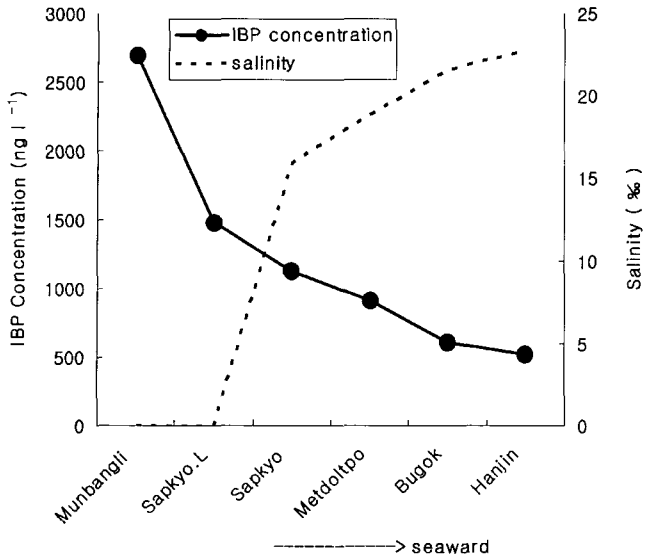


Fig. 4. IBP concentrations in the surface waters of Asan Bay in July 2004.

temporally (Fig. 6). The concentrations of diazinon were about an order of magnitude higher in freshwater than in seawater. The concentration of diazinon generally decreased with increasing distance from the mouth of Asan Bay. Relatively high concentrations of diazinon occurred from June to October. The concentrations of diazinon at Sapkyo peaked on October 2004 at a level of 209.5 ng l<sup>-1</sup>. Elevated concentrations of diazinon were also observed in June 2004 at Sapkyo (36.1 ng l<sup>-1</sup>) and at Eumsum (28.6 ng l<sup>-1</sup>). This result was inferred from the fact that diazinon is not only used for rice paddy field but also for other various dry field agricultures. Diazinon is also detected

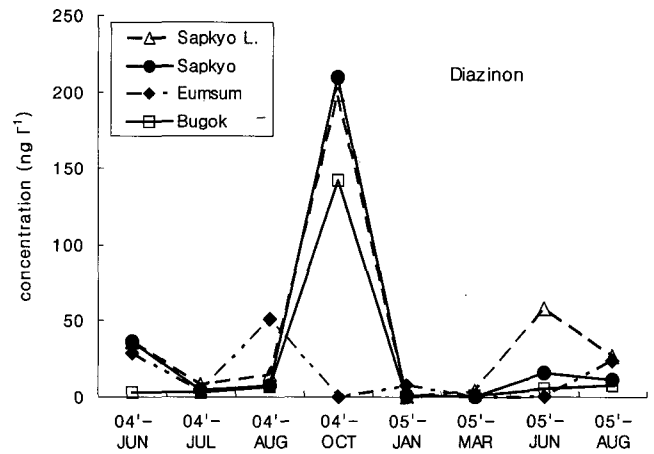


Fig. 6. Seasonal variation of diazinon in the surface waters of Asan Bay.

frequently at relatively high concentration in Asan Lake. Measured concentrations of diazinon in seawater sample did not exceed the seawater quality standard of Korea (20,000 ng l<sup>-1</sup>). According to the Japanese water quality standard for the aquacultural purpose diazinon should be lower than 100 ng l<sup>-1</sup> for seawater and 40 ng l<sup>-1</sup> for freshwater. Yu *et al.* [2001] reported that diazinon concentrations were the highest at a station located in the lower estuary (8.1 ng l<sup>-1</sup>) in Dangang Bay in 1997. Diazinon and methidathion were found to be the important organophosphorus pesticides at San Joaquin river in California (Domagalski *et al.* [1997]; Albanis *et al.* [1998]).

3.1.4 Malathion

Malathion is highly toxic to aquatic invertebrates and to the aquatic stages of amphibians (Johnson *et al.* [1980]; U.S. Pub-

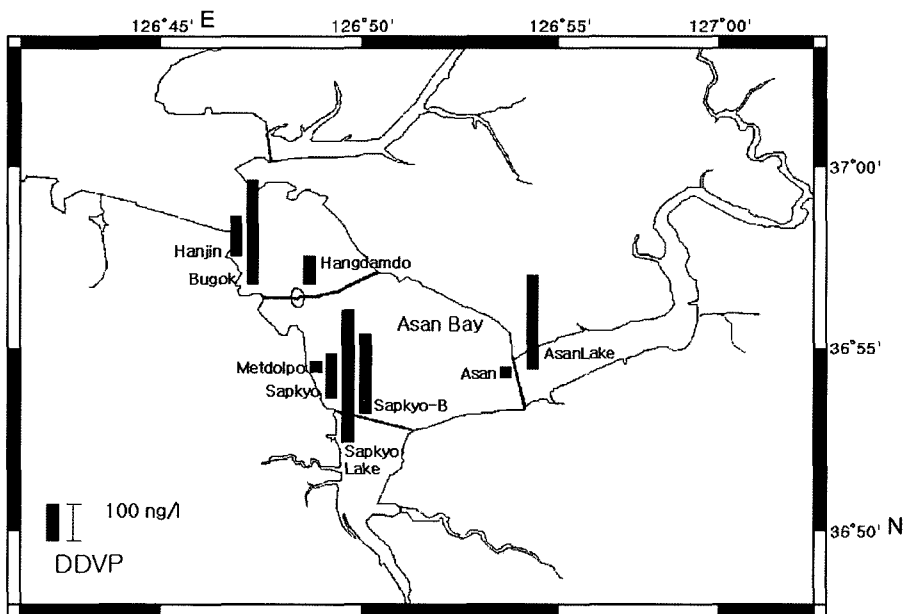


Fig. 5. Distribution of DDVP in the surface waters of Asan Bay in June 2005.

lic Health Service [1995]). Because of high acute toxicity the concentration of malathion in seawater is regulated by the seawater quality standard of Korea. During the sampling period, concentration of malathion varied from 0.5 mg l<sup>-1</sup> to 371.4 mg l<sup>-1</sup>. Relatively high concentrations were observed in May 2005 (N.D.~371.4 ng l<sup>-1</sup>) and in July 2005 (N.D.~127.1 ng l<sup>-1</sup>). Malathion concentrations in Asan Bay were far below 250,000 ng l<sup>-1</sup> which is a limit set by the seawater quality standard of Korea.

### 3.1.5 Parathion

Parathion and parathion methyl were detected at 9 and 26 samples respectively out of 78 samples analyzed in the surface waters of Asan Bay. The concentrations of parathion ranged from N.D. to 23.6 ng l<sup>-1</sup> which were well below 60,000 ng l<sup>-1</sup> which is a limit set by the seawater quality standard of Korea.

### 3.1.6 Ethoprophos

Ethoprophos is effective against soil-dwelling insects and has a wide spectrum of uses with applications against many underground vegetable pests. In Asan Bay relatively high concentrations of ethoprophos were detected at sites receiving input from the freshwater reservoir. Ethoprophos is used for dry field farming rather than for rice paddy field. The highest concentration of ethoprophos was detected in June 2005 at Sapkyo (124.4 ng l<sup>-1</sup>). The next highest concentration of ethoprophos was measured in August 2005 at Sapkyo (72.3 ng l<sup>-1</sup>).

### 3.1.7 Methidathion

In the surface waters of Asan Bay, methidathion could be detected at concentrations ranging 4~334 ng l<sup>-1</sup> during the sampling period. The concentrations of methidathion was relatively high in June 2004 (20.9~84.6 ng l<sup>-1</sup>) and in August 2005 (21.4~74.6 ng l<sup>-1</sup>). In subsequent samples the concentrations of methidathion were considerably lower. Methidathion and diazinon were found to be the highest concentrations of organophosphorus pesticides detected at San Joaquin river in California (Domagalski *et al.* [1997]; Albanis *et al.* [1998]). The compound is very highly toxic to aquatic organisms (both vertebrate and invertebrate); the reported LC<sub>50</sub> values of this compound are 10 to 14 µg l<sup>-1</sup> in rainbow trout and 2 to 9 µg l<sup>-1</sup> in bluegill sunfish (Kidd *et al.* [1991]; Mayer *et al.* [1986]).

### 3.1.8 Other organophosphorous pesticides

During the study period, the concentration range of phorate was from N.D. to 142.6 ng l<sup>-1</sup>. Relatively high concentrations of phorate in the surface water was detected from June to August 2004. Phorate was not detected from October to February since this pesticide is commonly used for potato and is practically not used after harvesting season. Phorate is highly toxic to fish. Reported 96-hour LC<sub>50</sub> values ranged from 2 to 13 µg l<sup>-1</sup> in

cutthroat trout, bluegill sunfish and largemouth bass (Johnson [1980]). In Asan Bay, the measured concentration of tokuthion ranged from N.D. to 157.2 ng l<sup>-1</sup>. It was found at 11 samples out of 78 samples analyzed. The highest concentration of tokuthion was measured in June 2005 at Eumsum (157.2 ng l<sup>-1</sup>). During the sampling period, merphos was frequently detected at concentrations ranging from N.D. to 56.7 ng l<sup>-1</sup>. Carbophenothion was detected frequently at relatively low concentration. And the highest concentration was measured in March 2005 (N.D.~27.0 ng l<sup>-1</sup>). Carbophenothion is highly toxic to fish, crustaceans, marine organisms and amphibians (Wagenet [1985]). Dyfonate was detected almost every month ranging from N.D. to 20.2 ng l<sup>-1</sup>. The concentrations of mevinphos which is essentially used for dry field farming ranged N.D. to 157.3 ng l<sup>-1</sup> with maximum occurring in March 2005.

Disulfoton is especially effective against sucking insects. The observed concentration range of disulfoton was from N.D. to 50.0 ng l<sup>-1</sup>. Generally, the relatively high concentration of disulfoton was found from June to August which is the application period of this pesticide. Fenitrothion concentrations ranged from N.D. to 54.8 ng l<sup>-1</sup> and the highest concentration was measured in July 2005 (N.D.~54.8 ng l<sup>-1</sup>). Azinphos-methyl, azinphos-ethyl and merphos could be measured in the surface waters of Asan Bay with a detection frequency of 41, 29 and 34 respectively out of 78 samples. Along with the above pesticides, detectable amounts of trichloronate, ethion and EPN were observed during the sampling period. Fenthion, fenamiphos, pirimifos-methyl, sulfotep and fensulfothion were rarely measured in Asan Bay. Their detection frequency was below 10 out of 78 samples analyzed.

## 3.2 Organophosphorous pesticides adsorbed onto suspended particle

Equilibrium partitioning models (DeToro *et al.* [1991]) and field studies (Domagalski and Kuivila [1993]) indicate that some pesticides may be concentrated on suspended sediments. Adsorption of pesticides onto the particle phase is an essential process driving the fate and mobility of pesticides in the environment. Since particles are a primary source of nutrition for filter feeding organisms, pesticides associated with particles may have different environmental effects in estuaries than dissolved pesticides. Because suspended particles may carry appreciable amounts of associated pesticides, sediment transport may be an important mechanism for introduction of pesticides into the Asan Bay.

Suspended particle samples collected concurrently with the water samples were analyzed for pesticide content. In comparison to dissolved pesticides in water sample, relatively few pesti-



cides adsorbed pesticides were found in the samples. DDVP (max=200.63 ng l<sup>-1</sup>), ethoprophos (max=72.0 ng l<sup>-1</sup>), phorate (max=74.8 ng l<sup>-1</sup>), stirofos (max=20.8 ng l<sup>-1</sup>), diazinon (max=40.9 ng l<sup>-1</sup>), IBP (max=642.2 ng l<sup>-1</sup>), EPN (max=33.12 ng l<sup>-1</sup>), azinphos-methyl (max=79.58 ng l<sup>-1</sup>) and fenithrothion (max=2.98 ng l<sup>-1</sup>) were detected in suspended particles of Asan Bay during this study. Detectable amounts of malathion, trichlorate, chlorfenvinfos, methidathion, merphos, fenamiphos, ethion, carbofenothion, azinphos-methyl were observed in suspended particles collected in Asan Bay during the sampling period. It was shown that DDVP, phorate, stirofos, EPN azinphos-methyl and IBP appeared to have high adsorption capacity onto suspended particles.

The degree of adsorption depends on both the pesticides and particle properties. The pesticides-soil adsorption coefficient ( $K_d$ -soil) is a basic parameter used by pesticides scientist and regulatory agencies worldwide to describe the environmental fate and behavior of pesticides (Chen *et al.* [2004]). We calculated the pesticide-particle adsorption coefficient,  $K_d$ -particle (l kg<sup>-1</sup>), of OPs measured at Sapkyo Lake in June, 2004 (Fig. 7) and at Eumsum in July, 2004 (Fig. 8). Calculated  $K_d$ -particle values in this study are the ratio of pesticides adsorbed onto suspended particle to dissolved pesticides in water samples. Calculated  $K_d$ -particle values of each pesticide were compared with the previously reported pesticides-soil adsorption coefficient ( $K_d$ -soil). As shown in Fig. 7 and 8, our observed  $K_d$ -particle values were related to the reported pesticides-soil adsorption coefficient ( $K_d$ -soil). This suggests that organophosphorous pesticides in Asan Bay are in

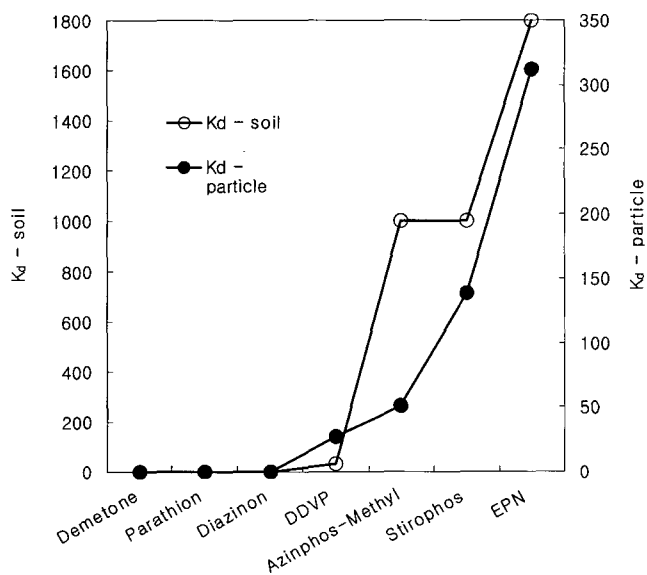


Fig. 7. Calculated  $K_d$ -particle and reported  $K_d$ -soil (June 2004, Sapkyo Lake).

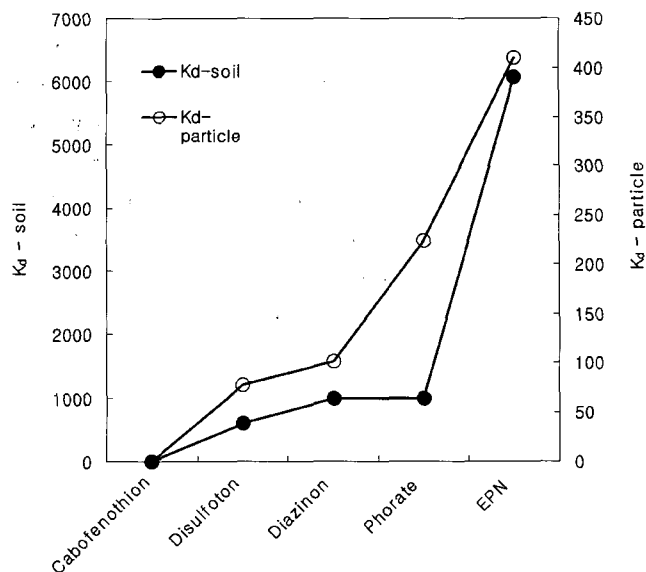


Fig. 8. Calculated  $K_d$ -particle and reported  $K_d$ -soil (June 2004, Eumsum).

equilibrium between water and particles. Pesticides are not usually in equilibrium between water and particles in the estuarine environment. Bergamaschi *et al.* [1999] found poor relation between the concentrations of pesticides adsorbed onto particles and  $K_{oc}$  of pesticides in San Francisco Bay. He suggested that observed particle-associated pesticide concentrations may reflect disequilibrium between sedimentary and aqueous phases resulting from long equilibration times at locations where pesticides were applied, and relatively short transit times for re-equilibration to occur. Particle associated pesticide concentration are generally have been influenced by amount of pesticides applied in drainage basin. The mechanism governing sorption interactions are complex and are not always simply related to the concentration of particles (Cooke *et al.* [2004]).

#### 4. CONCLUSION

In this study, distribution characteristics of organophosphorous pesticides from June 2004 to August 2005 in the surface waters and the suspended particles collected in Asan Bay, Korea employing a GC/NPD analytical technique. During this study, detected organophosphorous compounds were; DDVP, mevinphos, ethoprophos, phorate, sulfotep, dyfonate, disulfoton, diazinon, IBP, parathion-methyl, fenitrothion, pirimifos-methyl, malathion, parathion, trichloronate, fenthion, chlorfenvinfos, methidathion, tokuthion, merphos, fenamifos, stirofos, ethion, fensulfothion, carbofenothion, EPN, azinphos-methyl and azinphos-ethyl. Conclusions of this study are as follows.

1. During the sampling period, the most commonly detected organophosphorus pesticides in the surface waters were IBP (max=6343.7 ng l<sup>-1</sup>). DDVP, diazinon, ethoprophos and methidathion were also observed at relatively high concentrations. The observed seasonal variation of organophosphorous pesticides can be explained by their seasonal application pattern. The concentrations of diazinon, malathion and parathion in the surface waters of Asan Bay was well below a limit set by the seawater quality standard of Korea.

2. The concentration of organophosphorous pesticides generally decreased with increasing distance from the mouth of Asan Bay. This result implies progressive dilution of the pesticides in the marine environment.

3. Organophosphorous pesticides adsorbed onto suspended particles were also studied. DDVP, phorate, stirofos, EPN, azinphosmethyl and IBP had higher adsorption capacity onto suspended particles than other pesticides. Calculated pesticide-particle adsorption coefficient ( $K_d$ -particle) for samples collected in Asan Bay were closely related to the reported pesticides-soil adsorption coefficient ( $K_d$ -soil).

4. To understand the behavior and fate of organophosphorous pesticides, mechanisms of its transport, including adsorption capacity onto different types of sediment particles, should be carefully studied in the future. More studies on bio-availability and toxicity are needed to predict adverse impacts of organophosphorous pesticides on marine ecosystems.

## ACKNOWLEDGEMENTS

This work was supported by Korea Ocean Research and Development Institute through the research project entitled; Land-Ocean Interactions in the Coastal Zone - Land-based sources of input in Asan Bay, Korea (PE96000 and PE97102).

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2006년 4월 10일 원고접수

2006년 8월 16일 수정본 채택