

GC-MS Analysis of Organophosphorus Pesticide Residue in Seawater From the Kwangyang Bay, Korea

Mi-Ok Park and Jeom-Sook Park

Department of Oceanography, Pukyong National University, Busan 608-737, Korea
(Manuscript received 3 November, 2005; accepted 27 March, 2006)

Sea water samples collected in August, 1994 from 20 stations in the Kwangyang Bay were analyzed by gas chromatography/mass spectrometry-selected ion monitoring (GC/MS-SIM) to investigate persistence and distribution pattern of four organophosphorus pesticides (DDVP, Diazinon, IBP, EDDP). Except for IBP, the contamination by DDVP, Diazinon, and EDDP in marine aquatic environment in Korea has not been reported previously. In this study, however, all these four pesticides were detected in all stations (except DDVP) and their concentrations were in ng/L level. The concentrations ranged from detection limit to 15.3ng/L for DDVP, 1.8-27.7ng/L for Diazinon, 7.3-63.5ng/L for IBP, and 22.2-1100.1ng/L for EDDP. It is noteworthy that the measured concentrations of IBP and EDDP in this study would be much lower than usual, since the use of IBP and EDDP was less than 50% of average annual consumption due to unusually dry and hot weather condition in the summer of 1994. It was very surprising to find that the highest concentrations of organophosphorus pesticides were observed at stations near Daesa Streamlet instead of Seomjin River, which has more point source of the pesticides. This result suggests that the small river discharge during heavy rain period in summer can give harmful effect on marine biota (both wild and aqua-cultured) with its organophosphorus pesticide residue, despite of their short residence time in aquatic environment. In order to protect the marine life properly from acute toxicity of the organophosphorus pesticides, it needs to be emphasized that monitoring the level of agricultural pesticides in river run-off should be done during active consumption period rather at regular intervals.

Key Words : GC/MS-SIM, Seawater, Organophosphorus pesticides, DDVP, Diazinon, IBP, EDDP

1. Introduction

Pesticides, which are used to protect agricultural crops from insects and diseases, remain in soil and are eventually washed off by rain. The residue of pesticides in river run-off is known to give harmful effects on non-target aquatic biota. Scott *et al.*¹⁾ reported that mortality of 71 species of fish among 127 species killed at the coast of South Carolina was related with pesticide residues. Among the pesticides, the organophosphorus pesticides are known to be destroyed in a relatively short time scale by light and bacteria compared to organochlorine pesticides or carbamates^{2,3)}. Especially Eichelberger *et al.*⁴⁾ reported that methyl parathion, malathion, fenthion are de-

graded up to 90% in 2 weeks. However, in spite of short residence time of the organophosphorus pesticides in aquatic environment, their acute toxicity to marine biota can be lethal even at low concentration of LD₅₀⁵⁾. For example, Schimmel *et al.*⁶⁾ reported that LD₅₀ of chlorpyrifos for *Mysidopsis bahia* as 0.035 µg/L. National institute of environmental research has been conducting bimonthly monitoring of water quality for most river estuaries in Korea since 1970. However, there has been no report regarding the presence of organophosphorus pesticides by National institute of environmental research up until now. As a result, the potential harmful effect of organophosphorus pesticides in marine environment was neglected. Partly, it is because of low sensitivity in analytical method (GC) and the selection of sampling timing. The test is routinely performed bimonthly, without consideration of intensive use of pesticides in short periods.

In general, chromatographic methods⁷⁻⁹⁾ are used

Corresponding Author : Mi-Ok Park, Department of Oceanography, Pukyong National University, Busan 608-737, Korea
Phone: +82-51-620-6217
E-mail: mopark@pknu.ac.kr

for qualitative and quantitative analysis of pesticide residues in crops and foods. The presence and distribution of organophosphorus pesticides in marine environments were reported by Schimmel et al.⁶⁾, Hinckley and Bidleman¹⁰⁾, Kucklick and Bidleman¹¹⁾. In Korea, except a report by Jeon and Yang¹²⁾ about the residues of IBP at Suncheon Bay, there was no report about presence and distribution of organophosphorus pesticides in marine environment of Korea.

In Korea, most aquaculture beds, distributed at the south and west coastal region, are closely located near the agricultural land like rice paddy. For this reason, it is highly probable that pesticide residues can be introduced to marine environment before complete degradation. During summer time, the use of pesticides (such as IBP and EDDP) for rice paddy is increased to prevent the rice blast disease especially after heavy rain. The combination of these two factors (the short travel time and intensive use of these pesticides near the coastal region) imposes potential hazardous impacts on marine biota with their acute toxicity. This study use the sensitive and accurate analytical method of GC/MS-SIM to measure the level of concentrations of organophosphorus pesticides in seawater at Kwangyang Bay area, including the mouth of Seomjin River estuary, which is relatively less polluted river in Korean peninsula.

2. Materials and Methods

2.1. Materials

List of the organophosphorus pesticides is shown in Table 1. According to the guideline by FAO (Food and Agriculture Organization) and WHO, DDVP and Diazinon are categorized as highly toxic to fishes and banned the use of the pesticides near river, a fish farm

Table 1. List of standard organophosphorus pesticides

pesticides ^a	uses ^b	application range ^c
DDVP	insecticide	cotton plant, vegetables, fruit tree, flowering plants
Diazinon	insecticide	rice(rice-stem borer), fruit tree, flowering plants
IBP	fungicide	rice(rice-plant fever)
EDDP	fungicide	rice(rice-plant fever)

^a common name,

^{b,c} refer to Agrochemical Year Book(1994)

in Korea¹³⁾. Standards of DDVP, Diazinon, IBP and EDDP were obtained from WAKO Pure Chemical Industries, LTD. (JAPAN). Purities of the standards were 99.3%, 99.8%, 98.8% and 99.7% respectively. Solvent used for the standards was methanol (Fisher Scientific, USA) and internal standard was profenofos (purity 99.9%), which was purchased from Chemical service (USA). The solvent used for profenofos was dichloromethane (Fisher Scientific, USA).

2.2. Study Area

Kwangyang bay, which located at the central southern coast of Korea is geographically semi-closed shape and surrounded by small industrial cities, such as Kwangyang, Hadong, Yeochun and Namhae. The distance along the east-west and north-south is about 27km and 15km¹⁴⁾, respectively and the bay area is about 200 km². In this study area, the northern part is mostly shallow in depth less than 5 m and far east part along the Namahe Island is relatively deeper (above 20 m) with fast current. At the western part of the bay, POSCO - huge steel factory facilities are located near Myodo. The sampling was mostly made on the eastern side of the bay to find out the persistence and distribution of organophosphorus pesticides residue in sea water. As fresh water sources, there are two major rivers (Seomjin river and Sueo river) and several minor streamlets in Namhae Island (including Daesa, Kalwha and Chonpo streamlet). Agricultural activities scattered along the rivers introduce the pesticides through the run-off to marine environments. Rice paddies are scattered along the Seomjin river, Sueo river and Daesa streamlet and citron trees are growing at the western coast of Namhae Island. Fig. 1 shows the locations of sampling stations in the Kwangyang bay, including stations near the mouth of Seomjin river.

2.3. Sampling

Sea water samples were collected by pre-washed brown bottles from the surface water below 0.5 m depth. In order to prevent the adsorption on the surface of collecting vessel, 1.5 L of sea waters are collected in 2.5L brown glass bottles¹⁵⁾ and transferred to the lab as frozen in dry ice immediately. All the samples were analyzed in a week. Temperatures of the surface water were measured by thermometer up to 0.1°C. Salinity and pH were measured by Salinometer (model E-2, Tsurumi Seiki Co.) and pH meter (model SP-7) respectively.

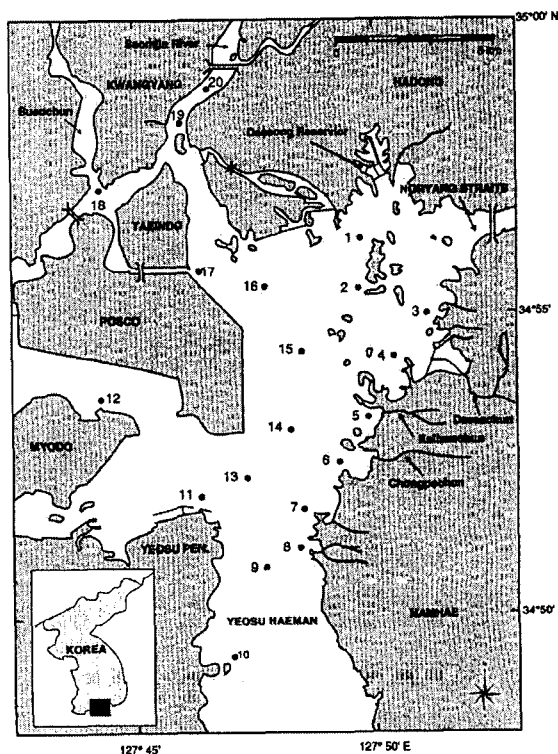


Fig. 1. Map showing sampling stations in the Kwangyang Bay.

2.4. Extraction and concentration procedure

Since the concentrations of pesticides residue are very low, all seawater samples are concentrated after extraction procedure before the GC-MS analysis. 1 L of sea water samples filtered through GF (glass microfiber filter, 0.45 μm) and 60mL of dichloromethane (CH₂Cl₂) are combined in a separating funnel and shaken for 300 times by hand. After sitting for 15-30 min at room temperature, the mixture is separated by sea water and organic solvent layers. The supernatant layer of organic phase was passed through the column (20cm×1cm) filled with 1-2cm of sodium sulfate anhydrate (Na₂SO₄) and collected in 300mL of round flask. The remained sea water phase was extracted twice with 60mL of dichloromethane. For concentrating the pesticide residue in extracts, the organic solvent was evaporated in rotary evaporator in 40-45 °C water bath. The concentrated 3-5mL of extracts was transferred to 10mL test tube and completely evaporate the organic solvent under the nitrogen gas flow. The internal standard, profenofos was added and dichloromethane was also added to make final volume as 1mL before injection to GC for analysis.

2.5. GC/MS analysis

2μL from 1mL concentrated extracts of sea water was injected to GC injection port for GC/MS analysis. Instruments used for analysis of organophosphorus pesticides were Fisons 8000 gas-chromatograph and Fisons Trio-1000 mass spectrometer. The analysis conditions for GC/MS are shown in Table 2. The chromatogram of four standards and internal standards are obtained (Fig. 3) and mass spectra for identification are shown in Fig. 4. Retention times for standards and relative retention time to internal standards are listed in Table 3. This analysis used

Table 2. GC/MS condition used for analysis of organophosphorus pesticides residue

GC condition	
column :	SPB-5(30m×0.25mm i.d., 0.25 μm)
carrier gas :	He
flow rate of carrier gas :	0.9 ml/min
GC injection port temperature :	280 °C
split mode :	splitless mode
GC temperature programming	
	80 °C was kept for 3 min at the start
	Then it increases 20 °C / min and
	finally 300 °C was kept for 5 min
Mass condition	
transport line temperature :	280 °C
ion source temperature :	200 °C
ionization mode :	EI-SIM(Selected Ion Monitoring)
electron energy of ion source :	70 eV

Table 3. Retention time and characteristic fragment of standard organophosphorus pesticides

pesticides	R.T ^a (R.R.T) ^b	characteristic fragments(m/z)									
		R. A ^c (%)									
DDVP	6.78(0.53)	47	79	109*	145	185	187	220	222**		
		10	35	100	10	30	10	5	3		
Diazinon	10.68(0.83)	93	97	137	152	153	179*	199	304**		
		40	30	80	60	35	100	45	25		
IBP	10.96(0.86)	65	91*	123	204	246	288**				
		20	100	40	85	20	10				
profenofos ^d	12.81(1.00)	95	125	139	206	208*	337	339	372**		
		90	45	95	78	100	94	85	45		
EDDP	13.72(1.07)	65	77	109*	173	186	201	310*			
		35	10	100	95	20	30	35			

^a R.T = retention time
^b R.R.T = relative retentiontime
^c R.A = relative abundance of the peak to the base peak
^d internal standard pesticide: refer to Hong *et al.*(1993)
* the base peak(peak of highest intensity)
** molecular weight

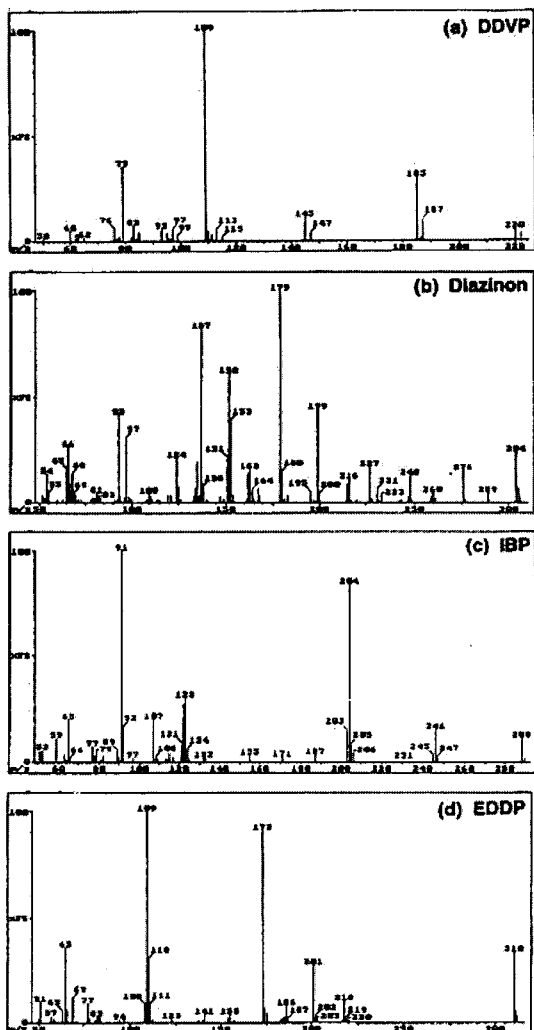


Fig. 4. Mass Spectra of standard organophosphorus pesticides.

relative retention times to internal standards and peak area ratio for the selected ions of standards and unknown samples (Table 3 & 4). A peak of which relative retention time matches with the corresponding standard in less than ± 0.05 min is assigned to the same kind of pesticide in the samples. The concentrations of each pesticide were calculated by following equation (Eq. 1).

$$A = B \times (C \times D) \times (1/E) \dots \dots \dots (\text{Eq. 1})$$

- A: the concentration of pesticide in sea water (ng/L)
- B: mass from the calibration curve (ng)
- C: final volume for analysis (mL)

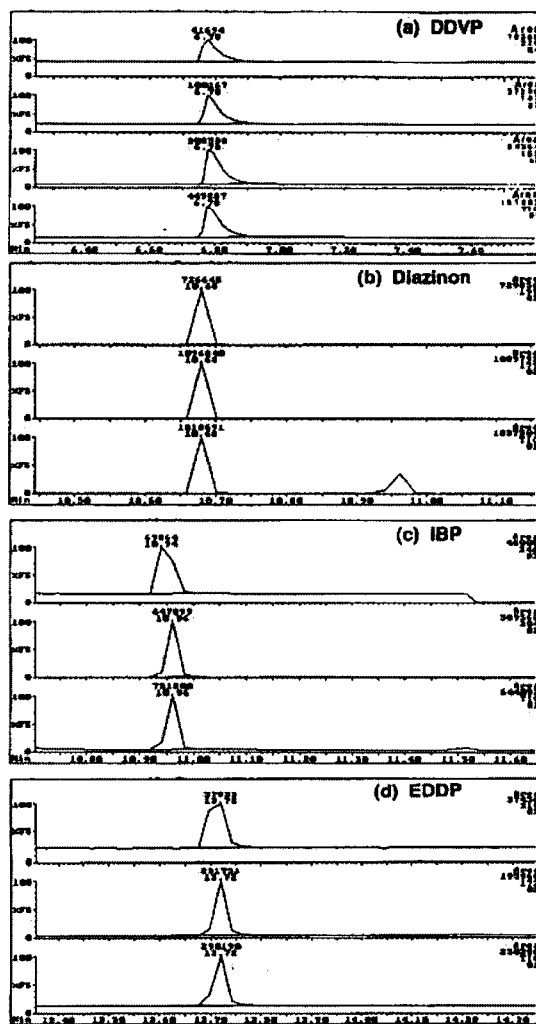


Fig. 5. Mass chromatogram of selected ion of standard organophosphorus pesticides.

- D: injection volume of C solution (μL)
- E: total volume of sample (L)

In this study, B was calculated as concentration ($\mu\text{g/L}$) instead of mass (g). Fig. 6 shows the calibration curves for concentrations vs STD/ISTD peak ratio and primary equation by least square method with r

Table 4. Selected fragment and peak area ratio of selected fragment

pesticides	selected fragment	peak are ratio
DDVP	185 : 187 : 220	3.08 : 1 : 0.42
Diazinon	179 : 199	1.15 : 1
IBP	204 : 246	9.27 : 1
EDDP	173 : 310	4.00 : 1

Table 5. Reproducibility test of organophosphorus pesticides

pesticides	STD ^a /ISTD ^b mean	SD ^c	CV ^d
DDVP	0.1019	0.0044	4.318
Diazinon	0.2089	0.0072	3.452
IBP	0.2235	0.0174	7.785
EDDP	0.0894	0.0050	5.539

^aSTD=standard solution

^bISTD=internal standard solution

^cSD=standard deviation

^dCV=coefficient of variation

=percentage of relative standard deviation ...refer to Horwitz(1982)

(correlation coefficient).

3. Results and Discussions

3.1. Distribution pattern of organophosphorus pesticides in sea water

The organophosphorus pesticides in seawater were measured in February and August in 1994. Total amount pesticides used for agriculture is closely related with the weather conditions in every year. Especially in Korea, long rain spell between June and September causes various diseases and vermin. Along the river the rice paddies are located to receive the water for irrigation. Summer (August) is the time for farmers to use of IBP and EDDP, in order to prevent the rice blast diseases, especially after heavy rain. Since the rice crop is harvested after fall, the use of pesticides in winter is very rare. So the concentrations of IBP and EDDP in winter (February) can be used minimum background level which is persistent throughout the year. The measurements of the organophosphorus pesticides residues on the same 5 stations on both summer and winter were made to compare the maximum and minimum concentrations of the pes-

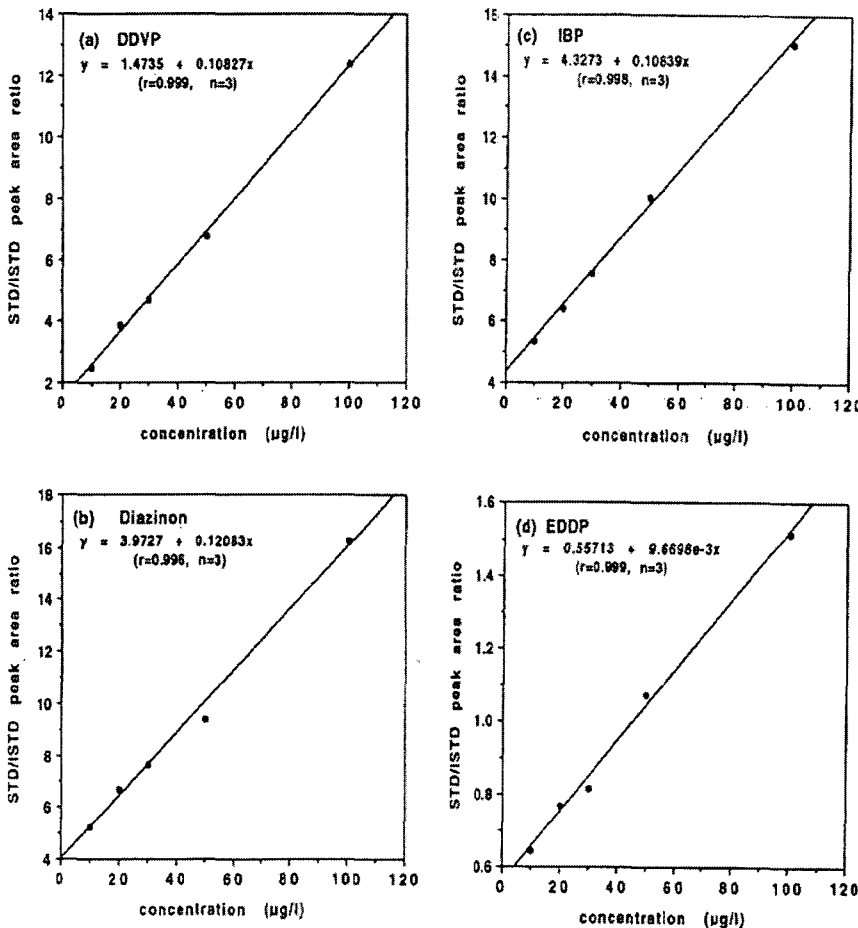


Fig. 6. Calibration curve used for quantitative analysis of organophosphorus pesticides residue.

Table 6. Range and mean concentration(ng/l) of organophosphorus pesticides residue in surface seawate (August, 1994)

	organophosphorus pesticides residue			
	DDVP	Diazinon	IBP	EDDP
range	*~15.3	1.8~27.7	7.3~65.5	22.2~1100.1
mean ^a	3.5	12.2	25.2	263.2

^abelow detection limit

^bvalues below detection limit were excluded from calculation of mean value.

ticides in sea water. The stations were selected to found a point source and distributions of the pesticides in Kwangyang Bay, which is typical bay in Korea.

3.1.1. August

All DDVP, Diazinon, IBP and EDDP were detected at all stations (except 4 stations for DDVP) in the study area during August. The level of the pesticides in seawater was ng/L level. The range and mean concentrations of the organophosphorus pesticides residue in the surface seawater are shown in Table 6. DDVP, Diazinon and IBP was detected in ng/L level, on the other hand, EDDP was relatively found as higher concentrations, from tens to maximum upto 1100ng/L. The distribution pattern of the organophosphorus pesticides residues in Kwangyang bay are shown in Fig. 7~Fig. 10. The concentrations of the pesticides are relatively higher at the region near the river mouth or irrigation reservoirs. Among the detected pesticides, DDVP showed the lowest residue concentrations in the surface seawater in Kwangyang bay. The low concentrations of DDVP can be attributed to the volatile property of this insecticide for flowering plant and fruit trees. Diazinon, which is also an insecticide for fruit tree and flowering plants as well as rice (rice-stem borer) was detected as the second lowest concentrations with mean value of 12.2ng/L. The range of Diazinon was from 1.8ng/L to 27.7ng/L.

EDDP and IBP, both as fungicides against rice blast diseases were detected at much higher concentrations than DDVP and Diazinon with their mean concentrations as 263.2ng/L and 25.2ng/L respectively. Especially the concentrations of EDDP residue were higher than any other pesticides analyzed. And the distribution pattern of EDDP showed a unique tongue

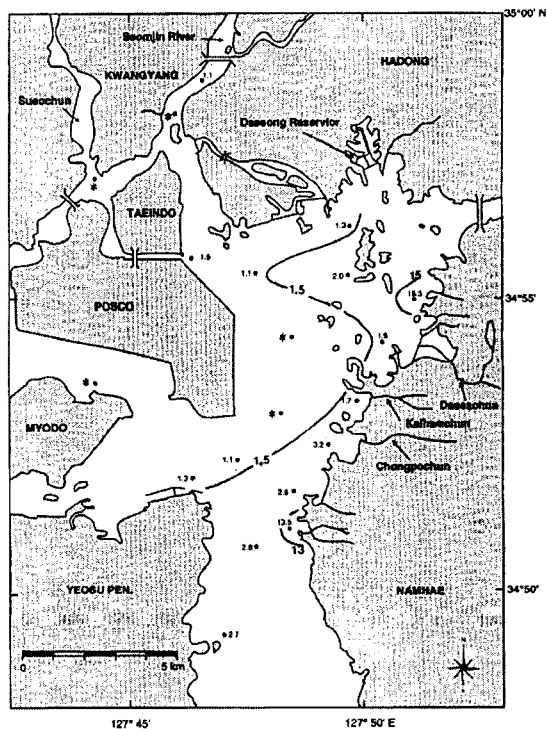


Fig. 7. Distribution of DDVP in surface seawate(unit: ng/l) (August, 1994) (* below detection limit).

shape from Daesa Reservoir. EDDP residue in marine environments has not been reported before, but in this study the concentrations of EDDP in seawater were detected in the range of 22.2 - 1100.1ng/L at all the stations. The highest concentrations were measured at St. 4 near Daesa Reservoir. Compared to concentrations at St. 19 and St. 20, which are located at the mouth of Seomjin river and St. 18 which is located at the mouth of Sueo river, the concentrations of EDDP at St. 4 is at least 20 times higher. The size of river and amount of water discharge from the Seomjin and Sueo river is much greater than Daesa reservoir, which is used for agricultural irrigation. The reason for the exceptionally high concentration of EDDP at st. 4, 13, 14 along the current direction could be attributed to the short length of Daesa river and accumulation of pesticide residue in the Daesa reservoir. The short travel time for pesticide from the agricultural soil before it is introduced into the sea water would not allow the pesticide to decompose in aquatic environment by natural decomposition by light or microorganisms or sink to bottom by adsorption onto the suspended particles in the river. The gate of Daesa

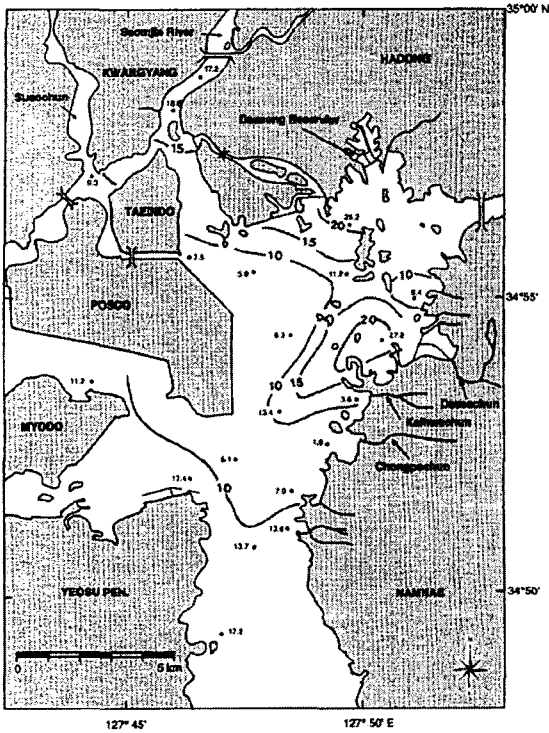


Fig. 8. Distribution of Diazinon in surface seawater (unit: ng/l) (August, 1994).

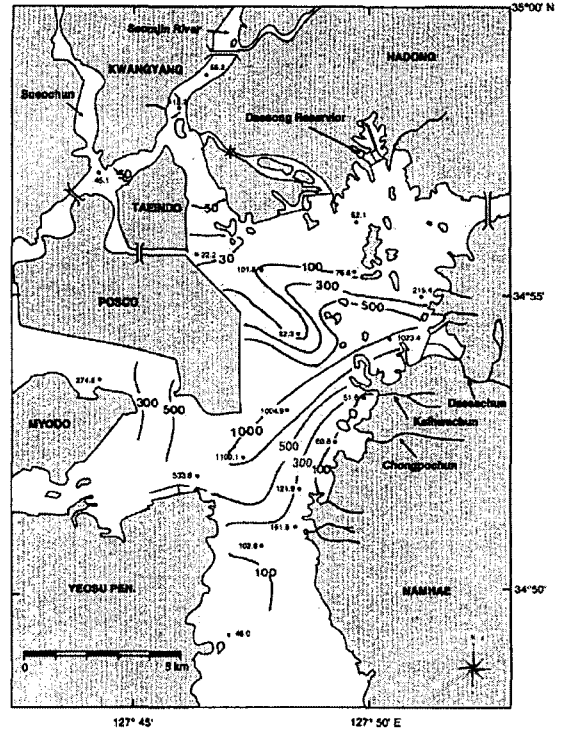


Fig. 10. Distribution of EDDP in surface seawater(unit: ng/l) (August, 1994).

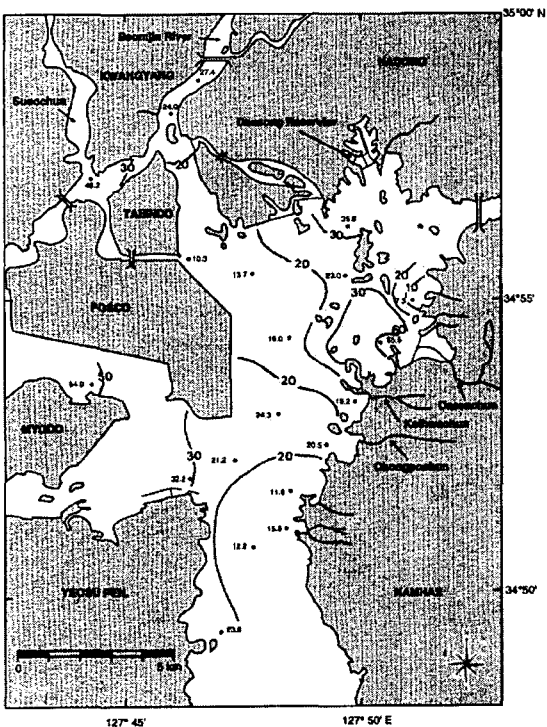


Fig. 9. Distribution of IBP in surface seawater(unit: ug/l) (August, 1994).

reservoir is opened in the event of flood. The pattern of high concentration of EDDP in August in Kwangyang bay shows the influence of discharge of water in the Daesa reservoir as an opening gate event and the current movement. Thus the adverse influence of organophosphorus pesticides with acute toxicity is limited only to the region, which the pesticides were used and arrived in spatially and temporally^{5,12}. The lower COD (3.03 mg/L) and lower pH (7.80, acidic) at st 4 compared to the adjacent stations (COD= 3.53-5.22, pH= 8.05-8.21) showed that very active decomposition of particulate organic matters was in progress at st. 4. Not only close to source of accumulated pesticide in reservoir, but also the chemical environment (low pH enhanced the preservation of organophosphate in seawater upto 10 times longer in half-lives.) provided the conditions to keep high concentration of pesticide at st. 4.

IBP is a fungicide which is widely used in rice farming during June to September with EDDP. The measured concentrations of IBP were lower than EDDP, and higher than DDVP and Diazinon. The mean concentration of IBP was 25.3ng/L and its

range was 7.3~65.5ng/L. Although the maximum concentration of IBP was found at st. 4, three different stations of high IBP concentration ($> 30\text{ng/L}$) in the Kwangyang bay showed that there are 3 different point sources of IBP from land through the Seomjin river, Suyo river, Daesa streamlet.

Diazinon was detected at all stations and the concentrations were higher near the point source, such as Seomjin river, Daesa and Daesong reservoir than rest of the area. Again the level of Diazinon was higher at seawater compared to brackish water which has a short travel time from the source to aquatic environment. The concentration was from 1.8~27.7ng/L and mean value was 12.2ng/L. The highest concentration was measured at st. 4 near Daesa streamlet. And similar concentration was measured at st. 1 (25.2ng/L) near Daesong reservoir. Although Diazinon is used as insecticide for rice, mostly it is used as insecticide for soil and the time for active use are widely spread out and to the various plants, too. Since adsorption coefficient of Diazinon to soil (1000g/mL) is higher than its solubility (60mg/L), the net transport of Diazinon to river and/or marine aquatic environment is relatively small¹⁷⁾. The presence of Diazinon in riverine water were reported as 4~10ng/L at the mouth of Mississippi river and 20ng/L from the river water samples from Illinois river¹⁷⁾.

DDVP was measured at 15 stations from 20 stations with the lowest concentration among the organophosphorus pesticides analyzed. The highest concentration, 15.3ng/L was measured at St. 3 and at St. 8 comparable concentration, 13.5ng/L was measured. Except these two stations near small streamlet, at most stations the concentrations of DDVP were much lower than average concentration, 3.5ng/L or under the detection limit (0.95ng/L). St. 3 and St. 8, which showed higher level of DDVP in seawater are located in Namhae Island. DDVP is used for mostly to dry field farming, especially for fruit trees. Extensively in Namhae Island, Citron trees are growing as one of the special products even in winter season. The possible main source of DDVP in seawater seems to be the use of this pesticide for Citron tree farming in Namhae Island. The lowest concentrations of DDVP in seawater can be attributed to the volatility of DDVP, which leaves little amounts on soil, to be washed off to river and ocean. Except IBP, the pres-

ence of DDVP, Diazinon, EDDP in marine environment of Korea is reported for the first time in this study.

3.1.2. Correlation between salinity and concentration of organophosphorus pesticides residues

In Fig. 11, salinity of each station and concentration of organophosphorus pesticides residue in seawater are plotted to find a relationship between these two factors. Since Seomjin River is the most dominant source for fresh water discharge to the Kwangyang bay, concentrations of the pesticides residue were expected to be decrease as it gets far from the mouth of Seomjin river by mixing and degradation along the path to ocean. So the gradients of concentration of the organophosphorus pesticide residue to salinity Fig. 11. Correlation between and concentration of were expected to be present along the Seomjin river to the ocean. However, the distribution of organophosphorus residue in Fig. 7-10, and Fig. 11, did not reflect any direct relationship between salinity and concentrations of the pesticides. As shown in Fig. 11, there was no relationship between salinity and concentrations of the pesticides, in general.

Among 20 stations, st. 16~st. 20 are the stations which are located in mixing zone with salinity 22~29 ‰. In this 5 stations, Diazinon and IBP showed negative correlation with salinity and DDVP showed a moderately positive correlation. EDDP didn't correlates with salinity in this region. Especially IBP correlates well with salinity with r (correlation coefficient), 0.963 and DDVP, Diazinon, and EDDP correlates poorly with coefficients, 0.700, 0.434 and 0.053 respectively. The good correlation of IBP with salinity implies the source of the IBP to this mixing zone is Seomjin river and Suyo river. Although the concentration of DDVP were very low and concentrations at two stations out of 5 stations were under the detection limit, the positive correlation with salinity seems to related with adsorption at the mouth of river with low salinity and higher suspended matter in the water and desorption from the surface of sediments at higher salinity seawater¹⁸⁾. At stations with salinity 29-31‰, the concentrations of the organophosphorus pesticide residue were varied from maximum to below the mean values. This showed that organophosphorus pesticide residues in the seawater were varied ex-

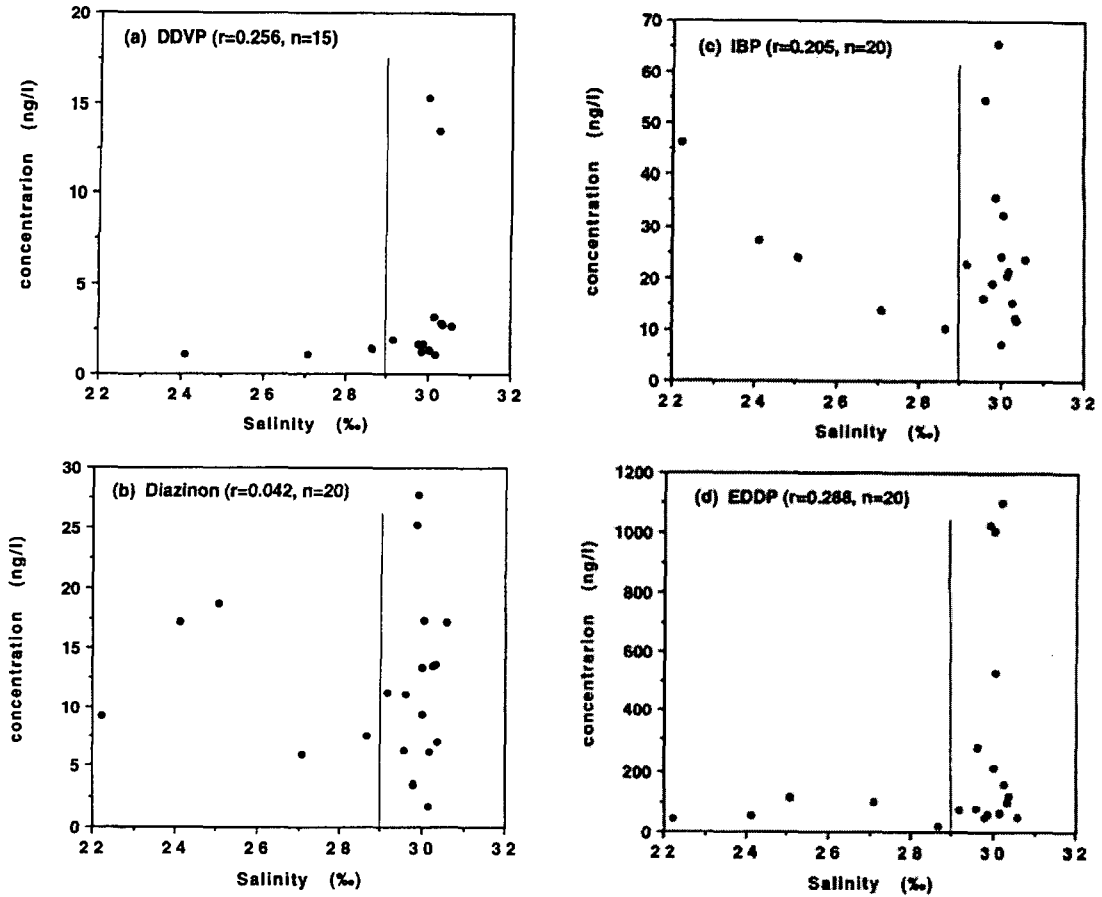


Fig. 11. Correlation between and concentration of organophosphorus pesticides residue.

tensively in their concentrations. Interestingly, at st. 4, all pesticides except DDVP showed the maximum or near maximum concentrations, which implies that there is very close regional source to the ocean. The point source for high level of pesticide residues in sea water suggested the Daesa streamlet was the important in the Kwangyang bay during summer of 1994.

3.2. Comparison of level of organophosphate pesticide residue between August and February

In order to find out the difference in the level of pesticide residue between summer(active consumption season) and winter (inactive consumption season), the concentrations of 4 pesticides residue in sea water were measured on 5 selected stations (Table 7). All 4 pesticides showed the decrease in the concentration level in various amounts from summer to winter. Seasonal change in the level of concentrations of pesticide residue was clearly observed. The pesticide residue in seawater in August was decreased to 77%

Table 7. Concentrations(ng/l) of organophosphorus pesticides residue in surface seawater (February and August, 1994)

St.	DDVP		Diazinon		IBP		EDDP	
	Feb.	Aug.	Feb.	Aug.	Feb.	Aug.	Feb.	Aug.
1	*	1.3	0.6	25.2	3.7	35.8	*	62.1
5	1.3	1.7	*	3.6	*	19.2	*	51.6
8	6.4	13.5	*	13.6	2.9	15.3	*	161.8
11	1.0	1.3	4.4	17.4	8.3	32.2	*	533.8
17	3.1	1.5	1.2	7.5	27.1	10.3	3.7	22.2
mean ^a	3.0	3.9	2.1	13.5	10.5	22.6	3.7	10.63

*below detection limit

^avalues below detection limit were excluded from calculation of mean value.

(DDVP), 46%(IBP), 16%(Diazinon), 3.5%(EDDP) in February. The decrease in amount depending on active and inactive season was greatest for EDDP and Diazinon. Especially the concentration of EDDP was lower than detection limit at 4 out of 5 stations tested

Appendix 5. Consumptions of organophosphorus pesticides in Namhae, Hadong province branch office at 1993 and 1994

pesticides	Namhae province branch office		Hadong province branch office	
	'93 con.	'94 con. (R.C,%) ^b	'93 con.	'94 con. (R.C,%) ^b
IBP (GR) ^c	2,504	862 (42.0)		1,470
IBP (GR) ^d	17,900	8,355 (46.7)	14,519	6,134 (42.2)
EDDP (EC)	11,412	6,256 (54.8)	13,579	4,857 (35.8)

^a formulation quantity

^b relative consumptions to '93 consumption

^c granule (3kg/a paper bag)

^d emulsifiable concentrate (500ml/a bottle)

in February.

However, the level of IBP in winter was not negligible in spite of its active consumption was made only during summer season. About 50% of IBP residue in seawater in summer was still present in seawater in winter. The location of high concentration of IBP (27.1ng/L) was measured in st. 17 near Taein Island. The measured high concentration of IBP on st.17 in winter seems to be resulted from desorption of IBP from the surface of particulate matter in sediment, not from river run-off. The pH values (8.11) at st. 17 was lower than surrounding stations near Taein Island (st. 14-16, 8.12-8.27) and lower COD (3.99 mg/L) than st. 14-16 (5.14-5.77). These values showed that there is an active degradation of organic particles at st. 17. Except st. 17, the concentration of other stations decreased to 11% of IBP in summer. The high concentration of IBP at st. 17 implies the preserved pesticide residue on the particulate sediment can supply the non-degraded pesticide residue into seawater by desorption process. Meanwhile it is not surprising that concentration of DDVP was not decreased as much as IBP, EDDP, since DDVP is known to be used in winter season for citron farming at Namhae Island. For DDVP and IBP, the differences in concentration of pesticides were relatively smaller than for Diazinon and EDDP. And EDDP showed the greatest change from summer to winter.

4. Conclusion

The four organophosphorus pesticides, DDVP, Diazinon, IBP and EDDP in seawater were analyzed by GC-MS-SIM and detected from all 20 stations in

the Kwangyang bay except DDVP in August, 1994. The correlation between the concentrations of pesticide residue and salinity showed that the main source of the pesticide residue in seawater was Daesa streamlet in the study area. And at mixing zone, Seomjin reiver or Sueo river was main sources for IBP. The short distance of Daesa reservoir to ocean contributed to introduction of non-degraded pesticide to the seawater. The measured concentrations of pesticide residues in seawater were from ND to 1100 ng/L in August, 1994. The seasonal change in the concentration level of pesticide residues was clearly observed and it was the most prominent for EDDP (96% reduction in winter). And the residues of DDVP and IBP in seawater were detected in non-negligible level even in winter. This result suggested that the marine biota can be affected by high concentration (> 1µg/L) of the toxic pesticide residue from the adjacent rice paddy, without remaining any detectable amount of the pesticide residue in seawater. Thus it is desirable to monitor the organophosphorus pesticides during period of active consumption (summer) rather than regular intervals. The GC-MS-SIM provided the accurate and sensitive analysis for organophosphorus residue in seawater.

Acknowledgement

The authors are grateful to Dr. Hong and Dr.Chang at KBSI for providing valuable advices for the analysis.

References

- 1) Scott, G. I., D. S. Baughman, A. H. Trim and J. C. Dee, 1987, Lethal and sublethal effects of insecticides commonly found in nonpoint source agricultural runoff to estuarine fish and shellfish, In: Pollution physiology of estuarine organism edited by Vernberg, W.H., A. Calabreze, F. P. Thurberg, F. J. Vernberg, University of South Carolina Press, Columbia, SC, 251-274.
- 2) Manahan, S. E., 1979, Environmental chemistry (3rd ed.) Willard Grant Press, Boston, 168pp.
- 3) Drapper, W. H. and D. G. Crosby, 1984, Solar photooxidation of pesticides in dilute hydrogen peroxide, J. Agric. Food Chem., 32, 231-237.
- 4) Eichelberger, J. W. and J. J. Lichtenberg, 1971, Persistence of pesticides in river water, Environ. Sci.

- Technol., 2, 541-544.
- 5) Stoker, H. S. and S. L. Seager, 1976, Environmental chemistry air and water pollution (2nd edition), Foresman and Company, Dallas, 157-175.
 - 6) Schimmel, S. C., R. L. Garnas, J. M. Patrick and J. C. Moore, 1983, Acute toxicity, bioconcentration, and persistence of AC 222, 705, benthocarb, chlorpyrifos, fenvalerate, methyl parathion, and permethrin in the estuarine environment, J. Agric. Food Chem., 31, 104-113.
 - 7) Ault, J. A., C. M. Schofield, L. D. Johnson and R. H. Waltz, 1979, Automated gel permeation chromatographic preparation of vegetable, fruits, and crops for organophosphate residue determination utilizing flame photometric detection, J. Agric. Food Chem., 27, 825-828.
 - 8) Di Muccio, A., A. Ausili, L. Vergori, I. Camoni, R. Dommarco and L. Gambetti, 1990, Single-step multi-cartridge clean-up for organophosphate pesticide residue determination in vegetable oil extracts by gas chromatography, Analyst, 115, 1167-1169.
 - 9) Hong, J. K., Y. W. Eo, J. S. Rhee and T. J. Kim, 1993, Simultaneous analysis of 25 pesticides in crops using gas chromatography and their identification by gas chromatography-mass spectrometry, Journal of Chromatography, 639, 261-271.
 - 10) Hinckley, D. A. and T. F. Bidleman, 1989, Analysis pesticides in seawater after enrichment onto C₈ bonded-phase cartridges, Environ. Sci. Technol., 23, 995-1000.
 - 11) Kucklick, J. R. and T. F. Bidleman, 1994, Organic contaminants in Winyah Bay, South Carolina I : Pesticides and polycyclic aromatic hydrocarbons in subsurface and microlayer waters, Mar. Environ. Res., 37, 63-78.
 - 12) Jeon, D. S. and J. S. Yang, 1990, Determination of organophosphorus pesticides in Suncheon Bay, J. Oceano. Soc. Korea, 25, 21-25.
 - 13) Agrochemical Tech Organization, 1991, Guide to agrochemical use for '91, Junghwa press, 27-29.
 - 14) Park, K. S., 1987, Exchange of Sea water through entrance of Kwangyang Bay, Master thesis of National Fisheries University, p.2.
 - 15) Sharom, M. S. and K. R. Solomon, 1981, Adsorption and desorption of permethrin and other pesticides on glass and plastic materials used in bioassay procedures, Can. J. Fish. Aquat. Sci., 38, 199-204.
 - 16) Horwitz, W., 1982, Evaluation of analytical methods used for regulation of food and drugs, Anal. Chem., 54, 67A-76A.
 - 17) Perelra, W. E. and F. D. Hostettler, 1993, Nonpoint source contamination of the Mississippi River and its tributaries by herbicides, Environ. Sci. Technol., 27, 1542-1552.
 - 18) Duinker, J. C. and M. T. J. Hillebrand, 1979, Behavior of PCB, pentachlorobenzene, α -HCH, γ -HCH β -HCH, dieldrin, endrin and p,p'-DDD in the Rhine-Meuse estuary and adjacent coastal area, Neth. J. Sea. Res., 13, 256-281.