

Determination of Organophosphorous Pesticides in Suncheon Bay

DEOK SAN JEON AND JAE SAM YANG

Korea Ocean Research and Development Institute, Ansan P.O.Box 29, Seoul 425-600, Korea

순천만 유기인제제 농약의 측정

전득산 · 양재삼

한국해양연구소 극지연구부

Eleven water samples were analyzed for organophosphorous pesticides in Suncheon Bay with Gas Chromatography Mass Spectrometry. For the first time in Korea, Kitazin-P was found in marine environment and the concentrations ranged upto 2.2 mg/l. The regional and temporal variations of the pesticide were also studied.

Gas Chromatograph Mass Spectrometry(GC/MS)를 이용하여 순천만 유역내 유기인제제 농약의 분포특성을 규명하기 위해 해수, 담수 및 기수 시료가 분석되었다. 우리나라에서 최초로 유기인제제 농약 Kitazin-P가 해양환경에서 검출되었으며 그 농도는 최고 2.2mg/l를 기록하였다. 또한 순천만 유역내의 지역적인 변화와 시간적인 분포도 아울러 연구되었다.

INTRODUCTION

Global use of various kinds of synthesized pesticides have increased every year to protect crops from insects. In Korea, over 6 million tons (commercial wet weight) of pesticides are consumed every year (NACF, 1988). They are organophosphates, carbamates, organochlorines, organosulfurs, organoarsenics, and antibiotics. Although their productions are different year by year, organophosphates are one of the most commonly used pesticides in Korea (NACF, 1988). The organophosphates are generally more acutely toxic than any other alternative pesticides, and are also more soluble in water and as a consequence are less to accumulate in biological tissue. They are believed less resistant in bacterial decomposition and under sunlight, so their persistence in natural environment is believed much less than the organochlorines.

Therefore, organophosphates are generally a concern in more localized situations than are the organochlorines.

Like other organic pollutants, some residue of pesticides in farming land flow into rivers and lakes and eventually reach to coastal waters. On the way, these pesticides continue to decompose through bacterial activity and photooxidation. Nonetheless, recent studies (Strachan *et al.*, 1982) argued that the organophosphates sustain in natural aquatic environment much longer than believed before.

Recently, desk-top models of gas chromatography mass spectrometry (GC/MS) became available with significant developments of hardware and software, consequently GC/MS becomes an alternative to analyze organopollutants such as dioxines and PCBs from environmental samples. Recent models of GC/MS have extensive index libraries of reference

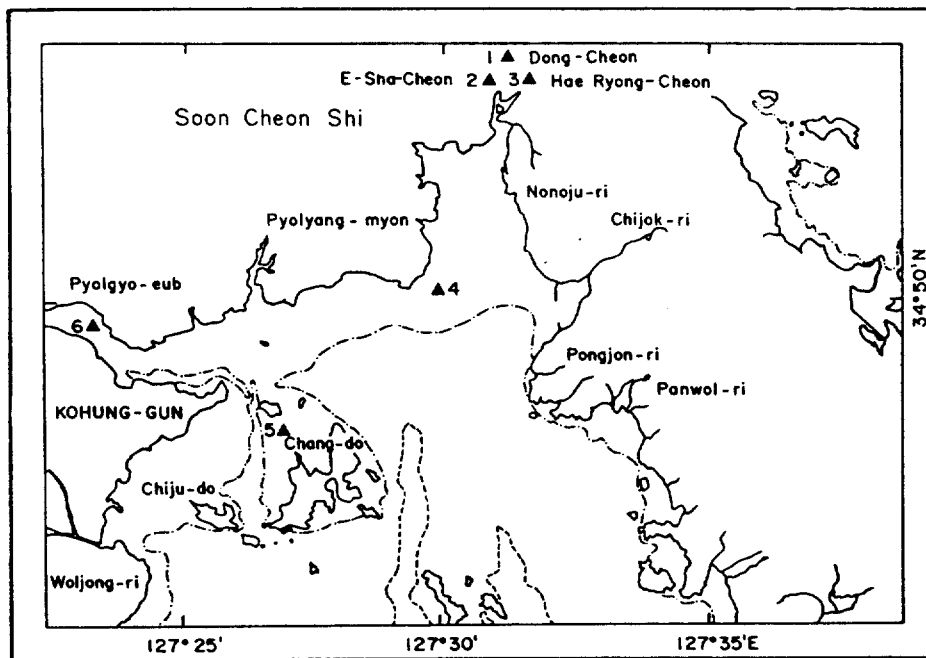


Fig. 1. Study area and sites.

organic compounds, which is helpful to identify the unknown organic compounds. The development of a software, "Selected Ion Monitoring Program", which detects just several typical ions of the spectrum from an organic compound, enable us to detect the concentrations of organic compounds down to the levels of pg/l .

Kitazin-P and Hinosan (commercial names) are two of the most commonly used organophosphates in the study area (NACF, 1989). Herein, water samples were analyzed to understand the regional and temporal distributions of these two pesticides in Suncheon Bay area.

MATERIALS AND METHODS

Sampling: Eleven water samples were obtained from 6 locations in Suncheon Bay area, South Coast of Korea (Fig. 1). Three sampling (St. 1-3) stations were for fresh water, one (St. 6) for brakish water and two (St. 4,5) for seawater. The samples were taken twice in late July and early August, 1989. The July samples were ob-

Table 1. General sequence for pesticide residue analysis

1. Sampling	3.6 l glass bottle
2. Sample preservation	-20 °C
3. Extraction	Organic phase: hexane and chloroform
4. Concentration	Kuderna-Danish Apparatus in water bath Nitrogen Gas Blowing
5. Determination	GC/MS

tained during heavy rainfall and the August samples were collected during clear days to figure out the temporal differences of the pesticide distribution. The samples were collected in 3.6 l glass bottles, frozen in iceboxes and transported to the laboratory and kept at -20°C. The analysis were carried out within 1 month after the sampling.

The analytical procedures are summarized in Table 1. The procedures are composed of 3 steps; extraction, concentration and determination steps.

Table 2. Operating conditions for the GC/MS

Mass Spectrometer-GC/MSD HP 5970 Selective Detector interfaced to an HP 5890 Gas Chromatograph configured to an HP 7946 computer linked with an HP 1000 Data System	
Ion Source: 250°C	Multiplier Voltage: 1800V
Transfer Line: 280°C	Entrance Lens: 60 mVv/AMU
Analyzer: 250°C	Repeller: 10.20V
Run Time: 21 min	Ion Focus: 0.0
Scan Start Time: 3 min	Axis Gain: 17
X-Ray: 56.0V	Axis Offset: 16
AMU Gain: 142	AMU Offset: 58

Gas Chromatography

Injector: 250°C, splitless mode

Column: 25m, 0.20 mm i.d., fused silica capillary column.
film thickness: 0.11 micron

Run Time 18.00, Equilibration Time 0.50 Purge Off Time 0.75

Level	Initial temp (°C)	Initial time (min.)	Rate (°C/min.)	Final temp(°C)	Final time(min.)	Total time(min.)
1	85	3.00	45.0	220	5.00	11.00
2			45.0	240	5.00	16.44

Extraction:

Five hundred ml of a water sample in a 100 ml separatory funnel was shaken vigorously with 7.5 ml of hexane (HPLC grade, Baker Chemical Co.) and 42.5 ml of chloroform (HPLC grade, Baker Chemical Co.) for 5 minutes. The separatory funnel was stood for 15 minutes and the organic phase was decanted to a 250 ml Kuderna-Danish Apparatus, filtering through a column filled with 10 g of anhydrous sodium sulfate (Analytical Grade, Wako Purechemical LTD.).

Concentration:

The Kuderna-Danish Apparatus was installed in a water bath at the temperature of 75-80°C. After 50 minutes, the volume of the extract became approximately 5 ml. The inside and joint parts of the Apparatus was rinsed with hexane from the top and eventually the extract became to the volume of 10 ml. The extract within the collector part of the Apparatus was separated from the Apparatus, then the extract was concentrated with gentle flow of nitrogen gas to the

volume of 0.5 ml.

Determination:

One ul from the concentrated extract was injected to the Gas Chromatography Mass Spectrometer (Hewlett Packard 5890A-5970). The operating condition is shown in Table 2. The pesticides were identified from their retention times and mass spectrums. The mass spectrums were compared with those in NBS library and from standards (IBP and EDDP standard solution, 0.5 ml, 98%, Wako Purechemical LTD.) of the pesticides. The standard solutions were diluted to become 0.2, 0.4 mg/l and 1.5 mg/l for each standards, from which calibration curves were obtained.

Precision and Calibration Curve:

Because Kitazin-P and Hinosan are commercial names of IBP and EDDP, respectively, an IBP standard (s-Benzyl di-iso-propyl Phosphothiolate) was used for the determination of Kitazin-P and an EDDP standards (O-Ethyl

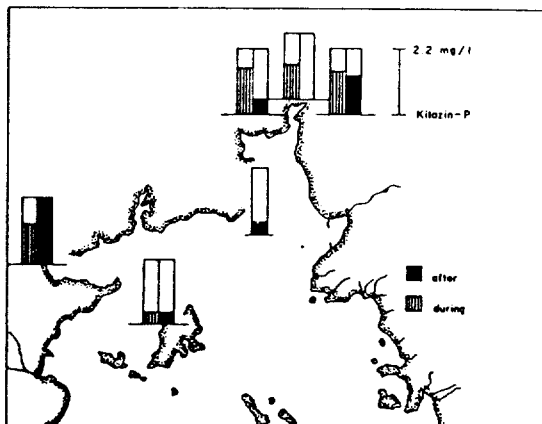


Fig. 2. Regional variations of Kitazin-P during and after heavy rainfall.

S, S-Diphenyl Dithiophosphate) for Hinosan. Relative standard deviation were 0.04 and 0.05% for IBP and EDDP, respectively, from 4 replicate analyses of 1 mg/l standard solutions.

Recovery Yields:

A half ml of 1 mg/l IBP and EDDP standards were spiked to 4 blank samples and were followed the analytical procedures. One μ l of the concentrated extract (5 ml) which was obtained from the procedures was injected to the GC/MS and its signal intensity was compared with that of original 1 mg/l standard solution. The recovery yields for IBP and EDDP standards were 95 and 94%, respectively, from 4 replicate analysis.

Detection Limit:

The detection limits of Kitazin-P and Hinosan were estimated as 0.2 and 0.4 mg/l, respectively, which were set twice the background noise.

Identification:

Retention times and mass spectrum of any peaks from the samples were compared with those of IBP and EDDP standards and NBS lib-

Table 3. Concentration of Kitazin-P in Suncheon Bay area

	25 Jul.	8 Aug.	(Unit: mg/l)
1	1.2	not detected	Dong Cheon (Fresh water)
2	1.6	0.5	E-Sha Cheon (Fresh water)
3	1.5	1.3	Hae Ryong Cheon (Fresh water)
4	not analyzed	0.4	Ma San Ri (Sea Water)
5	0.4	0.4	Chang Do (Sea Water)
6	1.3	2.2	Pyol Gyo Cheon (Brakish water)

rary, and confirmed the identification when they matched perfectly each other. The peaks of Kitazin-P and Hinosan were eluted at the retention times of 8.344 and 12.051 minutes, respectively at the condition of the GC/MS described in Table 2.

RESULTS AND DISCUSSION

An organophosphorous pesticide, Kitazin-P was identified from its mass spectrum and retention time. The concentrations of Kitazin-P ranged from not-detectable to 2.2 mg/l (Table 3), while Hinosan was not detected.

Generally, the concentrations of Kitazin-P were found above 0.4 mg/l except St. 1, Dongcheon in August, while the highest concentration of Kitazin-P was found from St. 6, Pyol Gyo Cheon in August (Table 3 and Fig. 2). The seawater samples from St. 4 and 5 showed consistantly 0.4 mg/l in both July and August, which probably due to the strong tidal mixing.

As mentioned in the experimental section, the sampling in July was executed during heavy rainfall and the sampling in August was obtained during clear days. In heavy rainfall, the concentrations in brakish and fresh water samples from St. 1,2,3 and 6 show similar concentration of Kitazin-P, while the concentrations became very diverse in clear days in August (Table 3 and Fig. 2). These findings are due to the dilution of the pesticide during the

heavy rainfall in the study area in July. On the contrary, in August, the consumption of the pesticides increased tremendously after the heavy rainfall (personal communication). This probably enhanced the marked local difference in the concentration of Kitazin-P. St. 6 is mostly agricultural area, while St. 1, 2, and 3 are a combination of municipal, industrial and agricultural areas. The heavy consumption of the pesticide in clear days after rainfall is very common situation in many agricultural areas, which probably contribute to the high concentration of the pesticide in St. 6, the agricultural area.

Organophosphorous pesticides are thought less resistant in bacterial decomposition and under sunlight than organochlorines, yet this work proved their existence in coastal environment. The concentrations were upto 2.2 mg/l, which was proved well over 96 hour LC50 for fish larvae with similar kind of organophosphorous pesticide (Shin, 1989). This finding indicates a potential contamination of organophosphates in coastal environment. Especially, since the residence times of the river water are short because of the short lengths of the rivers in Korea, the natural decomposition of the pesticides on the way to coastal waters is hard to expect. In addition, many coastal areas are occupied for both agriculture and aquaculture. Under this situation, a significant danger might be brought about to the quality of aquacultured seafoods from the south and west coasts of Korea where farming and aquaculture are carried out in adjacent area. The contamination

problems of drinking water due to the overuse of pesticides are frequently issued, still very seldomly same problem was raised in marine environment. A finding of detectable amount of an organophosphate which was believed the least persistent pesticide group in natural aquatic environment raises a necessity for a better understanding of the distributions of the pesticides used in coastal environment.

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