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Determination of pesticides in river water by gas chromatography–mass spectrometry–selected-ion monitoring

H. Kobayashi*, K. Ohyama, N. Tomiyama, Y. Jimbo, O. Matano and S. Goto

Chemistry Division, The Institute of Environmental Toxicology, 4321 Uchimoriya-cho, Mitsukaido-shi, Ibaraki 303 (Japan)

ABSTRACT

A highly sensitive and specific method for the determination of trace levels of pesticides in river water has been developed. The method is based on reversed-phase (C_{18}) solid phase extraction, followed by gas chromatography–mass spectrometry–selected-ion monitoring. Recoveries at the 0.5- or 2.5 $\mu\text{g/l}$ fortification level were between 79 and 98%. The detection limits were 0.05 $\mu\text{g/l}$ for chlornitrofen and 0.01 $\mu\text{g/l}$ for other pesticides.

INTRODUCTION

Environmental pollution caused by chemical compounds including pesticides has become a serious problem. Some pesticides are released into the environment during and/or after application to crops, and may be harmful to human beings and other species. Therefore, monitoring the residual levels of pesticides is very important for human health and environmental control.

Butachlor, pretilachlor, oxadiazon, chlornitrofen, simetryn and thiobencarb have been utilized as herbicides in rice paddy fields during the cultivation season. Determination of these pesticides has usually been carried out by extraction with solvent, clean-up on a chromatographic column and analysis by GC. Recently, solid-phase extraction (SPE) has been used to extract pesticides from water [1–7]. This extraction is a simple and rapid technique in comparison with liquid–liquid extraction. GC–MS–selected-ion monitoring (SIM) is suited for the quantification of $\mu\text{g/l}$ or ng/l levels of pesticides in environmental samples. We have applied these

techniques and developed a method for multiresidue analysis of these pesticides in river water.

EXPERIMENTAL

Chemicals

A Sep-Pak C_{18} cartridge (0.4 g) was obtained from Waters Assoc. Before use, the cartridge was rinsed with 5 ml of methanol, followed by 10 ml of distilled water for cleaning and conditioning. Butachlor and pretilachlor were purchased from Monsanto Japan and Ciba-Geigy Japan, respectively. Oxadiazon, chlornitrofen and simetryn were obtained from Wako. Thiobencarb was purchased from Kumiai. All standards were of >99% purity. All other reagents were of analytical reagent grade. Reagent-grade water was obtained from a Milli-Q water purification system (Millipore, Yonezawa, Japan).

Applications

Applications of butachlor, pretilachlor, oxadiazon, chlornitrofen, simetryn and thiobencarb were used for weed control in rice paddy fields. In 1987 and 1988, the amounts of active ingredient applied to the rice paddy fields during the farming period

* Corresponding author.

were 97–5612 kg in the Kokai River (K-River) watershed of Ibaraki Prefecture and 7.2–552.9 kg in the Saita River (S-River) watershed of Kagawa Prefecture. The K-River watershed comprises a flatland and an agricultural village. The S-River watershed is a mountain village, and at the middle of the watershed several small rivers join.

Sampling

Water was sampled from upper, middle and/or lower rivers at depths of 30–50 cm, at 3 to 7 day intervals during the farming periods. Samples of water of 3 l each were placed in dark containers, stored in a refrigerator at a temperature of 4°C until analysed, and analysed within 1 day of receipt. The distance from the upper river point to the lower river point in K-River is about 45 km. The length of S-River is about 30 km, and the middle river point is 15 km from the mouth of river.

Determination

A 1000-ml sample of river water was transferred into a 1000-ml separatory funnel connected to two Sep-Pak C₁₈ cartridges, which was rinsed with 5 ml of methanol, followed by 10 ml of water for cleaning and conditioning. Water samples were aspirated through the Sep-Pak C₁₈ cartridge. Trapped pesticides were eluted from the column with 10 ml of methanol after being rinsed with 3 ml of water-methanol (70:30, v/v), and the effluent was evaporated to dryness with a stream of nitrogen. The residue obtained was dissolved in 1 ml of acetone. 2-Aliquots (2- μ l) of the solution were injected into the GC-MS system.

Monitoring ions used were as follows: butachlor, m/z 176; pretilachlor, m/z 238; oxadiazon, m/z 175; chlornitrofen, m/z 319; simetryn, m/z 213; thiobencarb, m/z 257. The peak areas of these pesticides on the chromatogram were measured, and the concentration of each pesticide was determined from its calibration curve. Duplicate water samples were analysed.

Preparation of calibration curves

A 25-mg portion of each standard was dissolved in 500 ml of acetone to give a 50-ppm stock solution. Each 50-ppm stock solution was serially diluted to prepare the standard solutions of 0.01–1.0 ng for butachlor, pretilachlor, oxadiazon, simetryn

and thiobencarb, and 0.05–5.0 ng for chlornitrofen in acetone.

Gas chromatography-mass spectrometry

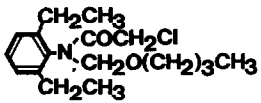
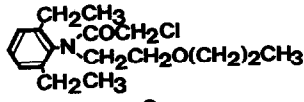
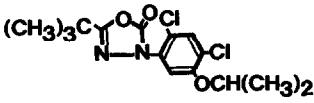
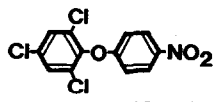
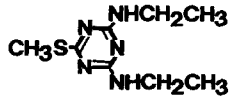

A Hewlett-Packard 5890 gas chromatograph was coupled to a JMS-DX 300 (JEOL) mass spectrometer. The mass spectrometer was equipped with a JMA-DA 5000 (JEOL) data system. The ionization voltage and the ion-source temperature were set at 70 eV and at 150°C, respectively. An SPB-1 fused-silica capillary column was used (15 m \times 0.53 mm I.D. and 0.5 μ m film thickness). Helium was used as carrier gas, and the flow-rate was 30 ml/min. The temperatures of the column, separator and injection port were maintained at 170°C, 250°C and 250°C, respectively.

RESULTS AND DISCUSSION

The structures of the pesticides monitored, their solubilities in water and their vapour pressures are given in Table I. The solubility in water of simetryn, and the vapour pressure of chlornitrofen and thiobencarb are higher than those of other pesticides. In electron impact (EI) mass spectra of the pesticides monitored, butachlor, pretilachlor, oxadiazon, chlornitrofen, simetryn and thiobencarb, molecular ions are present at m/z 311, 311, 344, 317, 213 and 257, respectively. Other structurally significant ions were found m/z 237, 176 and 160 for butachlor, m/z 238, 176 and 162 for pretilachlor, m/z 302, 258 and 175 for oxadiazon, m/z 287, 236 and 173 for chlornitrofen, m/z 170 and 155 for simetryn and m/z 125, 100 and 72 for thiobencarb. The low intensities of the molecular ions of butachlor and pretilachlor precluded their use as monitoring ions for the quantitation. In those cases, the most intense or characteristic ions for each compound were selected as the quantitation ions. These ions were m/z 176 for butachlor, m/z 238 for pretilachlor, m/z 175 for oxadiazon, m/z 319 [M + 2] for chlornitrofen, m/z 213 for simetryn m/z 257 for thiobencarb.

Solid-phase extraction reduced the analysis time and solvent consumption compared with traditional methods such as liquid-liquid extraction. No further clean-up was necessary before determination by GC-MS. The peak areas of the monitoring ions on the chromatograms were measured, and the concentration of each pesticide was determined from each calibration curve.

TABLE I
CHEMICAL STRUCTURE, SOLUBILITY AND VAPOR PRESSURE OF THE PESTICIDES EXAMINED

Pesticide	Structure	Solubility (mg/l of water)	Vapour pressure (mPa)
Butachlor		23	0.6
Pretilachlor		50	0.133
Oxadiazon		0.7	<0.133
Chlornitrofen		0.25	4.67 · 10 ⁴ (109°C)
Simetryn		450	0.095
Thiobencarb		30	2.93

The calibration curves were generated with a linear correlation coefficient of 0.999.

Selected-ion chromatograms of standard, control and recovery samples showing the ion trace for each selected mass are presented in Fig. 1. No significant interfering peaks were observed on the ion chromatograms derived from control sample extracts.

Recovery studies were performed at the 2.5- $\mu\text{g/l}$ level for chlornitrofen and 0.5 $\mu\text{g/l}$ for other pesticides. As summarized in Table II, the recoveries were between 79 and 98%. When chlornitrofen was eluted from the column with 5 ml of tetrahydrofuran after being eluted with 10 ml of methanol, the recovery was 85%. However, chlornitrofen was not quantitatively recovered. This phenomenon may be attributed to the adsorption of chlornitrofen in the C₁₈ cartridge. The detection limits in water were 0.05 $\mu\text{g/l}$ for chlornitrofen and 0.01 $\mu\text{g/l}$ for other pesticides when a 2- μl aliquot of the final solution (1 ml) obtained from a 1000-ml sample was injected into the GC-MS system.

This method was applied to the analysis of the

pesticides released into rivers after application to crops.

The stabilities of the six pesticides in water during transportation and storage were estimated by using distilled water. As shown in Table III, their recoveries were higher than 88% after 7 days at room temperature.

TABLE II
RECOVERY OF PESTICIDES ADDED TO DISTILLED WATER AND LIMIT OF DETECTION

Values are the mean of triplicate experiments.

Pesticide	Added ($\mu\text{g/l}$)	Recovery (%)	Limit of detection ($\mu\text{g/l}$)
Butachlor	0.5	95	0.01
Pretilachlor	0.5	96	0.01
Oxadiazon	0.5	98	0.01
chlornitrofen	2.5	79	0.05
Simetryn	0.5	90	0.01
Thiobencarb	0.5	89	0.01

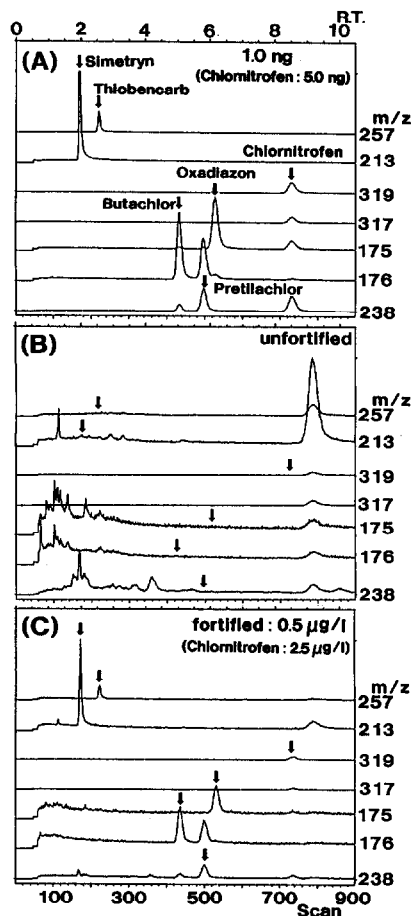


Fig. 1. Mass fragmentograms of (A) pesticides examined, (B) control sample and (C) recovery test sample.

The amounts of pesticides applied to the paddy fields are listed in Table IV as the amount of the active ingredients. All the pesticides except for thiobencarb were used in the similar amounts during 1987 and 1988, that is 97–5612 kg of active ingredient. In 1988, however, the use of thiobencarb increased by 50%. Thiobencarb and chlornitrofen were applied in amounts of 2000–5612 kg. The amounts of active ingredients used in the S-River watershed during the farming period varied from 0.2 kg of simetryn to 553 kg of thiobencarb. Pretilachlor was not used during the same period.

Representative ion monitoring chromatograms of K-River water are shown in Fig. 2. These ions were free from interfering peaks in the control water sample. Pretilachlor and oxadiazon showed similar retention times. However, as shown in this figure, these pesticides were easily separated and determined by monitoring the selected characteristic ions.

The analytical findings of surface water samples collected from rivers indicate that most of the pesticides were detected in river water at 1 to 10 µg/l levels for the first 2–4 weeks after application in the fields. They were reduced below the limits of detection at 4–6 weeks. On the whole, the levels of pesticides detected in the S-River were lower than those in the K-River. In 1987, the concentrations of butachlor and pretilachlor were found to be about 1–4 µg/l in the K-River. These pesticides were present only during the first few weeks after application and then decreased rapidly. Similar behaviour was found for oxadiazon and chlornitrofen. Simetryn

TABLE III

STABILITY OF BUTACHLOR, PRETILACHLOR, OXADIAZON, CHLORNITROFEN, SIMETRYN AND THIOBENCARB ADDED TO DISTILLED WATER STORED AT ROOM TEMPERATURE

Values are the means of triplicate experiments. Amount added: 0.5 µg/l (chlornitrofen 2.5 µg/l).

Storage period (days)	Recovery (%)					
	Butachlor	Pretilachlor	Oxadiazon	Chlornitrofen	Simetryn	Thiobencarb
0	95	96	98	79	90	88
3	101	112	100	86	96	97
7	101	100	99	88	93	89

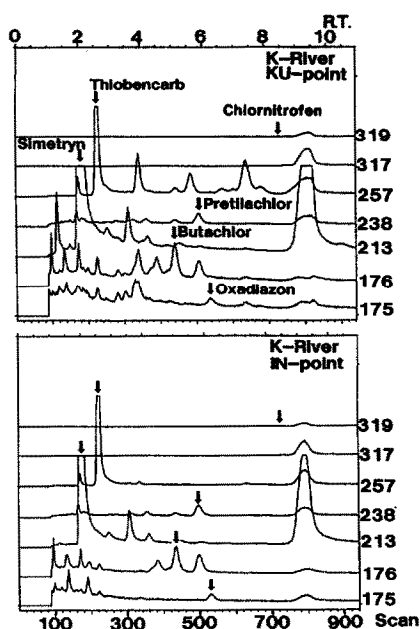


Fig. 2. Typical mass fragmentograms of butachlor, pretilachlor, oxadiazon, chlornitrofen, simetryn and thiobencarb residue in K-River water. Sampling date: June 7, 1988. Injection volume/final solution volume from 1000 ml sample: 2 μ l/1 ml.

was observed at the highest residue level (3.0–13.3 μ g/l) about 4 weeks after application. Except for chlornitrofen and simetryn, the detected levels of

pesticides were generally consistent with the amounts applied to the rice paddy fields.

In spite of the use of a large amount of chlornitrofen, the level of chlornitrofen detected was much lower than those of other pesticides. This may be attributed to the lower solubility in water, to the higher vapour pressure and to adsorption onto soil.

In contrast to chlornitrofen, simetryn was observed at high concentration during 1987 and 1988. Simetryn is very soluble in water, and may be rapidly transported into the river when the water levels in the rice paddy fields increase after rainfall.

The amount of pesticide during sampling date X_i is $C_i f_i$, in which C_i and f_i are the concentration of pesticide detected in river water and water flow at sampling date X_i , respectively. Therefore, the amount of pesticide transported into a river over period between one sampling date and the next (W_i) can be defined as:

$$W_i = 1/2[(C_i f_i + C_{i+1} f_{i+1})(X_{i+1} - X_i)]$$

The total amount of pesticides (TW) transported into a river during the farming period is thus:

$$TW = \sum_{i=1}^n W_i$$

TABLE IV

AMOUNTS OF PESTICIDES-ACTIVE INGREDIENTS APPLIED TO RICE PADDY FIELDS IN THE K-RIVER WATERSHED

The areas of paddy fields are 8084 ha for the upper K-River watershed, 14 700 ha for the lower K-River watershed, 124 ha for the upper S-River watershed, 713 ha for the middle S-River watershed and 557 ha for the lower S-River watershed.

Pesticide	Amount of pesticide applied (kg)									
	K-River watershed				S-River watershed					
	1987		1988		1987			1988		
	Upper	Lower	Upper	Lower	Upper	Middle	Lower	Upper	Middle	Lower
Butachlor	651	1677	540	1220	75.3	1.2	52.2	18.5	177.6	305.6
Pretilachlor	606	1543	640	1500	—	—	—	—	—	—
Oxadiazon	97	315	80	200	13.7	307.2	315.3	16.8	244.4	271.7
Chlornitrofen	2743	5612	2709	4476	7.2	475.3	166.6	3.6	295.6	256.0
Simetryn	1792	1859	1500	1614	—	—	—	—	—	0.2
Thiobencarb	2111	3473	3659	5294	8.5	552.9	191.4	4.4	368.8	344.3

Run-off (R) of pesticide transported into the river is then calculated using the following equation:

$$R = TW / TA \times 100$$

where TA is total amount of pesticide used at the river watershed. The TA used were calculated by adding the total amount of pesticide used at the upper and middle river watersheds for the middle river and at the upper, middle and lower river watersheds for the lower river.

On the basis of the calculations, the run-off of pesticides transported into the river was from 0.1% chlornitrofen to 33% simetryn for the K-River, and from 0.01% chlornitrofen to 2.4% butachlor, but 3.9% oxadiazon, for the S-River. Pesticides that are very soluble in water, such as simetryn, are efficiently transported into rivers. The influence of pesticide solubility on their mobility is an important factor in their transportation in the aquatic system [8]. In addition, it seems that the difference in the results for the K-River and the S-River can also be ascribed to the properties of soil. The soil of the K-River watershed is loam, and the pesticides used in paddy fields, except for the chlornitrofen adsorbed on soil, were transported into the rivers. On the other hand, the soil of the S-River watershed is sand, and the pesticides in the field were transported into the river after being removed into soil.

CONCLUSIONS

A multiresidue analysis of butachlor, pretila-

chlor, oxadiazon, chlornitrofen, simetryn and thio-bencarb in river water samples was developed. The method was based on solid-phase extraction, followed by GC-MS-SIM. By this method, the detection limits were 0.05 $\mu\text{g/l}$ for chlornitrofen and 0.01 $\mu\text{g/l}$ for other pesticides. The results for river water indicate that most of the pesticides were present at low levels for the first 2–4 weeks after application in the fields. Pesticide concentrations decreased below detectable levels at 4–6 weeks. The levels of pesticides in river water were generally consistent with the amounts of pesticides applied. In addition, pesticides that are very soluble in water are efficiently transported into river when water levels in the paddy field increase after rainfall.

The GC-MS-SIM method provides a rapid, sensitive and accurate technique for the analysis of pesticides in river water.

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