NOTE

Pesticide Residue Flux from Rainwater into Lake Nakanuma in the Rainy Season

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ABSTRACT

Pesticide residues in rainwater were investigated for the estimation of pesticide flux into a lake in Ibaraki Prefecture during the 1990 rainy season. The maximum concentration of oxiadiazon in the rainwater was $4.2 \mu\text{g l}^{-1}$. The maximum concentrations of fenobucarb, fenitrothion and edifenphos in the rainwater were 0.58, 0.53 and $0.36 \mu\text{g l}^{-1}$, respectively. The annual ratio of fenitrothion redeposition by rainfall was estimated at 1.5% of the total shipping amount in Ibaraki Prefecture. There was no significant difference between redepositions of pesticides by rainfall and shipping amounts in the prefecture ($\alpha = 0.05$). Pesticide residues in lake water were investigated in Lake Nakanuma, Ibaraki Prefecture, from March to December 1990. The concentrations of molinate, simetryn, iprobenfos, and thiobencarb in irrigation canal water were in the high range ($>1.2 \mu\text{g l}^{-1}$). The concentrations of diazinon, malathion, and fenthion in the water were at a lower level ($<0.2 \mu\text{g l}^{-1}$). The maximum concentration of simetryn in the lake was $0.91 \mu\text{g l}^{-1}$. Except for chlornitrofen, the maximum concentration of pesticide in the lake ($<1.0 \mu\text{g l}^{-1}$) was about one-tenths in that of irrigation canals. The amount of pesticide from rainfall was a major factor from the viewpoint of estimating the environmental viability of the lake.

Key words : environmental fate, Lake Nakanuma, pesticide, rainfall

INTRODUCTION

Pesticides applied to rice paddies and golf courses for pest and/or weed control contaminate aquatic ecosystems. These pesticide residues have been detected in rivers surrounded by paddy fields in Japan (SUZUKI, 1982; IMANAKA *et al.*, 1985; MARU, 1985; FUKUSHIMA, 1991; HATAKEYAMA *et al.*, 1991; TAKAMURA *et al.*, 1991; NUMABE *et al.*, 1992; IWAKUMA *et al.*, 1993; NOHARA and IWAKUMA, 1996a). Water which is used over and over for irrigation finally enters lakes. However, little is known about the long-term effects and types of pesticide residues of in lake water (IMANAKA *et al.*, 1985; SHIRAISHI *et al.*, 1988; NOHARA and IWAKUMA, 1996a, b). Lakes are a very important sources of drinking water, as well as being used for fisheries, and providing a habitat for aquatic organisms. Some pesticides

escape as vapor from agriculture fields and golf courses (GROVER, 1974 ; OKUMURA, 1991 ; FUSHIWAKI *et al.*, 1993 ; HAYAKAWA *et al.*, 1996). However, some level of vaporized pesticides seem to return to the ground with rainwater (TARRANT and TATTON, 1968 ; VISWESWARIAH *et al.*, 1975 ; UNO *et al.*, 1986 ; HOLOUBEK *et al.*, 1990 ; GALASSI *et al.*, 1993 ; HATFIELD *et al.*, 1996 ; SUZUKI, 1996). Such pesticide concentrations in rainwaters and their ratio of inflow into lakes are still unknown.

The purpose of the present study was to clarify the changes in pesticide concentrations in rainwater during the rainy season, and to determine the ultimate ecological impacts of pesticide flux into a lake.

MATERIALS AND METHODS

The sampling site for rainwater by the National Institute for Environmental Studies (NIES, 140°07' E, 36°02' N) is located in the eastern part of the Kanto Plain about 50 km northeast of Tokyo (Fig. 1). Rainwater was collected during June and July 1990. Lake Nakanuma (140°09' E, 35°53' N) is located 18.2 km south of the NIES in Ibaraki Prefecture, Japan. The lake is the deepest (13.0 m) in the Kanto Plain, and is elliptical in shape with an area of 10,750 m². According to the topographical map (NI-54-19-13-2) made on a scale of 1 : 25,000 by the Geographical Survey, land use around the lake (6×6 km) is classified as paddy field (69.0%), town (17.5%), grassland (5.1%), open water (3.3%), farmland (3.1%), and forest (2.0%). The water of one irrigation canal connected with the Kokai River enters the lake. The irrigation water was collected at a site nearest to the lake. Lake water was collected at depth intervals of 2 m in the center of Lake Nakanuma. Both collections once a week from May to July 1990, and once a month from March to April and from August to December 1990. Daily rainfall data at the Tateno Station, located 0.5 km east of NIES, were obtained from the Mito Local Meteorological Observatory. Following every steady rainfall, rainwater for pesticide analysis was collected in a stainless steel 10-liter container, stored in a refrigerator, using a stainless steel sink (47×55 cm) and polytetrafluorethylene tube, and brought back to the laboratory the next day. The water samples were filtered through precombusted (450 °C, 3 h) Whatman GF/C glass fiber filters to remove suspended matter.

The filtered water was passed through an ODS-packed column (Bond-Elute C18, Analytichem International, U.S.A.) with an aspirator at a rate of about 20 ml min⁻¹ to absorb any pesticides present. The column was then centrifuged once at 3,000 rpm for 20 min to remove the water, and twice at 1,000 rpm for 15 min with 0.5 ml acetone to extract the absorbed pesticides. The extract was finally brought to a level of 1 ml with 50 µl azobenzene and triphenyl phosphate as internal standards (0.1 mg l⁻¹).

The pesticide concentration was determined with a gas chromatograph (Model 5980A, Hewlett Packard, U.S.A.) fitted with a capillary column (SPB-5, fused silica 0.25 µm, 0.32 mm inner diameter×30 m long) and

Fig. 1. Map of sampling locations, lakes and major rivers in central Japan. Solid square: rainwater sampling site of National Institute for Environmental Studies (NIES); solid circle: lake water sampling site of Lake Nakanuma; solid triangle: sampling site of irrigation canal into Lake Nakanuma.

equipped with an autoinjector (Model 7673A, Hewlett Packard, U.S.A.). The peak area of the pesticide signal on the gas chromatogram was determined with a chromatographic data processor (Model 3396, Hewlett Packard, U.S.A.). A nitrogen-phosphorus detector gas chromatograph (GC/NPD) was used for the determination of fenitrothion (MEP), fenthion (MPP), diazinon, fenobucarb (BPMC), molinate, simetryn, malathion, thiobencarb, butachlor, oxadiazon, chlonitrofen (CNP), edifenphos (EDDP) and iprobenfos (IBP). The column was heated gradually from 50 to 300 °C with an injector temperature of 250 °C and a detector temperature of 300 °C. Helium was used as the carrier gas at a flow rate of 54 ml min⁻¹. The detection limits were 0.02 µg l⁻¹ for water.

Fig 2. Changes in rainfall and concentrations of major pesticides in rainwater, June and July 1990. Open square : fungicide ; solid circle : herbicide ; open triangle : insecticide. EDI : edifenphos ; IPR : iprobenfos ; OXI : oxadiazon ; CHL : chlonitrofen ; MOL : molinate ; FNO : fenobucarb ; FNI : fenitrothion ; DIA : diazinon ; MAL : malathion.

RESULTS

The maximum concentration of edifenphos, a fungicide, in rainwater was $0.36 \mu\text{g l}^{-1}$ in late July (Fig. 2). The concentration of iprobenfos, a fungicide, was highest ($0.17 \mu\text{g l}^{-1}$) in July. The concentration of oxadiazon, a herbicide, was highest ($4.2 \mu\text{g l}^{-1}$) of any pesticide in mid-June. The maximum concentrations of chlornitrofen and molinate were 0.19 and $0.10 \mu\text{g l}^{-1}$, respectively. Fenobucarb had the highest level ($0.58 \mu\text{g l}^{-1}$) among insecticides. Fenitrothion was detected throughout in June and July. Diazinon and malathion had the lowest levels ($<0.2 \mu\text{g l}^{-1}$) among insecticides. There was no significant difference between each pesticide concentration in rainwater and the amount of continuous rainfall ($\alpha=0.05$).

Table 1. Water solubility, vapor pressure of pesticide, range of maximum concentration of pesticide and redeposition by rainfall in aquatic ecosystems.

Pesticide	Water solubility ¹⁾ (mg l^{-1})	Vapor pressure ¹⁾ (mPa)	Shipping amount ²⁾ (Ibaraki) (t)	Range of maximum concentration ($\mu\text{g l}^{-1}$)					Redeposition by rainfall (μgm^{-2} month^{-1}) ¹⁰⁾
				River ^{3),4),5),6)}	Lake Kasumi-gaura ^{7),8),9)}	Lake Nakanuma ¹⁰⁾	Irrigation canal ¹⁰⁾	Rain ¹⁰⁾	
Molinate	880	746	39.1	1.2-23	0.5	0.67	4.96	0.10	1.32
Fenobucarb	660	47	21.5	18-30	1.0-1.6	0.13	0.34	0.58	4.05
Simetryn	450	0.1	14.8	2.9-11	1.1-4.8	0.91	3.51	ND	0.00
Iprobenfos	430	0.30	59.7	3.2-18	3.4-24	0.66	2.52	0.17	2.34
Malathion	145	5.3	10.5		0.18	0.07	0.36	0.18	1.29
Diazinon	40	0.097	34.4	0.2-1.0	0.1-0.8	0.03	0.11	0.15	5.47
Thiobencarb	30	2200	44.9			0.17	1.20	0.07	1.31
Butachlor	23	0.6	17.2	1.5-9.0	0.05	0.45	0.79	0.02	0.23
Fenitrothion	21	0.15	41.6	0.2-20		0.05	0.04	0.53	14.7
Fenthion	2	4	50.0	2.6-2.8	1.9	0.00	0.02	0.12	1.18
Oxiadiazon	0.7	<0.13	10.2	1.1-3.1	0.66	0.06	0.21	4.23	2.99
Chlonitrofen	0.25	3.2	29.3	0.6-4.1		0.63	0.31	0.19	0.10
Edifenphos	insol.	no data	12.1		0.36	ND	ND	0.36	0.56

1) WORTHING and HANCE, 1991; 2) AGRICULTURAL PRODUCTION BUREAU, 1990; 3) NAKAMURA and OSAKI, 1984; 4) HATAKEYAMA *et al.*, 1992; 5) NUMABE *et al.*, 1992; 6) IWAKUMA *et al.*, 1993; 7) SHIRAI-SHI *et al.*, 1988; 8,9) NOHARA and IWAKUMA, 1996a,b 10) present study

Concentrations of molinate, simetryn, iprobenfos and thiobencarb in irrigation canal water were in the high range ($>1.0 \mu\text{g l}^{-1}$, Table 1). Those pesticides had high solubility in water ($30-880 \text{ mg l}^{-1}$). The maximum concentration of any pesticide (except for chlornitrofen) in the lake ($<1.0 \mu\text{g l}^{-1}$) was lower than any found in irrigation canal water. The maximum concentrations of fenobucarb, diazinon, fenitrothion, fenthion, oxiadiazon and edifenphos in rainwater were higher than tiny in the water of irrigation canals. The maximum concentration of simetryn in Lake Nakanuma was $0.91 \mu\text{g l}^{-1}$. Simetryn was not detected in rainwater. The total shipping amounts of 13 pesticides detected in Ibaraki Prefecture ($6,094 \text{ km}^2$ area) in 1990 was about 385 tons. There was no significant difference between the redeposition amount of each pesticide by rainfall and the shipping amount in

Ibaraki Prefecture ($\alpha = 0.05$).

DISCUSSION

The annual redepositions of pesticides by rainfall are $0.11\text{--}8.1\ \mu\text{g m}^{-2}\text{ year}^{-1}$ ($0.01\text{--}1.0\ \mu\text{g m}^{-2}\text{ month}^{-1}$) in Nara Prefecture (UNO *et al.*, 1986). Their study found iprobenfos, fenitrothion, diazinon, malathion, methidathion, and cyanophos in preserved rainwater during one month. In the present study, the redepositions of pesticides by rainfall during two months was in the high range of as $0.10\text{--}14.7\ \mu\text{g m}^{-2}\text{ month}^{-1}$ (Table 1). The flux of redeposition to the entire prefecture by rainfall was $35\ \mu\text{g m}^{-2}\text{ month}^{-1}$ ($0.25\ \text{mg m}^{-2}\text{ year}^{-1}$, from April to October). Pesticides with higher vapor pressure and lower solubility in water show higher volatility (YUKIMOTO *et al.*, 1979). Fenitrothion also shows both high vapor pressure and low solubility in water (Table 1). It is worth noting that high levels of fenitrothion are used for aerial spraying over pine forest around the present study area (AGRICULTURAL PRODUCTION BUREAU, 1990; HATAKEYAMA *et al.*, 1990). Therefore, redeposition of fenitrothion by rainfall seemed to be higher than for other pesticides. Based on the mean data of redeposition (Table 1), the redeposition ratio of fenitrothion by rainfall was an estimated 1.5% of the total shipping amount in Ibaraki Prefecture. That ratio was higher than that of 13 other pesticides (0.4%). Fenitrothion is also the most frequently detected pesticide in rainwater in Hyogo Prefecture (FUJIMORI *et al.*, 1994).

In the last ten years, there have been many studies which involved the monitoring of pesticides in aquatic ecosystems in Japan (FUKUSHIMA, 1991; NUMABE *et al.*, 1992; IWAKUMA *et al.*, 1993; SHIRAISHI *et al.*, 1988; NOHARA and IWAKUMA, 1996a, b). Such monitoring has been restricted to rivers and lakes. The maximum concentration of pesticides except for chlornitrofen in Lake Nakanuma ($<1.0\ \mu\text{g l}^{-1}$) was about one-tenth that of the irrigation canal. The amount of pesticide from rainwater was a major factor in estimating the eventual ecological viability of Lake Nakanuma (Table 1). Therefore, the results of the present study suggested the environmental necessity of monitoring the flux of pesticide residues in rainwater into lake ecosystems.

Pesticides can exist in the atmosphere absorbed in soil particles, and can later be redeposited by rainfall on land remote from the site of the original deposition (VISWESWARIAH *et al.*, 1975). They can also enter the atmosphere by volatilization. The falling amounts of pesticides are not clearly related to the retectural shipment amounts (SUZUKI, 1996). In the present study, there was no significant difference between the redeposition amount of each pesticide by rainfall and the shipping amount in Ibaraki Prefecture. Pesticide residues in rainwater are detected only around application areas, and few pesticides are diffused widely in the air (SUZUKI, 1996). This makes it difficult to estimate the origin of the pesticides in rainwater. The question of origin aside, in Japan there seems to be no area without pesticide residues in its rainwater. We need many more monitoring sites in Japan for the

study of pesticide residues in rainwater and their long-term ecological impact.

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茨城県中沼の湖水と梅雨期の降水中の農薬残留濃度

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摘 要

湖への農薬の負荷量を把握するために、1990年の梅雨期の雨水中の農薬濃度を茨城県で測定した。降水中の最大農薬残留量はオキサジアゾンで $4.2 \mu\text{g l}^{-1}$ であった。雨水中のフェノベンカーブ(BPMC)、フェニトロチオン(MEP)、エジフェンフォス(EDDP)の濃度は $0.58, 0.53, 0.36 \mu\text{g l}^{-1}$ 以下であった。フェニトロチオンの雨水からの年間降下量の割合は出荷量の1.5%と見積もられた。雨水による各農薬降下量は雨量や茨城県の農薬出荷量との有為な関係は見られなかった。1990年3月から12月に茨城県中沼の湖水及び一時的に流入する農業用水の中の農薬濃度を測定した。モリネート、シメトリン、イプロベンフォス(IBP)、チオベンカーブの農業用水の中濃度は $1.2 \mu\text{g l}^{-1}$ 以上と高い範囲にあった。ダイアジノン、マラソン、フェンチオン(MPP)の農業用水の中濃度は $0.2 \mu\text{g l}^{-1}$ 以下と低い範囲にあった。湖水中のシメトリンの最大濃度は $0.91 \mu\text{g l}^{-1}$ であった。クロルニトルフェン(CNP)を除いて、湖水中の最大の濃度は農業用水の約1/10程度であった。湖沼への農薬流入を見積もる上で雨水を介しての流入は重要な流入源の一つである事が明らかになった。