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Concentration and Distribution of Several Pesticides Applied to Paddy Fields in Water and Sediment, from Sugao Marsh, Japan

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In Japan, many studies have been carried out on the fate of pesticides in the environment, especially on pesticides applied to paddy fields. These studies have carried out pesticide fate in and runoff from the paddy fields (Tanigawa and Nishimura, 1999) in addition to their monitoring in water at several rivers and lakes (Maru, 1985; Nohara et al., 1997; Kondo et al., 2001). On the other hand, sediment is a very important medium for pesticide behavior in aquatic ecosystems. So, several studies on the behavior of pesticides in sediment have been carried out (Long J.L.A. et al., 1998; Kreuger, J. et al. 1999). However, the concentrations of pesticides applied to paddy fields in sediments have been rarely investigated in Japan (Nakamura et al., 1985; Ohyama et al., 1987) where about half the total pesticide application is to paddy fields (Kanazawa, 1991). Although the marsh connected with paddy fields at plain area has rich bio-diversity and may be affected by pesticide, the investigation about pesticide concentration in sediment in a marsh have not carried out. The purpose of this study was to monitor the concentration of the selected pesticides both in water and sediment in a marsh connected with paddy fields, and to elucidate the distribution and persistence of the pesticides in sediment.

MATERIALS AND METHODS

Sugao marsh is located in the southwestern part of Ibaraki Prefecture, northeast of Tokyo, Japan. The Iinuma, Higashinire and Egawa Rivers flow into the marsh (Figure 1). This marsh is mostly surrounded by paddy fields and partly by an urban area. The size of this marsh is about 5 km to the south and north and about 0.6 km to the east and west, having a surface area of about 2.32 km^2 with about 80% being covered with various hygrophytes and rich bio-diversity (Ibaraki Nature Museum., 1996). Water samples were collected at five representative sites. Sites 1 to 4 were placed along the flow from the upper to lower reaches of the marsh and the other site called RI was placed at the Iinuma River (Figure 1). Considering the application timing of the pesticides in paddy fields, the period for monitoring and collection of water samples was from April 15th to August 29th 2002. Namely, the frequency of the sample collection was about once a week from April 15th to

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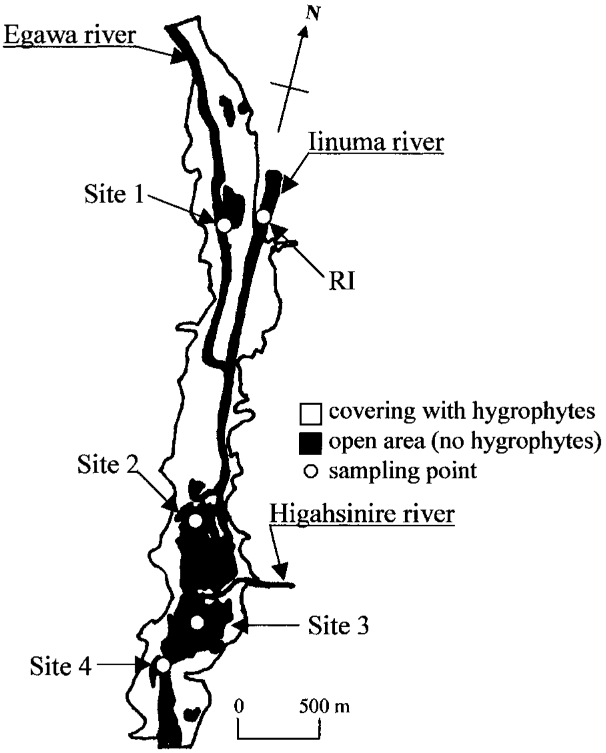

Figure 1. The location of sampling points at Sugao marsh.

June 9th when the water quality was expected to change due to agricultural practices in the paddy fields and about once a month after this period. Water samples were collected with a stainless beaker (2 L in volume). Samples were stored in brown glass bottles (3 L in volume). The samples from the RI site were obtained on April 25th. Sediment samples were also collected from the identical sites at the same time as the water samples, except April 25th, from the sediment surface at about 5 cm depth with a 3 m dipper and stored in glass bottles (900 mL in volume). Samples could not be collected from site 3 in July.

Four kinds of herbicides including esprocarb (*S*-benzyl 1,2-dimethylpropyl (ethyl) thiocarbamate), thiobencarb (S-4-chlorobenzyldiethyl- thiocarbamate), dimethametryn (N^2-(1,2- dimethylpropyl)-N^4-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine) and pretilachlor (2-chloro-2',6'- diethyl-*N*-(2-propoxyethyl) acetamide) were selected and analyzed in the present study. The selection was based on the commercial amounts of pesticides sold by the Japan Agricultural Association in the relevant areas of Ibaraki Prefecture, Japan. All standard pesticides used in this study were obtained from Wako Jyunyaku Kogyo, Co., Ltd., except for dimethametryn which was provided by Kanto Kagaku, Co., Ltd. Chemical properties of the pesticides studied are shown in Table 1.

Five hundred milliliter of the water sample was shaken with 50 mL of ethyl acetate for 5 min after addition of 30 g of NaCl and the organic layer filtered through anhydrous Na_2SO_4. The aqueous layer was shaken again and filtered in the same manner. The combined filtrates were evaporated to approximately 1 mL with a rotary evaporator and dried under N_2 and further purified on a florisil column (200 mm length, 10 mm internal diameter). The column was prepared with 1.5 g anhydrous Na_2SO_4 placed on 1.0 g florisil, 4 v/w% of water, previously conditioned with each 10 mL of acetone and n-hexane. The residue was dissolved in 10 ml of the solvent (n-hexane : acetone = 85 : 15 (v/v)) and applied onto the column. Then, 10 mL of the same solvent was applied to obtain a 20 mL eluate. This eluate was evaporated to about 1 mL with a rotary evaporator and dried under N_2. The residue was again dissolved in 1 mL acetone containing 0.05 μgmL^{-1} phenanthrene-d_{10} as an internal standard and finally analyzed by GC/MS.

Sediment samples were passed through a 2 mm sieve and thoroughly mixed, centrifuged at 3000 rpm for 20 min and the supernatant was discarded. 10 g dry weight of the sample was shaken with 50 mL acetone for 30 min and filtered with a 1.0 µm glass filter (Whatman GF/B). Then, the sample was combined in a 200 mL of 5% NaClaq and shaken with 30 mL of ethyl acetate for 30 min. The organic layer was filtered through anhydrous Na_2SO_4 and the aqueous layer was shaken again and filtered in the same manner. The combined filtrates were evaporated to approximately 1 mL with a rotary evaporator and dried under N_2 and further purified on a silica gel column (200 mm length, 10 mm internal diameter). The column was prepared with 1.5 g anhydrous Na_2SO_4 placed on 1.0 g silica gel, contained 4 v/w% of water, previously conditioned with each 10 mL of acetone and n-hexane. After column conditioning, the dried residue dissolved in 10 mL of the solvent (n-hexane : acetone = 95 : 5 (v/v)) was applied onto the column, and 20 mL of the same solvent was applied to obtain a 30 mL eluate. This eluate was concentrated to 1 mL with a rotary evaporator and dried under N_2. The residue was further purified by graphite carbon cartridge (Supelco, Co., Ltd.). The cartridge volume of 500mg/5mL was previously conditioned with 30 mL acetone. After conditioning, the residue was dissolved in 5mL of

Table 1. Several physicochemical properties of the pesticides studied.[a]

Pesticide	chemical formula	M.W.	water solubility (20°C)(mgL^{-1})	Kow[b]
Esprocarb	$C_{15}H_{23}NOS$	265.4	4.9	4.6
Thiobencarb	$C_{12}H_{16}ClNOS$	257.8	30	3.42
Dimethametryn	$C_{11}H_{21}N_5S$	255.4	50	3.8
Pretilachlor	$C_{17}H_{26}ClNO_2$	311.9	50	4.08

[a] Cited from The Pesticide Manual 12th. (2000)

[b] 1-octanol/water partition coefficient.

the solvent (n-hexane: acetone = 95 : 5 (v/v). The sample was applied to cartridge and another 20 mL of acetone 20 mL was applied to the cartridge. Both eluates were combined and concentrated to 1 mL with a rotary evaporator and dried under N_2. The residue was again dissolved in 5 mL acetone including 0.05 $\mu g mL^{-1}$ phenanthrene-d_{10} as an internal standard and analyzed by GC/MS. Part of the sediment samples was air-dried and analyzed for carbon content (determined by NC analyzer using a SUMIGRAPH NC-900, Sumika Bunseki Center, Co., Ltd.).

All samples were analyzed by Hewlett Packard 6890 GC equipped with a fused silica capillary column (MDN-5S, 30 m length and 0.30 mm internal diameter, 0.25 μm film) and with 5973N MS operated in the selected ion monitoring mode. Their detection limits were 0.02-0.04 $\mu g mL^{-1}$ in water and 4-10 $\mu g kg^{-1}$ in sediment. Recoveries (%) were 95-109% (C.V.=4-7%, n=5) in water and 49-81% (C.V.=4-5%, n=5) in sediment.

RESULTS AND DISCUSSION

Periodic changes in the concentrations of pesticides in water samples appeared from late April to early May (Figure 2). These periodic peaks of the pesticide concentrations were considered to be due to the timing of pesticides application, as pointed out in other previous studies (Maru, 1985; Kondo et al., 2001). The patterns of pesticide concentration peaks clearly corresponded to the timing of application to this study area because the transplanting of rice seedlings was initiated from April 25th and almost finished on May 9th. Comparing the concentrations of dimethametryn, esprocarb and pretilachlor between the sampling sites, they were relatively lower in the marsh water than the site of river water, approximately one half or one third of the marsh (Figure 2). The pesticide concentrations in marsh water were also lower than the irrigation canals entering into the marsh as observed at the marsh of Nakanuma (Nohara et al., 1997). This phenomenon may be caused by the dilution effect of water discharged into the study marsh. In addition dimethametryn, esprocarb and pretilachlor showed a time lag in their concentration changes between the RI and site 2 (Figure 2) where the appearance of concentration peaks in site 2 was delayed as compared to site RI. According to the previous study on Lake Kasumigaura, a time lag of about one month was observed in pesticide concentration peaks at the river mouth, the central part and the out flow (Shiraishi et al., 1998). However, as observed in Lake Kibagata (Tsukabayashi et al., 1996) having a comparable size with Sugao marsh, the mean residence time for pesticides in the present study were shorter than that observed for the Lake Kasumigaura.

The highest pesticide concentrations in the sediment detected at site 1 (Figure 3). The concentrations of pesticides in the sediments at sites 1, 2 and 3 of the marsh were higher than at the sites RI and 4, input and output points for Sugao marsh, respectively (Figure 3).

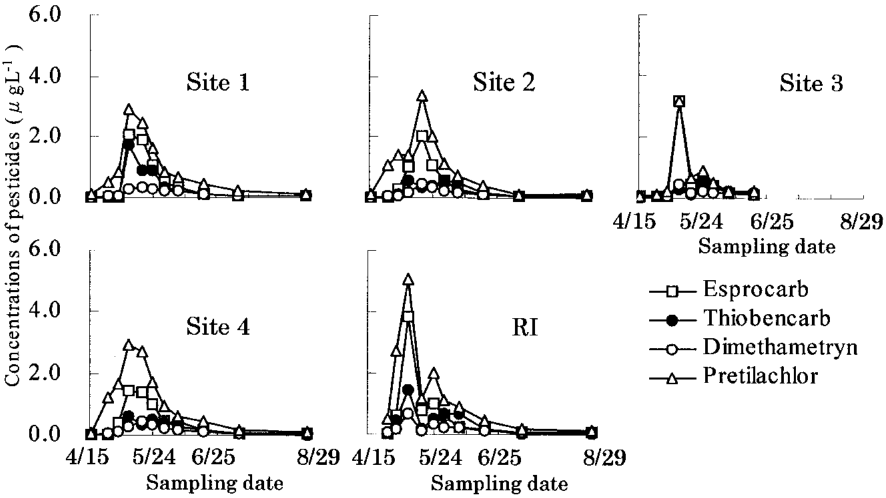

Figure 2. Concentration of pesticides in the water at sampling

The frequency of detection in sediment (expressed as the number of samples detected vs. the number of samples analyzed) was in the following order; esprocarb (46/47), thiobencarb (43/47), dimethametryn (42/47), pretilachlor (34/47). The frequency of detection in "Chemicals in the environment" (Environmental Health and Safety Division, Environmental Agency JAPAN, 2002) was 3/165 for thiobencarb. Higher frequency was observed in the present study for thiobencarb in the sediments. The concentration peaks of pesticides in the sediment appeared in late May to early June (Figure 3). Although the concentration peaks are probably caused by the timing of application as observed in the case of water samples, the pesticides concentration peaks were appeared at later periods than in water. The lately appearance of the pesticides concentration peaks in the sediment was also reported at the irrigation canal surrounding the paddy fields (Nakamura et al., 1985). Moreover, simetryn, butachlor and CNP were detected even at November in the sediment at the downstream area of the Ishikari River, about 150 km distance from the paddy field area (Ohyama et al., 1987). Thus, the pesticides used for paddy fields persist for a long period and are widely spread from irrigation canal to river and marsh sediment.

In general, hydrophobic chemical compounds were apt to adsorb to organic matter in the sediments. As shown in Table 2, the concentrations of four pesticides correlated very well with the carbon content in the sediment (significant level at 1%), suggesting the possibility that the pesticides are adsorbed on organic matter in the sediment at Sugao marsh. Since the highest content of carbon was detected in the sediment at site 1 (Table 3), the pesticide concentration in the sediment at site 1 was higher than for other sampling sites. According to Long J.L.A. et al.(1998) the deposition processes of suspended solids due to a decrease in flow rate affects various properties of sediments and the quantity of persistent organic

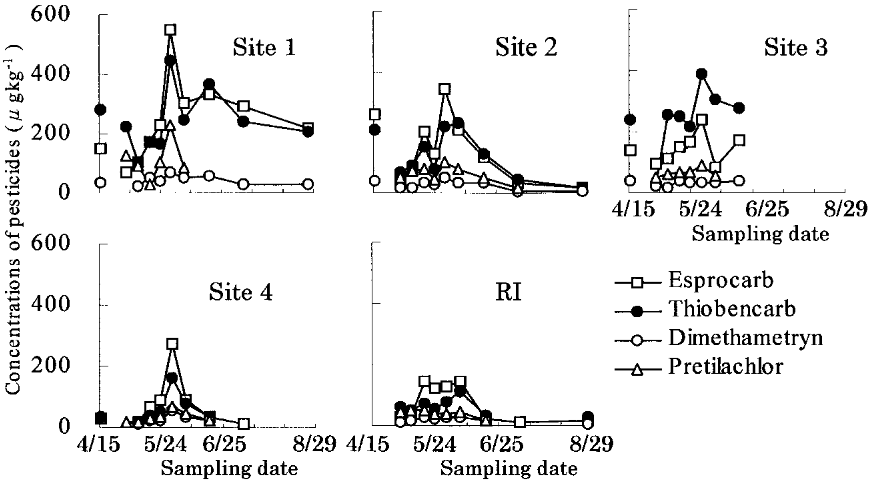

Figure 3. Concentration of pesticides in the sediment at sampling sites.

Table 2. Correlation between pesticide concentration and carbon content in sediment samples.

Pesticide	Number of samples	Correlation coefficient
Esprocarb	n=46	0.511**
Thiobencarb	n=43	0.646**
Dimethametryn	n=41	0.550**
Pretilachlor	n=34	0.552**

**Significant at p<0.01

Table 3. Avarage carbon content in sediment samples.

	Number of samples	average carbon content (%)	coefficient of variation (%)
Site 1	n=11	7.7	4.8
Site 2	n=11	3.6	30.4
Site 3	n=8	5.6	23.9
Site 4	n=11	4.0	18.9
RI	n=10	1.7	43.6

chemicals in the sediments. Site 1 was most conformed to this condition because relatively slow water flow was observed.

Focusing on changes in thiobencarb concentrations both in water and sediment, there were a distinct difference in the concentrations between the sediment and water (Figure 2 and 3). According to Tanigawa and Nishimura (1999), the concentration of thiobencarb in the plow layer of paddy fields readily increased after application and decreased slowly. On the other hand, thiobencarb was not detected soon after the inflow at the input river mouth of Lake Kasumigaura, probably because of photo-dissociation and volatilization (Shiraishi et al., 1998). However, in the present study, thiobencarb was detected in sediments when it was not detected in water. Therefore, the disappearance of thiobencarb from water may not only be by photo-dissociation and vaporization, but also due to translocation to the sediment.

It seems still necessary to monitor pesticide concentrations in sediments because the possibilities that aquatic plants absorb pesticides from the sediment (Nohara et al., 1988) and the affect of pesticides on benthos in lake sediment by in vivo experiment (Hatakeyama and Sugaya, 2000) are often concern. Data obtained from this study suggests that the sediments in Sugao marsh may prevent pesticide run off to down stream through intimate interactions. However, since the water-sediment system is always in a non-equilibrium condition between pesticides concentrations in water and those in sediments, further study on the role of marsh sediment at non-equilibrium condition is necessary.

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