Concentration and loading of several pesticides in water, suspended solids and sediment during ordinary water discharge in Sugao marsh, Ibaraki Prefecture, Japan

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Concentrations of esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn in water, suspended solids and sediment were studied during ordinary water discharge over the course of a year in Sugao marsh, Ibaraki Prefecture, Japan. Periodic changes in pesticide concentrations in water were similar to those in suspended solids. Pesticides were mostly present as dissolved form in water. Namely, the partition ratios of total suspended solids in whole water samples were 0.37–2.5% as the median, and the ratios of pesticide loading as adsorbed form on suspended solids against total pesticide loading were 0.42–4.6%. However, the concentrations of pesticides were higher in fine suspended solids (0.5 to 1.0 μm) than coarse suspended solids (more than 1.0 μm). Fine suspended solids loaded with pesticides were estimated to be 18 to 59% of all suspended solids, indicating their important role as a carrier of pesticides. Moreover, vertical distributions of pesticides in sediment down to a depth of 15 cm were not clearly shown, probably due to the disturbance of sediment at the surface by actual water flow. © Pesticide Science Society of Japan

Keywords: pesticide loading, suspended solids, particle size, sediment, ordinary water discharge.
Materials and Methods

1. Brief description of study sites and collection of samples

Sugao marsh is located in the southwestern part of Ibaraki Prefecture, northeast of Tokyo, Japan. The Inuma, Hi-gashinire and Egawa Rivers flow into the marsh (Fig. 1). This marsh is surrounded mostly by paddy fields and partly by an urban area, having a surface area of about 2.32 km² nearly 80% of which is covered with various hygrophytes. All samples were collected at two sites, Fureaibashi and Inuma river, located at inner mash and river mouth, respectively (Fig. 1). Taking into consideration the timing of pesticide application in paddy fields, the collection of water, suspended solid and sediment sample was conducted from April 23, 2003 to March 10, 2004. The sample collection was carried out at the study sites during ordinary water discharge conditions, defined as a period when the water table of the river was constant and the weather was fine at last two days before sampling. Samples were collected about once a week from April 23 to July 3 when the water quality was expected to change due to agricultural practices in the paddy fields, and about once a month after this period. The sediment sample of was not collected from the Inuma river site on June 21.

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Water samples were collected with a stainless beaker and stored in brown glass bottles. Suspended solids samples were collected from a very large volume (100 liters) of water collected with a polyethylene beaker and stored in five 20 liter polyethylene tanks. Suspended solids samples of different size in water were obtained through filtering as described in the section “Sample processing.” The core samples of sediment were collected with a Multi-sampler (DIK-180A, Daiki Rika Kogyo Co., Ltd.) at Fureaibashi, divided into layers of 0–5 cm and 5–15 cm, and stored in glass bottles. At the river mouth, sediment samples were collected at a depth of about 5 cm with a dipper because of difficulty to obtain a core sample.

The data on water discharge were provided by the Sakai Branch Office of Civil Engineering Department, Ibaraki Prefecture, and were obtained from observations made three times a month at Maaraibashi, about 1.5 km up-stream from the sampling site on the Inuma river. Since water quantity would be similar between the Maaraibashi and Inuma river sites with no major input occurring, water discharge at Maaraibashi ought to be comparable with that at the Inuma river site. The average monthly discharge was calculated as the arithmetic mean of each month’s measurements, excluding any data which differed remarkably from other measurements in the same month. The water discharge data were used to estimate the loading with suspended solids and pesticides from April to July, because the frequency of sampling was reduced to once or twice a month after August.

2. Pesticides

Five pesticides, esprocarb (5-benzyl 1,2-dimethylpropyl- (ethyl)thiocarbamate), thiobencarb (S-4-chlorobenzyldiethylthiocarbamate), dimethametryn (N₂-(1,2-dimethylpropyl)-N⁴-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine), pretilachlor (2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetamide) and simetryn (4,6-bis(ethylamino)-methylthio-1,3,5-triazine), were analyzed in this study (Table 1). All these pesticides are used as herbicides in paddy fields. Their selection was based on amounts of pesticides sold by the Japan Agricultural Association in relevant areas of Ibaraki Prefecture, Japan. All standard pesticides used in this study were obtained from Wako Pure Chemical Industries, Ltd., except for dimethametryn which was provided by Kanto Kagaku, Co., Ltd. Chemical properties of the pesticides and amounts sold during the period April 2002 to March 2004 are shown in Table 1.

3. Sample processing and analysis of pesticides

3.1. Water samples

Five hundred milliliters of water samples were filtered through 1.0 μm and 0.5 μm glass-fiber filters (ADVANTEC GA-100 and GC-50). Suspended solids of these size fractions on the filters were abbreviated as SS₁.₀ and SS₀.₅, respectively. The filters were dried at 105°C for 24 hr and the weights of suspended solids were measured. The filtrated water samples were shaken by hand with 50 ml of ethyl acetate for 5 min after the addition of 30 g of NaCl, and the organic layer was filtered through anhydrous Na₂SO₄. The aqueous layer was shaken again and filtered in the same manner. The combined filtrates were evaporated to about 1 ml with a rotary evaporator, dried under N₂, and further purified on a Florisil cartridge (Waters Sep-Pak-Plus) washed with 5 ml of n-hexane before sample loading. The residue was dissolved in 5 ml of n-hexane and applied onto the cartridge. Then, 5 ml of n-hexane
was passed through the cartridge and the pesticide retained in the cartridge was extracted with 10 ml of n-hexane/acetone, 85/15 (v/v). This extract was evaporated to about 1 ml with a rotary evaporator and dried under N₂. The residue was dissolved in 1 ml of acetone containing 0.05 µg/ml of phenanthrene-d₁₀ as an internal standard and finally analyzed by GC-MS.

3.3. Sediment sample

Sediment samples were passed through a 2 mm sieve, thoroughly mixed, and centrifuged at 3000 rpm for 20 min. The supernatant was discarded. Ten grams of sample as dry weight was shaken with 50 ml of acetone for 30 min and filtered with a 1.0 µm glass fiber filter (Whatman GF/B). Then, the sample was evaporated to about 10 ml with a rotary evaporator, and 100 ml of 5% aq. NaCl was added and shaken with 30 ml of ethyl acetate for 30 min. The organic layer was filtered through anhydrous Na₂SO₄ and the aqueous layer was shaken again and filtered in the same manner. The combined filtrates were evaporated to about 1 ml with a rotary evaporator and dried under N₂. The residue was dissolved in 5 ml of acetone containing 0.05 µg/ml of phenanthrene-d₁₀ as an internal standard and analyzed by GC-MS.

4. Analysis of carbon and clay contents of suspended solids and sediment samples

Another twenty liters of water sample was filtered with 1.0 µm and 0.5 µm membrane filters (ADVANTEC Mixed Cellulose Ester) for the analysis of the carbon content of suspended solids. The samples thus obtained were freeze-dried. The carbon content of SS₁₀ was measured by NC analyzer (SUMIGRAPH NC-900, Sumika Bunseki Center, Co., Ltd.). However, this was not possible for SS₀.₅ samples because of

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Chemical formula</th>
<th>Water solubility (20°C) (mg/l)</th>
<th>logKow&lt;sup&gt;ab&lt;/sup&gt;</th>
<th>Koc&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Sales (kg)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Apr 2002–Mar 2003</th>
<th>Apr 2003–Mar 2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>C₁₂H₂₃NOS</td>
<td>4.9</td>
<td>4.6</td>
<td>580</td>
<td>9643</td>
<td>9716</td>
<td></td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>C₁₂H₁₆ClNOS</td>
<td>30</td>
<td>3.42</td>
<td>676</td>
<td>3426</td>
<td>2806</td>
<td></td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>C₁₁H₂₁N₅S</td>
<td>50</td>
<td>3.8</td>
<td>254</td>
<td>397</td>
<td>394</td>
<td></td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>C₁₇H₂₆ClNO₂</td>
<td>50</td>
<td>4.08</td>
<td>628</td>
<td>2994</td>
<td>2978</td>
<td></td>
</tr>
<tr>
<td>Simetryn</td>
<td>C₈H₁₅N₅S</td>
<td>400</td>
<td>2.6</td>
<td>333</td>
<td>1522</td>
<td>1393</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> According to ref. 16.

<sup>b</sup> 1-octanol/water partition coefficient.

<sup>c</sup> According to ref. 17.

<sup>d</sup> Amount of pesticide sold by the Japan Agricultural Association in the relevant areas of Ibaraki Prefecture, Japan.
the shortage of volume obtained.

The carbon content of the sediment sample, which was air-dried at room temperature, was also measured by NC analyzer. Moreover, the clay content of the sediment sample was determined using the pipette method.18)

Results and Discussion

1. Characteristics of suspended solids

As shown in Fig. 2, the concentrations of suspended solids (SS0.5 and SS1.0) were high from late April to early May, probably because of run-off from paddy fields. After this period, the concentrations decreased, except for the samples of October 29. The carbon content (%) and C/N ratio of suspended solids were 5.5 to 23 (average=8.4, median=7.1) and 5.9 to 10 (average=8.0, median=8.2), respectively (Fig. 2). During ordinary water discharge, the amounts of suspended solids loading to Sugao marsh from April to July were 235.2 kg and 9.5 kg for SS1.0 and SS0.5, respectively, which were estimated from their concentrations and the monthly water discharge data.

2. Pesticides in water

In water samples, periodic changes in the concentrations of esprocarb, thiobencarb, dimethametryn and pretilachlor appeared from late April to early May (Fig. 3a). On the other hand, the concentration of simetryn changed from late May to June (Fig. 3a). These periodic peaks of the pesticide concentrations were considered to be due to the timing of pesticides application.9) The amounts of pesticides loading as dissolved form to Sugao marsh were calculated as the sum of arithmetic means of each month from April to July (Table 3). Although sales of simetryn were lower than sales of esprocarb and thiobencarb, loading of simetryn as dissolved form was larger than esprocarb and thiobencarb (Tables 1 and 3). A similar

![Fig. 2. Concentrations of suspended solids and carbon content and C/N ratio in suspended solids. (Carbon content data of January 12, 2004, were not determined because of low concentrations of suspended solids.)](image)
tendency was reported in other studies where the run off ratio of simetryn from paddy fields was higher than that of esprocarb and thiobencarb due to its high water solubility and low logKow value.\textsuperscript{1,12) On the other hand, pretilachlor and thiobencarb differed in water solubility and sales, though pretilachlor had a higher logKow value than thiobencarb (Table 1). However, the concentration of pretilachlor in water was higher than that of thiobencarb (Fig. 3). It was also reported\textsuperscript{12) that the run off ratio of pretilachlor from paddy fields was higher than that of thiobencarb. Considering that compared to thiobencarb, pretilachlor had a lower adsorption ratio for several kinds of paddy soils\textsuperscript{19) and a lower Koc (Table 1), the

Fig. 3. Concentrations of pesticides in water, suspended solids and sediment at the study sites, Fureaibashi and Linuma river. (Sediment sample of June 21, 2003 was not collected from the Linuma river site.)
amount of pretilachlor loading as dissolved form in this study would be greater than that of thiobencarb or esprocarb.

3. Pesticides in suspended solids

Periodic changes in the concentration of pesticides in suspended solids collected at the two sampling sites appeared analogous to those in water (Figs. 3b, c, g and h). Although very low concentrations of pesticides as dissolved form were detected after August, the pesticides were frequently detected in suspended solids. Moreover, the concentrations of pesticide in SS0.5 were about 10 to 20 times higher than those in SS 1.0 (Figs. 3b, c, g and h). This might be due to the difference in surface area between the two fractions of suspended solids and strong hysteresis.14,20) As shown in Figs. 3b, c, g and h, the concentrations of esprocarb in suspended solids were higher than those of other pesticides, and thiobencarb was detected in relatively higher concentrations in SS0.5 at the Iinuma river site, and dimethametryn in SS 1.0 at Fureaibashi. Here, the partition ratio of suspended solids (PRss) is defined as below and calculated:

\[
PRss(\%) = \frac{100 \times C_{ss1.0}}{C_{w} + C_{ss1.0} + C_{ss0.5}}
\]

where \(C_{ss}\) is the weight of pesticides in suspended solids from a given size fraction, \(C_{w}\) is the weight of pesticides in filtered water, and \(C_{ss1.0}\) and \(C_{ss0.5}\) are the weights of pesticides in each fraction of suspended solids. Calculated average, median and maximum values of PRss are listed in Table 4. It is clear that most of the pesticides in whole water samples \((C_{w} + C_{ss1.0} + C_{ss0.5})\) were present in filtered water, namely the PRss of total suspended solids was only 0.37–2.5% as the median value (Table 4). Esprocarb, thiobencarb had higher PRss values than pretilachlor and simetryn in both size fractions (Table 4), probably because the latter two pesticides had lower water solubility and higher logKow and Koc values (Table 1). Although most of the pesticides were present as dissolved forms, the PRss was over 5% by calculation in some case (Table 4). Moreover, the pesticides were detected in suspended solids, even if their concentration in water was low or undetectable (Figs. 3a, c, f and g). With rain fall event, the ratio of esprocarb adsorbed suspended solids in run off water from paddy fields was about 20%,11) probably because of the higher concentration of suspended solids compared with ordinary water discharge. The average and median values obtained from the small samples of water in the previous study13) were higher than those in the present study. This might be partly attributed to the higher frequency of detection

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Dissolved</th>
<th>SS total(^a)</th>
<th>SS1.0</th>
<th>SS0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount (kg)</td>
<td>Amount (g)</td>
<td>% of total loading(^a)</td>
<td>Amount (g)</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>23</td>
<td>1.1×10(^3)</td>
<td>4.6</td>
<td>6.1×10(^2)</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>9.4</td>
<td>3.4×10(^2)</td>
<td>3.5</td>
<td>1.4×10(^2)</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>9.0</td>
<td>2.6×10(^2)</td>
<td>2.8</td>
<td>1.9×10(^2)</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>43</td>
<td>3.6×10(^2)</td>
<td>0.84</td>
<td>2.4×10(^2)</td>
</tr>
<tr>
<td>Simetryn</td>
<td>21</td>
<td>8.9×10(^1)</td>
<td>0.42</td>
<td>7.3×10(^1)</td>
</tr>
</tbody>
</table>

\(^a\) Sum of SS1.0 and SS0.5

\(^b\) SS total/(dissolved+SS total)×100

\(^c\) SS1.0 (or SS0.5)/SS total×100

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>PR of SS total (%)</th>
<th>PR of SS1.0 (%)</th>
<th>PR of SS0.5 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n(^a)</td>
<td>Median</td>
<td>Average</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>23</td>
<td>2.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>17</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>26</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>16</td>
<td>0.56</td>
<td>0.79</td>
</tr>
<tr>
<td>Simetryn</td>
<td>15</td>
<td>0.37</td>
<td>0.47</td>
</tr>
</tbody>
</table>

\(^a\) Number of samples used for the calculation.
in this study. In turn, the sample volume of this study was thought to be appropriate to grasp the change in concentration and distribution of pesticides in suspended solids.

The amounts of pesticides loading as adsorbed form on suspended solids in Sugao marsh were calculated as the sum of the arithmetic means of each month from April to July (Fig. 4). The amount of esprocarb loading as total suspended solids (SS1.0 and SS0.5) in Sugao marsh from April to July was $1.1 \times 10^3 \text{ g}$, and it was higher than for any other pesticide (Table 3). On the other hand, the amounts of esprocarb loading with suspended solids during the monitoring period including rain fall events were higher than in this study. In this study, the amount of pesticide loading as adsorbed form was lower than that of dissolved form and the ratios of adsorbed forms against total pesticide loading were 0.42–4.6% (Table 3). Comparing the relative loading ratio of the pesticide adsorbed on SS1.0 and SS0.5 against total suspended solids, esprocarb and thiobencarb adsorbed on SS0.5 showed about one half of total suspended solids (Table 3). The amount of pesticide loading to Sugao marsh by suspended solids was much smaller than the amount of dissolved form.

However, the pesticide loading by suspended solids could be critical since the finer the particles of run off material, the stronger the adsorption–desorption hysteresis. It was thought that most of the pesticide adsorbed on suspended solids was not desorbed and hence accumulated in the sediment through sedimentation. It was also pointed out that the sedimentation by suspended solids on which pesticides were adsorbed was more important for the accumulation of pesticides in sediment than in water. The results of this study suggested that the smaller fraction was important for the loading to sediment.

4. Pesticides in sediment

A change in texture from clay to sand occurred at the Fureaibashi site during the monitoring period, and coincided with the decrease in the carbon content of sediment (Fig. 5). Since the concentrations of pesticides in sediments are recognized to be correlated with the carbon and the clay content of sediment, periodic changes in pesticide concentrations in sediments differed between the Iinuma river and Fureaibashi sites (Figs. 3d, e and i), probably resulting from the change in texture of the sediment. The concentrations of esprocarb and thiobencarb in sediment were higher than those of other pesticides. This is because these pesticides had lower water solubility and higher logKow and Koc values (Table 1). In April at the Fureaibashi site, these two pesticides were detected in sediment before the application of pesticides in paddy fields (Fig. 3). Since the same tendency was recognized previously, these pesticides might have remained to be adsorbed on sediment rich in clay and organic matter from the preceding year.

However, the texture of the sediment changed at the

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**Fig. 4.** Amounts of loading of pesticides as dissolved and adsorbed forms (SS1.0 and SS0.5) from April to July, 2003, at Iinuma river.

**Fig. 5.** Carbon and clay content of sediment.
Fureaibashi site during this study (Fig. 5). Therefore, the pesticide concentrations might have decreased since autumn at the Fureaibashi site. Moreover, vertical distributions of pesticide concentrations in sediment at the Fureaibashi site were not clearly shown between 0–5 cm and 5–15 cm samples (Figs. 3d and e) which might be due to the continuous disturbance of sediment by actual water flow.

5. Relationships of pesticides between in water, suspended solids and sediment

The patterns of change in pesticide concentrations in water were similar to those in suspended solids, but not those in sediment (Fig. 3). This is surely because the concentrations of pesticide in water, suspended solids and sediment are not always in equilibrium as shown in laboratory experiments.19) Furthermore, when suspended solids are smaller, the rate of deposition is slower in almost an exponential manner according to Stokes’s law.21) However, the sedimentation rate of suspended solids with pesticides and the characteristics of suspended solids as an adsorbent of pesticides were still obscure in the case of ordinary water discharge and of rain fall event. Further study of the role of suspended solids as a carrier of pesticides is necessary in the field and also in laboratory experiments.

Acknowledgments

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