Behavior of Several Herbicides Applied to Paddy Fields in Water-Sediment System

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Summary

Pesticides are applied to agricultural lands and released intentionally into the environment, resulting in the pollution in the environment and serious influences upon the various ecosystems. Therefore, the pesticides with low toxicity and short residual period have been considered as their important properties for their development and application. Rice production is the characteristic of Japanese agriculture, and about a half of the total pesticides is applied to paddy fields. So, many previous investigations on pesticides applied to paddy fields have been carried out on the behavior in and the runoff from paddy fields, and on their monitoring in river, lake and marsh water. Considering the behavior of pesticides in aquatic environment, sediment is very important because pesticides finally reach to sediment. In addition, suspended solids are also thought to be very important as a carrier of pesticides in water-sediment system. But, the fate of pesticides in sediment and suspended solids, their adsorption-desorption phenomena and their degradability in sediment were not sufficiently investigated. The objective of this study is to clarify the behavior of several herbicides applied to paddy fields in water-sediment system.

In the present study, five herbicides (esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn) applied to paddy fields were investigated, and their concentration change, distribution and loading amounts in water, suspended solids and sediment were monitored during two years at Sugao marsh, Ibaraki prefecture, Japan. In addition, the adsorption-desorption phenomena and the degradability of herbicides studied in water-sediment system were also investigated in the laboratory. Main results obtained were as follows:

1) Although the periodical changes in the concentrations of herbicides in water, suspended solids and sediment were caused by the timing of herbicide application in paddy fields, the concentration peaks of herbicides in the sediment were appeared later than those in water and
suspended solids. Furthermore, concentrations of herbicides in the sediment from inner marsh were higher compared with the input or output sites of Sugao marsh. It might be caused by the sedimentation of suspended solids with adsorbed herbicides. Concentrations of herbicides in the sediment were also affected by the change in the texture of sediment due to the disturbance by actual water flow. Loading of herbicides to marsh was mostly present as dissolved form. Concentrations of herbicides in fine suspended solids (0.5 to 1.0 μm) were higher than those in coarse suspended solids (more then 1.0 μm). Partition ratio of total suspended solids were 0.37-2.5% as the median value. The ratio of herbicide loading as adsorbed form against total herbicide loading were 0.42-4.6%. Herbicide loading by the fine suspended solids was estimated to be 18 to 59 % of total suspended solids, indicating their important roles as a carrier of herbicides.

2) All herbicides reached their adsorption equilibrium within 72 hours, and the adsorption ratios of esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn were 81.3, 78.9, 59.0, 57.6 and 78.8 (%), respectively. All adsorption data of herbicides studied fitted well to Freundlich equation. The extent of Freundlich coefficient, \( K_f \), increased in the following order: pretilachlor < dimethametryn < simetryn < thiobencarb < esprocarb. It was strongly suggested that the adsorption site of herbicides on sediment might be not only organic matter, but also mineral surface in sediment, especially for simetryn, dimethametryn and pretilachlor. The hysteresis of adsorption-desorption phenomena was observed for all herbicides studied. The process of dimethametryn and pretilachlor in adsorption-desorption hysteresis was affected by the presence of organic matter in sediment. The \( K_{oc} \) values obtained in this study were higher than the \( K_{oc} \) values for soils in the previous study. The \( K_{oc} \) values with sediment may not appropriate to predict the concentration of herbicide in the aquatic environment.

3) The amounts of esprocarb, thiobencarb and pretilachlor were decreased and degraded rapidly during 16 to 32 days after their application, and it might be caused by microorganisms
and dechlorination. On the other hand, the degradation of simetryn and dimethametryn in a simple water-sediment system were probably due to chemical decomposition, and these herbicides in sediment were in more persistence than other herbicides.

Based on the foregoing results, following discussion and conclusion can be deduced:

1) Sediment could act as a sink of herbicides in water-sediment system at river and marsh during ordinary water discharge. However, the sediment might become a source of herbicides when the sediment is disturbed by water flow and the fine particles with adsorbed herbicides in sediment are re-suspended in water. So, the sediment has a possibility to become either source or sink of herbicides in the aquatic environment depending on the hydrological conditions.

2) Adsorption-desorption characteristics and the degradability of herbicides obtained by the laboratory experiments as well as their chemical properties could not sufficiently explain for their residual tendency in the fields. It might be controlled by the adsorption characteristics of herbicides on the various and heterogeneous surfaces of organic matter and/or mineral structure. Furthermore, aging effect of herbicides in sediment might also affect the behavior of herbicides.

3) The present study on the behavior of several herbicides applied to paddy fields in water-sediment system will contribute to the prediction on the behavior of herbicides and other chemical substances in water-sediment system, and will be applicable to the appropriate usage of herbicides in agricultural lands.
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Chapter 1

Introduction

1-1 Background of this study

Various artificial chemical substances present in the environment are potentially harmful for the organisms in various ecosystems. These chemical substances are able to be distinguished by the manner of releasing them: accidentally or intentionally into the environment. In the case of the chemical substances released accidentally, they are usually used in closed system, and are able to be controlled by taking various counter measures at the points of release. However, the pesticides are applied to agricultural lands and released intentionally into the environment. Therefore, the pesticides have polluted the environment and exerted serious influences upon the various ecosystems. Rachel Carson was the first person who indicated the harmful influences of pesticides on ecosystem in her well-known book "Silent Spring" (Carson, 1962). Since the toxicity for wild animals and the persistence period of the pesticides had not been considered at that time, those pesticides have been widely used and remained in the environment, such as the persistent organic pollutants (POPs) and the endocrine disrupters (Tanabe, 2002). In Japan, the pesticides with low toxicity, short residual period and high selectivity have been considered as their important properties for their development and the application in the agricultural fields, especially since the Agricultural Chemicals Regulation Law was revised in the year of 1971. Therefore, serious pollution of pesticides has not been reported in Japan since 1971. Pesticides have contributed to the stable production of agricultural products and the reduction in farm working hours, and are indispensable as agricultural materials up to now. By the use of herbicides and machineries, over 50 hours of labor needed to work on 10a paddy fields in the 1950s have been reduced to under 2 hours at present time (Ueji and Inao, 2000). However, it is a growing concern that the fates and
influences of pesticides in the environment should not be over-looked, because they are released intentionally into the environment.

Many previous studies have been carried out to understand the behavior of pesticides in the environment. For example, the fate of pentachloronitrobenzene (PCNB) used as a fungicide in the intensive farming area was investigated, and it was shown that the concentration of PCNB in river water reflected the type of land use and the loading of PCNB into river during rainfall event. This was due to the soil particles containing PCNB which were run off from crop land (Fushiwaki et al., 1994). It was also shown that the run off ratio of pesticides applied to the orchard was far lower than that of paddy field (Sasaki, 1999). The fates of pesticides in soil environment were also studied. For example, the leaching of several pesticides in the upland field of Andosol was studied under natural rainfall condition (Suzuki, 2000). Moreover, due to the volatilization from water and soil surface, the pesticides with high Henry’s law constants were frequently detected in rainwater at even the off-period of their application (Suzuki et al., 2003). Furthermore, the investigation of pesticides applied to golf links was also carried out (Sudo and Kunimatsu, 1995). Thus, in Japan, many previous studies on the fates of pesticides in the various environments have been carried out.

Rice production is the characteristic of Japanese agriculture and about a half of the total pesticides is applied to paddy fields (Kanazawa, 1991). Since the herbicides applied to paddy fields were directly exposed to irrigation water, their run off ratios were higher than other pesticides (Kanazawa, 1991). The environmental risk assessment of herbicides applied to paddy fields requires the risk management, based on the evaluation of their toxicity (hazard assessment) and their exposure (exposure analysis) (Ueji and Inao, 2001). Hazard assessment requires the estimation of predicted no-effect concentration (PNEC), based on the result of herbicides toxicity test, and the exposure analysis also requires the estimation of predicted environmental concentration (PEC). After all, the environmental risk management of herbicide
is carried out, based on the characterization of PNEC and PEC. Estimation of PEC requires the monitoring in aquatic environment and the application of mathematical simulation models. Moreover, the estimation of PEC in aquatic environment should include the behavior and adsorption / desorption characteristics of herbicides in sediment. In addition, from the viewpoint of risk assessment in the aquatic ecosystem, the adsorption of the micro-organic pollutants on sediment was very important (Warren et al., 2003), since the pesticides applied to paddy fields were shown to influence on the lives of benthos and aquatic plants (Iwakuma et al., 1988; Hatakeyama and Sugaya, 2000).

Previous investigations on pesticides applied to paddy fields have been carried out, especially on the behavior in and the runoff from paddy fields (Hankawa, 1985; Numabe et al., 1992; Nagafuchi, 1999; Tanigawa and Nishimura, 1999; Yamamoto et al., 1999; Fajardo et al., 2000) in addition to their monitoring in river water (Maru, 1985; Iizuka, 1989; Yamaguchi et al., 1991; Sasagawa et al., 1996; Kondo et al., 2001) and that in lake and marsh water (Imanaka et al., 1985; Shiraishi et al., 1988; Tsuda et al., 1996; Tsukabayashi et al., 1996; Nohara et al., 1997; Nagafuchi et al., 2002; Sudo et al., 2002). However, these previous studies were not carried out on the fate of pesticides in sediment. Most of studies on sediment have been carried out for pesticides with high persistency in the past. For example, the fates of dichlorodiphenyltrichloroethane (DDT), chlordane and endrin were studied. Although the fates of pesticides used at present time have been investigated scarcely (Warren et al., 2003), some pesticides in present use were investigated in the sediments at the Humber river in UK (Long et al., 1998), Liao-He and Yangtse in China (Gfrerer et al., 2002), the Blackwater and the Whitewater rivers in UK (Daniels et al., 2000) and the pond at water catchments area in Sweden (Kreuger, 1999). The pesticides detected in these studies were used for crop land. Since the most of pesticides in Japan were applied to paddy fields, Ministry of the Environment have investigated the concentrations of various chemical substances in sediment including the
pesticides applied to paddy fields. However, the results of this investigation published in "Chemicals in Environment" (Environmental Health and Safety Division, Ministry of the Environment, 2002) could not evaluate the fate of pesticides in sediment, because the sampling points and the periods were somewhat unreasonable considering their actual application conditions. Some studies on the fate of pesticides applied to paddy fields in sediment were carried out at the irrigation canal surrounding the paddy fields (Nakamura et al., 1985), the Ishikari river (Ohyama et al., 1987) and the Koise river (Iwakuma et al., 1993). But, the data of pesticides in sediment were not sufficient, especially those for the fate of pesticides applied to paddy fields in lake and marsh sediments. In addition, although the adsorption and desorption phenomena of pesticides in sediment was thought to be very important to determine the fate of pesticides in sediment, the number of previous investigations in sediment are less than those in soils (Kanazawa, 1989; Hayakawa et al., 1994; Kibe et al., 2000a; Kibe et al., 2000b; Fushiwaki and Urano, 2001; Ebato et al., 2001). Furthermore, some investigations on the degradability of pesticides in water-sediment system have been carried out (Kitano and Minami, 1996 and 1997; Araki et al., 2003; Kodaka et al., 2003). However, the degradability of pesticides applied to paddy fields was not investigated in these studies. Since the estimation of PEC requires the information for adsorption and desorption phenomena and degradability of herbicides in sediments both in fields and laboratory conditions, the investigation of pesticides on these aspects in sediment is necessary. It was thought that the sedimentation of suspended solids with adsorbed pesticides was also important for the translocations of pesticides from water to sediment (Inoue et al., 2002). And, the investigation on the concentration change and the loading amount of pesticides in suspended solids is thought to be very important with respect to the loading of pesticides on sediment. The previous studies of pesticides in suspended solids have been carried out on their adsorption in the laboratory condition and the run off from paddy fields during the rainfall event in rice transplanting (Numabe et al., 1992; Sasagawa et al.,
Unfortunately, to our knowledge, the concentration change and the loading amount of pesticides in suspended solids were not investigated.

1-2 Objective of this study

Objective of this study is to clarify the behavior of several herbicides applied to paddy fields in water-sediment system. In this study, esprocarb (\(S\)-benzyl 1,2-dimethylpropyl (ethyl) thiocarbamate), thiobencarb (\(S\)-4-chlorobenzyl(diethyl- thiocarbamate), dimethametryn (\(N^2\)-(1,2- dimethylpropyl)-\(N^\prime\)-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)-2- methylthio -1,3,5-triazine) were selected as the target herbicides. Sugao marsh located at the southwestern part of Ibaraki prefecture was chosen as a study area, and its general descriptions and the characteristics of water quality were described in chapter 2. In chapter 3, the concentration change and the distribution of these herbicides in water and sediment were investigated at five study sites in Sugao marsh. In chapter 4, the concentration change of herbicides in water, suspended solids and sediment were investigated at the two study sites located at the inner marsh and the river mouth, and the amounts of herbicides loading in water and suspended solids of two size fractions during ordinary water discharge were also investigated at the river mouth. In chapter 5, the adsorption and desorption characteristics of herbicides in sediment were examined, and both the roles of organic matter and mineral surface for adsorption and desorption phenomena were investigated. In chapter 6, the characteristics of herbicides degradability in a simple water-sediment system were examined. In chapter 7, based on previous chapters, over-all discussion on the behavior of several herbicides applied to paddy fields was presented in water-sediment system.

1-3 Herbicides investigated in this study
As mentioned above, five herbicides, esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn were investigated in this study. These herbicides are applied to paddy fields, and widely used in the study area. Pesticides are able to be classified based on their usage and chemical structure (Roberts, 1998). Esprocarb and thiobencarb are classified as thiocarbamate herbicide, pretilachlor as chloroacetanilides herbicide, and dimethametryn and simetryn as 1,3,5-triazine herbicides (Figure 1-1), and the chemical structures of herbicides studied were described in Figure 1-2. Chemical properties of herbicides studied and their commercial amounts sold by the Japan Agricultural Association in the relevant areas of Ibaraki prefecture were described in Table 1-1.
Table 1-1. Several physicochemical properties of herbicides studied and their amounts of sales.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Chemical formula</th>
<th><em>Water solubility (20°C)(g L⁻¹)</em></th>
<th><em>b</em> logKow</th>
<th><em>c</em> Koc</th>
<th>d The amount of sales (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>C₁₃H₁₂N₂OS</td>
<td>4.9</td>
<td>4.6</td>
<td>580</td>
<td>8441</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>C₁₂H₁₆ClNOS</td>
<td>30</td>
<td>3.42</td>
<td>676</td>
<td>1133</td>
</tr>
<tr>
<td>Dimethametrin</td>
<td>C₁₁H₂₁N₂S</td>
<td>50</td>
<td>3.8</td>
<td>254</td>
<td>351</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>C₁₇H₂₂ClNO₂</td>
<td>50</td>
<td>4.08</td>
<td>628</td>
<td>2661</td>
</tr>
<tr>
<td>Simetryn</td>
<td>C₂₂H₁₄N₄S</td>
<td>400</td>
<td>2.6</td>
<td>333</td>
<td>1176</td>
</tr>
</tbody>
</table>

*a* according to The pesticide manual 12th (2000).  
*b* 1-octanol/water partition coefficient.  
*c* according to Kanazawa (1996).  
*d* amount of herbicides sold by the Japan Agricultural Association in the relevant areas of Ibaraki prefecture, Japan.
Pesticides

Usage
- herbicides
- insecticides
- fungicides
- plant growth regulators
- attractants
- repellents
- raticides
- spreading agents
- others

Chemical structure
- amides
- anilides
- arylalanines
- aryloxyalkanamides
- aryloxyalkanoic acids
- arylphenoxypropionic acids
- benzofuranyl alkanesulfonates
- benzoic acids
- bipyridilium herbicides
- bis-carbamates
- chloracetanilides
- cyclohexanedione oximes
- dinitroanilines
- dinitrophenols
- diphenyl ethers
- hydroxybenzonitriles
- imidazolinones
- isoxazoles
- organophosphorus herbicides
- pyridazinones and pyrazoles
- pyridine acids
- 4-pyridones
- quinolinicarboxylic acids
- sulfonylureas
- thiocarbamates
- 1,3,5-triazines
- 1,2,4-triazines
- triazoles
- triazolopyrimidines
- uracils
- ureas

Herbicides in this study
- pretilachlor
- esprocarb
- thiobencarb
- simetryn
- dimethametryn

Figure 1-1. Classification of pesticides by their usage and chemical structures (Roberts 1998).
Figure 1-2. Chemical structure of a) esprocarb [(S-benzyl 1,2-dimethylpropyl (ethyl) thiocarbamate], b) thiobencarb [(S-4-chlorobenzyldiethyl- thiocarbamate ], c) pretilachlor [2-chloro-2',6'- diethyl-N-(2-propoxyethyl) acetamide], d) dimethametryn [N2-(1,2- dimethylpropyl)-N′-ethyl-6- methylthio-1,3,5-triazine-2,4-diamine], and simetryn [4,6-bis (ethylamino)-2-methylthio-1,3,5-triazine].
Chapter 2

General description of study area, and characteristics of water quality

2-1 Introduction

As mentioned in chapter 1, fates of herbicides were monitored at Sugao marsh in this study. However, as the basin of this marsh is surrounded by paddy fields and partly by residential area it was thought that the aquatic environmental of this marsh was affected by the inflow water having various kinds of water qualities. So, it was very important to investigate the influence of hydrological conditions and land use of surrounding area on water quality at sampling sites. The aim of this chapter is to describe the study area and to show the characteristics of general water quality at study sites.

2-2 General information on the study area

Sugao marsh is located at the southwestern part of Ibaraki prefecture, about 40 km northeast of Tokyo, Japan. The Inuma and Egawa Rivers flow into north side of the marsh, and the Higashinire River flow into east side of the marsh (Figure 2-1). These rivers flow through the paddy field area and partly urban area, and the marsh is also mostly surrounded by paddy fields and partly by a residential area. The topographical slope at the basin of Sugao marsh is quite gentle. Therefore, it was recognized that the river water was occasionally in the condition of stagnation or even in backward flow at the some locations. The Inuma River flow out from this marsh and join to the Tone River about 4 km south from this marsh.

The size of this marsh is about 5 km from north to south, and about 0.6 km from the east to west, having a surface area of about 2.32 km² where about 80% being covered with various hygrophytes in rich bio-diversity (Ibaraki Nature Museum., 1996). So, this marsh is designated as the nature conservation area of Ibaraki prefecture since 1975. And, fine-earth,
sand particles and plant debris had been accumulated, and hydrarch succession had been progressed at this marsh since 1950’s (Obata et al., 1996).

2-3 Materials and methods

2-3-1 Descriptions of sampling sites and collection of samples

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 Linuma River (Figure 2-1). Collection of water samples were conducted from April 15th, 2002, to February 18th, 2003, and the frequency of the sample collection was about once a week from the middle of April to the end of May when the water quality was expected to be changed due to the agricultural practices in the paddy fields, and twice a month in June, January and February, and once a month in July and August. Water samples were collected with a stainless beaker, and stored in polypropylene bottle (250 mL in volume). The sample from the RI site was obtained since April 25th, 2002. Samples were not be collected from site 3 since July, 2002.

2-3-2 Analytical methods of water quality

pH value was measured by glass electrode (HM-11P, Toa Denpa Corporation). Electric conductivity was measured by platinum electrode (CM-11P, Toa Denpa Corporation). When water sample was collected, the pH and electric conductivity values were measured simultaneously. Water sample was filtered through 0.20 μm cellulose acetate membrane filter (ADVANTEC, DISMIC-25CS) for measuring the concentration of dissolved organic carbon and inorganic ions. The concentration of dissolved organic carbon was measured by TOC-5000 (Shimadzu Corporation). The inorganic ions determined in this study included potassium, ammonium, sodium, magnesium and calcium as cation, and fluoride, chloride, nitrite, nitrate,
Phosphate and sulfate as anion. These ions were measured by ion chromatograph (DX-500, Dionex Corporation) except for nitrite and nitrate ions. They were detected by ultraviolet detector (SPD-10AVP, Shimadzu Corporation). Concentration of total phosphorus in water sample was measured following after JIS method (Japanese Standards Association, 2002).

2-4 Results and discussion

2-4-1 pH

The pH of the water samples from study sites were in the range from 6.87 to 9.33, and the change in pH were shown in Figure 2-2. The change in pH of the water samples from site3 was somewhat larger than other sites. In general, pH of water from lake and marsh are between 6 to 8 (Saijyo and Mitamura, 1995). However, the pH over 9 are often observed in the present study. This is probably because phytoplankton consumes dissolved carbon dioxide by photosynthesis (Saijyo and Mitamura, 1995).

2-4-2 Electric conductivity

Changes in electric conductivity were shown in Figure 2-3. The average value of electric conductivity of river water in Japan is 0.130 dS m⁻¹ (Saijyo and Mitamura, 1995). On the other hand, the electric conductivity obtained from this study area were higher than that average value, and were in the range from 0.232 to 0.447 dS m⁻¹. Moreover, relatively higher values of electric conductivity were observed in winter period. A reason of high electric conductivity values might be due to the inflow of domestic and agricultural wastes water having high electric conductivity (Murayama et al., 2001) in addition to the decrease in the quantity of inflow water during winter period.

2-4-3 Concentrations of dissolved organic carbon
Concentrations of dissolved organic carbon were shown in Figure 2-4. The range was from 1.75 to 8.66 mg L\(^{-1}\). The concentrations of dissolved organic carbon increased at early June, and somewhat higher concentrations were measured in winter. Since the high concentration of dissolved organic carbon was observed from domestic wastewater (Murayama et al., 2001), the higher concentrations obtained from this study might be due to the inflow of domestic waste water.

**2-4-4 Concentration of cations and anions**

Changes in the concentrations of cation and anion were shown in Figure 2-5 and 2-6, respectively. Higher concentrations of sodium, calcium, chloride, nitrate and sulfate ions were detected compared with other ions. These ions were possibly affected by the use of fertilizers and other agricultural practices (Murayama et al., 2001). High concentration of chloride ion was also reported in the previous study (Hirayama, 1985), suggesting that the factors of higher concentration of chloride ion were derived from fertilizers of potassium chloride, inflows of domestic waste water and depositions of sea salt (Matsuo, 1989; Murayama et al., 2001). Furthermore, the use of irrigation water in paddy fields around Sugao marsh basin from Lake Kasumigaura, having higher concentration of chloride ion (Murayama et al., 2001), would be also a reason for the high concentration of chloride ion. Concentrations of nitrate ion were decreased during the period of agricultural practices, and increased after this period. The same tendency as for the present study was also reported in the previous studies in Lake Kasumigaura basin (Suzuki and Tabuchi, 1984; Murayama et al., 2001). They found that the concentration of nitrate ion decreased in river water after agricultural practices both for the basin inflow and the irrigation water from Lake Kasumigaura (Murayama et al., 2001). While the increase in nitrate ion concentration might be affected by the inflow of agricultural waste water having the higher concentration of nitrate ion in that period (Suzuki and Tabuchi, 1984). Phosphate ion was not
detected for almost all water samples, because phosphate ion would be mostly adsorbed on suspended solids (Kondoh et al., 1993; Murayama et al., 2001).

2-4-5 Concentration of total phosphorus

Concentrations of total phosphorous were shown in Figure 2-7. It was in the range from 0.09 to 1.26 mg L\(^{-1}\). The variation of the total phosphorous concentration was large during the period of agricultural practices, probably due to the higher discharge of run off of suspended solids with adsorbed phosphorous during this period (Kondoh et al., 1993; Murayama et al., 2001). The highest concentration of total phosphorous sample was observed at Site2 on February 18th, 2003, probably being affected by the highest population of migratory birds that were observed in winter at circumference of Site 2 (Yanagisawa et al., 2003). Since the concentrations of total phosphorous, and nitrate and ammonium ions in paddy field were increased in the period of migratory birds in winter (Ohata and Yamamoto, 1999), this was probably affected by the migratory birds.

2-5 Conclusion

Water quality in this study area changed at every sampling sites and periods. The pH and electric conductivity were increased from May to June, probably due to the agricultural practices, but the concentration of nitrate ion was decreased. The electric conductivity and the concentrations of nitrate and ammonium ions were increased from autumn to winter period, probably due to the inflow of domestic and agricultural wastes waters together with small water discharge. Furthermore, the water quality was also affected by the irrigation water from Lake Kasumigaura in addition to the activities of migratory birds.
Figure 2-1. Location of sampling sites at Sugao marsh.
Figure 2-2. Periodic changes in pH at sampling sites.
Figure 2-3. Periodic changes in EC at sampling sites.
Figure 2-4. Periodic changes in DOC concentration at sampling sites.
Figure 2-5. Periodic changes in the concentrations of cations at sampling sites. (a:Na⁺, b:Ca²⁺, c:Mg²⁺, d:K⁺, e:NH₄⁺)
Figure 2-6. Periodic changes in the concentrations of anions at sampling sites. (a: SO$_4^{2-}$, b:Cl$^-$, c:NO$_3^-$, d:NO$_2^-$, e: F$^-$)
Figure 2-7. Periodic changes in the concentrations of total phosphorus at sampling sites.
Chapter 3
Concentration and distribution of several herbicides applied to paddy fields in water and sediment from Sugao marsh

3-1 Introduction

In Japan, as mentioned in chapter 1, 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 (Hankawa, 1985; Numabe et al., 1992; Tanigawa and Nishimura, 1999; Yamamoto et al., 1999; Fajardo et al., 2000) in addition to their monitoring in water at several rivers (Maru, 1985; Yamaguchi et al., 1989; Sasagawa et al., 1996; Kondo et al., 2001) and lakes (Shiraishi et al., 1988; Tsukabayashi et al., 1996; Nohara et al., 1997; Sudo et al., 2002). 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 et al., 1998; Kreuger et al. 1999; Daniels et al., 2000; Gfrerer et al., 2002). 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 of the total pesticides are applied to paddy fields (Kanazawa, 1991). Although the marsh connected with paddy fields at plain area has rich bio-diversity and may be affected by pesticides, the investigations about pesticides concentrations in sediment in a marsh have not been carried out. So, it is very important to clarify the tendency of pesticide concentration change and distribution in water and sediment in a marsh. The aim of this chapter was to monitor the concentration of the selected herbicides both in water and sediment in a marsh connected with paddy fields, and to elucidate the distribution and persistence of the herbicides in sediment.
3-2 Materials and methods

3-2-1 Brief descriptions of the sampling sites and collection of samples

As shown in the previous chapter, water samples were collected at five representative sites at Sugao marsh, Ibaraki prefecture, Japan. 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 Inuma River (Figure 2-1).

Considering the application timing of the herbicides 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 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 of 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.

3-2-2 Herbicides

Four herbicides (esprocarb, thiobencarb, pretilachlor, dimethametryn) were selected and analyzed in this chapter. The selection was based on the commercial amounts of herbicides sold by the Japan Agricultural Association in the relevant areas of Ibaraki prefecture, Japan (Table 1-1). All standard herbicides used in this study were obtained from Wako Jyunyaku Kogyo, Co., Ltd., except for dimethametryn which was provided by Kanto Kagaku, Co., Ltd. The chemical properties and structural formulas of the herbicides studied were described in Table 1-1 and Figure 1-2 in chapter 1, respectively.
3-2-3 Sample processing for herbicides analysis

*Water sample*

Five hundred milliliter of the water sample was shaken with 50 mL of ethyl acetate for 5 minutes after addition of 30 g of NaCl, and the organic layer filtered through anhydrous Na$_2$SO$_4$. 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$_2$SO$_4$ placed on 1 g florisil containing 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 of acetone containing 0.05 µg mL$^{-1}$ phenanthrene-d$_{10}$ as an internal standard and finally analyzed by GC/MS.

*Sediment sample*

Sediment samples were passed through a 2 mm sieve and thoroughly mixed, centrifuged at 3000 rpm for 20 minutes and the supernatant was discarded. 10 g dry weight of the sample was shaken with 50 mL of acetone for 30 minutes 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 minutes. The organic layer was filtered through anhydrous Na$_2$SO$_4$ 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 Na₂SO₄ placed on 1.0 g silica gel containing 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 N₂. The residue was further purified by graphite carbon cartridge (Supelco, Co., Ltd.). The cartridge volume of 500 mg/5 mL was previously conditioned with 30 mL of acetone. After conditioning, the residue was dissolved in 5 mL of the solvent (n-hexane : acetone = 95 : 5 (v/v)). The sample was applied to cartridge and another 20 mL of acetone was applied to the cartridge. Both eluates were combined and concentrated to 1 mL with a rotary evaporator and dried under N₂. The residue was again dissolved in 5 mL of acetone including 0.05 μg mL⁻¹ phenanthrene-d₁₀ 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.).

**Analysis of herbicide**

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 and recoveries were shown in Table 3-1 and the data were not corrected by these recoveries.

**3-3 Results and discussion**

**3-3-1 Herbicides in water**

Periodic changes in the concentrations of herbicides in water samples appeared from late April to early May (Figure 3-1). These periodic peaks of the herbicide concentrations were
considered to be due to the timing of herbicides application, as pointed out in other previous studies (Maru, 1985; Yamaguchi et al., 1989; Sasagawa et al., 1996; Kondo et al., 2001). The patterns of herbicide concentration peaks clearly corresponded to the timing of application in 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 a half or one third of the marsh (Figure 3-1). The pesticides 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 discharge 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 3-1) 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 herbicides in the present study were shorter than that observed for the Lake Kasumigaura.

3-3-2 Herbicides in sediment

The highest herbicide concentrations in the sediment were detected at site 1 (Figure 3-2). The concentrations of herbicides 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 3-2). 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 shown in “Chemicals in the environment” (Environmental Health and Safety Division, Ministry of the Environment, 2002) was 3/165 for thiobencarb. Higher frequency was observed in the present study for thiobencarb in the sediments. The concentration peaks of herbicides in the sediment appeared in late May to early June (Figure 3-2). Although the concentration peaks are probably caused by the timing of application as observed in the case of water samples, the herbicides concentration peaks were appeared at later periods than in water. The later appearance of the herbicides 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 in the sediment even at November at the downstream area of the Ishikari River, about 150 km distance from the paddy field area (Ohyama et al., 1987). Thus, the herbicides 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 3-2, the concentrations of four herbicides correlated very well with the carbon content in the sediment (significant level at 1%), suggesting the possibility that the herbicides 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 3-3), the herbicide concentration in the sediment at site 1 was higher than other sampling sites. According to Long et al., (1998), the deposition processes of suspended solids due to a decrease in flow rate affect various properties of sediments and the quantity of persistent organic 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 (Figures 3-1 and 3-2). 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 due to photo-dissociation and vaporization, but also translocation to the sediment.

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

3-4 Conclusion

The concentrations of four herbicides in water and sediment were monitored to clarify their periodical change and distribution in Sugao marsh. Although the periodical changes in the concentrations of herbicides in water and sediment were caused by the timing of herbicide application, the herbicides concentration peaks in the sediment were appeared at later periods than in water. The concentrations of herbicides in the marsh water were relatively lower than the site of river water, probably due to the dilution effect. The concentrations of herbicides in the sediments at sampling sites located inner marsh were higher than at sampling sites located at input or output points of Sugao marsh. The concentrations of four herbicides in sediments correlated very well with the carbon content in the sediment (significant level at 1%). It was
suggested that the herbicides might be adsorbed on organic matter in the sediment at Sugao marsh.
### Table 3-1. Detection limits and recoveries of herbicides studied.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Detection limits</th>
<th></th>
<th>Recoveries</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water (µg L⁻¹)</td>
<td>sediment (µg kg⁻¹)</td>
<td>water (%)</td>
<td>sediment (%)</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>0.02</td>
<td>8.0</td>
<td>98</td>
<td>4.1</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>0.04</td>
<td>10</td>
<td>95</td>
<td>5.8</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>0.02</td>
<td>4.0</td>
<td>104</td>
<td>4.8</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>0.04</td>
<td>10</td>
<td>109</td>
<td>7.2</td>
</tr>
</tbody>
</table>
Table 3-2. Correlation between herbicide concentration and carbon content in sediment samples.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Number of samples</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>n=46</td>
<td>0.511**</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>n=43</td>
<td>0.646**</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>n=41</td>
<td>0.550**</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>n=34</td>
<td>0.552**</td>
</tr>
</tbody>
</table>

**Significant at p<0.01
Table 3-3. Average carbon content in sediment samples.

<table>
<thead>
<tr>
<th></th>
<th>Number of samples</th>
<th>Average carbon content (%)</th>
<th>Coefficient of variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>n=11</td>
<td>7.7</td>
<td>4.8</td>
</tr>
<tr>
<td>Site 2</td>
<td>n=11</td>
<td>3.6</td>
<td>30.4</td>
</tr>
<tr>
<td>Site 3</td>
<td>n=8</td>
<td>5.6</td>
<td>23.9</td>
</tr>
<tr>
<td>Site 4</td>
<td>n=11</td>
<td>4.0</td>
<td>18.9</td>
</tr>
<tr>
<td>RI</td>
<td>n=10</td>
<td>1.7</td>
<td>43.6</td>
</tr>
</tbody>
</table>
Figure 3-1. Concentration of herbicides in water at sampling sites.
Figure 3-2. Concentration of herbicides in sediment at sampling sites.
Chapter 4

Concentration and loading of several herbicides in water, suspended solids and sediment during ordinary water discharge in Sugao marsh

4-1 Introduction

In Japan, as mentioned in the previous chapters, many studies have been carried out on the behavior of pesticides applied to paddy fields in the aquatic environment. These studies have investigated their fate in the paddy fields and the run off (Hankawa, 1985; Numabe et al., 1992; Tanigawa and Nishimura, 1999; Yamamoto et al., 1999) and their concentrations monitored during a certain period in water from rivers (Maru, 1985; Yamaguchi et al., 1989; Sasagawa et al., 1996; Kondo et al., 2001) and lakes (Shiraishi et al., 1988; Tsukabayashi et al., 1996; Nohara et al., 1997; Sudo et al., 2002). Especially, the studies on the pesticide residues in sediment become indispensable for benthos and aquatic plants, because the disappearance rate of persisted pesticide in sediment is generally delayed comparing with other natural conditions (Gao et al., 1997). It was observed that the pesticide concentration in sediment was changed when the physicochemical properties of sediment were changed with the rate of water flow (Nakamura et al., 1985; Long et al., 1998; chapter 3 of this study), suggesting that the accumulation of pesticides in sediment probably related with the precipitation of suspended solids on which pesticides were adsorbed (Inoue et al., 2002). So, the behavior of pesticide in suspended solids in rivers and lakes should be investigated not only at rainfall event but also during ordinary water discharge. However, the studies on the pesticide concentration in suspended solids have been carried out mainly at rainfall event (Numabe et al., 1992; Sasagawa et al., 1996; Nakano et al., 2004). This is because enough amounts of suspended solids for analysis could be obtained. Although several studies were conducted during ordinary water discharge, the frequencies of detection of pesticide in suspended solids were very low because
of the shortage in the amounts of sample enough to be analyzed (Tanabe et al., 1998; Inoue et al., 2002; Nakano et al., 2004). Among suspended solids, fine particles were important as a carrier for pesticide in run off materials (Wu et al., 2003). Therefore, it is necessary to prepare ample amounts of suspended solids and to conduct the study on the concentration of pesticide in different size of suspended solids during ordinary water discharge.

The aim of this chapter is to analyze the concentrations of the herbicides in suspended solids of two size fractions together with those in water and sediments in marsh and river of the study sites, and to estimate the amount of herbicide loading both as dissolved form in water and as adsorbed forms on suspended solids during ordinary water discharge.

4-2 Materials and methods

4-2-1 Brief descriptions of the sampling sites and collection of samples

All samples in this chapter were collected at two sites, Fureaibashi (Site 2) and Inuma river (RI), located inner mash and river mouth, respectively (Figure 2-1).

Considering the application timing of the herbicides in paddy fields, collection of water, suspended solids and sediment samples were conducted from April 23th, 2003 to March 10th, 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 least two days before sampling. The frequency of the sample collection was about once a week from April 23th, 2003 to July 3th, 2003 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 June 21th, 2003 was not collected from RI site.

Water samples were collected with a stainless beaker and stored in a brown glass bottles. Suspended solids samples were collected from very large volume of 100 L of water sample collected with a polyethylene beaker and stored in each five 20 L polyethylene tanks.
Suspended solids samples of different size in water were filtrated as describe later in the section of “Sample processing”. The core samples of sediment were collected with Multi-sampler (DIK-180A, Daiki Rika Kogyo Co., Ltd.) at Site 2, and divided into two layers of 0-5 cm and 5-15 cm, and stored in glass bottles. At the river mouth, RI site in this study, sediment samples were collected from the surface of about 5 cm depth with a dipper because of the difficulty to obtain core sample.

4-2-2 Data of water discharge

The data of water discharge were provided from Sakai Branch Office of Civil Engineering Department, Ibaraki prefecture, and were obtained from the observation frequency of three times a month at Maaraibashi, about 1.5 km upper stream from the RI site. Since the water quantity may be similar between Maaraibashi and RI site where no large input is present, water discharge at Maaraibashi is sought to be comparable with that at RI site. The average of monthly water discharge was calculated from the arithmetic means at each measurement times in a month, excluding the exceptional data which were remarkably different from other measurement data in a same month. These water discharge data from April to July were used to estimate the loading of suspended solids and herbicides, because the frequency of sampling was reduced to once or twice a month after August.

4-2-3 Herbicides

Five herbicides (esprocarb, thiobencarb, pretilachlor, dimethametryn, simetryn) were selected and analyzed in this chapter. The selection was based on the commercial amounts of herbicides sold by the Japan Agricultural Association in the relevant areas of Ibaraki prefecture, Japan (Table 1-1). All standard herbicides used in this study were obtained from Wako Jyunyaku Kogyo, Co., Ltd., except for dimethametryn which was provided by Kanto Kagaku,
Co., Ltd. The chemical properties and structural formulas of the herbicides studied were described in Table 1-1 and Figure 1-2 in chapter 1, respectively.

4-2-4 Sample processing for herbicides analysis

Water sample

Five hundred mL of water samples were filtered through the 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 SS_{1.0} and SS_{0.5}, respectively. These filters were dried at 105°C for 24 hours and the weights of suspended solids were measured. The filtrated water samples was shaken by hand with 50 mL of ethyl acetate for 5 minutes after addition of 30 g of NaCl, and the organic layer was filtered through anhydrous Na_{2}SO_{4}. 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 N_{2}, 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 n-hexane was passed through the cartridge and the herbicide retained in the cartridge was extracted with 10 mL n-hexane/acetone, 85/15 (v/v). This extract was evaporated to about 1 mL with a rotary evaporator and dried under N_{2}. The residue was dissolved in 1 mL of acetone containing 0.05 µg mL^{-1} phenanthrene-d_{10} as an internal standard and finally analyzed by GC-MS.

Suspended solids sample

Eighty liter of water samples was filtered with 1.0 µm and 0.5 µm glass-fiber filters (ADVANTEC GA-100 and GC-50) for the collection and analysis of herbicides concentrations in suspended solids. These filters were extracted two times with 200 mL of acetone by ultrasonic wave. As for the SS_{0.5} samples, 50 mL of acetone was used for extraction in the same
manner (in the following sentences, figures in a parenthesis are expressed for the SS0.5 samples). Then, acetone extract was evaporated to about 100 mL (10 mL) with a rotary evaporator and combined in 200 mL (100 mL) of 5% NaClaq and shaken with 50 mL (30 mL) of ethyl acetate for 30 minutes. 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. After drying, the residue was dissolved in 5 mL of n-hexane and was passed through the silica gel cartridge (Waters Sep-Pak-Plus) washed with 5 mL of n-hexane before sample loading. Then, 5 mL of n-hexane was passed through the cartridge and the herbicide retained in the cartridge was extracted with 6 mL of n-hexane/acetone, 4/1 (v/v). This extract was evaporated to approximately 1 mL with a rotary evaporator and dried under N2. Then, the residue was dissolved in 2 mL of n-hexane/acetone, 1/1 (v/v), and passed through graphite carbon cartridge (Supelco, Co., Ltd. 500 mg / 6 mL) washed with 5 mL of each n-hexane and acetone before sample loading. And, 5 mL of n-hexane/acetone, 1/1 (v/v) was passed through the cartridge. Seven mL of eluate was concentrated to about 1 mL with a rotary evaporator and dried under N2. The residue was dissolved in 3 mL (1 mL) of acetone containing 0.05 μg mL⁻¹ phenanthrene-d₁₀ as an internal standard and finally analyzed by GC-MS.

*Sediment sample*

Sediment samples were passed through a 2mm sieve, thoroughly mixed and centrifuged at 3000 rpm for 20 minutes. And the supernatant was discarded. Ten grams as dry weight of the sample was shaken with 50 mL of acetone for 30 minutes and filtered with a 1.0 μm glass filter (Whatman GF/B). Then, the sample was evaporated to about 10 mL with a rotary evaporator, and 100 mL of 5% NaClaq was added and shaken with 30 mL of ethyl acetate for 30 minutes. 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 n-hexane, and sulfur was removed by copper shot column. Then, the sample was cleaned up by both silica gel and graphite carbon in the same manner as for suspended solids. Finally, the sample was dissolved in 5 mL of acetone containing 0.05 µg mL⁻¹ phenanthrene-d₁₀ as an internal standard and analyzed by GC-MS.

Analysis of herbicides

All samples in the present study were analyzed by Hewlett Packard 6890 GC equipped with a fused silica capillary column (DB-5, 30 m length and 0.25 mm internal diameter, 0.25 µm film) and with 5973N MS operated in the selected ion monitoring mode. Their detection limits and recoveries were shown in Table 4-1 and the data were not corrected by these recoveries.

Sample processing for carbon and clay content analysis

Another twenty liter of water sample was filtered with 1.0µm and 0.5 µm membrane filters (ADVANTEC Mixed Cellulose Ester) for the analysis of carbon content of suspended solids. Suspended solids 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 the shortage of sample volume obtained.

Carbon content of the sediment sample, which was air-dried at room temperature, was also measured by NC analyzer. Moreover, clay content of the sediment sample was determined by the pipette method (Soil Environmental Analysis Committee, 1997).
4-3 Result and discussions

4-3-1 Characteristics of suspended solids

As shown in Figure 4-1, the suspended solids concentrations (SS₀.₅ and SS₁.₀) rose in the period from late April to early May because of the runoff from paddy fields by agricultural practices. And, after this period, the concentration was decreased, except for the samples of October 29th, 2003. The carbon content (%) and C/N ratio of suspended solids were from 5.5 to 23 (Average = 8.4, Median = 7.1) and from 5.9 to 10 (Average = 8.0, Median = 8.2), respectively (Figure 4-1). During ordinary water discharge, the amounts of suspended solids loading to Sugao marsh from April to July estimated from their concentration and monthly water discharge data were 235.2 kg and 9.5 kg for SS₁.₀ and SS₀.₅ respectively.

4-3-2 Herbicides in water

In water samples, periodic changes in the concentrations of esprocarb, thiobencarb, dimethametryn and pretilachlor were appeared from late April to early May (Figure 4-2a). On the other hand, change in the concentration of simetryn were appeared from late May to June (Figure 4-2a). The reason for these periodic peaks of the herbicide concentrations were considered to be due to the timing of herbicides application as mentioned in chapter 3. The amounts of herbicides loading as dissolved form to Sugao marsh were calculated as arithmetic means of each month from April to July (Table 4-2). Although the amounts of sale of simetryn were lower than esprocarb and thiobencarb, loading of the former as dissolved form was larger than the latters (Tables 1-1 and 4-2). Similar tendency was also reported in several studies where the run off ratio of simetryn from paddy field areas was higher than esprocarb and thiobencarb because of its high water solubility and the low logKow (Numabe et al., 1992; Nakano et al., 2004). On the other hand, pretilachlor and thiobencarb shows similar water solubility and the amounts of sales, and pretilachlor shows higher logKow than thiobencarb.
(Table 1-1). However, the concentration of pretilachlor in water was higher than thiobencarb (Figure 4-2), and it was also reported that its run off ratio from paddy field was higher than thiobencarb in the previous study (Nakano et al., 2004). The adsorption ratio of pretilachlor for several kinds of paddy soils was lower than thiobencarb (Kibe et al., 2000a), and the Koc of pretilachlor was lower than thiobencarb (Table 1-1). Thus the amount of pretilachlor loading as dissolved form in this study might be higher than those of thiobencarb and esprocarb.

4-3-3 Herbicides in suspended solids

Periodic changes in the concentration of herbicide in suspended solids appeared analogous with those in water (Figures 4-2b, c, g and h). Although very low concentrations of herbicide as dissolved form were detected in the period after August, the herbicides in suspended solids were frequently detected. Moreover, the concentrations of herbicide in SS_{0.5} were about 10 to 20 times higher than those in SS_{1.0} (Figures 4-2b, c, g and h). This might be due to the difference in the surface area of two size fractions of suspended solids and strong hysteresis (Gao et al., 1998a; Wu et al., 2003). As shown in Figures 4-2b, c, g and h, the concentrations of esprocarb in suspended solids were higher than other herbicides, and thiobencarb was detected in relatively higher concentration in SS_{0.5} at RI, and dimethametryn in SS_{1.0} at Site 2. Here, the partition ratio (PR) is defined as below and calculated:

\[
PR_{ss} (\%) = 100 \times \frac{C_{ssi}}{(C_{w} + C_{ss1,0} + C_{ss0,5})}
\]

where C_{ssi} is the weight of herbicides in suspended solids from a given size fraction; C_{w} is the weight of herbicides in filtered water sample; C_{ss1,0} and C_{ss0,5} are the weights of herbicides in each of size fraction of suspended solids. Calculated average, median and maximum values of PR_{ss}, not used for 0 and 100% values in calculation, were shown in Table 4-3. It is clear that the most of the herbicides in whole water samples (C_{w} + C_{ss1,0} + C_{ss0,5}) were present in filtered water, namely PR_{ss} of total suspended solids was only 0.37–2.5% as the median value (Table
Values of PRss for esprocarb and thiobencarb were higher than those of pretilachlor and simetryn in both size fractions (Table 4-3), because these herbicides were lower in water solubility and higher in logKow and Koc (Table 1-1). Although the most of the herbicides were present as dissolved form, PRss over 5% was occasionally recognized by calculation in some case (Table 4-3). Moreover, the herbicides in suspended solids was detected, even if their concentration in water was low or out of detection (Figures 4-2a, c, f and g). At rainfall event, the ratio of esprocarb adsorbed on suspended solids in run off water from paddy field was about 20% in the previous study (Sasagawa et al., 1996). This was because the concentration of suspended solids was higher than ordinary water discharge. The average and median values in the previous study (Tanabe et al., 1998) using small volume of water sample were higher than those in the present study. This might be due to their higher frequency of detection in this study. In turn, the sample volume of this study was thought to be appropriate to grasp the concentration change and distribution of herbicide in suspended solids.

The amounts of herbicides loading as adsorbed form on suspended solids in Sugao marsh were calculated as the arithmetic means of each month from April to July (Figure 4-3). The amount of esprocarb loading as total suspended solids (SS1.0 and SS0.5) in Sugao marsh from April to July was $1.1 \times 10^3$ g, and it was higher than other herbicides (Table 4-2). On the other hand, the amounts of esprocarb loading as suspended solids during monitoring period including rain fall event (Nakano et al., 2004) were higher than this study. The amounts of herbicide loading as adsorbed form was lower than that of dissolved form, and the ratio of adsorbed form against total herbicide loading were 0.42-4.6% (Table 4-2). Comparing the relative loading ratio of the herbicide adsorbed on SS1.0 and SS0.5 against total suspended solids, herbicides adsorbed on SS0.5 showed 18-59% to total suspended solids (Table 4-2). As shown in foregoing discussion, the amount of herbicide loading to Sugao marsh by suspended solid was much smaller than that of dissolved form. However, the herbicide loading by suspended solid
was not able to be disregarded from the viewpoint of loading to sediment. Since more fine particles of runoff materials had strong adsorption-desorption hysterisis (Wu et al., 2003), it was thought that the most of herbicide adsorbed on suspended solids was not desorbed and probably accumulated to sediment by sedimentation. And, it was also pointed that the sedimentation by suspended solids with adsorbed pesticides were more important for the accumulation of pesticides in sediment than dissolved pesticide in water (Inoue et al., 2002). The results of this study suggested that the importance of smaller size fraction to estimate the herbicide loading to sediment.

4-3-4 Herbicides in sediment

The change in texture from clay to sand at Site 2 coincided the decrease in carbon content of sediments (Figure 4-4). And, the concentrations of herbicides in sediments were correlated with carbon and clay content of sediment as shown in the chapter 3. Therefore, periodic changes in herbicide concentration in sediments (Figures 4-2d, e and i) were different between the sites of RI and Site 2, probably resulted from the change in texture of sediment. The concentrations of esprocarb and thiobencarb in sediment were higher than those of other herbicides, because these herbicides were lower water solubility and higher logKow and Koc (Table 1-1). And, esprocarb and thiobencarb were detected in sediment at Site 2 before the period for herbicide application (Figure 4-2), and same tendency was recognized in the previous study (Nakamura et al., 1985) and in chapter 3. These herbicides might be remained to be adsorbed on clay and organic matter in sediment from the preceding year because of high contents of clay and carbon in the sediment at Site 2 in April. However, as the texture of sediment was abruptly changed at Site 2 during the present study (Figure 4-4), the herbicide concentrations might be decreased at this site since autumn. Moreover, difference in vertical distributions of herbicide concentration in sediment at Site 2 were not clearly shown between
0-5cm and 5-15cm samples (Figures 4-2d and e). This might be due to the continuous disturbance of sediment surface by actual water flow in different scale.

4-3-5 Relationships among herbicides in water, suspended solids and sediment

The patterns of herbicide concentration change in water were similar to those in suspended solids, and were not similar to those in sediment (Figure 4-2), since the concentrations of herbicide in water, suspended solids and sediment were not always in the equilibrium condition as obtained in the laboratory experiment (Kibe et al., 2000a). Furthermore, when suspended solids are smaller, the rate of deposition is slower in almost an exponential manner according to Stokes’s law (Suzuki and Kondo, 1994). However, sedimentation rate of suspended solids with herbicides and characteristics of suspended solids as adsorbent of herbicides were still obscure during ordinary water discharge as well as in rainfall event. Further study on the role of suspended solids as the carrier of herbicides is necessary in the field and also in laboratory experiments.

4-4 Conclusion

Concentrations of the esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn in water, suspended solids and sediment were studied during ordinary water discharge of a year in Sugao marsh. Periodic changes of herbicide concentration in water were similar to those in suspended solids. Herbicides were mostly present as dissolved form. Concentrations of herbicides in fine suspended solids (0.5 to 1.0 μm) were higher than those in coarse suspended solids (more then 1.0 μm). Partition ratio of total suspended solids to total water sample were 0.37-2.5% as the median value. The ratio of herbicide loading as adsorbed form against total herbicide loading were 0.42-4.6%. Herbicides loading by the fine suspended solids were estimated to be 18 to 59 % of total suspended solids, indicating their important roles as a carrier
of herbicides. Differences in vertical distributions of herbicides in sediment down to 15 cm in depth were not clearly shown, probably due to the disturbance of sediment surface by actual water flow.
Table 4-1. Detection limits and recoveries of herbicides studied.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Detection limits</th>
<th>Recoveries</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water (μg L⁻¹)</td>
<td>suspended solids* (mg kg⁻¹)</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Dimethametyn</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Simetryn</td>
<td>0.04</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Values of suspended solids were obtained from SS₄₀.
<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Dissolved amount (kg)</th>
<th>Dissolved amount (g)</th>
<th>Dissolved % of total loading</th>
<th>SS total amount (g)</th>
<th>SS total % of SS total</th>
<th>SS$_{0.05}$ amount (g)</th>
<th>SS$_{0.05}$ % of SS total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>23</td>
<td>$1.1 \times 10^3$</td>
<td>4.6</td>
<td>$6.1 \times 10^2$</td>
<td>57</td>
<td>$4.6 \times 10^2$</td>
<td>43</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>9.4</td>
<td>$3.4 \times 10^2$</td>
<td>3.5</td>
<td>$1.4 \times 10^2$</td>
<td>41</td>
<td>$2.0 \times 10^2$</td>
<td>59</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>9.0</td>
<td>$2.6 \times 10^2$</td>
<td>2.8</td>
<td>$1.9 \times 10^2$</td>
<td>74</td>
<td>$6.6 \times 10^1$</td>
<td>26</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>43</td>
<td>$3.6 \times 10^2$</td>
<td>0.84</td>
<td>$2.4 \times 10^2$</td>
<td>67</td>
<td>$1.2 \times 10^2$</td>
<td>33</td>
</tr>
<tr>
<td>Simetryn</td>
<td>21</td>
<td>$8.9 \times 10^1$</td>
<td>0.42</td>
<td>$7.3 \times 10^1$</td>
<td>82</td>
<td>$1.6 \times 10^1$</td>
<td>18</td>
</tr>
</tbody>
</table>

* Sum of SS$_{1.0}$ and SS$_{0.5}$

*SS total / (dissolved + SS total) * 100

* SS$_{1.0}$ (or SS$_{0.5}$) / SS total * 100
<table>
<thead>
<tr>
<th>Herbicide</th>
<th>PR of SS total (%)</th>
<th></th>
<th>PR of SS(_{1.0}) (%)</th>
<th></th>
<th>PR of SS(_{0.1}) (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n^*) median</td>
<td>average</td>
<td>maximum</td>
<td>(n^*) median</td>
<td>average</td>
<td>maximum</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>23</td>
<td>2.2</td>
<td>3.1</td>
<td>8.6</td>
<td>22</td>
<td>1.8</td>
</tr>
<tr>
<td>Thioanobencarb</td>
<td>17</td>
<td>2.1</td>
<td>2.1</td>
<td>6.1</td>
<td>12</td>
<td>1.6</td>
</tr>
<tr>
<td>Dimethametryln</td>
<td>26</td>
<td>2.5</td>
<td>3.5</td>
<td>12</td>
<td>26</td>
<td>1.9</td>
</tr>
<tr>
<td>Pretillachlor</td>
<td>16</td>
<td>0.56</td>
<td>0.79</td>
<td>4.2</td>
<td>14</td>
<td>0.37</td>
</tr>
<tr>
<td>Simetryn</td>
<td>15</td>
<td>0.37</td>
<td>0.47</td>
<td>1.2</td>
<td>14</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*Number of sample used for the calculation
Figure 4-1. Concentration of suspended solids and, carbon content and C/N ratio in suspended solids from Site 2 and RI Site (carbon contents for January 12th, 2004 were not determined because of low concentrations of suspended solids)
Figure 4-2. Concentration of herbicides in water, suspended solids and sediment at Site 2 and RI Site (sediment sample of June 21th, 2003 was not collected from RI Site)
Figure 4-3. Amount of loading of herbicides as dissolved and adsorbed forms (SS$_{1.0}$ and SS$_{0.5}$) from April to July, 2003, at RI Site.
Figure 4-4. Carbon and clay content of sediment from Site 2 and RI Site.
Chapter 5

Adsorption and desorption characteristics of several herbicides on sediment

5-1 Introduction

Adsorption phenomena of pesticides in soil are very important for the behavior of pesticides in the environment. So, many previous investigations on the adsorption phenomena of pesticides in soil had been carried out using various kinds of soils (Kanazawa, 1989; Kobayashi et al., 1996; Nakamura et al., 1996; Wang et al., 1999; Kibe et al., 2000a; Kibe et al., 2000b; Fushiwaki and Urano, 2001; Ebato et al., 2001; Nemeth-Konda et al., 2002; Lesan and Bhandari, 2003; Li et al., 2003). Adsorption phenomena of pesticides in sediment are also very important for the fate and influence of pesticides in aquatic environment, because the sediment is thought as one of the sink of the pesticides exposed for aquatic environment where pesticides finally reached. Furthermore, the adsorption characteristics of pesticides on sediment are necessary for predicting pesticide concentration in aquatic environment. However, few investigations on adsorption characteristics of pesticides in sediment have been carried out (Hayakawa et al., 1994; Gao et al., 1998a; Gao et al., 1998b; Madsen et al., 2000; Tao and Tang, 2004), compared with those on pesticides in soils. In addition, desorption phenomena of pesticides in sediment are also very important to determine the persistency and mobility of pesticides in sediment. Although desorption process was frequently assumed to be in the reverse reaction with adsorption, the hysteresis in the adsorption-desorption phenomena in sediment was reported (Gao et al., 1998a) and thought to affect the dissipation of pesticides in sediment. Therefore, the investigation on the desorption characteristics of pesticides from sediment is also necessary for predicting pesticide concentration in aquatic environment. In general, the adsorption amounts of the hydrophobic pesticides on soil or sediment were thought to be related with the amount of organic matter in them. So, the hydrophobic property was
assumed to be an index of the amounts of pesticides adsorbed on sediment. However, it is the fact that the higher concentrations of pretilachlor in the water and its higher run off ratio were observed compared with other pesticides having lower hydrophobicity than pretilachlor (Nakano et al., 2004; chapters 3 and 4 in this study). So, it is necessary to investigate the effects of organic matter in sediment on the pesticides adsorption and desorption phenomena.

The aim of this chapter is to clarify the adsorption and desorption characteristics of several herbicides in sediment, and to examine the effects of organic matter on the adsorption and desorption of several herbicides in sediment.

5-2 Materials and methods

5-2-1 Herbicides

Five herbicides (esprocarb, thiobencarb, pretilachlor, dimethametryn and simetryn) investigated in chapters 2 and 3 were examined for the adsorption and desorption phenomena in this chapter. The chemical properties and structural formulas were described in Table 1-1 and Figure 1-2 in chapter 1, respectively.

5-2-2 Sediment sample

Sediment sample (0-15 cm depth) was collected with Multi-sampler (DIK-180A, Daiki Rika Kogyo Co., Ltd.) at Site 2 (Figure 2-1) from October 30, 2004. Then, the sediment sample was dried in the air and passed through a 2 mm sieve. Carbon content of sediment sample was measured by NC analyzer (SUMIGRAPH NC-900, Sumika Bunseki Center, Co., Ltd.). The pH of the sediment sample was measured in the mixture of sediment and 0.01M CaCl₂ solution (1:5 as weight bases) using glass electrode. Particle size distribution of sediment sample was determined by the pipette method (Soil Environmental Analysis Committee, 1997). The mineral components of clay fraction in sediment sample were analyzed by X-ray
diffraction using Cu Kα radiation (Geiger FREX 2012, Rigaku) after the deferration (Mehra and Jackson, 1960) and magnesium and potassium ions saturation (Wada, 1966). The XRD spectrum obtained from the sample saturated with magnesium ion was shown in Figure 5-1. In addition, the amounts of Al, Fe and Si for the clay fraction separated from the sediment sample were determined in the extracts with acid ammonium oxalate and also with sodium dithionite-citrate (Soil Environmental Analysis Committee, 1997). Amounts of Al, Fe and Si were measured by inductively coupled plasma emission spectroscopy (ICAP-575, Jarrell Ash Co., Sydney).

5-2-3 Adsorption / desorption experiment

Experimental conditions and procedures

Adsorption and desorption experiment was carried out in the batch mode according to the OECD guideline 106 (OECD, 2000), which was modified in this study, where 5 g of dried sediment sample were taken in a glass centrifuge tube, sealed with Teflon screw cap, and mixed with 25 mL of 0.01M CaCl2 solution (sediment : solution ratio = 1 : 5) including 0.02% sodium azide to inhibit biotransformation (Gao et al., 1998a). Then, this glass centrifuge tube was shaken during a given experiment time at 20°C (±1°C) under the absence of light on a horizontal shaker. The suspension was centrifuged at 3000 rpm for 15 minutes, and 20 mL of the supernatant was obtained for the analysis of herbicide. The supernatant was shaken with 5 mL of n-hexane for 1 minute by hand after the addition of 5 g of NaCl to increase the extraction efficiency of n-hexane for simetryn (Kibe et al., 2000a). The organic layer was filtered though anhydrous Na2SO4. The aqueous layer was shaken again with 5 mL of n-hexane and filtered in the same manner. The combined filtrates were evaporated and dried under N2. Then, the residue was dissolved in 2 mL of acetone and finally analyzed by Hewlett Packard 6890 GC equipped with a fused silica capillary column (HP-5MS, 30 m length and 0.32 mm internal diameter, 0.25
μm film) and with nitrogen-phosphorus detector (NPD). The recoveries in the extraction of each herbicide from water by above method were shown in Table 5-2, and the data were not corrected by these recoveries.

Blank sample was prepared in the same manner without herbicides, and the herbicides were not detected in water under these experimental conditions. The amounts of the adsorbed herbicides were calculated as the difference between the initial herbicide concentration and the resulting supernatant concentration after centrifugation at a given reaction time.

**Adsorption**

To examine the adsorption equilibrium rate of the herbicides on the sediment sample, the shaking times were designed as 0.15, 0.3, 1, 2, 3, 4, 8, 12, 24, 48 and 72 hours, and the initial concentration of herbicide in 0.01M CaCl₂ solution was fixed to be 2.0 mg L⁻¹. This experiment was carried out in duplicate for every herbicide.

For adsorption isotherm, a series of 25 mL of 0.01M CaCl₂ solution containing 0.02, 0.2, 0.5, 1.0 and 2.0 mg L⁻¹ of a given herbicide was added to 5 g of the sediment, and shaken for 72 hours and analyzed by the same manner described above. This shaking time (72 hours) as equilibrium time was obtained from this study of adsorption rate. This experiment carried out in duplicate for every herbicide.

**Desorption**

Desorption studies were carried out for all herbicides with the initial concentration of 2.0 mg L⁻¹. After a given adsorption equilibrium time, the supernatant of 20 mL was replaced by the same volume of 0.01M CaCl₂ solution containing no herbicide. The sediment in centrifugation tubes was agitated to disperse the sediment pellet, and it was shaken again as described in the adsorption experiment. The desorption equilibration process was carried out.
once a day, and repeated for four times. The herbicide concentration in the solution was determined after each desorption step. The amount of herbicide adsorbed on the sediment was calculated as the difference between the initial amount adsorbed and the amount desorbed. This experiment carried out in quadruplicate for every herbicide.

Removal of organic matter, and adsorption / desorption experiment for \( \text{H}_2\text{O}_2 \)-treated sediment

Organic matter was removed from sediment sample and used for adsorption and desorption experiments. By adding 150 mL of 30\% \( \text{H}_2\text{O}_2 \) to 50 g of the dried sediment sample, allowing it stood at room temperature. After the foaming originated from decomposition of organic matter was disappeared, the sediment sample was further heated till the foaming from \( \text{H}_2\text{O}_2 \) was completely disappeared. This \( \text{H}_2\text{O}_2 \) treatment was repeated several times. Then, the sediment sample was dried at 40\°C for 24 hours. Carbon content of this sediment sample was measured after this \( \text{H}_2\text{O}_2 \) treatment, and showed a removal of 75\%. pH value of this sediment sample was measured as described before. The adsorption and desorption experiments using \( \text{H}_2\text{O}_2 \)-treated sediment sample were carried out in the same manner as described above. However, the adsorption equilibrium rate and the adsorption isotherm were examined during the shaking time for 24 hours.

5-3 Results and discussion

5-3-1 Some properties of sediment

The pH of original sediment and \( \text{H}_2\text{O}_2 \)-treated sediment samples were 6.06 and 5.28, respectively. The carbon content of original sediment sample was 0.64\%. Its particle distribution was as follows: coarse sand, fine sand, silt and clay fractions = 54.3, 30.9, 7.2 and 7.6 (\%), respectively. The amounts of Al, Fe and Si extracted with acid ammonium oxalate and sodium dithionite-citrate were shown in Table 5-1. Fe extracted with acid ammonium oxalate
might be ferryhydrite (Soil Environmental Analysis Committee, 1997). And, the difference in the amounts of Fe and Si between two extraction methods might be derived from iron oxides like goethite as well as amorphous silicate mineral like allophane and imogolite. Since the difference in amount of Al between two extractions was very small, the amorphous silicate minerals of Al might be absent (Soil Environmental Analysis Committee, 1997). Moreover, the presence of crystalline minerals having Fe/Si molar ratio of 1/2 was postulated by this extraction method. Furthermore, the result of X-ray diffraction indicated the existence of some secondary minerals, possibly smectite, chlorite, illite and kaolin minerals (Figure 5-1). So, the characteristics of this sediment is low in organic carbon and clay content, and contain ferryhydrite, amorphous iron silicate mineral in addition to some secondary clay minerals.

5-3-2 Adsorption / desorption kinetics

The adsorption rates of herbicides on the original sediment sample were shown in Figure 5-2. It was confirmed that all herbicides reached their adsorption equilibriums within 72 hour, and two adsorption steps with rapid and slow adsorption were recognized (Figure 5-2). This tendency of adsorption was similar to the previous studies in which adsorption of some pesticides and their metabolites by pond sediment were investigated (Gao et al., 1998a), and that of the same herbicides as this study by three kinds of paddy soils were studied (Kibe et al., 2000b). The rapid adsorption was occurred within 4 hours where about 50 – 75% of the added herbicides were adsorbed, especially 44 – 67% of herbicides within 0.25 hour (Figure 5-2). The amounts of esprocarb, thiobencarb and simetryn adsorbed on sediment were about 80% of their added amount at equilibrium, while those of pretilachlor and dimethametryn were about 60 % (Table 5-3).

The amounts of herbicides desorbed from the original sediment sample after the first desorption step (24 hour) were 26, 21, 16, 13 and 12% of the initial adsorbed amount of
dimethametryn, pretilachlor, thiobencarb, esprocarb and simetryn, respectively (Figure 5-3). And, the amounts of herbicides desorbed from the original sediment sample after four times of desorption procedures were 57, 49, 46, 39 and 37% of the initial amount, that was analogous with the order in the first step of desorption mentioned above (Figure 5-3 and Table 5-3). The desorption curves of all herbicides were slightly declined after the initial step (Figure 5-3). And, even after the fourth desorption step, adsorbed herbicides were not completely desorbed. Since some pesticides and their metabolites adsorbed on pond sediment became more difficult to be desorbed with the increased incubation time (Gao et al., 1998a), the herbicides studied in this study might also become more difficult to be desorbed from the sediment sample.

5-3-3 Adsorption / desorption isotherm

All adsorption data of herbicides studied fitted well to Freundlich equation (1):

\[ Q = K_f C^{1/n} \]  

where \( Q \) (mg kg\(^{-1}\)) is the amounts of pesticide adsorbed on sediment (mg) per dry-sediment (kg); \( C \) (mg L\(^{-1}\)) is the concentration of pesticide in water; \( K_f \) (L kg\(^{-1}\)) and \( 1/n \) are the adsorption coefficient and adsorption constant, respectively. Freundlich coefficient, \( K_f \), express the affinity between adsorbent and adsorbate, the adsorption capacity of adsorbent and the amount of the structural adsorption site of adsorbent (Urano et al., 1981; Kondo et al., 2001). On the other hand, the constant \( 1/n \) is a parameter that reflects the pore volume distribution and the intrinsic physicochemical characteristics of adsorbate (Urano et al., 1981; Gao et al., 1998a; Kondo et al., 2001).

The adsorption isotherms of herbicides studied were described in Figure 5-4, and the values of adsorption coefficient \( K_f \) and constant \( 1/n \) were also shown in Table 5-4. The extent of the \( K_f \) values increased in the following order: pretilachlor < dimethametryn < simetryn < thiobencarb < esprocarb (Table 5-4). The inverse relationship has been often recognized
between the adsorption ratio of pesticide on soil or sediment and that of water solubility (Gao et al., 1998a; Wang et al., 1999; Fushiwaki et al., 2001). However, the $K_f$ value of simetryn in this study was relatively higher in spite of the highest water solubility among the herbicides studied (Table 1-1). There was no significant tendency between the $K_f$ values and water solubility of the herbicides in this study. Furthermore, the $K_f$ value of pretilachlor was the lowest among the herbicides studied. The adsorption phenomena of several herbicides applied for paddy fields were also investigated using five kinds of paddy soils (Kibe et al., 2000a). The 1/n value express the linearity of isotherm theoretically, and if the 1/n value is below 1.0, the sorption curve is classified as L type, where as the adsorption sites are increasingly occupied and more difficult for adsorbate to find vacant sites (Gao et al., 1998a; Kondo et al., 2001). The extent of the 1/n values in this study was increased in the following order: pretilachlor < simetryn < thiobencarb < dimethametryn < esprocarb, and only esprocarb showed the value of over 1.0 (Table 5-4). Since the lower values of 1/n for some pesticides were associated with the higher organic matter contents in sediments (Weber et al., 1992), it was thought that the 1/n value of hydrophobic pesticide was to be lower. However, the 1/n value of esprocarb was high (Table 5-4) in spite of its most hydrophobicity among the herbicides studied (Table 1-1). In contrast, although the Kow value of simetryn was the lowest in this study (Table 1-1), the value of 1/n was lower than other herbicides, except for pretilachlor. So, it could be inferred that organic matter in sediment in this study was not only the dominant adsorption site for herbicides, but the mineral surface might be important for adsorption of herbicides as well.

When the value of $n$ is 1.0, equation (1) is expressed in Henry equation as follows:

$$Q = K_d C$$  \hspace{1cm} (2)

where $K_d$ (L kg$^{-1}$) is the adsorption constant of the adsorbate in liquid and solid phase. Furthermore, when the adsorption of pesticide on soil and sediment is discussed, the $K_d$ value is generally normalized to Koc using following equation by organic carbon content. This is
assumed that pesticide is adsorbed on the organic matter in soil and sediment, especially for more hydrophobic pesticide.

\[ K_{oc} = \left( \frac{K_d}{C_{org}} \right) \times 100 \]  

where \( K_{oc} \) is the adsorption constant based on the content of organic matter and \( C_{org} \) (%) is organic carbon content in soil or sediment. The \( K_d \) and \( K_{oc} \) values have often been used in the previous studies for predicting pesticide concentration in soil and aquatic environment (Nofziger et al., 1994; Shirmohammadi and Knisel, 1994). The \( K_d \) and \( K_{oc} \) values of herbicides in this study were calculated and shown in Table 5-4. Differences between the value of \( K_d \) and \( K_f \) became larger when the values of \( 1/n \) were low (Table 5-4). The \( K_{oc} \) values obtained in this study were higher than the \( K_{oc} \) values for soils reported by the previous study (Tables 1-1 and 5-4). It was reported that the \( K_{oc} \) values of carbon tetrachloride and 1,2-dichlorobenzene for sediments were higher than these \( K_{oc} \) values for soils (Chiou, 2002). Therefore, the high \( K_{oc} \) values in this study were not only due to low organic matter content in sediment, but also to the differences in chemical properties between soil organic matter and sediment organic matter. Furthermore, since other adsorption parameters such as clay and other minerals contents were excluded in \( K_{oc} \) values, Henry equation and the adsorption constant \( K_{oc} \) may not be appropriate to predict the concentration of herbicide in water and sediment.

All desorption data also fitted well to Freundlich equation (1), and were shown in Figure 5-4. If the adsorption and desorption of pesticides in the sediment are reversible in reaction, the \( 1/n \) value during the desorption is theoretically equal to that of the adsorption. However, in this study, all the values of \( 1/n_{des} \) were lower than that of \( 1/n_{ads} \) (Table 5-4). Both \( 1/n_{ads} \) and \( 1/n_{des} \) values indicated the existence of hysteresis in adsorption and desorption processes of herbicides in sediment. This was also recognized from the adsorption and desorption isotherms with different slopes (1/n) (Figure 5-4). The ratio of \( (1/n_{ads} / 1/n_{des}) \) was assumed to express the intensity of hysteresis (Gao et al., 1998a), and the increase in this ratio
meant that hysteresis was stronger. In the present study, the ratio of \(1/n_{ads}/1/n_{des}\) of pretilachlor was the highest, and the relatively higher values were obtained for simetryn and dimethametryn compared with those of esprocarb and thiobencarb (Table 5-4). The \(K_r\) value of pretilachlor was the lowest among the herbicides studied, but its hysteresis was the largest (Table 5-4). Therefore, it might be postulated that pretilachlor had not enough adsorption site in the original sediment sample but showed high affinity. However, the mechanism of hysteresis is not clear yet (Gao et al., 1998a), and more examination is necessary.

**5-3-4 Effect of organic matter removal on the adsorption / desorption of herbicides**

The adsorptions of herbicides on \(H_2O_2\)-treated sediment sample reached the equilibrium very quickly, and the adsorption curves were flat during examination time (Figure 5-5). The amounts of herbicides adsorbed on \(H_2O_2\)-treated sediment sample were 99.6, 88.4, 70.0, 66.1, and 52.9% of the added amounts for simetryn, dimethametryn, pretilachlor, esprocarb and thiobencarb, respectively (Table 5-3). The adsorption amounts of simetryn, dimethametryn and pretilachlor on \(H_2O_2\)-treated sediment sample were increased, while those of esprocarb and thiobencarb were decreased in comparison with the original sediment sample without \(H_2O_2\) treatment. According to Gao et al., (1998a), the rapid and slow adsorption might be a diffusing surface phenomenon into organic matter and mineral structure, respectively. The amounts of herbicides desorbed from \(H_2O_2\)-treated sediment sample after the fourth desorption step were 80, 68, 61 and 30% of the initial adsorbed amount for thiobencarb, esprocarb, pretilachlor and dimethametryn, respectively (Table 5-3 and Figure 5-6). Simetryn was adsorbed very strongly on \(H_2O_2\)-treated sediment sample and desorbed hardly during fourth desorption steps. So, the adsorption of simetryn might be considered to be specific adsorption on mineral surface.

Simetryn and dimethametryn are classified as 1,3,5-triazine group, and the herbicides
of this group show weakly base in reaction. The pKa values of simetryn and dimethametryn are 4.0 and 4.1, respectively (British Crop Protection Council, 2000). Since the pH of H2O2-treated sediment sample was lower than the original sediment sample without H2O2 treatment, it was thought that simetryn and dimethametryn in H2O2-treated sediment sample were more ionized than in the original sediment sample under the pH values of this experiment condition. Since it was thought that H2O2-treated sediment sample had more mineral surface area than the original sediment sample, the adsorption amounts of these herbicides on H2O2-treated sediment sample might be higher than the original sediment sample. Therefore, simetryn and dimethametryn might be adsorbed on clay or mineral surface by ionic adsorption though its positive charge of the triazine ring with the negative charges of clay and mineral surface (Kibe et al, 2000a). On the other hand, the adsorption amount of pretilachlor was also increased for H2O2-treated samples (Figure 5-5). Pretilachlor was classified as chloroacetanilide herbicide (Robert, 1998). It was shown that the chloroacetanilide herbicide was bounded to clay and humic acid by hydrogen bond and charge-transfer bonds (Liu et al., 2000). Therefore, it was considered that the adsorption mechanism of pretilachlor on H2O2-treated sediment sample might be different from those of simetryn and dimethametryn.

All adsorption and desorption data of the herbicides on H2O2-treated sediment sample fitted Freundlich equation, and the isotherms of herbicides were shown in Figure 5-7. The Kf value of esprocarb and thiobencarb were lower than those of dimethametryn, simetryn, and the Kf value of pretilachlor were higher comparing with those of the original sediment sample (Table 5-4). Since all the values of 1/n_{des} were also lower than those of 1/n_{ads} in H2O2-treated sediment sample, it was considered that there is the hysteresis reaction (Table 5-4) between adsorption and desorption. Since the ratios of (1/n_{ads} / 1/n_{des}) of dimethametryn and pretilachlor were lower compared with that for the original sediment sample (Table 5-4), the hysteresis of dimethametryn and pretilachlor might be caused by organic matter in sediment.
5-4 Conclusion

To investigate adsorption and desorption characteristics of several herbicides on a sediment sample, kinetics, isotherms, hysteresis and effect of organic matter were examined. All herbicides reached their adsorption equilibrium within 72 hour, and both rapid and slow adsorption steps were recognized. The extent of adsorption ratio increased in the following order: pretilachlor < dimethametryn < simetryn < thiobencarb < esprocarb. Comparison of the data with H$_2$O$_2$-treated sample, it is strongly suggested that the adsorption site of herbicides on sediment might be not only the organic matter, but also the mineral surface in sediment. The hysteresis of adsorption-desorption phenomena were observed for all herbicides. The hysteresis process for sediment was affected by the presence of organic matter in sediment. Furthermore, mineral surface was assumed to be adsorption sites, and was in particularly very important for the adsorption of simetryn, dimethametryn and pretilachlor.
<table>
<thead>
<tr>
<th>Element</th>
<th>A (mmol kg(^{-1}))</th>
<th>S (mmol kg(^{-1}))</th>
<th>S - A (mmol kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.78</td>
<td>0.79</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.53</td>
<td>1.09</td>
<td>0.56</td>
</tr>
<tr>
<td>Si</td>
<td>0.33</td>
<td>1.32</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Table 5-1.** Amounts of Al, Fe and Si extracted by acid ammonium oxalate and sodium dithionite-citrate from clay fraction of sediment.

A: extracted by acid ammonium oxalate.
S: extracted by sodium dithionite-citrate.
Table 5-2. Recoveries of the herbicides studied.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Recoveries (%)</th>
<th>C.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>96</td>
<td>3.8</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>97</td>
<td>2.6</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>97</td>
<td>3.0</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>97</td>
<td>4.1</td>
</tr>
<tr>
<td>Simetryn</td>
<td>94</td>
<td>2.6</td>
</tr>
<tr>
<td>Herbicide</td>
<td>Original sediment</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>------------------</td>
<td>----------------</td>
</tr>
<tr>
<td></td>
<td>the ratio of</td>
<td>the ratio of</td>
</tr>
<tr>
<td></td>
<td>adsorption (%)</td>
<td>desorption (%)</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>81.3</td>
<td>38.6</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>78.9</td>
<td>47.5</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>59.0</td>
<td>56.6</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>57.6</td>
<td>48.7</td>
</tr>
<tr>
<td>Simetryn</td>
<td>78.8</td>
<td>36.5</td>
</tr>
</tbody>
</table>
Table 5-4. Adsorption and desorption coefficients of herbicides studied.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Original sediment</th>
<th>H₂O₂-treated sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_d</td>
<td>Koc</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>22.2</td>
<td>3475</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>18.8</td>
<td>2939</td>
</tr>
<tr>
<td>Dimethametrin</td>
<td>6.34</td>
<td>990</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>15.8</td>
<td>2466</td>
</tr>
<tr>
<td>Simetryn</td>
<td>6.96</td>
<td>1088</td>
</tr>
</tbody>
</table>
Figure 5.1. X-Ray diffraction pattern of clay fraction saturated with magnesium ion in sediment where peaks are corresponding to quartz (Q), plagioclase (P), smectite (S), kaolin (K), illite (I), chlorite (Ch), α-cristobalite (Cr).
Figure 5-2. Adsorption rate of herbicides on original sediment (added amount: 50 µg).
Figure 5-3. Desorption rate of herbicides on original sediment (added amount: 50 μg).
Figure 5-4. Adsorption and desorption isotherms of herbicides on original sediment.
Figure 5-5. Adsorption rate of herbicides on $\text{H}_2\text{O}_2$-treated sediment sample (added amount: 50 $\mu$ g).
Figure 5-6. Desorption rate of herbicides on H₂O₂-treated sediment sample (added amount: 50 μg).
Figure 5-7. Adsorption and desorption isotherms of herbicides on H$_2$O$_2$-treated sediment sample.
Chapter 6
Degradation of several herbicides in water-sediment system

6-1 Introduction

Pesticides are affected by various degradation processes in the aquatic environment after their application to paddy fields; mainly by photochemical degradation in surface water caused by sunlight (Armbrust, 1999) and by decomposition with microorganisms in river and lake water (Kanazawa, 1992; Sarai et al., 1993). And, some pesticides containing halogen in their chemical structure were decomposed through dehalogenation in reduced condition (Moon and Kuwatsuka, 1984; Fajardo et al., 2000). Furthermore, pesticides are affected by these degradation processes, and finally reach to sediment in the aquatic environment. So, the degradation of pesticides in sediment was very important to the behavior of pesticides in the aquatic environment.

Kanazawa (1987) studied the degradation of 12 kinds of pesticides under aerobic and anaerobic conditions using activated sludge, soil and river sediment as the inoculum. Although the method of Kanazawa’s study (1987) was fitted for the understanding of the characteristics of pesticide degradation, the metabolic pathways and their metabolites, the results of this study was not directly applicable to the pesticide degradation in the sediment under monitoring condition. Fushiwaki and Urano (1988) investigated the seasonal change of chlornitrophen degradability in river water and sediment using modified methods of river die-away. Sarai et al. (1994) examined the degradation of pesticides in sediment by soil die-away method. However, these investigations methods might not evaluate completely the degradation processes in the actual water-sediment system. In addition, the degradation of pesticides applied to golf field were studied in water-sediment system (Kitano and Minami, 1996 and 1997; Araki et al., 2003), and the degradation of some organophosphorus pesticides were also investigated in
water-sediment system (Kodaka et al., 2003). Satsuma et al. (2002) investigated the metabolic pathway of atrazine in water-sediment microcosm, and showed that the benthic microbes with the degradation ability for atrazine existed in sediment surface. According to Ying and Williams (2000), the dissipation rates of pesticides in water-sediment system were delayed compared with those of pesticides in water. However, to our knowledge, degradation of pesticides applied to paddy fields in water-sediment system was rarely investigated.

The aim of this chapter is to study the herbicide degradation in a sediment collected from Sugao marsh, and to evaluate the differences in their degradation rates under a simple sediment-water system.

6-2 Materials and methods

6-2-1 Herbicides

Five herbicides (esprocarb, thiobencarb, pretilachlor, dimethametryn and simetryn) investigated in chapters 3, 4 and 5 were examined in the degradation experiment of this chapter. The chemical properties and structural formulas were described in Table 1-1 and Figure 1-2 in chapter 1, respectively.

6-2-2 Sediment sample

Sediment sample (0-15 cm depth) was collected with Multi-sampler (DIK-180A, Daiki Rika Kogyo Co., Ltd.) at Site 2 (Figure 2-1) on July 21th, 2005. Sediment sample was passed through a 2 mm sieve, thoroughly mixed and centrifuged at 3000 rpm for 20 minutes, and the supernatant was discarded. This sediment sample was used for degradation experiment. Carbon content of sediment sample was measured by NC analyzer (SUMIGRAPH NC-900, Sumika Bunseki Center, Co., Ltd.). Particle size distribution of sediment sample was determined by the pipette method (Soil Environmental Analysis Committee, 1997). The carbon
content of the sediment sample was 0.49%. The particle distribution was as follows: relative amounts of coarse sand, fine sand, silt and clay fractions were 51.5, 24.0, 16.3 and 8.2 (%) on dry weight basis, respectively.

6-2-3 Degradation experiment

Five gram of wet sediment sample was taken into the glass centrifuge tube (25 mm internal diameter) and mixed with 25 mL of distilled water containing five herbicides fixed to 5.0 mg L\(^{-1}\) (vertical position of water and sediment surfaces were 35 mm and 10 mm high in the tube, respectively). Then, this tube with the permeable silicone plug was agitated once and left for standing at 20°C under the absence of light. The concentrations of herbicides in water and sediment were measured on 0, 2, 4, 8, 16, 32 and 64 days after their application. On each of these days, the glass centrifuge tube was centrifuged at 3000 rpm for 15 minutes, and the supernatant and precipitate were obtained as water and sediment sample, respectively. This experiment was carried out in triplicate.

The herbicides in water were extracted and dehydrated by the same manner described in chapter 5, where the sample was dissolved in 4 mL of acetone and analyzed by GC-NPD. The sediment sample separated from water by centrifugation was shaken with 30 mL of acetone for 30 minutes, and filtered with a 1.0 μm glass filter (Whatman GF/B). Then, the sample was cleaned up by the same manner described in chapter 4, where the sample was dissolved 5 mL of acetone and also analyzed GC-NPD. All samples in the present study were analyzed by Hewlett Packard 6890 GC equipped with a fused silica capillary column (HP-5MS, 30 m length and 0.32 mm internal diameter, 0.25 μm film) and with nitrogen-phosphorus detector (NPD). The recoveries for the methods mentioned above were shown in Table 6-1, calculated as total recoveries of water-sediment system, and the experimental data were not corrected by these recoveries.

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6-3 Results and discussion

The residual amounts of herbicides during their degradation experiment were shown in Table 6-2 and Figure 6-1. Residual ratios of herbicides against initial amounts in total water-sediment system were also calculated and shown in Table 6-3. As shown in Table 6-2, the partition ratios of herbicides between water and sediment were different from those in the adsorption experiment in chapter 5, probably due to the absence of horizontal shaking in this degradation experiments. Since esprocarb and thiobencarb were more strongly adsorbed on sediment than other herbicides, they were present in the lower amounts in water than other herbicides (Figure 6-1 and Table 6-2).

The residual amounts of herbicides in water were decreased soon after the herbicide application, and esprocarb and thiobencarb were not detected in water on 32 days after herbicide application (Figure 6-1). The dissipation rate of herbicides were in the following order: esprocarb ≅ thiobencarb > pretilachlor > simetryn > dimethametryn (Figure 6-1). One of the reasons of herbicides dissipation in water might be due to their translocation into sediment, because the amounts of herbicides in sediment were increased at the same time (Figure 6-1) in addition to the chemical and biochemical degradation process in herbicide dissipation. As mentioned above, the residual amounts of herbicides in sediment were increased after herbicide application. However, the amounts of esprocarb, thiobencarb and pretilachlor were decreased rapidly on 16 to 32 days after herbicide application, while that of simetryn and dimethametryn became constant since 8 days after herbicide application (Figure 6-1). The residual ratio of herbicides against initial amounts in total water-sediment system were slightly decreased or nearly constant during 4 days after herbicide application, and all herbicides were decreased clearly on 8 days after herbicide application. The rates of herbicide dissipation in water-sediment system were in the following this order: esprocarb ≅ thiobencarb >
pretilachlor > simetryn ≅ diethametryn (Figure 6-1). As mentioned above, according to Ying and Williams (2000), the dissipation rates of pesticides in water-sediment system were delayed compared with that of pesticides in water. In this study, the degradations of herbicides in sediment were also delayed than in water (Figure 6-1). So, the sediment had the ability to retard the degradation in water-sediment system by adsorbing pesticides.

The degradation of thiobencarb caused by a specific kind of microorganisms in soil under aerobic and anaerobic conditions was reported (Nakamura et al., 1977). Moon and Kuwatsuka (1984) also examined the dechlorination of thiobencarb using 17 kinds of soil samples under flooded conditions. They reported that the degradation of thiobencarb by dechlorination started after 10 to 20 days of lag period from its addition in two soil samples, and the lag period of thiobencarb was shorten by the pre-incubation of soil. And, they concluded that specific microorganisms caused the dechlorination of thiobencarb. In this study, thiobencarb also began to decompose within 10 to 20 days after its application. So, the rapid dissipation of thiobencarb in sediment might be realized by microorganisms. Esprocarb was also decomposed rapidly in this study (Figure 6-1). Although esprocarb and thiobencarb were classified as thiocarbamate group (Roberts, 1998) esprocarb does not include halogen in its chemical structure. Therefore, the degradation of thiobencarb might be not only by dechlorination, but also by another decomposition pathway by microorganisms (Roberts, 1998).

On the other hand, the degradation ratio of pretilachlor in sediment was 62.4 % on 16 days after its application in this study (Table 6-3). The degradation of pretilachlor by dechlorination under reduced condition and the half lives of pretilachlor (DT$_{50}$) at the 0 to 1 cm layer of paddy soil under filed conditions during three years were shown in the previous study (Fajardo et al., 2000). According to Fajardo et al. (2000), DT$_{50}$ of pretilachlor in the 0 to 1 cm layer of paddy soil was observed on 7 to 10 days after herbicide application due to its leaching and degradation by dechlorination. Furthermore, it was reported that the herbicides classified as acetanilide
group showed the faster degradation rate in soil under anaerobic condition than aerobic condition, and this rapid degradation was due to reductive dehalogenation and microorganisms (Roberts, 1998). So, the degradation of pretilachlor in sediment might be caused by the dechlorination and microorganisms. DT$_{50}$ of simetryn and dimethametryn in soil under laboratory condition were on 52 to 179 days and 140 days, respectively (Kanazawa, 1992). These values were larger than other pesticides (Kanazawa, 1992). Furthermore, simetryn and dimethametryn classified as 1,3,5-triazine group showed a dominant chemical decomposition by hydrolysis with less biological decomposition (Roberts, 1998), leading to longer persistence than other herbicides in water-sediment system.

6-4 Conclusion

The degradation rates of herbicides in a simple sediment-water system were investigated. The sediment sample collected from Sugao marsh and five herbicides (esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn) were investigated in this study. The amounts of each herbicide in water-sediment system were slightly decreased during 4 days after herbicide application. Then, the amounts of esprocarb, thiobencarb and pretilachlor were decreased rapidly during 16 to 32 days. Especially, the amounts of esprocarb and thiobencarb in water were not virtually detected on 32 days after herbicides application. The degradations of these herbicides might be caused by microorganisms and dechlorination, while the main degradation process of simetryn and dimethametryn in water-sediment system were probably due to chemical decomposition. The latter might be suggested from the herbicides persistence during 64 days after their application.
### Table 6-1. Recoveries of herbicides calculated as total recoveries of water-sediment system.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Recoveries (%)</th>
<th>C.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>95</td>
<td>1.7</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>93</td>
<td>1.8</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>96</td>
<td>1.8</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>99</td>
<td>1.7</td>
</tr>
<tr>
<td>Simetryn</td>
<td>96</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Table 6-2. Residual amounts (μg) of herbicides in water and sediment, and their total amounts.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>0 days</th>
<th>2 days</th>
<th>4 days</th>
<th>8 days</th>
<th>*16 days</th>
<th>32 days</th>
<th>64 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>median</td>
<td>mean</td>
<td>C.V.</td>
<td>median</td>
<td>mean</td>
<td>C.V.</td>
<td>median</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>5.8</td>
<td>5.7</td>
<td>5.9</td>
<td>4.1</td>
<td>4.1</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>6.7</td>
<td>6.8</td>
<td>4.5</td>
<td>5.0</td>
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<td>4.6</td>
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<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>8.6</td>
<td>8.8</td>
<td>4.8</td>
<td>7.2</td>
<td>7.5</td>
<td>5.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>8.2</td>
<td>8.5</td>
<td>5.6</td>
<td>6.7</td>
<td>6.9</td>
<td>4.7</td>
<td>6.6</td>
</tr>
<tr>
<td>Simetryn</td>
<td>8.9</td>
<td>9.0</td>
<td>5.6</td>
<td>7.0</td>
<td>7.1</td>
<td>4.0</td>
<td>6.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Water</th>
<th>Sediment</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esprocarb</td>
<td>5.6</td>
<td>11.2</td>
<td>16.8</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>4.8</td>
<td>9.9</td>
<td>12.8</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>2.6</td>
<td>18.9</td>
<td>18.5</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>2.9</td>
<td>10.8</td>
<td>11.7</td>
</tr>
<tr>
<td>Simetryn</td>
<td>2.0</td>
<td>16.4</td>
<td>18.4</td>
</tr>
</tbody>
</table>

*The median and C.V. were not able to calculated because the examination were conducted in duplicate at 16 days.
Table 6-3. Residual ratio (%) of herbicides against initial amounts in total water-sediment system.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>2 days</th>
<th>4 days</th>
<th>8 days</th>
<th>*16 days</th>
<th>32 days</th>
<th>64 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>median</td>
<td>mean</td>
<td>C.V.</td>
<td>median</td>
<td>mean</td>
<td>C.V.</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>96.0</td>
<td>94.9</td>
<td>2.6</td>
<td>94.0</td>
<td>93.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>98.9</td>
<td>98.3</td>
<td>2.7</td>
<td>99.5</td>
<td>99.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Dimethametryn</td>
<td>94.6</td>
<td>96.3</td>
<td>3.2</td>
<td>100.5</td>
<td>100.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>91.4</td>
<td>92.2</td>
<td>2.8</td>
<td>93.0</td>
<td>92.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Simetryn</td>
<td>92.3</td>
<td>92.7</td>
<td>2.3</td>
<td>94.9</td>
<td>92.2</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| *The median and C.V. were not able to calculated because the examination were conducted in duplicate at 16 days.
Figure 6-1. Changes in residual ratio of herbicides studied.
Chapter 7

Over-all Discussion

7-1 Introduction

In this study, monitoring the concentrations of five herbicides (esprocarb, thiobencarb, dimethametryn, pretilachlor and simetryn) applied to paddy fields were conducted in water, suspended solids and sediment during two years at Sugao marsh, Ibaraki prefecture, to clarify the behavior of these herbicides in water-sediment system (chapters 3 and 4). Furthermore, the adsorption and desorption characteristics of these herbicides on sediment as well as their degradability in water-sediment system were also examined (chapters 5 and 6). In this chapter, over-all discussion on the characteristics of herbicides behavior in water-sediment system at river and marsh environment were done, based on the result of monitoring in the field and the laboratory experiments in the previous chapters. And, at the end of this chapter, further studies needed are pointed out with regard to the behavior of herbicides in water-sediment system in the aquatic environment.

7-2 Behavior of herbicides applied to paddy fields in water-sediment system of river and marsh environment

Two different processes of herbicide translocation from water into sediment might be existed (Figure 7-1). These include the adsorption of dissolved herbicide on sediment, and the sedimentation of suspended solids with adsorbed herbicide onto sediment. It was shown that most of the herbicides applied to paddy fields flowed into marsh from river were present as dissolved form, because the loading amounts of herbicides in water were larger than those in suspended solids (Figure 4-3). However, it was assumed that the translocation of herbicides from water to sediment was not only caused by the adsorption of dissolved herbicides, but also
by the sedimentation of suspended solids. As shown in chapters 3 and 4, the herbicides concentration peaks in the sediment were appeared at later periods than in water, probably due to the sedimentation of suspended solids with adsorbed herbicides. Moreover, the higher herbicides concentrations were detected in the sediment from inner marsh where slower water flow was observed (Figure 3-2). Therefore, the sedimentation of suspended solids with adsorbed herbicides might be a possible process of herbicide translocation into the sediment in water-sediment system.

It was argued that whether sediment became a sink or source for pesticides (Gao et al., 1998a). As shown in the present monitoring study, the concentrations of herbicides in water were not parallelly increased with those in sediment (chapters 3 and 4). And, when the concentrations of herbicides in water became low, the increase of herbicides concentrations in water through desorption from sediment was not recognized (chapters 3 and 4). In addition, all herbicides studied here showed the hysteresis of adsorption-desorption process on sediment (Table 5-4). Therefore, the sediment could act as a sink of herbicides in water-sediment system at marsh during ordinary water discharge (Figure 7-1). However, the sediment might become a source of herbicides when the sediment is disturbed by water flow and the fine particles with adsorbed herbicides in sediment are re-suspended in water (Figure 7-1). So, it is plausible that the sediment has a possibility to become a source of herbicides for aquatic environment depending on hydrological conditions.

7-3 Residue and persistence of herbicides in water-sediment system of river and marsh environment

In Table 7-1, herbicides studied here were arranged according to their order in terms of residual amount, adsorption-desorption characteristics and degradability both in the field and laboratory. From the monitoring study shown in chapters 3 and 4, concentration of herbicides in
water were increased approximately in the following order: dimethametryn < thiobencarb < esprocarb = simetryn < pretilachlor, while those in suspended solids and sediment were increased approximately in the following order: dimethametryn < simetryn = pretilachlor < thiobencarb < esprocarb. However, from a laboratory experiment in chapter 5, the extent of adsorption ratio on sediment was increased in the following order: pretilachlor < dimethametryn < simetryn < thiobencarb < esprocarb. The tendency of this result was approximately similar to the result of monitoring study. However, the hysteresis of herbicides adsorption-desorption on sediment were different from this tendency, and the hysteresis intensities of simetryn, dimethametryn and pretilachlor were stronger than those of esprocarb and thiobencarb.

Since the amounts of sale for esprocarb (Table 1-1) and its adsorption ratio (Table 5-3) were relatively higher than other herbicides, the residual amounts of esprocarb in suspended solids and sediment became higher than other herbicides (Figure 4-2). And, since the adsorption ratio of thiobencarb on sediment was relatively higher among the herbicides studied (Table 5-3), the residual amount of thiobencarb in suspended solids and sediment was also higher than other herbicides (Figure 4-2). The degradation rate of esprocarb and thiobencarb were faster among the herbicides studied, probably due to microbial degradation (Figure 6-1), but high concentrations of esprocarb and thiobencarb were detected in sediment before herbicide application in paddy fields (Figures 3-2 and 4-3). The formation of some chemical substances defined as bound residues were reported (Barraclough et al., 2005) and it were originally defined by the International Union of Pure and Applied Chemistry (IUPAC) as “chemical species originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues.” Furthermore, it was pointed that these chemical substances became more non-bioavailable in the environment (Barraclough et al., 2005). Therefore, esprocarb and
thiobencarb might be persistent in sediment for all the year round as non-bioavailable form like bound residues. In addition, the degradation of thiobencarb in sediment from river and marsh was also affected by dechlorination inhibiter (Ueki and Inao, 2001).

Although hydrophobic property of pretilachlor was relatively higher among the herbicides studied (Table 1-1), the concentration of pretilachlor was higher in water, and lower in suspended solids and sediment (Figure 4-3). Same tendency was also recognized in the previous study (Nakano et al., 2004). The reason for this tendency is not understood yet. However, following possibilities would be important: high adsorption affinity of pretilachlor for sediment was somewhat limited by the number of adsorption sites (chapter 5), and pretilachlor was decomposed under the reduced condition (Fajardo et al., 2000). Accordingly the residual amount of pretilachlor in sediment was lower than those of thiobencarb, although these two herbicides had similar amounts of sale.

Since water solubility of simetryn is high (Table 1-1), it became higher in the concentration in water (Figures 3-1 and 4-3). And, since the amount of sale of dimethametryn was lower than other herbicides (Table 1-1), it was detected in lower concentrations in water, suspended solids and sediment (Figure 4-3). However, the adsorption affinity of simetryn and dimethametryn for the mineral surface in sediment was higher than that for organic matter in sediment (chapter 5), and their adsorption-desorption hysteresis on sediment were stronger than esprocarb and thiobencarb (Table 5-4). In addition, simetryn and dimethametryn were more persistent in sediment in water-sediment system among the herbicides studied (Figure 6-1). Therefore, dimethametryn was detected in low concentration in sediment for all the year round.

As mentioned above, in some cases, adsorption-desorption characteristics and degradability of herbicides based on laboratory experiment could not explain sufficiently their residual tendency in fields. Although chemical properties of herbicide such as Kow and water solubility was related with the residual tendency in fields, and the adsorption characteristics
were investigated in the previous studies, it is still difficult to explain the data obtained from this study in some cases. It might be controlled by the adsorption characteristics of herbicide on the various surfaces of organic matter or mineral structure, because the adsorption sites of organic matter and mineral structure were heterogeneous and its detail is not clarified yet. Furthermore, aging effect of pesticides in sediment might be also influential on the behavior of pesticides in the aquatic environment (Barraclough et al., 2005).

7-4 Further studies needed

Water-sediment system in aquatic environment is important for determining the behavior of herbicides applied to paddy fields. Further studies are necessary to investigate the role of sediment for herbicides as sink or source, more detailed characteristics of adsorption and desorption phenomena, and their exact degradation processes in sediment under the non-equilibrium condition. Moreover, experimental flume channels (Allan et al., 2004) are necessary to estimate the herbicides behavior and PEC (Predicted Environment Concentrations). In addition, the monitoring study at river, lake and marsh is still scarce and it is very important to investigate the behavior of herbicides in water-sediment system, because the data obtained from monitoring is sure to be reflected by the actual environmental conditions. Considering new chemical compounds developed and registered as herbicides, the studies on the appropriate management of herbicide usage are still necessary to prevent their ecological effects.
Table 7-1. Herbicides in the order of their residual amount, adsorption-desorption characteristics and degradability.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Suspended solids</th>
<th>Sediment</th>
<th><strong>Adsorption capacity</strong></th>
<th><strong>Adsorption affinity</strong></th>
<th>*<strong>Hysterisis</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>In filed</td>
<td>dimethametryn &lt;</td>
<td>dimethametryn &lt;</td>
<td>dimethametryn &lt;</td>
<td>pretilachlor &lt;</td>
<td>esprocarb &lt;</td>
<td></td>
</tr>
<tr>
<td>Suspended solids</td>
<td>simetryn =</td>
<td>simetryn =</td>
<td>simetryn =</td>
<td>thiobencarb &lt;</td>
<td>esprocarb &lt;</td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td>esprocarb =</td>
<td>pretilachlor &lt;</td>
<td>thiobencarb &lt;</td>
<td>esprocarb &lt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*based on adsorption ratio and $K_F$.
**based on the value of $1/n_{adv}$.
***based on the ratio of $((1/n_{ads})/(1/n_{dec}))$. 
Figure 7-1. Schematic presentation of herbicides behavior in water-sediment system, focusing on the role of sediment (○: herbicide, ◯: particle of suspended solids or a part of sediment, a: in the period of herbicides flowing into water-sediment system at ordinary water discharge, b: in the period of rare detection of herbicides in water at ordinary water discharge, c: in the case that sediment is distracted by water flow).
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References


Environmental Health and Safety Division, Ministry of the Environment Japan 2002: Chemicals in the environment, 368p, Environmental Health and Safety Division, Ministry of the Environment Japan, Tokyo (in Japanese)

Fajardo F., Takagi K., Ishizaka M. and Usui K. 2000: Pattern and rate of dissipation of pretilachlor and mefenacet in plow layer and paddy water under lowland field conditions:
A three-year study, *J. Pestic. Sci.*, 25, 94-100


Iwakuma T., Shiraishi H., Nohara S. and Takamura K. 1993: Runoff properties and change in concentrations of agricultural pesticides in a river system during a rice cultivation period, Chemosphere, 27, 677-691


Kanazawa J. 1996: The data of pesticide environmental characteristics and toxicities, 382p, Godo syuppan, Tokyo (in Japanese)


Kondoh T., Misawa S. and Toyota M. 1993: Characteristic of effluents of nitrogen and phosphorous in paddy fields during the paddling and transplanting season, *Trans. JSIDRE*,

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Murayama S., Komada M., Baba K. and Tsumura S. 2001: Characteristics and the seasonal changes in water quality of small rivers in a rural agricultural catchment area, *Jpn. J. Soil


OECD 2000: Guideline for testing of chemicals 106, OECD, Paris


Satsuma K., Tanaka H., Sato K. and Kato Y. 2002: Role and behavior of benthic microbes able to degrade herbicide atrazine in naturally derived water/sediment microcosm, *Microbes and Environments*, 17, 179-184


Soil Environmental Analysis Committee 1997: Soil environmental analysis, pp. 24-29, Hakuyusya, Tokyo (in Japanese)


Ueji M. and Inao K. 2001: Rice paddy field herbicides and their effects on environment and ecosystems, Weed Biol. Manag., 1, 71-79


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