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Pesticides in Water and Sediment from Littoral Area of Lake Biwa

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Abstract A survey of 29 pesticides was performed for water and sediment from two littoral areas of Lake Biwa in 2007. Two insecticides, 5 fungicides and 13 herbicides in the water and an insecticide, 4 fungicides and 7 herbicides in the sediment were detected from the present survey. Pesticide accumulation potential in the sediment was calculated as "Pesticide concentration ratio" from the results of the survey on water and sediment in Lake Biwa. Correlation was investigated for each of the detected pesticides between sediment ignition loss and pesticide concentration ratio or between sediment particle size and pesticide concentration ratio. The ignition loss correlated well with the pesticide concentration ratio for pyrokiron, simetryn, and isoprothiolane ($p < 0.01$ to $p < 0.001$) but did not for molinate, bromobutide and pretilachlor. Further, the <0.025 mm particle size ratio correlated well with the pesticide concentration ratio for pyrokiron, simetryn, flutolanil, isoprothiolane and mefenacet ($p < 0.01$ to $p < 0.001$) but did not for bromobutide and pretilachlor. The correlation between <0.025 mm particle size ratio and pesticide concentration ratio had almost the same tendency as that between ignition loss and pesticide concentration ratio, suggesting sediment with higher <0.025 mm particle size ratio had higher weight (%) of ignition loss.

Keywords Pesticide · Lake Biwa · Water · Sediment

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Pesticide contamination of river, lake and marsh from agriculture use is a problem of worldwide importance. Many field data on the pesticide contamination of surface waters and sediments in the aquatic environments have been reported in Japan (Ministry of the Environment, Japan 1993, 1994; Yoshizawa 1996; Kawakami et al. 2005, 2006) and in foreign countries (Osfor et al. 1998; Hela et al. 2005).

In the past, we reported various pesticide contaminations of water and fish from rivers flowing into Lake Biwa in Japan (Tsuda et al. 1996, 1997, 1998, 1999). Recently, we reported that about 30 pesticides were detected from the survey in surface waters of Lake Biwa in 2006 (Nakamura et al. 2008). However, few surveys have been performed for pesticides in sediment from Lake Biwa (Ministry of the Environment, Japan 1993, 1994) or from rivers flowing into Lake Biwa.

In this report, the same pesticides in the Lake Biwa survey (Nakamura et al. 2008) were surveyed for water and sediment from two littoral areas of Lake Biwa in 2007 and pesticide accumulation potential in the sediment was calculated as "Pesticide concentration ratio" from the results of the survey. Further, correlation was investigated for each of the detected pesticides between sediment ignition loss and pesticide concentration ratio or between sediment particle size and pesticide concentration ratio.

Materials and Methods

A standard solution of 68 pesticide mixtures and internal standards (Chrysene-d_{12} and phenanthrene-d_{10}) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Florisil PR (60/80 mesh) from Wako Pure Chemical Industries Ltd (Osaka, Japan) after activation at 130°C for

16 h was used for column clean-up. Pesticide-grade solvents and chemicals were used throughout.

Water and sediment samples were collected from littoral area of Lake Biwa (Fig. 1) once or twice every month from April to August in 2007. Sediment samples were collected using an Eckman sampling device from the top 10-cm layer at each sampling location.

The concentrations of 29 pesticides in water samples were determined by the following procedure (Nakamura et al. 2008). In brief, a measured volume (500 mL) of water sample was passed through an Aqusis PLS-3 column and eluted with 4 mL of dichloromethane after drying with air stream at room temperature for 40 min. The eluate was analyzed using GC/MS after evaporation to 0.5 mL and addition of the internal standards. Average recoveries (n = 3) were 78%–130% for the 29 pesticides at a spiked level of 0.1 μg/L. Quantification limits were 0.1 μg/L for propiconazole-1 and propiconazole-2, 0.05 μg/L for cafenstrole, 0.02 μg/L for isoprocarb, fenitrothion, pyrokiron, dimethametryn, pyributicarb, anilofos and mefenacet and 0.01 μg/L for the other 19 pesticides.

Determination of the pesticides in sediment samples was performed using the method of Ministry of the Environment, Japan (2002). In brief, about 10 g of the 2 mm sieve-passed sample was shaken 10 min and extracted ultrasonically 10 min with 25 mL of acetone and centrifuged 10 min (2,000 rpm). The acetone layer was poured into the 250 mL of 5% NaCl prepared in 500 mL of separatory funnel. The same operation was repeated and the mixture was shaken twice 5 min with 50 mL of dichloromethane. The combined dichloromethane layer was mixed with 50 mL of hexane, dehydrated with anhydrous Na_2SO_4 and rotary-vacuum evaporated to 1 mL at 40°C, added three times with 20 mL of hexane on the way to eliminate dichloromethane. The concentrated was passed through a 30 × 1.0 cm I.D. glass clean-up column containing 5 g of hexane-rinsed Florisil PR and 1 g of anhydrous Na_2SO_4. The column was eluted with 125 mL of acetone and hexane (10 + 90) after washing with 10 mL of hexane. The eluate was analyzed using GC/MS after evaporation to 1 mL and addition of the internal standards. Average recoveries (n = 7) were 60% for pyributicarb and

Fig. 1 Map of sampling locations

72%–105% for the 25 pesticides except fenthion, propiconazole-1 and propiconazole-2 at a spiked level of 50 μg/kg, respectively. Quantification limits were 5 μg/kg for cafenstrole, 2 μg/kg for pyrokiron, simazine, anilofos and mefenacet and 1 μg/kg for the other 21 pesticides except fenthion, propiconazole-1 and propiconazole-2. The GC/MS (Finnigan Trace GC 2000 gas chromatograph and Finnigan GCQ/Polaris ion trap mass spectrometer) operating conditions were as follows:

Gas Chromatography

Column: RESTEK Rtx-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness).

Column temperature: 50°C (2 min) → 20°C/min → 180°C (5 min) → 4°C/min → 300°C, injection temperature: 250°C.

Carrier gas: He 1.0 mL/min, injection volume: 1 μL, injection mode: splitless.

Mass Spectrometry

Ionization voltage: 70 eV, ionization current: 27 μA, interface temp.: 250°C.

Ion source temperature: 200°C, scan mode: full scan, mass range: 50–550.

Table 1 Pesticide concentrations in water and sediment from southern basin and northern basin of Lake Biwa

Pesticides	Use	Littoral zone of Akanoi Bay (n = 3) in southern basin		East littoral zone of northern basin (n = 3)	
		Water (μg/L) (n = 21)	Sediment (μg/kg dry wt) (n = 21)	Water (μg/L) (n = 21)	Sediment (μg/kg dry wt) (n = 21)
Isoprocarb	Insecticides	<0.02 to <0.02	<1 to <1	<0.02 to <0.02	<1 to <1
Fenobucarb		<0.01 to 0.04	<1 to <1	<0.01 to 0.02	<1 to <1
Diazinon		<0.01 to 0.28	<1 to 2	<0.01 to 0.01	<1 to <1
Fenitrothion		<0.02 to <0.02	<1 to <1	<0.02 to <0.02	<1 to <1
Fenthion		<0.01 to <0.01	–	<0.01 to <0.01	–
Dichlobenil	Fungicides	<0.01 to 0.01	<1 to <1	<0.01 to 0.01	<1 to <1
Pyrokiron		0.02 to 0.53	<2 to 15	0.02 to 0.37	<2 to <2
Iprobenfos		<0.01 to <0.01	<1 to <1	<0.01 to <0.01	<1 to <1
Fthalide		<0.01 to 0.02	<1 to <1	<0.01 to <0.01	<1 to 2
Flutolanil		<0.01 to 0.06	<1 to 5	<0.01 to 0.02	<1 to 2
Isoprothiolane		0.01 to 0.12	<1 to 9	0.01 to 0.06	<1 to 11
Propiconazole-1		<0.1 to <0.1	–	<0.1 to <0.1	–
Propiconazole-2		<0.1 to <0.1	–	<0.1 to <0.1	–
Molinate	Herbicides	<0.01 to 1.40	<1 to 7	<0.01 to 0.53	<1 to <1
Simazine		<0.01 to <0.01	<2 to <2	<0.01 to <0.01	<2 to <2
Propyzamide		<0.01 to <0.01	<1 to <1	<0.01 to <0.01	<1 to <1
Bromobutide		0.02 to 5.77	<1 to 14	0.03 to 1.90	<1 to 2
Simetryn		0.03 to 3.44	<1 to 44	0.03 to 1.11	<1 to 18
Alachlor		<0.01 to 0.02	<1 to <1	<0.01 to 0.02	<1 to <1
Esprocarb		<0.01 to 0.44	<1 to 23	<0.01 to 0.07	<1 to 2
Thiobencarb		<0.01 to 0.06	<1 to 10	<0.01 to <0.01	<1 to 1
Dime thametryn		<0.02 to 0.13	<1 to <1	<0.02 to 0.06	<1 to <1
Dime piperate		<0.01 to <0.01	<1 to <1	<0.01 to <0.01	<1 to <1
Pretilachlor		<0.01 to 0.46	<1 to 1	<0.01 to 0.23	<1 to 1
Thenylchlor		<0.01 to 0.13	<1 to <1	<0.01 to 0.03	<1 to <1
Pyributicarb		<0.02 to <0.02	<1 to <1	<0.02 to <0.02	<1 to <1
Anilofos		<0.02 to 0.10	<1 to <1	<0.02 to <0.02	<2 to <2
Mefenacet		<0.02 to 2.65	<2 to 33	<0.02 to 0.57	<2 to 8
Cafenstrole		<0.05 to 0.09	<5 to <5	<0.05 to 0.08	<5 to <5

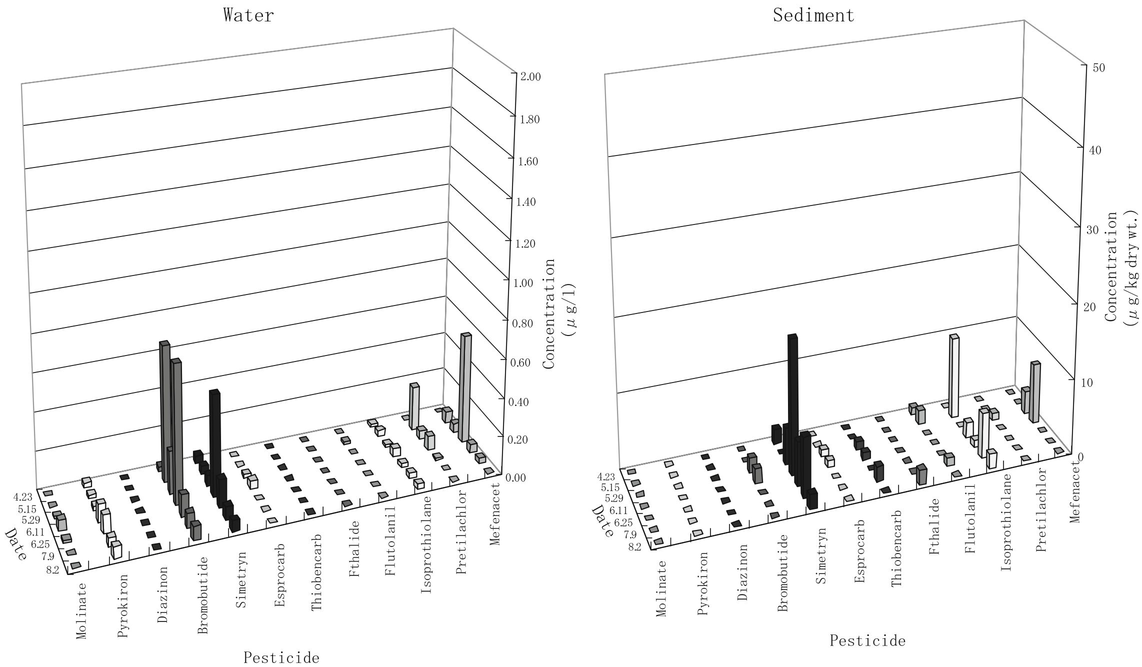

Fig. 2 Concentration changes of the 12 pesticides in the water and sediment from east littoral zone of northern basin of Lake Biwa (10C) throughout the survey from April to August in 2007

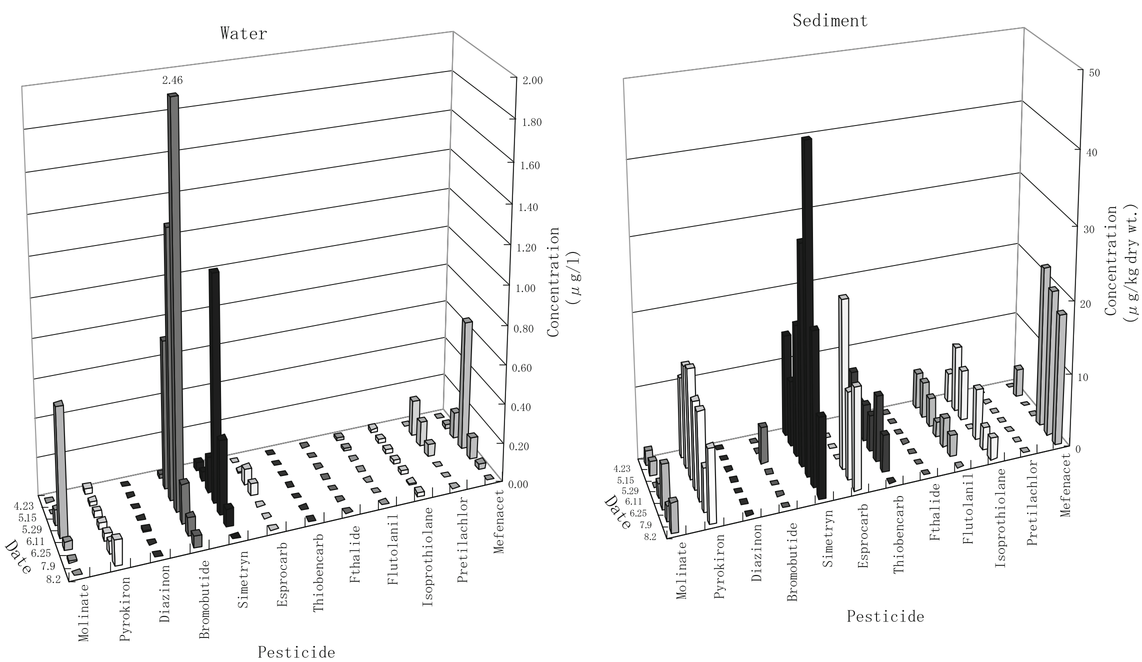

Fig. 3 Concentration changes of the 12 pesticides in the water and sediment from littoral zone of Akanoi Bay (South) in southern basin of Lake Biwa throughout the survey from April to August in 2007

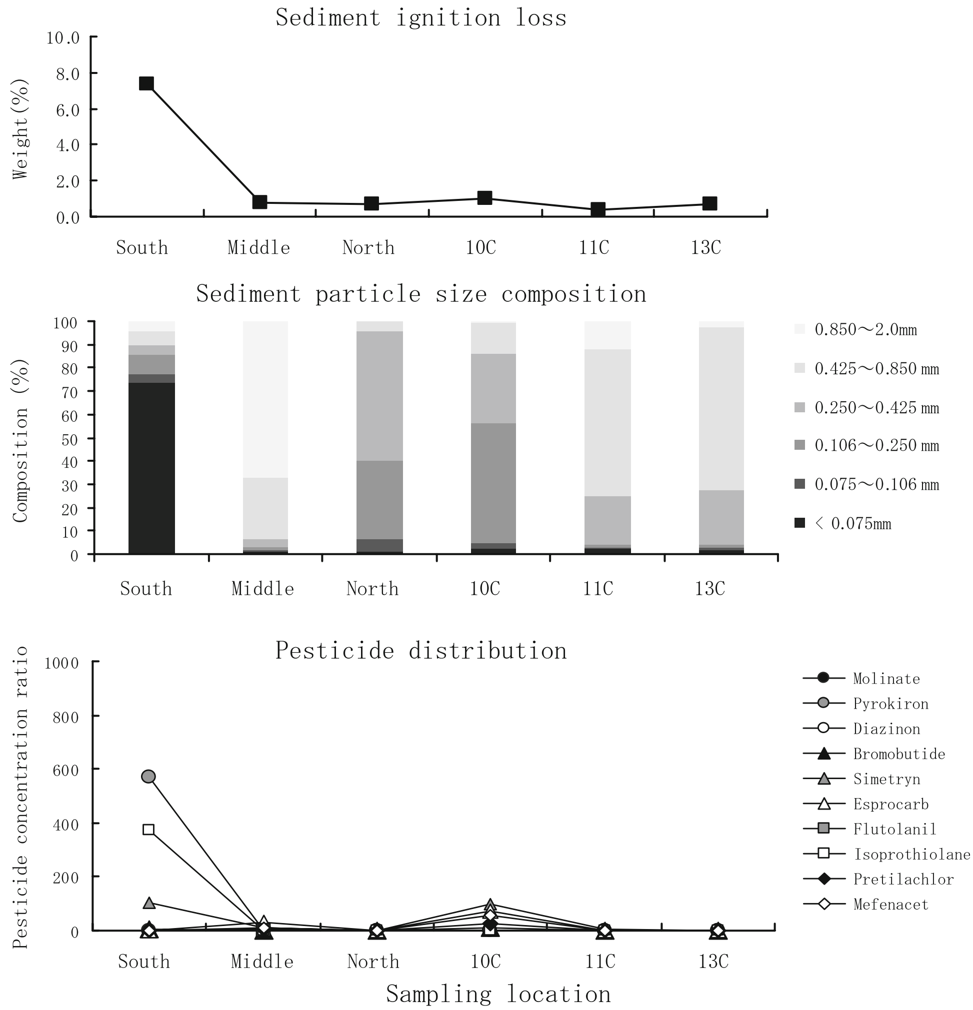

Fig. 4 Ignition loss, particle size composition and pesticide distribution in the sediments from six sampling locations in two littoral areas of Lake Biwa on May 29, 2007

Calculation of Pesticide Concentration Ratio

Pesticide concentration ratio was calculated using the following equation:

$$\text{Pesticide concentration ratio} = \frac{\text{pesticide concentration in sediment}}{\text{pesticide concentration in water}}.$$

Calculation was performed at each sampling time when the concentration of each pesticide could be determined for both water and sediment samples.

Results and Discussion

Results of the survey are summarized in Table 1 for east littoral zone (C_{10}, C_{11} and C_{13}) of northern basin of Lake Biwa and for littoral zone (North, Center and South) of Akanoi Bay in southern basin of Lake Biwa. Two insecticides, 4 fungicides and 10 herbicides in the water and 3 fungicides and 6 herbicides in the sediment were detected from the east littoral zone of northern basin of Lake Biwa. Two insecticides, 5 fungicides and 12 herbicides in the water and an insecticide, 3 fungicides and 7 herbicides were detected from the littoral zone of Akanoi Bay in southern basin of Lake Biwa. An insecticide (diazinon), 4 fungicides (pyrokiron, fthalide, flutolanil and isoprothiolane) and 7 herbicides (molinate, bromobutide, simetryn, esprocarb, thiobencarb, pretilachlor and mefenacet) were detected in the present sediment survey, so concentration changes of the 12 pesticides in the water and the sediment from the two littoral areas of Lake Biwa are shown in Figs. 2 and 3 throughout the survey from April to August in 2007. The concentrations of molinate, bromobutide, simetryne and mefenacet in the water were high in May and June. This result corresponded to the maximum use of the herbicides in paddy fields of Japan and detection of simetryn in the sediment corresponded well to that in the water.

However, the concentration of bromobutide in the sediment was very low compared with that in the water and detections of the other pesticides in the sediment did not correspond to those in the water.

In general, hydrophobic chemical compounds are apt to adsorb to organic matter in the sediments and the absorption ability is higher in case of higher composition of small sediment particle size. Here, an example of ignition loss (carbon contents), particle size composition and pesticide distribution in the sediments from six sampling locations (May 29, 2007) are shown in Fig. 4. Pesticides such as pyrokiron, isoprothiolane and simetryn had higher pesticide concentration ratio at the sampling locations where the values of ignition loss and the composition of small particle size were higher.

Correlation between sediment ignition loss and pesticide concentration ratio was investigated for the present survey data on the 12 pesticides. The correlation coefficients are summarized in Table 2. The ignition loss correlated well with the pesticide concentration ratio for pyrokiron, simetryn and isoprothiolane ($p < 0.01$ to $p < 0.001$) but did not for molinate, bromobutide and pretilachlor, suggesting the possibility that the adsorption of pesticide on organic matter in the sediment was strong for pyrokiron, simetryn and isoprothiolane but weak for molinate, bromobutide and pretilachlor. Kawakami et al. (2007) reported that the adsorption ratio of five herbicides on the sediment increased in the following order: pretilachlor < dimethametryn < simetryn < thiobencarb < esprocarb. The order of simetryn > pretilachlor was consistent with our experiment results.

Further, correlation between <0.025 mm sediment particle size ratio and pesticide concentration ratio was investigated for the present survey data on the 12 pesticides. The correlation coefficients are summarized in Table 3. The <0.025 mm particle size ratio correlated well with the pesticide concentration ratio for pyrokiron, simetryn, flutolanil, isoprothiolane and mefenacet ($p < 0.01$–$p < 0.001$) but did not for bromobutide and pretilachlor. The correlation between <0.025 mm particle size ratio and pesticide concentration ratio had almost the same tendency as that between ignition loss and pesticide concentration ratio, suggesting sediment with higher <0.025 mm particle size ratio had higher weight (%) of ignition loss.

Table 2 Relationship between ignition loss (%) and pesticide concentration ratio in Lake Biwa sediment

Pesticide	n	Correlation coefficient (*r*)
Molinate	22	−0.0608****
Pyrokiron	42	0.6051
Diazinon	5	−0.3506
Bromobutide	42	0.0436
Simetryn	42	0.4237**
Esprocarb	18	0.4839*
Thiobencarb	1	–
Fthalide	0	–
Flutolanil	15	0.3007
Isoprothiolane	42	0.4721***
Pretilachlor	21	−0.0663
Mefenacet	28	0.2102

* $p < 0.05$ ** $p < 0.01$ *** $p < 0.002$ **** $p < 0.001$

Table 3 Relationship between <0.025 mm particle size ratio and pesticide concentration ratio in Lake Biwa sediment

Pesticide	n	Correlation coefficient (*r*)
Molinate	22	0.1578
Pyrokiron	42	0.7410****
Diazinon	5	−0.2750
Bromobutide	42	0.0141
Simetryn	42	0.6166****
Esprocarb	18	−0.2402
Thiobencarb	1	–
Fthalide	0	–
Flutolanil	15	0.8328****
Isoprothiolane	42	0.6975****
Pretilachlor	21	−0.0959
Mefenacet	28	0.4953**

** $p < 0.01$ **** $p < 0.001$

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