RESEARCH PAPER

**Miki Sudo · Takeshi Kawachi · Yoshifumi Hida
Takao Kunimatsu**

Spatial distribution and seasonal changes of pesticides in Lake Biwa, Japan

Abstract The spatial distribution and seasonal variation in the concentrations in Lake Biwa of pesticides used in paddy fields were studied. Lake Biwa is the largest lake in Japan and is a recognized water resource for 14 million people in the Kinki district. Samples were collected nine times from April to December 2001 at ten sites within the lake and at the mouths of six influent rivers. Weekly sampling was also carried out at a single site on an effluent river. Among the 20 pesticides analyzed, the detection frequencies in surface water were almost 100% for simetryn, bromobutide, and isoprothiolane; around 75% for molinate and pyroquilon; around 30% for three herbicides and one fungicide; and almost zero for the remaining substances. The maximum concentrations of pesticides detected frequently in the lake were in the range 0.1–$0.4 \mu g l^{-1}$. The occurrence of a few pesticides below the thermocline may be explained by thermal stratification and vertical circulation. Although the thermocline suppressed vertical diffusion in spring and summer during pesticide application periods, a few pesticides remaining at the surface of the lake in winter were transported to the hypolimnion by vertical circulation and remained there even after the reestablishment of the thermocline. The half-lives of pesticides in the lake were estimated to be more than a year for simetryn, half a year for bromobutide, 1.5 months for molinate, and 1 month for dimepiperate. The main cause of elimination for molinate and dimepiperate was estimated to be degradation, that for simetryn was outflow, and for bromobutide both degradation and outflow were significant.

Key words Pesticides · Water contamination · Vertical diffusion · Lake Biwa

M. Sudo (✉) · T. Kawachi · Y. Hida · T. Kunimatsu
School of Environmental Science, The University of Shiga
Prefecture, 2500 Hassaka, Hikone 522-8533, Japan
Tel. +81-749-28-8334; Fax +81-749-28-8477
e-mail: sudo@ses.usp.ac.jp

Introduction

In recent years there has been a rise in the number of reported incidents of contamination of public water from pesticides, largely caused by increasing use of intensive agricultural methods on upland fields (Dabrowski et al. 2002; Müller et al. 2002; Triano et al. 2001; Harman-Fetcho et al. 1999), paddy fields (Tanabe et al. 2001; Crepeau and Kuivila 2000; Albanis et al. 1994; Pereira and Hostettler 1993), golf courses (Ma et al. 1999; Sudo and Kunimatsu 1992, 1995), and urban areas (Hoffman et al. 2000). Little is known about the long-term, low-dose effects of many of these pesticides on public health, as well as on nontarget species. Therefore public water contamination from pesticides has become a growing source of anxiety, and many believe it will become a major environmental issue.

Lake Biwa is the largest lake in Japan, and water from it and the Yodo River, situated at the lower reaches of the lake, is used by 14 million people in the Kinki district as potable water and for industrial, recreational, and agricultural purposes. Understanding contamination data and the contamination mechanisms at work in rivers and lakes is necessary to quantify the fate and transport of pesticides released from agricultural fields. Although some researchers have studied the pesticide contamination in influent rivers (Sudo et al. 2002b; Tsuda et al. 1997; Sasagawa et al. 1996) and the effluent river (Sudo et al. 2002a, b; Fukushima et al. 1995; Yamaguchi et al. 1992) of the Lake Biwa basin, few extensive surveys of the lake water have been made. The objective of this study was to present the seasonal, spatial, and vertical variations in pesticides in Lake Biwa and to consider the relation between pesticide contaminations and the limnological characteristics of the lake.

Materials and methods

Study area

Lake Biwa has a surface area of $674 \, km^2$ and a water catchment area of $3174 \, km^2$, which closely corresponds to the

administrative limits of Shiga Prefecture. The ratio of the catchment area of Lake Biwa to the area of the prefecture is 93%. The lake is a mesotrophic lake. The climatic conditions of the Lake Biwa basin are characterized by an average annual temperature of 14.1°C and an average annual precipitation of 1740 mm (LBRI 1987). Although more than 100 rivers originating in the surrounding mountains flow into the lake, its outlets are the Seta River and three artificial canals flowing from the southern end of the lake.

Rice is a major crop in the Lake Biwa basin. In the catchment area, paddy fields occupy 17% of the total land use and rice is harvested in more than 400 km² of paddy fields each year. Upland fields and orchards occupy less than 1% of total land use. In the majority of the paddy fields, rice seedlings are transplanted between the end of April and the beginning of May, and harvested until late September. Preemergence herbicides are applied by sequential treatment or one-shot treatment up to 3 weeks after transplantation. In sequential treatment, a first-stage herbicide is applied up to 5 days after transplanting, followed by second-stage herbicide application between 2 and 3 weeks after that. In one-shot treatment, a one-shot herbicide is applied once between 3 and 14 days after transplanting. Fungicides and insecticides are used during June and August according to forecast and the occurrence of diseases and insect pests. Such treatments are often used to disinfect seedlings in spring.

Sample collection

The locations of the observation sites are shown in Fig. 1. Surface water samples were collected at water depths of 60, 20, and 10 m along three transect lines from the mouth of the Ado River to the Uso River (line A), from Myojinsaki Point to the Echi River (line B), and from the Otani River to the Hino River (line C). Vertical sample collection was also performed by using a Van-Dorn sampling bottle. Sampling depths in the lake, based on the vertical profiles of water temperature, were set up above the thermocline (depths of 0 and 5 m at all sampling sites) and below the thermocline (a depth of 15 m at A2, B2, C2, A1, B1, and C1, and a depth of 50 m at A1, B1, and C1). Water samples were also collected at the mouth of six major influent rivers along the coast from the Uso River to the Hino River, selected on the basis of the area of the watershed and paddy fields (R1–R6). The land use pattern of the rivers is shown in Table 1. Sample collections within the lake and influent rivers were conducted nine times from April to December 2001. Surface water was also collected once a week in 2001 at the Biwako Bridge (site D), the point that divides the lake into the North Basin (average depth 43 m) and the South Basin (4 m), and at the Seta River (site E), the only natural outlet of the lake.
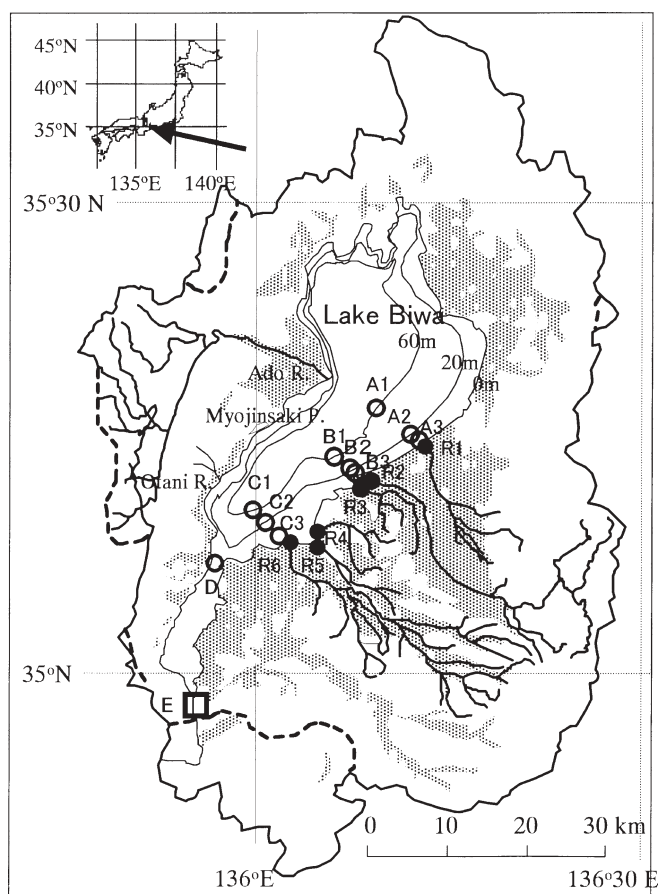
Fig. 1. Location of observation sites. ○ Sampling site in Lake Biwa; ● sampling site in influent river; □ sampling site in effluent river; — prefecture boundary; --- drainage basin boundary; ░ paddy fields

Table 1. Land utilization of observed rivers

Site	River	Total[a] (km²)	Land use[a]		
			Forests (km²)	Paddy fields (km²)	Others (km²)
R1	Uso	84.2	22.3	43.8	18.1
R2	Echi	203.3	161.9	19.1	22.3
R3	Daido	20.4	2.5	11.1	6.8
R4	Chomeiji	129.2	27.6	66.8	34.8
R5	Siratori	22.0	3.9	12.9	5.2
R6	Hino	210.1	106.0	57.8	46.3
E	Seta	3039.0	1844.4	675.8	518.8

[a] Integrated Planning of Water Resource Quality, Department of Environmental Engineering, Kyoto University (2000)

Table 2. Detection frequencies and annual maximum concentrations of pesticides in Lake Biwa and related rivers in 2001

Group	Agrochemical	Use	Application[a] (tons)	Lake water (surface) Frequency[b] (%)	Lake water (surface) Max.[c] (μg l^{-1})	Influent river water Frequency[b] (%)	Influent river water Max.[c] (μg l^{-1})	Effluent river water Frequency[b] (%)	Effluent river water Max.[c] (μg l^{-1})
I	Simetryn	H (R)	4.6	100	0.41	94	2.19	100	0.55
	Bromobutide	H (R)	1.9	98	0.21	76	2.83	100	0.27
	Isoprothiolane	F (R)	3.8	97	0.15	94	2.32	100	0.24
II	Molinate	H (R)	5.1	76	0.44	87	1.64	62	0.46
	Pyroquilon	F (R)	0.8	71	0.11	72	3.42	75	0.22
III	Dimepiperate	H (R)	6.1	44	0.15	46	0.76	23	0.04
	Thiobencarb	H (R,U)	14.0	30	0.04	39	0.73	12	0.11
	Pretilachlor	H (R)	4.6	31	0.09	30	3.04	23	0.10
	Flutolanil	F (R,U)	1.0	21	0.06	46	0.94	23	0.06
IV	Diazinon	I (R,U)	3.0	2	0.02	19	4.62	n.d.	–
	Esprocarb	H (R)	6.2	2	0.03	6	0.08	13	0.06
	Simazine	H (U,T)	0.1	1	0.02	11	0.06	n.d.	–
	Fenitrothion	I (R,U)	13.7	n.d.	–	2	0.04	n.d.	–
	Fenobucarb	I (R,U)	3.7	n.d.	–	n.d.	–	n.d.	–
	Fenthion	I (R,U)	2.8	n.d.	–	n.d.	–	n.d.	–
	Edifenphos	F (R)	1.6	n.d.	–	2	0.14	n.d.	–
	Iprobenfos	F (R)	1.4	n.d.	–	n.d.	–	n.d.	–
	Dichlorvos	I (U)	1.1	n.d.	–	n.d.	–	n.d.	–
	Pyributicarb	H (T)	1.1	n.d.	–	6	0.02	n.d.	–
	Chloroneb	F (U,T)	0.3	n.d.	–	n.d.	–	n.d.	–

H, herbicide; F, fungicide; I, insecticide; R, paddy fields; U, upland fields and orchards; T, turfgrass; n.d., not detected
[a] Application amount estimated as 93% of the shipment to Shiga Prefecture in 2001
[b] Detection frequency
[c] Maximum concentration

Sample analysis

The pesticides studied included nine herbicides, six fungicides, and five insecticides (Table 2). Standard pesticides and internal standards were purchased from Wako Pure Chemical Industries (Osaka, Japan) and Hayashi Pure Chemical Industries (Osaka, Japan). All chemicals were of pesticide analytical grade. The pesticides were determined as follows; prior to extraction using a Sep-Pak Plus PS-2 cartridge (265 mg styrene divinylbenzene copolymer, Nippon Millipore, Tokyo, Japan), 500- to 1000-ml samples were filtered through a 1.0-μm glass-fiber filter. Because the pesticides monitored in this study are known to exist mainly in the aqueous phase (Sudo et al. 2002a; Sasagawa et al. 1996), based on their sorptive characteristics such as greater aqueous solubilities and lower octanol–water partition coefficients, only the filtrate was analyzed to give the pesticide concentrations. Water after filtration was pumped through the cartridge at a flow rate of 10 ml min^{-1} using a piston pump with Teflon tubing. After extraction, the cartridge was centrifuged to remove excess water. The dried cartridge was eluted with 5 ml of acetone and concentrated to 1.0 ml under a gentle stream of nitrogen at 50°C. Acenaphthene-d10, anthracene-d10, fluoranthene-d10, and chrysene-d12 were added to all samples as internal standards. The extract sample was stored at −20°C before quantitative analysis. The sample was analyzed on a gas chromatograph (HP 6890, Hewlett-Packard, Palo Alto, CA, USA) coupled with a mass spectrometer (Joel Automass System II, JOEL, Tokyo, Japan) equipped with an ionization source (70 eV). The gas chromatograph/mass spectrometer (GC-MS) was fitted with a 30-m-long and 0.25-mm-thick film of dimethylpolysiloxane (DB-1, J&W, Folsom, CA, USA). The splitless injector, the GC–MS interface, and the source temperatures were maintained at 250°C. The initial oven temperature was maintained at 45°C for 4 min, increased to 180°C at 20°C min^{-1} followed by an increase to 250°C at 5°C min^{-1}, and held for 4 min.

Recovery efficiencies ranged from 74% (chloroneb) to 110% (fenobucarb) and the standard deviation ($n = 5$) ranged from 4% (fenitrothion) to 16% (flutolanil). No interfering peaks were found in the blank (organic-free water) extracts. The concentrations reported in this study were not corrected for recovery. A lower limit of quantification was calculated by determining the concentration that corresponded to an instrument signal/noise ratio of five. Because most of the pesticides analyzed by this method had a limit of quantitation at or below 0.01 μg l^{-1}, the limit of quantitation was chosen as 0.01 μg l^{-1} for these compounds. The concentration of pesticides detected at less than the limit was given as zero.

Results

Pesticide contamination in the surface water of the lake

The annual maximum concentrations of pesticides in the surface water of the lake (lines A, B, C and site D) and in the river water (six sites) are shown in Table 2. The detection frequencies, calculated via nine observations in lake

surface water at ten sites ($n = 90$), nine observations in influent rivers at six sites ($n = 54$), and via weekly observation in the effluent river ($n = 50$) are shown in the same table. Although the detection frequencies may be affected to some degree by the differences in timing between the sampling and the pesticide application period, the pesticides were divided into four groups based on detection frequencies in the surface water of the lake; pesticides detected in almost all samples (group I), in around 75% of samples (group II), in around 30% (group III), and in almost zero or not detected (group IV). The maximum concentrations were less than $0.5\,\mu g\,l^{-1}$ in the lake water. Pesticides classified in groups I, II, and III were composed of herbicides or fungicides and all of the insecticides monitored in this study were classified in group IV.

The detection frequencies in the influent rivers and the effluent river (site E) showed similar trends, however, the pesticides in group IV could be divided into two subgroups based on the observations in river water. One group is made up of the pesticides detected in river water with relatively low frequencies (group IV-1) and the other, the pesticides that were almost undetectable in river water (group IV-2).

Seasonal variations in pesticide concentrations

Concentrations of simetryn (group I), molinate and pyroquilon (group II), and dimepiperate (group III) in the surface lake water and the river water are shown in Fig. 2 as representative of the seasonal variation in each group. Simetryn and molinate were applied as second-stage herbicides in sequential treatment and dimepiperate was applied as a one-shot herbicide. The fungicide pyroquilon is mainly used to control rice leaf blast and panicle blast preventively or in the initial stage of the diseases from the end of June to early August. The fungicide was often used on seedlings before transplanting in April.

Fig. 2. a Seasonal changes in simetryn concentration in surface lake water and river water. *The scale of the circles in river water on June 8 is reduced fivefold because of their high values. b Seasonal changes in molinate concentration in surface lake water and river water. *The scale of the circles in river water on June 8 is reduced fivefold because of their high values. c Seasonal changes in pyroquilon concentration in surface lake water and river water. *The scales of the circles in river water on July 11 and July 31 are reduced tenfold and fivefold, respectively, because of their high values. d Seasonal changes in dimepiperate concentration in surface lake water and river water. *The scale of the circles in river water on June 8 is reduced twofold because of their high values
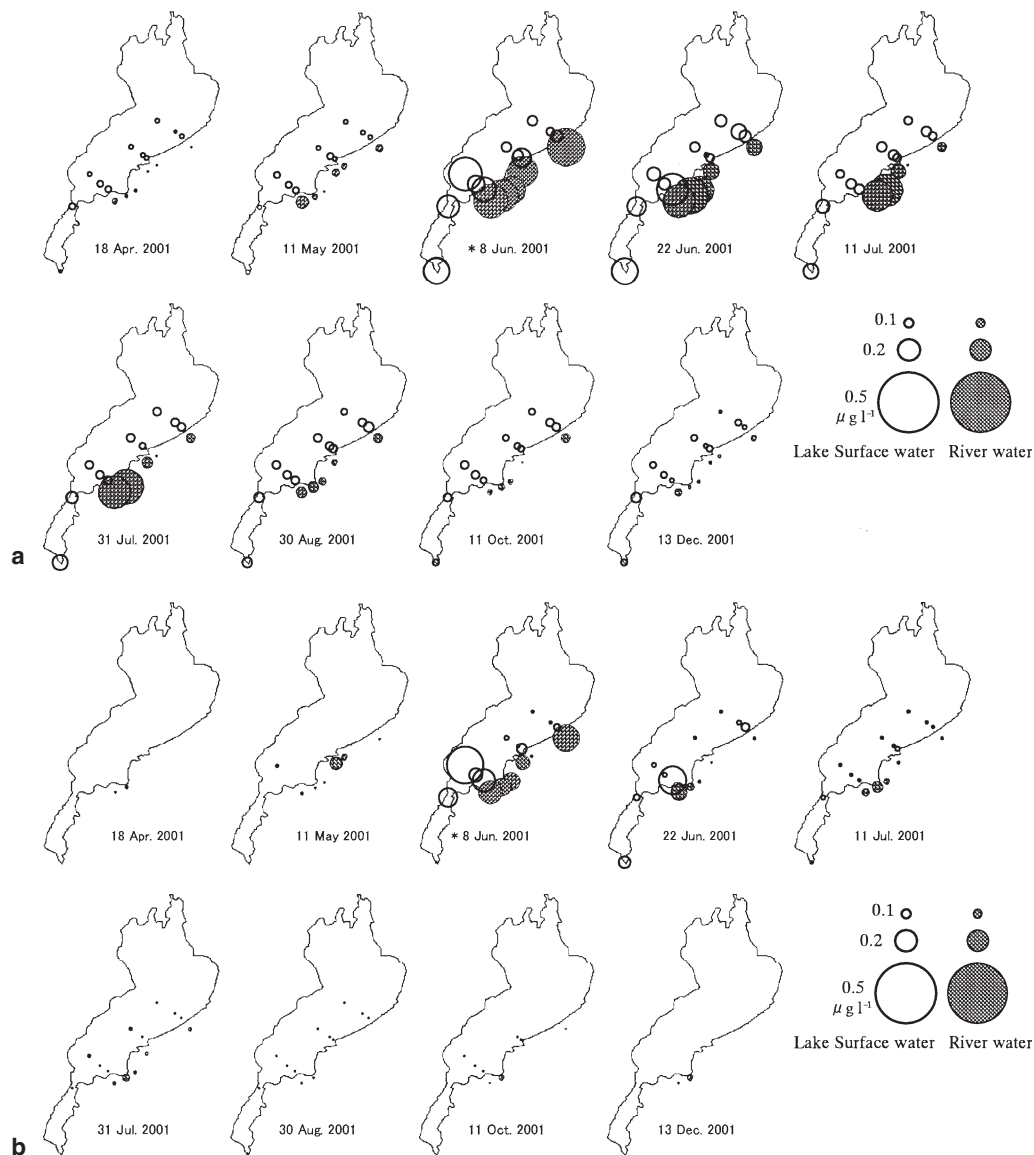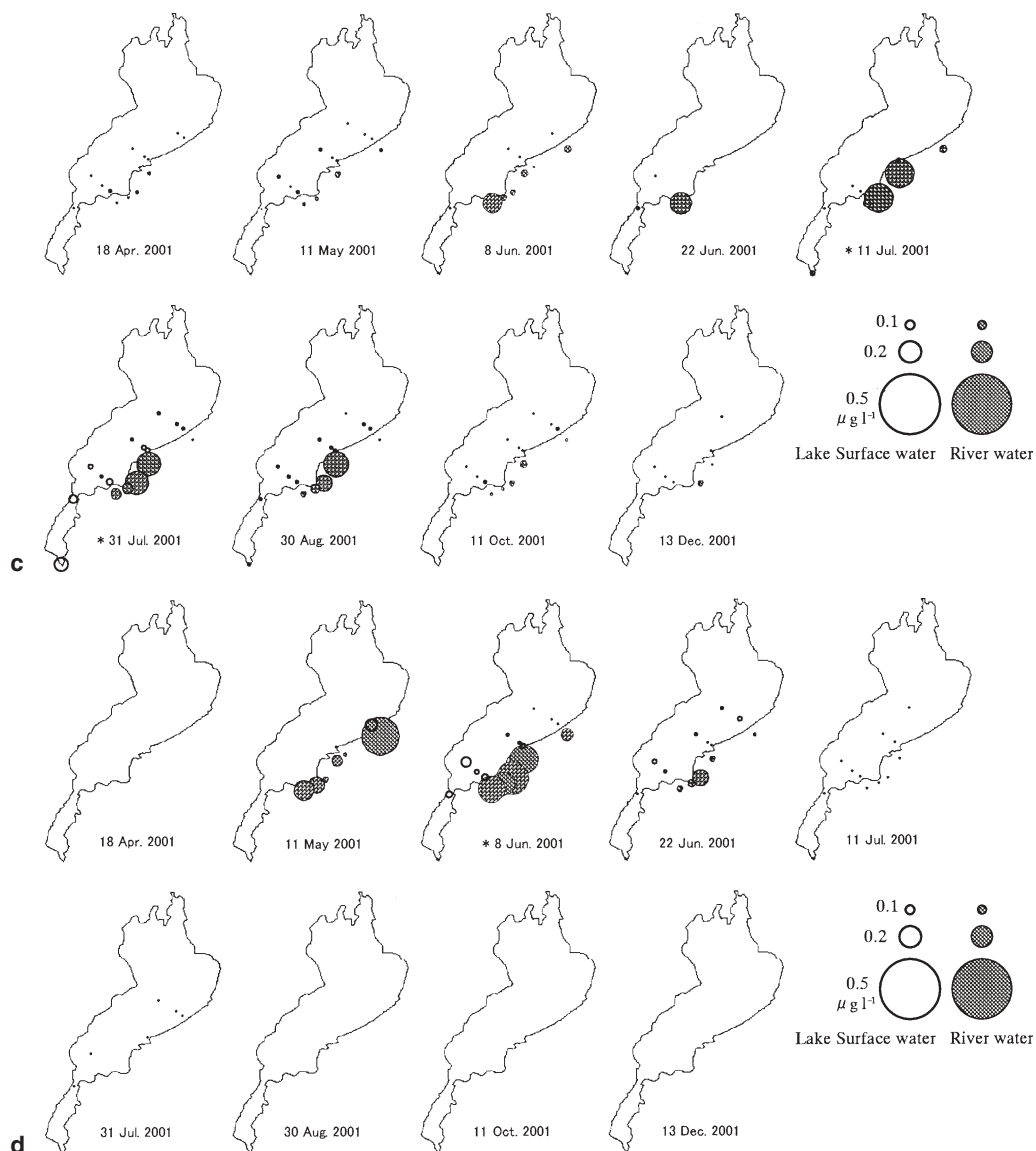
Fig. 2. Continued

Group I. Although it had been about a year since its previous application, simetryn was detected in the surface water of the lake at levels of around 0.05 μg l⁻¹ at every site in April in the surface water of the lake. Simetryn concentrations both in the littoral zone and the profundal zone increased rapidly at the beginning of June. Although the concentrations in the sample collected on June 8 were relatively higher at line C, site D, and site E, they were almost the same throughout the lake after the July observation. Following the high-contamination period, the concentration decreased gradually and remained at 0.1 μg l⁻¹ in the summer and 0.07 μg l⁻¹ in the winter. Compared with the concentrations in river-mouth water, the concentrations in the surface lake water were lower just before or immediately after the application period and shifted to be higher after the summer season. The concentration of the fungicide isoprothiolane in the lake and in the river increased to some degree during the application period in April, July, and August. The concentration during the remaining period was found to be around 0.03 μg l⁻¹ throughout the lake and in river waters.

Group II. Molinate contamination in the lake water emerged and peaked at 0.1–0.4 μg l⁻¹ in early June. The contamination levels then declined and remained under 0.05 μg l⁻¹ in the summer and autumn. No appreciable contamination in lake water or river water was observed in winter or early spring. The fungicide pyroquilon was detected throughout the surface lake water from April to early May and from late July to October. These values corresponded to the usage of the fungicide on seedlings in spring and usage to control rice blast in summer, respectively. In some of the influent rivers, relatively high concentrations were detected in June. The occurrence of pyroquilon contamination in the lake water in December was observed at 60% of sampling sites at concentrations of around 0.03 μg l⁻¹.

Group III. Contamination of the surface lake water and river water by pesticides in group III was observed for a few months after application only and was barely detected in the remaining period.

Group IV. The insecticide diazinon was detected in 20% of samples of river water in July and August, and the herbicides simazine, esprocarb, and pyributicarb were detected in 5%–10% of samples at relatively low contamination levels in May or June, relative to the application period.

Vertical profiles of pesticides in the lake

Figure 3 shows the vertical distribution of water temperatures and simetryn (group I), molinate and pyroquilon (group II), and dimepiperate (group III) at line A. The profiles of pesticide concentration and water temperatures at lines B and C were the same as those observed at line A. The water temperature changed seasonally between 10°C and 30°C at depths of 0 and 5 m, ranged from 10°C to 20°C at a depth of 15 m, and was stable at 8°C at 50 m. In the winter, the vertical distribution of water temperature reached a minimum. In group I, the concentration in surface water, or that above the thermocline (at a depth of 5 m), decreased gradually after the application period, and vertical distribution with changes in concentration were not observed in winter or early spring. Below the thermocline (at depths of 15 m and 50 m), pesticides in group I were detected throughout the year, at $0.07 \mu g l^{-1}$ for simetryn and at $0.02-0.03 \mu g l^{-1}$ for bromobutide and isoprothiolane.

In groups II and III, concentrations in water samples collected at a depth of 5 m were similar to those at the water surface. In group II, pyroquilon was detected almost all year round at $0.02-0.03 \mu g l^{-1}$ at depths of 15 m and 50 m, whereas molinate was almost undetectable. Group III chemicals were detected less frequently at a depth of 15 m, even in the high-contamination period, and were rarely detected at 50 m at concentrations greater than quantitation limits. For group IV, pesticide contamination was not observed at or below the thermocline, nor was it observed in the surface water.

Discussion

Contamination of surface water of the lake

The amounts of pesticide applied in the Lake Biwa basin, estimated as 93% of the total shipments to the prefecture, ranged from 0.1 to 14 ton/year (JPPA 2003); however, the detection frequencies and pesticide concentrations monitored in this study in the lake and river water were not in proportion to the amounts applied. The amount and the concentration of pesticides reaching the lake is affected not only by the application amounts but also by the local hydrogeological and meteorological conditions as well as pesticide properties such as mobility, rate of degradation, and evaporation.

As shown in Fig. 2, the simetryn concentration in the profundal zone increased in early June, two weeks after the greatest pesticide use, and the concentration was nearly uniform throughout the lake in the July observations. These changes may result from transportation by diffusion, circular currents, and internal waves established during the thermocline season as well as from the mass movement of water in the lake caused by wind and runoff from the rivers (LBRI 1987). Relatively higher concentrations found at line C during the application period were caused by high concentrations in adjoining influent rivers.

Although the concentration in the lake water of pesticides classified as group I and II had been lower than that in influent rivers during the application period, it shifted to being higher a few months later. This indicates that continuous pesticide input from the rivers is not an important factor by which pesticides remained in the lake. This phenomenon may result from the residue of the pesticides that flowed into the lake during the application period.

Contamination of the river water

Previous studies monitored in influent rivers of Lake Biwa showed maximum concentrations of 20 and $11 \mu g l^{-1}$ for simetryn and molinate, respectively (Sudo et al. 2002a), and 23, 4.1, 48, 4.6, and $2.9 \mu g l^{-1}$ for simetryn, isoprothiolane, molinate, thiobencarb, and diazinon, respectively (Sudo et al. 2002b). Tsuda et al. (1997) reported concentrations of 21.2, 7.6, 75.5, and $8.7 \mu g l^{-1}$ for simetryn, bromobutide, molinate, and pretilachlor, respectively, and Sasagawa et al. (1996) reported concentrations of about 50, 400, and $10 \mu g l^{-1}$ for simetryn, pretilachlor, and molinate, respectively. In these studies water samples were collected more than once a week above the mouth of the river. To a small extent, the lower pesticide concentrations in river water obtained in this study could be explained by variations in hydrological conditions and pesticide application. Moreover, the biweekly sample collection in this study may have failed to collect the peak concentration during the high-contamination period and sample collection at the mouth of rivers may contribute to decreases in the concentration by dilution with lake water.

Among the pesticides in group IV, diazinon was detected at relatively high frequency and high maximum concentration in river water. This pesticide may be decomposed effectively before diffusion in the lake because it is significantly degraded by light at wavelengths below 290 nm (Kanazawa 1992). Other pesticides in group IV-1 may be diluted and degraded soon after inflowing to the lake. Pesticides in group IV-2 were considered to be either readily degradable in the aquatic environment or less migratory from paddy fields.

Contamination of lake water below the thermocline

The water temperature of the influent rivers was similar to or slightly higher than that of the surface water of the lake

except in the winter season. The vertical diffusion of river water flowing into the northern lake were suppressed by a marked thermocline established at a depth of around 15 m between May and August. Therefore, pesticide concentrations increased markedly just above the thermocline (at depths of 0 and 5 m) during the thermal stratification period.

The occurrences of pesticides such as simetryn, bromobutide, isoprothiolane (group I) and pyroquilon (group II) in the hypolimnion of the lake may be the result of the following mechanisms. In winter and early spring, the water circulates vertically as indicated by the disappearance of the thermocline (Somiya 2000). Pesticides found to remain in the surface water when the thermocline disappears are thought to be transported from the epilimnion to the hypolimnion and subsequently distributed throughout the entire water column. Because residues in the hypolimnion may be less degradable as a result of low temperatures and reduced possibilities for degradation by sunlight or elimination by evaporation, residues may remain there, and over time the thermocline is established again. Desorption from the sediment could also be a cause of the occurrence of pesticides in the hypolimnion; however, the finding of no residue of any of the pesticides monitored in this study in the sediment collected at A3 and C3 (data not shown) suggests that there was no interaction between sediment and the water body. In the case of molinate and pesticides in group III, these chemicals may be undetected in the hypolimnion throughout the course of a year because no residue remained in surface water prior to the overturn of the water column in winter.

Elimination rate of pesticides in the surface lake water

Pesticides in Lake Biwa were eliminated during retention in the lake. The lumped first-order decay function is used to relate the mass of pesticides in the lake as follows:

$$\mathrm{d}L/\mathrm{d}t = -kL \tag{1}$$

where L is the pesticide mass in the lake and k is the elimination rate constant. Although herbicide concentration in the lake peaked once a year, fungicide concentration increased twice, reflecting its usage in spring and autumn. Therefore, elimination rate constants were analyzed only for herbicides in group I (simetryn and bromobutide), II (molinate), and III (dimepiperate) that showed a relatively high contamination level. To estimate the pesticide mass remaining in the entire lake, Lake Biwa was divided into an upper layer (depth 0–10 m) and a lower layer (depth >10 m), based on the depth at which the thermocline formed. The mass of pesticide was calculated as follows:

$$L = C_{\mathrm{upper}} \cdot V_{\mathrm{upper}} + C_{\mathrm{lower}} \cdot V_{\mathrm{lower}} \tag{2}$$

where C_{upper} is the mean of concentrations obtained at depths of 0 and 5 m, C_{lower} is that obtained at 15 and 50 m, and V_{upper} and V_{lower} are the water volumes of the upper and lower layers, respectively. The values of C_{lower} for molinate and dimepiperate were taken as zero because no consider-

able residues were observed in the lower layer. For practical reasons, the sampling date on which the maximum concentration was monitored was substituted as $t = 0$. The data set was analyzed up to December for group I and up to the sampling date on which the frequencies of detection decreased to less than 50% for groups II and III.

Figure 4 shows the elimination rates of pesticide mass. In group I, although the regression curves show some scatter, half-lives were more than 1 year for simetryn, and about half a year for bromobutide. In groups II and III, half-lives were estimated to be 1.5 months for molinate and 1 month for dimepiperate, respectively. A previous study also showed that both biological and nonbiological degradation of simetryn in water could be negligible (Kibe et al. 2000). Sudo et al. (2002a) reported that two straight lines plotted against a semilogarthmic scale were useful to approximate the elimination rate in influent rivers of the lake, and that the calculated half-lives of simetryn and molinate concentrations in influent rivers were 10 and 8 days. The disappearance of pesticide in river water may be mainly the result of a rapid decrease of pesticide runoff from paddy fields, and the result of the pesticide being washed away by discharges originating from nontreated areas. In contrast, the longer half-lives in the lake water may result from retention without the possibility of being washed away and the relatively low levels of elimination by degradation and evaporation.

The elimination of pesticides from the lake has two sources. One is outflow from the lake, which can be estimated based on observations at the effluent river; the other is the process of degradation, including chemical, biological, and physical reactions, that the pesticides undergo within the lake. Total amount eliminated per year (L_{elim}) was calculated as follows:

$$L_{\mathrm{elim}} = L_{\mathrm{max}}\left(1 - 10^{-kt}\right) \tag{3}$$

where L_{max} is the amount on the sampling date at which the maximum concentration was monitored, k is the elimination rate constant, and $t = 365$ days.

Pesticide output from Lake Biwa through the single effluent river and three artificial canals was calculated as follows:

$$L_{\mathrm{out}} = \sum C_{\mathrm{out}_i} Q_{\mathrm{out}_i}\left(t_{i+1} - t_{i-1}\right)/2 \tag{4}$$

where C_{out} and Q_{out} are the pesticide concentrations observed weekly at the Seta River and the total water volume discharged from the Seta River and three canals at time t_i, respectively.

Thus the amount of degradation (L_{deg}) was estimated to be the total amount eliminated minus the amount eliminated by outflow as follows:

$$L_{\mathrm{deg}} = L_{\mathrm{elim}} - L_{\mathrm{out}} \tag{5}$$

Table 3 shows that molinate and dimepiperate were eliminated mainly by degradation, that no substantial degradation of simetryn was observed, and that bromobutide was moderately eliminated. A previous study (Sudo et al. 2002b) showed that degradation in the lake in 1997 estimated from pesticide input from the entire river inflow

Fig. 3. a Seasonal changes in the vertical profiles of water temperature in 2001 at line A (*circles*), and the average temperature of river water (*arrows*). No data on river water was obtained on Aug. 30. **b** Seasonal changes in the vertical profiles of simetryn concentration in 2001 at line A. **c** Seasonal changes in the vertical profiles of molinate concentration in 2001 at line A. **d** Seasonal changes in the vertical profiles of pyroquilon concentration in 2001 at line A. **e** Seasonal changes in the vertical profiles of dimepiperate concentration in 2001 at line A
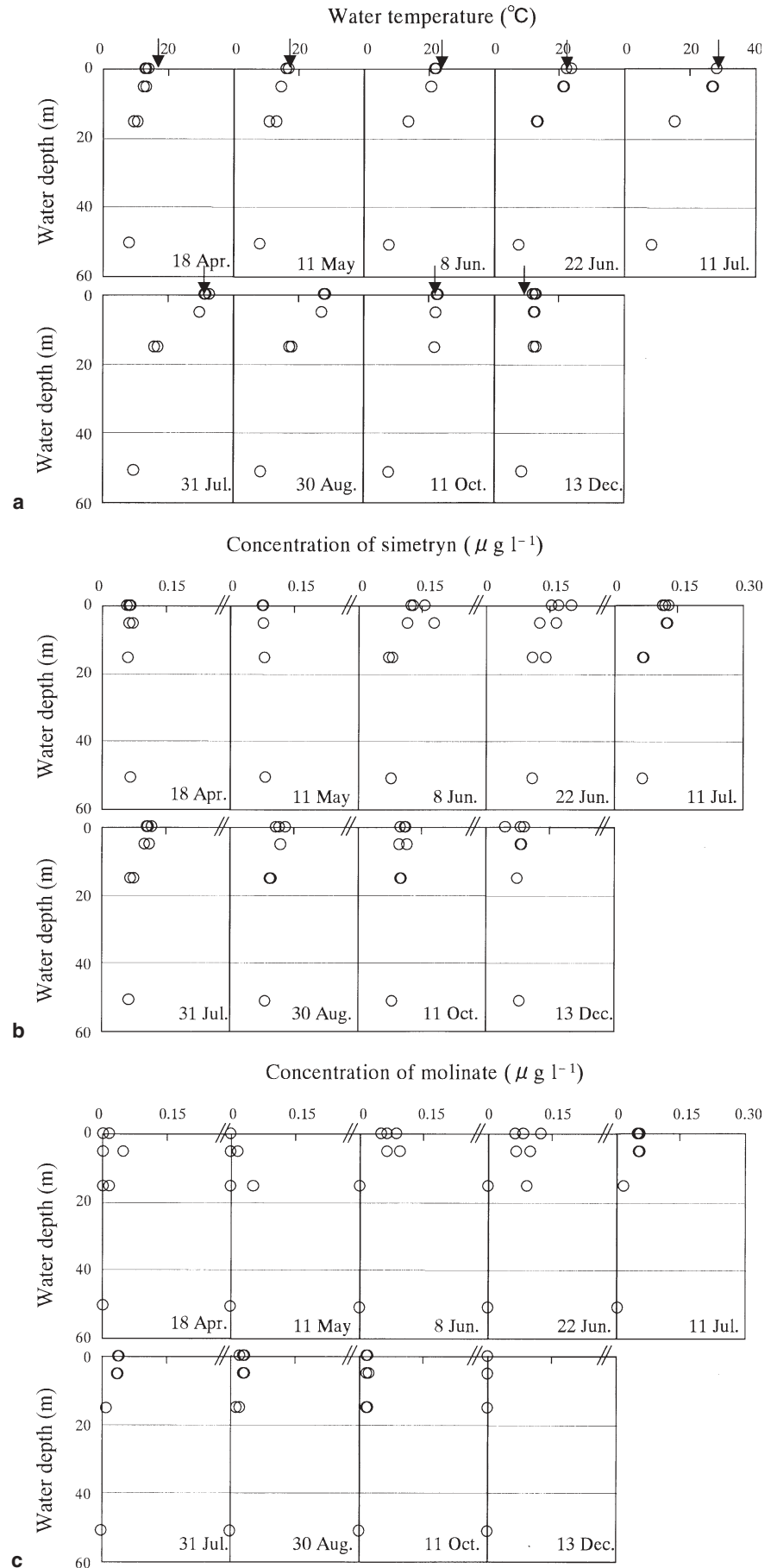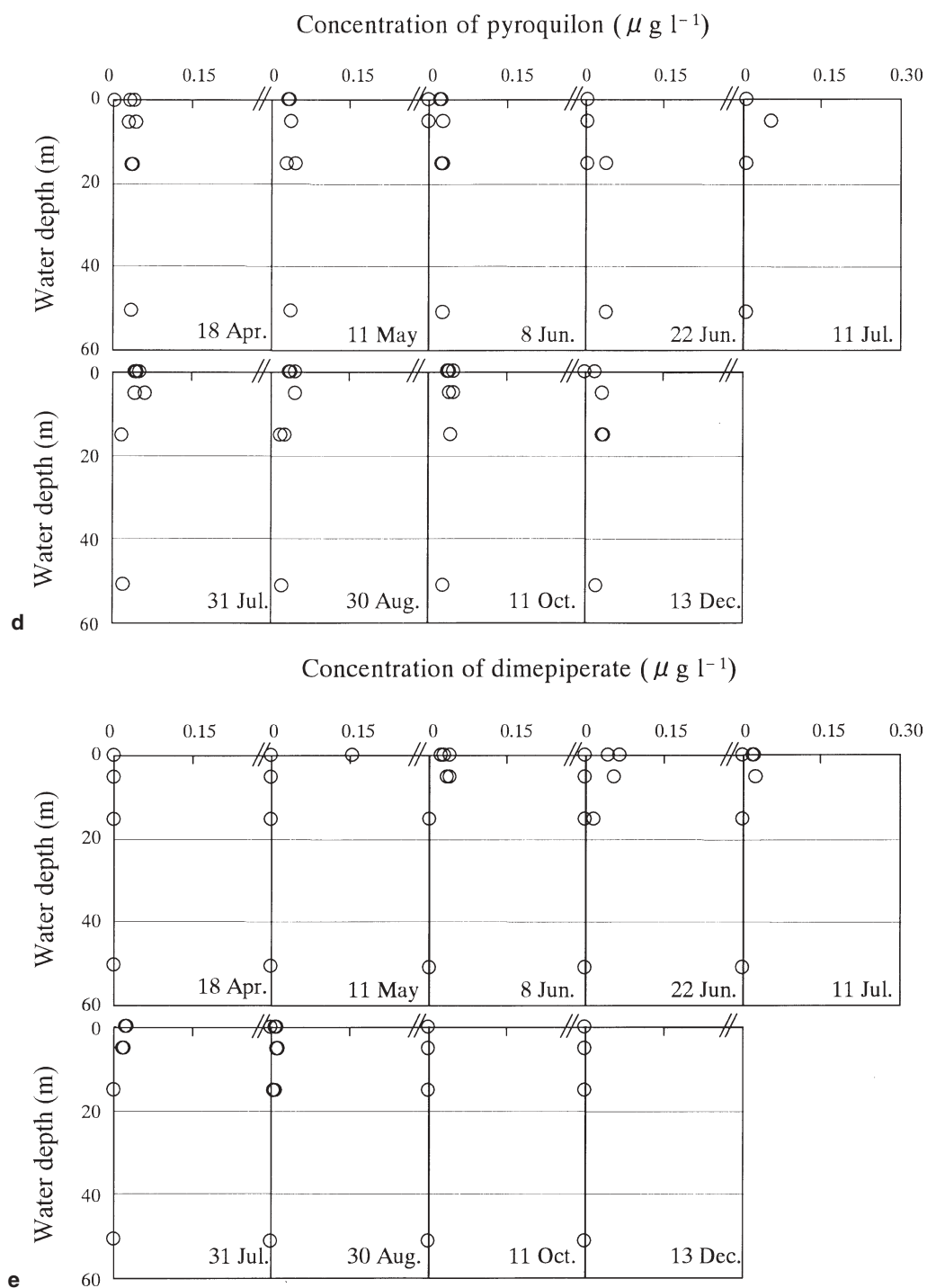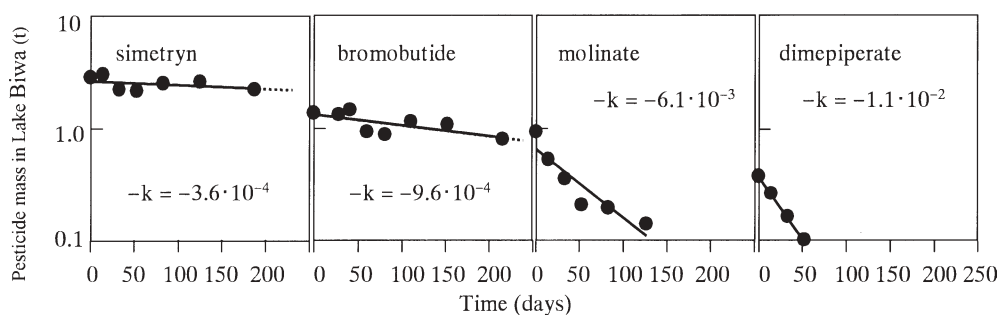
Fig. 3. Continued

Concentration of pyroquilon (μ g l^{-1})

18 Apr. 11 May 8 Jun. 22 Jun. 11 Jul.

31 Jul. 30 Aug. 11 Oct. 13 Dec.

d

Concentration of dimepiperate (μ g l^{-1})

18 Apr. 11 May 8 Jun. 22 Jun. 11 Jul.

31 Jul. 30 Aug. 11 Oct. 13 Dec.

e

Fig. 4. Elimination of pesticide mass from Lake Biwa. $-k$ is the elimination rate constant estimated by applying linear regression techniques

simetryn $\quad -k = -3.6 \cdot 10^{-4}$

bromobutide $\quad -k = -9.6 \cdot 10^{-4}$

molinate $\quad -k = -6.1 \cdot 10^{-3}$

dimepiperate $\quad -k = -1.1 \cdot 10^{-2}$

Pesticide mass in Lake Biwa (t)

Time (days)

Table 3. Elimination of pesticides from Lake Biwa in 2001

	Total (tons)	Elimination	
		Outflow (tons)	Degradation (tons)
Simetryn	0.8	0.66	0.1
Bromobutide	0.7	0.31	0.4
Molinate	0.9	0.21	0.7
Dimepiperate	0.4	0.03	0.4

reaching the lake and the outflow from the lake was 64% for molinate and 0% for simetryn. Although the practical transport characteristics of hydrodynamics within the lake are unknown, simetryn, which was observed to remain in the lake without marked degradation, was gradually discharged downstream. Molinate and dimepiperate may be degraded before reaching the effluent river and canals located at the southern end of the lake.

This study investigated and presented the characteristics of seasonal pesticide concentrations in the surface water of the lake, the relation of vertical circulation and thermal stratification to the vertical distribution of pesticides, and the elimination rate constant of pesticides in the lake. For future study, the fate and movement in the lake of additional pesticides should be studied intensively. We consider that it is essential to determine whether long-term exposure to relatively low pesticide concentrations dispersed throughout the lake poses a potential hazard to humans and the ecosystem.

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