Decrease in herbicide concentrations and affected factors in lagoons located around Lake Biwa

M. Sudo*, M. Nishino and T. Okubo****

*School of Environmental Science, The University of Shiga Prefecture, 2500 Hassaka Hikone, 522-8533, Japan (E-mail: *sudo@ses.usp.ac.jp*)

**Lake Biwa Environmental Research Institute, 5-34 Yanagihira 522-0022, Japan (E-mail: *nishino@lberi.jp*; *okubo-t@lberi.jp*)

Water Science & Technology **Vol 53 No 2 pp 131–138** © IWA Publishing 2006

Abstract The contamination levels and changes in the concentrations in four lagoons around Lake Biwa of paddy-use herbicide were studied. Four lagoons, Sone-numa (52 days of HRT (hydraulic residence time) estimated from the lagoon volume and the average discharge at the outlet, 21 ha area), Yanagihira-ko (40 days, 5.0 ha), Noda-numa (11 days, 6.0 ha), and Iba-naiko (2 days, 55.5 ha), were selected as monitoring sites. Intensive water sampling was carried out once a week from May to June at the outlet of each lagoon. Although twelve of the monitored herbicides were detected, the maximum concentrations did not exceed the guidelines for water-supply law in Japan. The relation between half-lives in herbicide concentrations and characteristics of a lagoon such as HRT and chlorophyll-a concentrations were examined. The shorter half-lives of herbicide concentrations in lagoons with shorter HRT means that replacement by influent water effectively decreased the pesticide concentrations. Shorter half-lives in lagoons with high chlorophyll-a concentrations between the lagoons with similar HRT suggest that biological degradation during the residence time worked more efficiently in the lagoon with high chlorophyll-a concentrations.

Keywords Half-life; herbicide; lagoons; Lake Biwa; water contamination

Introduction

Located on central Honshu Island, Lake Biwa has the largest surface area in Japan (674 km^2) and is used by 14 million people in the Kinki district as potable water and for industrial, recreational, and agricultural purposes. Although more than 30 lagoons have existed around Lake Biwa (1 ha – 1,150 ha), half of them have been altered entirely or partially, being established as drainage areas for paddy-fields or upland fields between 1944–1971 (LBRI, 1983). Recently, depression of agriculture and reevaluation of the environmentally beneficial aspects of lagoons have resulted in the development of several lagoon regeneration projects. Lagoons provide habitat for aquatic plants, microorganisms, insects, birds, and fishes, including some endemic species. Lagoons have also been recognized as active ecosystem components and are thought to be potential sites for the removal of nutrients before their flow into lakes (Fukushima *et al.*, 1989; Toda *et al.*, 1994; Okamoto *et al.*, 1997; Okubo, 1998; Okubo *et al.*, 2000). Pesticides, which may have a detrimental impact on human health and natural ecosystems, are a major source of non-point pollution in the Lake Biwa basin (Sudo *et al.*, 2002a,b) and are expected to be mitigated in lagoon areas during their retention. There are several studies reporting removal of pesticides used in upland fields (Kadlec and Hey, 1994; Detenbeck *et al.*, 1996; Schulz and Peall, 2001; Moore *et al.*, 2001; Kao *et al.*, 2001, 2002; Stearman *et al.*, 2003); however, there have been few published studies of paddy use pesticides in lagoons around Lake Biwa (Sudo *et al.*, 2003; Hinokio *et al.*, 1996). The objective of this study was to evaluate the actual environmental risk of pesticides and their potential for removal

doi: 10.2166/wst.2006.046

in lagoons under realistic environmental conditions. Although the pesticide budget based on long-term monitoring is essential to evaluating the accurate mass removal rate and mass removal efficiency, this study focused on pesticide concentrations at lagoon outlets. The comparison of pesticide concentrations among lagoons provides the relative contamination levels. The influence of residence time and biosphere activity as indicated by chlorophyll-a concentrations on half-lives in pesticide concentrations were examined to evaluate the lagoon buffer function and the pesticide-removing capabilities of a site.

Materials and methods

Study area

Prior to this study, pesticide concentrations were monitored in 20 lagoons around Lake Biwa once a month from May to August in 2001 (LBRI, 2002). Four of these 20 lagoons, Sone-numa, Yanagihira-ko, Noda-numa, and Iba-naiko, were selected as monitoring sites in this study on the basis of the maximum concentrations and the contaminations two or three months after the application period. Maps of the lagoons and the locations of the sampling sites are shown in Figure 1. Excluding the Noda-numa, water in the lagoons drains from a single outlet, although some rivers or canals are inflows to the lagoons. The areas and average water depths are also shown in Figure 1. The hydraulic residence time (HRT) estimated from the lagoon volume and the average discharge at the outlet, assuming no short-circuiting, are shown in Table 2.

Rice is a major crop in the catchment areas of lagoons, and related pesticides are drained through a discharge river and canal. In the majority of paddy fields, rice seedlings are transplanted between the end of April and the beginning of May, and are harvested until late September. Pre-emergence herbicides are applied by sequential treatments or a one-shot treatment up to 3 weeks after transplantation. In a 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 a one-shot treatment, a one-shot herbicide is applied once between 3 and 14 days after

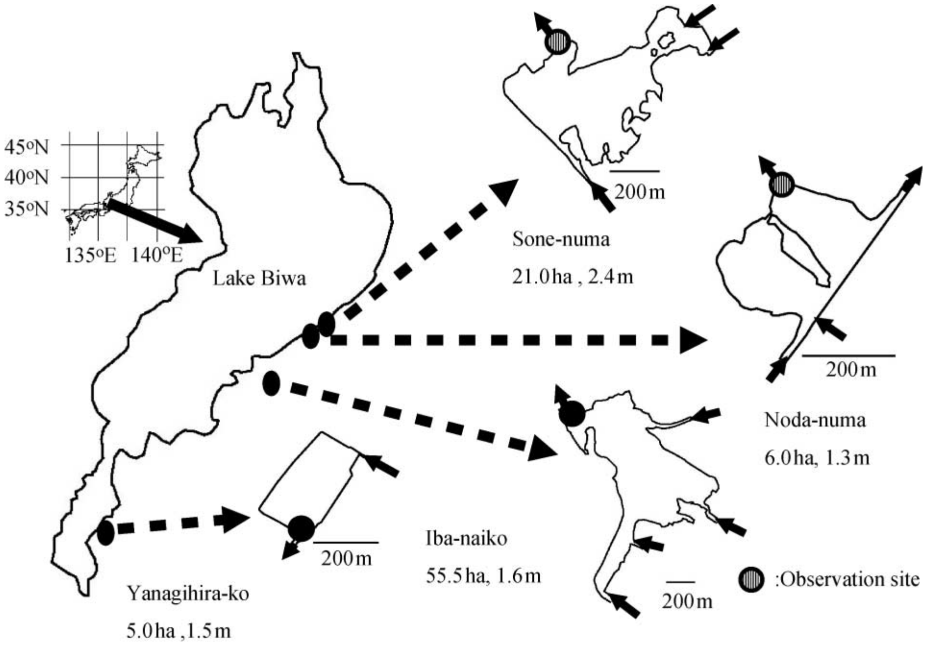

Figure 1 The locations, areas, and average water depths of observation sites in the lagoons

transplanting. A second-stage herbicide is often applied additionally when the one-shot herbicide does not work efficiently.

Sample collection and sample analysis

Water samples were collected at the single outlet of three lagoons and the outlet at the bottom of the Noda-numa once a week from May to early July. Sampling was also carried out every 2 weeks at the beginning of April and in the latter half of July. Water temperature, pH, conductivity, and discharge at the sampling site were also measured on-site. Water samples were analyzed for pesticide and chlorophyll-a concentrations. Twelve herbicides were analyzed (Table 1) according to our previously described method (Sudo *et al.*, 2004). Chlorophyll-a concentrations were measured using 90% acetone as the extract solvent according to the method of SCOR/Unesco (1966).

Results and discussion

Pesticide contamination in lagoons

The maximum concentrations of pesticides in the lagoons are shown in Table 1. The detection frequencies, calculated via 12 observations, are shown in the same table. Although the maximum concentrations and detection frequencies may be affected by the differences in application amounts in the catchment area and by the timing between sampling and the pesticide application period, all of the herbicides monitored in this study were detected more or less in four lagoons. Among the four lagoons, the concentrations in the Sone-numa and the Noda-numa were relatively high, suggesting that these lagoons may receive more agricultural non-point runoff loads and/or be less diluted with discharge originating from non-treated areas.

Among the pesticides detected in the four lagoons, the maximum concentrations of daimuron, mefenacet, and simetryn exceeded 5 μg/L. The water-supply law, which is designed to supply secure drinking water by securing water sources, was amended in 2004 and established guidelines for 101 pesticides. The values specified in the guideline are in general lower than the reported LC_{50} value for aquatic species such as carp,

Table 1 The maximum concentrations of herbicides and detection frequencies in lagoons in 2003

	Sone-numa		Yanagihira-ko		Noda-numa		Iba-naiko		Guideline*** μg/L
	Max.* μg/L	Freq.** %	Max. μg/L	Freq. %	Max. μg/L	Freq. %	Max. μg/L	Freq. %	
First-stage herbicide									
Bromobutide	4.72	83	1.12	83	2.90	83	1.29	75	40
Pretirachlor	0.64	58	0.91	67	1.49	58	1.94	58	40
Tenylchlor	0.61	92	0.19	75	0.59	83	0.17	100	200
One-shot herbicide									
Daimuron	8.43	92	5.11	92	7.27	92	5.82	92	800
Mefenacet	3.84	75	0.59	83	5.25	83	3.02	83	9
Thiobencarb	0.29	58	0.02	17	0.83	75	0.52	92	20
Esprocarb	0.13	83	0.08	33	0.78	83	0.77	83	10
Dimepiperate	0.14	17	0.05	17	0.54	75	0.36	33	3
Pyributicarb	0.12	75	0.12	67	0.09	50	0.13	67	20
Second-stage herbicide									
Simetryn	4.42	83	0.76	92	7.98	92	1.54	75	30
Benfresate	0.51	67	0.14	58	3.90	67	0.68	83	–
Molinate	0.32	75	0.11	50	1.28	92	0.18	50	5

*Maximum concentration
**Detection frequency
***Guideline for water-supply law in Japan

rainbow trout, and daphnia (Kanazawa, 1996). The maximum concentrations of mefenacet, bromobutide, pretirachlor, dimepiperate, simetryn, and molinate were within one order of magnitude lower than the guideline values. Those of other herbicides were beyond two orders of magnitude lower. Herbicide concentrations in influent water would be higher than that in lagoons; lagoons were effective for decreasing peak concentrations in contaminated water and decreasing toxicity for aquatic species by dilution and degradation.

Seasonal variations in herbicide concentrations

The following results and discussion focus on the concentrations of bromobutide, daimuron, mefenacet, and simetryn because of their high concentrations in the four lagoons. Bromobutide is applied between late April and mid May, as it is contained in both first-stage herbicides and one-shot herbicides. The application periods for daimuron and mefenacet are between early and late May, while that for simetryn is between late May and early June. Seasonal variations in the four lagoons are shown in Figure 2. In the lagoons with relatively short HRT, the Iba-naiko and the Noda-numa, the contamination levels of herbicides increased with almost direct correspondence to the application timing. The fall of concentrations occurred following the peak and remained at less than 1 μg/L for daimuron and 0.2 μg/L for the three herbicides in July.

In the Sone-numa and the Yanagihira-ko, the appearance of detectable contaminations tended to be delayed by approximately 1–2 weeks compared with the Iba-naiko and the Noda-numa, although the herbicides were applied at almost identical times in the catchment area. An exception with regard to the appearance of bromobutide concentrations may be due to the longer sampling interval in April. The high contamination periods also tended to be delayed and prolonged in these lagoons. The lag time may have been due to their long HRT. Following the peak concentrations, the concentrations gradually decreased and remained at 2 μg/L for daimuron and at more than 0.5 μg/L for the three herbicides in July.

Seasonal variations in chlorophyll-a concentrations

Seasonal variations in chlorophyll-a concentrations are shown in Figure 3. Concentrations in the Sone-numa ranged between 5 and 15 μg/L from April to early June, and increased to more than 30 μg/L in mid- and late June. A temporal increase was also observed at the Noda-numa in the middle of June. The concentrations in the Yanagihira-ko and the Iba-naiko remained relatively stable from April to June, ranging from 5–15 μg/L and 10–20 μg/L. In all lagoons, the concentrations decreased to less than 5 μg/L after mid-July.

Elimination rate of pesticides at the lagoon outlets

The lumped first-order decay function is used to relate the decrease in concentrations at the outlet in a lagoon as follows:

$$\mathrm{d}C/\mathrm{d}t = -kC$$

where C is the pesticide concentration and k is the elimination rate constant. Because herbicides are applied almost at the same time during a fixed application period, pesticide inputs from rivers or drains are limited at the period. Thus, the sampling date on which the maximum concentrations were determined was substituted as $t = 0$. The data set was analyzed up to early July. Table 2 shows the half-lives of pesticide concentrations calculated from gradients of the regression curve. Other parameters such as chlorophyll-a concentration, water temperature, pH and conductivity are also shown in

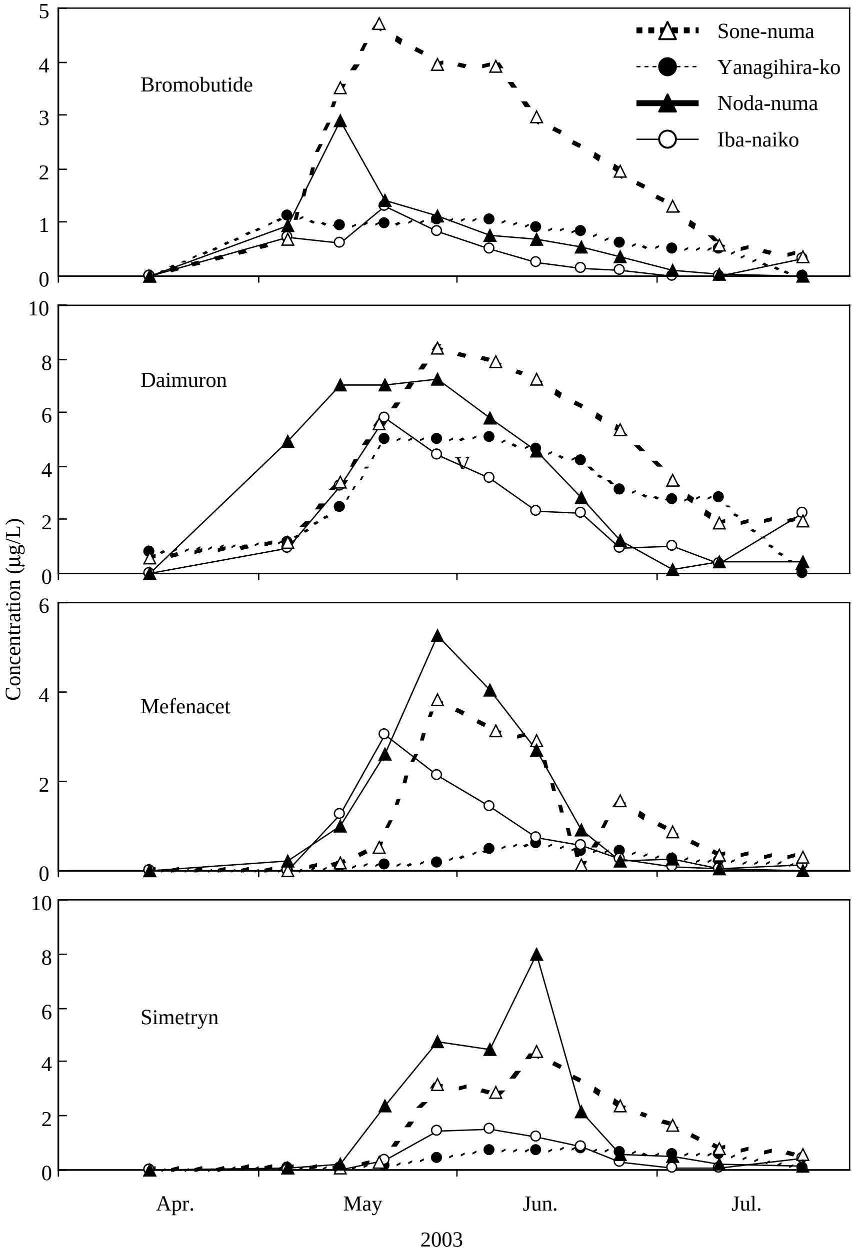

Figure 2 Seasonal variations in herbicide concentrations in the four lagoons

the same table. The chlorophyll-a concentrations were relatively high in the lagoons with higher conductivity, suggesting these lagoons may receive more nutrients from their catchment area. There are no significant differences in water temperature and pH among lagoons.

As shown in Table 2, the half-lives of herbicides in lagoons with relatively shorter HRT, the Noda-numa and the Iba-naiko, were estimated to be 5–10 days, while in those with longer HRT, the Sone-numa and the Yanagihira-ko, the half-lives were 20–30 days. The shorter half-lives in lagoons with shorter HRT means that replacement by influent water efficiently promotes pesticide disappearance.

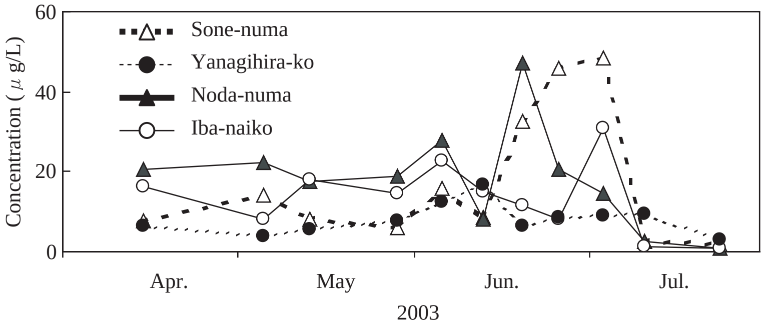

Figure 3 Seasonal changes in chlorophyll-a concentrations in the four lagoons

Table 2 HRT, half-life of herbicides and chlorophyll-a concentration in lagoons

			Sone-numa	Yanagihira-ko	Noda-numa	Iba-naiko
Half-life	Bromobutide	days	18.0	33.8	10.9	9.5
	Daimuron		24.5	28.9	10.2	14.5
	Mefenacet		14.7	18.9	11.7	8.6
	Simetryn		35.0	46.3	4.8	6.5
HRT		days	52	40	11	2
Chlorophyll-a*		μg/L	16.3	7.7	20.4	12.3
Water Temp.*		°C	24.6	22.8	23.0	22.1
pH*			7.75	7.70	7.60	7.96
Conductivity*		mS/m	19.3	18.2	23.6	13.8

*Average between May and June

If the half-lives of pesticides depend only on the HRT, half-lives in the Noda-numa could be expected to be longer than those of the Iba-naiko. But there was no significant difference in the half-lives between the lagoons. The fate of pesticide flow into a lagoon is degradation, outflow, internal storage and vaporization. Among them, internal storage can be considered negligible as the herbicides monitored in this study exist mainly in the aqueous phase due to their high water solubility and relatively low octanol-water partition coefficients. Vaporization can also be negligible because of their low Henry's law constant. Thus, the fate contributing to pesticide elimination during the residence time is degradation. Although each degradation process such as biological degradation and photo-degradation was not examined, they were lumped together into the chlorophyll-a concentration as an indicator of degradation. Chlorophyll-a concentrations represent the phytoplankton biomass, and the abundance of phytoplankton may depend on the abundance of aquatic biomass. Higher chlorophyll-a concentrations may bring advantages for the biodegradation process; however, they may reduce the ability of photo-degradation because of a decrease in transparency. Previous studies suggest that atrazine (McKinlay and Kasperek, 1999; Kao *et al.*, 2001; Kao *et al.*, 2002; Anderson *et al.*, 2002), azinphos-methyl, chlorpyriphos and endosulfan (Schulz and Peall, 2001) are degraded in wetland by biodegradation. As shown in Table 2, the shorter half-lives in the Noda-numa than in the Iba-naiko may be due to higher chlorophyll-a concentrations, suggesting that biological degradation during the residence time in the Noda-numa worked more efficiently to reduce pesticide concentrations than in the Iba-naiko. The difference between expected half-lives based on HRT and the observed ones in the Sone-numa and Yanagihira-ko could be explained in the same manner.

Conclusions

Herbicide concentrations were monitored at four lagoons around Lake Biwa during a 4-month period in 2003. Although the concentrations of herbicide were low, long-term effects on the aquatic environment are of concern in lagoons with long HRT because of the herbicide residue. Our results also suggest that lagoons with longer HRT and higher chlorophyll-a concentrations may reduce pesticide inputs to the lake. These conditions, however, are favorable to primary production, and they may lead to adverse effects on the water quality of a lagoon. It is therefore necessary to determine the most effective conditions and design best management practices for lagoons.

Acknowledgements

The authors express our appreciation to Tatsuhito Ogata and Misachi Shikimoto for their assistance in field sampling and laboratory analyses.

References

Anderson, K.L., Wheeler, K.A., Robinson, J.B. and Touvinen, O.H. (2002). Atrazine mineralization potential in two wetlands. *Water Res.*, **36**, 4785–4794.

Detenbeck, N.E., Hermanuts, R., Allen, K. and Swift, M.C. (1996). Fate and effects of the herbicide atrazine in flow-through wetland mesocosms. *Environ. Toxicol. Chem.*, **15**, 937–946.

Fukushima, T. and Iwata, Y. (1994). On water purification by aquatic plant (lotus) within a farm pond where domestic sewage is mixed. *Trans. Japanese Society Irrigation, Drainage Reclamations Engineering*, **142**, 99–105 (in Japanese).

Hinokio, R., Jiku, F. and Yokota, K. (1996). Fundamental study on pesticide storage and behavior in a lagoon around Lake Biwa. *Env. Conservation engineering*, **25**(8), 434–437 (in Japanese).

Kadlec, R.H. and Hey, D.L. (1994). Constructed wetlands for river water quality improvement. *Wat. Sci. Tech.*, **29**(4), 159–168.

Kanazawa, J. (1996). *Environmental Science of Pesticides*, Godo shuppan, Tokyo (in Japanese).

Kao, C.M., Wang, J.Y. and Wu, M.J. (2001). Evaluation of atrazine removal processes in a wetland. *Wat. Sci. Tech.*, **44**(11–12), 539–544.

Kao, C.M., Wang, J.Y., Dhen, K.F., Lee, H.Y. and Wu, M.J. (2002). Non-point source pesticide removal by a mountainous wetland. *Wat. Sci. Tech.*, **46**(6–7), 199–206.

LBRI (1983). Lagoons – its ecological function. *Lake Biwa Res. Inst. Bull.*, **2**, 46–54 (in Japanese).

LBRI (2002). *Characteristics of nutrient and pesticide concentration in lagoons around Lake Biwa*, Research Report 2002-01, Lake Biwa Research Institute, Otsu, Japan (in Japanese).

McKinlay, R.G. and Kasperek, K. (1999). Observations on decontamination of herbicide-polluted water by marsh plant systems. *Water Res.*, **33**, 505–511.

Moore, M.T., Rodgers, J.H. Jr., Cooper, C.M. and Smith, S. Jr. (2001). Mitigation of metolachlor-associated agricultural runoff using constructed wetlands in Mississippi, USA. *Agric. Eco. Environ.*, **84**, 169–176.

Okamoto, Y., Nakamura, K. and Kobayashi, H. (1997). Experiment for direct purifying on irrigation pond utilizing fallow paddy fields that were not expected to produce rice profitably. *Trans. Japanese Society Irrigation, Drainage Reclamations Engineering*, **187**, 151–160 (in Japanese).

Okubo, T. (1998). Water purification in wetlands and lagoons. *J. Water and Waste*, **40**(10), 35–45 (in Japanese).

Okubo, T., Tsujimura, S. and Sudo, M. (2000). Removal of pollutant loading in a lagoon. *Lake Biwa Res. Inst. Bull.*, **18**, 36–48.

SCOR/UNESCO Working Group 17 (1966). *Determination of photosynthetic pigments in sea water*, UNESCO, Paris, p. 69.

Schulz, R. and Peall, S.K.C. (2001). Effectiveness of a constructed wetland for retention of nonpoint-source pesticide pollution in the Lourens River Catchment, South Africa. *Environ. Sci. Technol.*, **35**, 422–426.

Stearman, G.K., George, D.B., Carlson, K. and Lansford, S. (2003). Pesticide removal from container nursery runoff in constructed wetland cells. *J. Environ. Qual.*, **32**, 1548–1556.

Sudo, M., Kunimatsu, T. and Okubo, T. (2002a). Concentration and loading of pesticide residues in Lake Biwa basin (Japan). *Water Research*, **36**(1), 315–329.

Sudo, M., Okubo, T., Kunimatsu, T., Ebise, S., Nakamura, M. and Kaneki, R. (2002b). Inflow and outflow of agricultural chemicals in Lake Biwa. *Lakes and Reservoirs*, **7**, 301–308.

Sudo, M., Okubo, T. and Kunimatsu, T. (2003). Herbicide loadings from paddy fields and purification effect in lagoon. *J. of Japanese society of Irrigation, Drainage and Reclamation Engineering*, **223**, 71–77 (in Japanese).

Sudo, M., Kawachi, T., Hida, Y. and Kunimatsu, T. (2004). Spatial distribution and seasonal changes of pesticides in Lake Biwa, Japan. *Limnology*, **5**, 77–86.

Toda, H., Matsumoto, E., Miyazaki, T., Shibano, K. and Kawashima, H. (1994). Nitrate disappearance in an irrigation pond. *Soil Science and Plant Nutrition*, **65**, 266–273 (in Japanese).