The spatial and temporal distribution of rice herbicides in Lake Biwa, Japan

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Abstract:

The plains on the lowlands surrounding Lake Biwa, Japan, have long been used for rice (Oriza sativa L.) cultivation. In 2007, we investigated the fate of herbicides commonly used in this agroecosystem. During the spring, the highest concentrations of simetryn, mefenacet, bromobutide and dymron were detected on the lake's surface and at the mid-depth (20 m), indicating that agricultural runoff enters the lake and directly affects its water quality. Our findings also suggest that these contaminants might serve as an indicator of the transport pathways of some agricultural pollutants into the lake.

KEYWORDS herbicide; water quality; paddy field; agricultural pollution; Lake Biwa

INTRODUCTION

Modern agricultural practices around the world rely on herbicides in order to maintain high productivity. In Japan, rice (Oriza sativa L.) that is especially vulnerable to weed competition would not be an economically viable crop without the use of herbicides.

Approximately 31,100 ha of the agricultural lands within Lake Biwa’s watershed are used for intensive production of irrigated rice (MAFF, 2004). Rice is usually grown by transplanting seedlings into freshly tilled and leveled fields. This activity usually takes place between late April and early May. Herbicides and other agrochemicals are usually applied up to three weeks after the seedlings have been transplanted. Rice is cultivated under flooded conditions and maintained by intermittent irrigation until late August, except for the midseason drainage that takes place between late June and early July (Sudo et al., 2005).

The impacts of herbicides on water quality are a growing public concern. Depending on how the water is managed, more than 30–50% of the applied chemicals leach from the paddy fields (Nakafuchi et al., 2001; Sudo et al., 2002; Watanabe et al., 2006, 2007). Although contamination of rivers by herbicides has been reported in many agroecosystems (Okamura et al., 2002; Tsuda, 2006; Ishihara, 2009), the issue has received little attention in lake studies. One of the few studies investigating vertical and spatial distribution of herbicides within lakes in the United States is reported by Schottler and Eisenreich (1994). Their data indicated that atrazine and metolachlor concentrations within the Great Lakes did not vary laterally or with depth. The only reference to vertical distribution of herbicides in Lake Biwa is a study by Sudo et al. (2004). They measured pesticide concentrations at four depths (0, 5, 15 and 50 m) along three transects and found vertical concentration differences with higher levels of simetryn and bromobutide on the lake surface. Recently, Nakamura et al. (2008) also reported detection of higher concentrations of herbicides on the surface between May and August at 18 sites. Sudo et al. (2005) investigated the movement of herbicides from land to Lake Biwa. The extent of pesticide sites were taken from the downstream reaches of the Uso River (Sta. R1), the Ane River (Sta. R2) and the Amano River (Sta. R3). These rivers are ideal for an herbicide study as they represent three of the largest drainage areas of their catchments. The land-use characteristics of the drainage basin for these rivers are shown in Table I. On 18 April and 23 May 2005, lake water samples were taken from 7 depths (0, 5, 10, 15, 20, 25, 30 m) at Sta. P4, a 40 m depth site approximately 4 km from the nearest shoreline. In 2006, lake water was collected from 5 depths (0, 10, 20, 30 and 50 m) on five dates during April to July at Sta. A3 and B3, both at approximately 60 m depth and located about 5 km from the nearest shoreline. In all surveys, surface water was collected using a 5-L bucket and vertical samples were collected using a 10-L Van...
Dorn sampler. Samples were kept refrigerated until analysis was performed. Sampling occurred between late April and mid-June, to cover the period of largest application of herbicides in the studied agroecosystem.

**Analytical procedures**

Water samples were first filtered through a pre-combusted glass fiber filter (Whatman, GF/F, pore-size 0.7 μm). Thirty-eight active chemical ingredients contained in the filtrates were extracted using a Waters Sep-Pak Plus PS-2 cartridge (Waters, Milford, MA, U.S.A.), and then measured using a gas chromatograph (Hewlett-Packard, HP 6890, Palo Alto, CA, USA) coupled with a mass spectrometer (JOEL, Automass System II, Tokyo, Japan) equipped with an ionization source (70 eV). Only the filtrates were analyzed because the chemical compounds studied are known to exist mainly in the aqueous phase (Sasagawa et al., 1996; Sudo et al., 2005). Details of analytical procedures are presented in Sudo et al. (2004). Standard herbicides 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 detection limit for all compounds was 0.02 μg L⁻¹. Concentrations below the detection limit were recorded as zero.

**RESULTS AND DISCUSSION**

Four herbicides, detected at higher concentrations, were selected as target compounds in this study. The selected herbicides were: simetryn [2,4-bis(ethylamino)-6-methylthio-1,3,5-triazine], mefenacet [2-(2-benzothiazolyl oxy)-N-methyl-N-phenylacetamide], bromobutide [2-bromo-3,3-dimethyl-N-(1-methyl-1-phenylethyl)butanamide] and dymron (3-(3,4-dichlorophenyl)-1,1-dimethylurea).

The concentrations measured in river water during 2004 are shown in Figure 2. In the Uso River, the water contamination level was higher than those of the Amano River and the Ane River for all four herbicides, but the three rivers showed a similar trend with peak concentrations between May and early June. The discrepancy in the herbicide concentrations obtained in water samples from the Uso River compared to the other two rivers can be explained by the land use of its drainage basin which is characterized by a larger proportion of paddy fields (see Table I). The later presence of concentration peaks for simetryn and mefenacet, compared to bromobutide and dymron, most likely reflects differences in application timing. The maximum concentrations were detected in the range of 0.44–3.61 μg L⁻¹ for simetryn, 0.31–2.63 μg L⁻¹ for mefenacet, 0.09–3.80 μg L⁻¹ for bromobutide and 0.71–10.65 μg L⁻¹ for dymron.

The residual concentrations of simetryn, mefenacet, bromobutide and dymron measured in lake surface water during 2004 are shown in Figure 3. At most sampling sites, these compounds became detectable from late April until mid May, reached a peak between

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**Table I. Land use characteristics of selected drainage basins (LBRI, 1988).**

| River | total area (km²) | Land use (%) |
|-------|-----------------|--------------|
| Uso   | 96.18           | 26 58 16     |
| Ane   | 369.03          | 90 6 4       |
| Amano | 306.90          | 73 3 24      |

Figure 1. Map of the study area showing sampling sites in Lake Biwa and at three of its tributaries. Circles indicate lake sampling sites, dotted line indicate the transect line and triangles indicate river sampling sites.

Figure 2. Temporal variation of (a) simetryn, (b) mefenacet, (c) bromobutide and (d) dymron in the Uso River (Sta. R1), the Ane River (Sta. R2) and Amano River (Sta. R3) during April–August 2004.
late May and mid June, and then decreased to trace amounts by August.

In 2005, vertical profiles were taken at Sta. P4. While low pesticide concentrations with no vertical differences were observed in the water column on 18 April (data not shown), vertical profiles taken at the same site on 23 May revealed vertical trends with higher concentrations of three herbicides (simetryn, mefenacet and dymron) both on the lake’s surface and at 20 m depth (Figure 4). The maximum concentrations found were in the range of ~0.08 \( \mu \text{g L}^{-1} \) for simetryn, 0.21–0.32 \( \mu \text{g L}^{-1} \) for mefenacet and 0.25–0.31 \( \mu \text{g L}^{-1} \) for dymron. The lack of vertical differences in bromobutide concentrations suggests that the major inputs of bromobutide might have not occurred at the same intensity and time as the other three herbicides.

In 2006, the vertical profiles for bromobutide and mefenacet were variable but higher concentrations of both herbicides were found at the lake’s surface and at 20 m depth in some samples (Figure 5). Peak levels for mefenacet were found on 16 May, 31 May and 14 June and those for bromobutide on 16 May and 14 June. Our results revealed a unique vertical distribution pattern for simetryn, mefenacet, bromobutide and dymron in Lake Biwa and showed that fluvial catchments under intensive agricultural activities directly affect lake water quality.

All pesticide residual concentrations measured in Lake Biwa in 2005 and 2006 were typically low, and in the same range of those previously reported (Sudo et al., 2004; Nakamura et al., 2008). However, even at low levels, the contamination of lake water needs to be considered since all herbicides are potentially toxic. For instance, several unicellular eukaryotic algae most common in freshwater (Chlorella, Chlamydomonas, Euglena) have been shown to be sensitive to photosynthetic inhibitor herbicides (Arvik et al., 1973). It has also been reported that some herbicides such as simetryn have a selective effect on microalgal communities, affecting green algae and promoting cyanobacterial growth (Yamagishi and Hashizume, 1974). Therefore, it will be important to monitor these compounds over time to determine their long-term effect on the water quality and ecosystem of the lake.

The driving mechanism for agrochemical contamination of the lake can not be elucidated based on this single study. However, we provide evidence that horizontal transport through the mid-depth level takes place in the North Basin of Lake Biwa. In an associated work, Tanaka et al. (in press) reported a widespread mid-depth (10–25 m) ammonium maximum formed in Lake Biwa from late April until mid-June. They suggest that ammonium derived from nitrogenous fertilizers enters the lake and is transported offshore by the combined effects of intrusion processes and internal waves. In Lake Kinneret, Israel, it has been reported that horizontal transport due to advection through the metalimnion may control the exchange between lake boundaries and the lake interior (Marti, 2004). The existence of a similar transport pathway can explain why high concentrations of herbicides are found at the mid-depths of Lake Biwa.
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