Environ Monit Assess (2010) 160:371–383
DOI 10.1007/s10661-008-0701-z

# Assessment of pesticide residues in freshwater areas affected by rice paddy effluents in Southern Japan

**Nathaniel Añasco · Seiichi Uno · Jiro Koyama · Tatsuro Matsuoka · Naoya Kuwahara**

Received: 7 May 2008 / Accepted: 20 November 2008 / Published online: 17 December 2008


**Abstract** Pesticide residues in five freshwater areas that are directly affected by rice paddy effluents in southern Japan were measured to determine their maximum concentrations and temporal variations. Water samples were collected every week during the 2005 rice planting season in Kagoshima Prefecture and stations were established in Amori River, Sudo River, Nagaida River (that drains into the bigger Kotsuki River), rice paddy drainage canal, and wastewater reservoir (that collects effluents from rice paddy fields). Of the 14 target pesticides examined, a total of 11 were detected in all stations. Mefenacet, fenobucarb, and flutolanil were the three pesticides with the highest maximum concentrations and were also detected frequently. Analysis of temporal variations of pesticides showed that herbicides had relatively higher concentrations in the earlier stages of the rice planting season, while insecticides and fungicides had relatively higher concentrations at the later stages. There was no significant difference among stations with regards to the temporal patterns of the top three pesticides. The calculated toxic units were less than 1 in all stations, implying low or negligible environmental risk of pesticides detected to freshwater organisms.

**Keywords** Pesticides · Rice paddy canal · Rivers · Wastewater reservoir · Concentrations · Temporal variation

N. Añasco
United Graduate School of Agricultural Sciences, Kagoshima University, Kagoshima, Japan

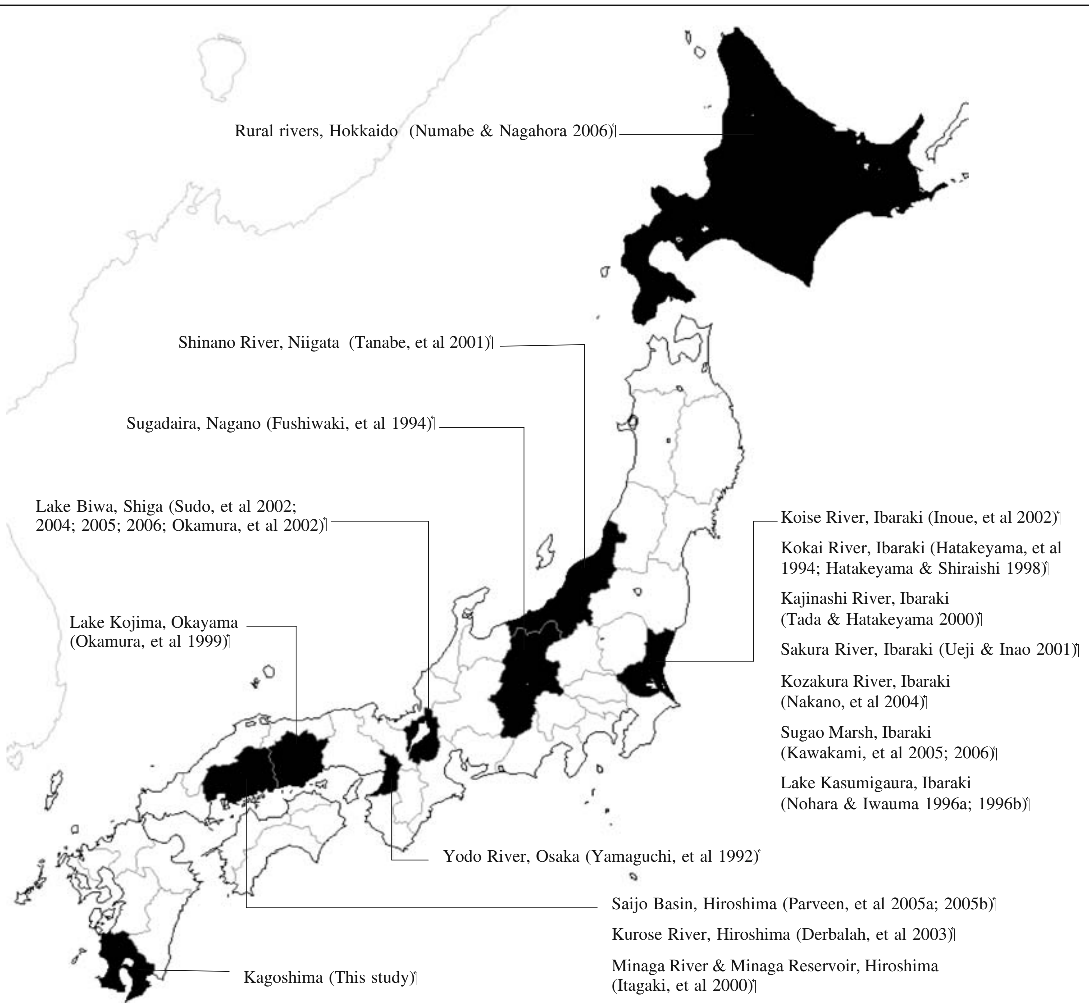
S. Uno · J. Koyama (✉) · T. Matsuoka · N. Kuwahara
Education and Research Center for Marine Resources and Environment, Kagoshima University Faculty of Fisheries, 4-50-20 Shimoarata, Kagoshima City, Kagoshima 890-0056, Japan
e-mail: koyama@fish.kagoshima-u.ac.jp

## Introduction

It is important to monitor the presence of pesticides in freshwater areas because hazardous effluents from rice paddy fields directly drain into them (Anderson et al. 2003), and they are the most important sources of pesticide contamination in coastal environments (Steen et al. 2001). Pesticides detected in coastal areas mostly come from river tributaries that received effluents from farming activities located upstream. In some instances, pesticides can pollute coastal environments through aerial spray drifts from agricultural lands (Gil and Sinfort 2005) or they can also be carried by rainfall (Sakai 2003; Suzuki et al. 2003), but these transport mechanisms rarely happen.

At present, less persistent pesticides still pose great risks to aquatic organisms (Cedergreen and Streibig 2005), including their transformation products (Belfroid et al. 1998). In addition, studies on the effects of pesticides to non-target organisms need some baseline information (Scholz and Hopkins 2006) such as their concentrations in the environment. Assessments, therefore, are commonly conducted in many countries to evaluate the potential impact of agrochemicals to aquatic ecosystems such as almond farming in California (Zhang et al. 2008), cocoa production in Ghana (Ntiamoah and Afrane 2008), and rice cultivation in France (Comoretto et al. 2007). Similarly, there are a number of published papers on pesticide residues in some freshwater areas of Japan, especially those that receive effluents from rice paddy fields. Several researchers studied the concentrations of rice pesticides particularly herbicides in river waters (Numabe and Nagahora 2006; Nakano et al. 2004; Derbalah et al. 2003; Inoue et al. 2002; Ueji and Inao 2001), paddy fields and drainage canals (Kawakami et al. 2005; Kibe et al. 2000), and lakes (Sudo et al. 2002, 2004). It is notable, however, that these studies were conducted mostly in the northern and central parts of Japan (see Fig. 1).

Thorough searches using the databases of Thomson Scientific (2007) and GeNii (2007)



*Map source*: http://www.craftmap.box-i.net

**Fig. 1** Study sites of most published papers on pesticide residue concentrations in freshwater areas around Japan for information regarding concentrations of pesticides in freshwater areas in southern Japan yielded negative results. As such, there is a necessity for an accessible information on the concentrations of pesticide residues in freshwater areas of southern Japan particularly in Kagoshima Prefecture, which has the largest cultivated land (Japan Statistical Bureau 2007) and the second highest usage of pesticides for agricultural purposes in Kyushu and Ryukyus regions as reported in the Pollutant Release and Transfer Register (PRTR) data (ORCERC 2007). Moreover, the near subtropical climate of southern Japan may have some effect on the usage of pesticides in rice farms, and consequently, their ultimate fate in the environment could be affected as well. Yet, whether there is a difference in the appearance of pesticides in freshwater areas between southern and northern–central Japan is not known. Hence, the objective was to determine the concentrations and temporal variations of pesticide residues in freshwater areas that received effluents from rice paddy fields in Kagoshima Prefecture and compare the results with published information from northern and central Japan. This study hoped to shed light on the latitudinal differences in the appearance of rice pesticides within Japan, which could also be useful to other countries with climatic differences between their southern and northern–central regions.

## Materials and methods

### Study area and sampling stations

Kagoshima Prefecture is the southernmost prefecture of Kyushu Island, Japan. Figure 2 shows

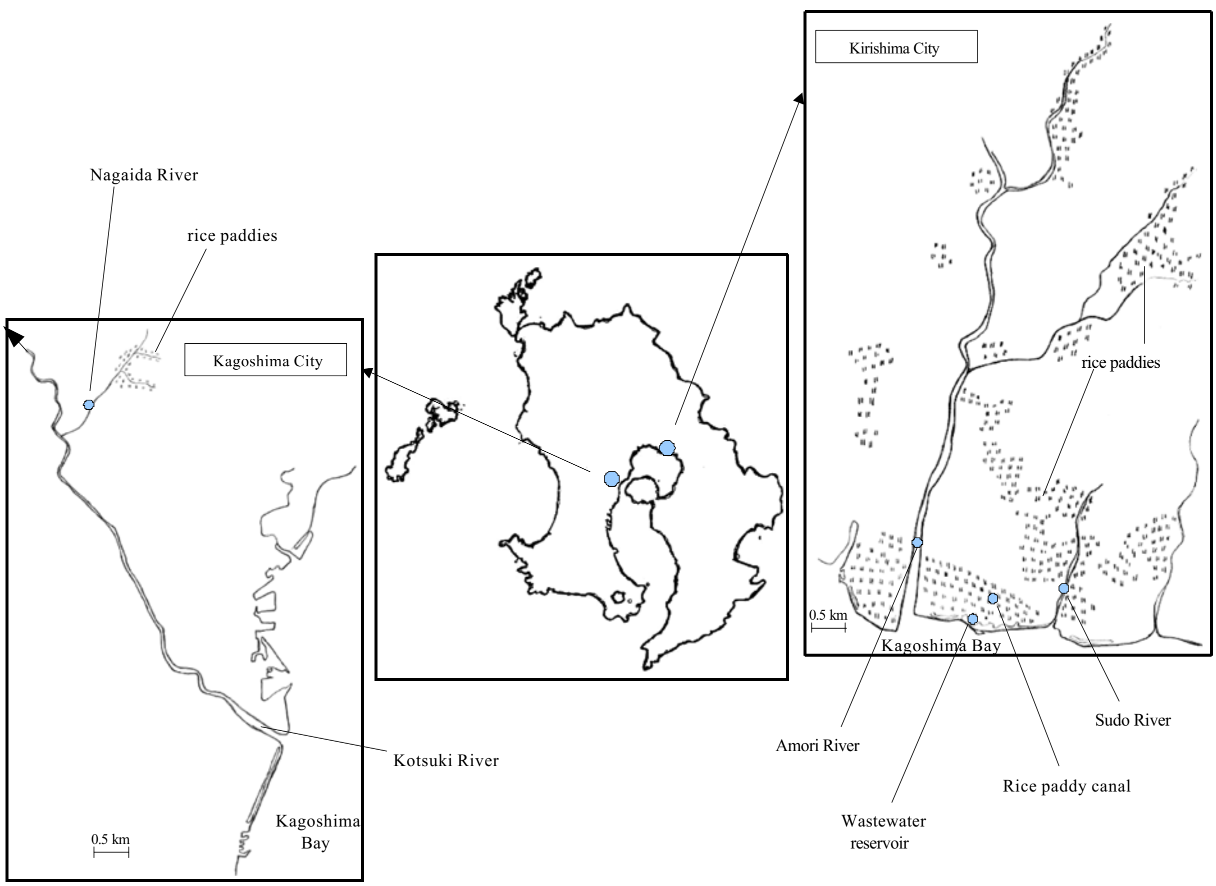



**Fig. 2** Study area and location of the five sampling stations

the study area and the location of the five sampling stations, namely, Amori River (42.5 km long with a drainage area of 411 $km^2$), Sudo River (2.5 km long with a drainage area of 10.5 $km^2$), rice paddy canal (just adjacent to outflows), wastewater reservoir (approximate area of 0.06 $km^2$), and Nagaida River (3.8 km long with a drainage area of 4.8 $km^2$) that drains into the Kotsuki River. All stations were situated adjacent to rice paddy fields and were assumed to receive effluents directly from these fields. The size of the paddy fields that are the probable sources of pesticides residues for Amori, Sudo, paddy canal, reservoir, and Nagaida sampling stations were 4.5, 2.8, 0.1, 1.6, and 0.1 $km^2$, respectively. The first four stations located in Kirishima City, which were relatively closer to the sea, were assumed to carry the paddy effluents directly into the coastal area. A reference sampling point was also established in Kagoshima City to represent a more inland station.

## Sampling strategy

During the 2005 rice planting season, water samples were collected for 20 weeks beginning third week of May until first week of October, taking into consideration that the start of the rice planting season in Kagoshima Prefecture is later than in Honshu Island, which normally starts by the end of April or beginning of May. Water samples were gathered in the earlier days of the week on the presumption that pesticides were applied during weekends when most part-time farmers were off-duty from their main jobs. To collect sample from each site, a transparent 1-L glass bottle was filled full of water by dipping just below the surface and great effort was made to avoid disturbing the sediment below. Samples were preserved while on transit to the laboratory using a cooler with ice packs.

## Target pesticides and recovery test

From the results of a preliminary investigation of 69 pesticides during the 2004 rice planting season, 14 target pesticides were selected for inclusion in the 2005 detailed survey. The target pesticides with their respective usage, chemical class, and mode of actions are presented in Table 1. Ten pesticides [fenobucarb, iprobenfos, flutolanil, phthalide, mefenacet, MEP (fenitrothion), chloroneb, malathion, isoprocarb, and pyributicarb] were included because they were detected in two or more stations in 2004. Three pesticides (etofenprox, pyriproxyfen, and mepronil) were considered because they were detected in the wastewater reservoir for more than four times. Finally, diazinon was added because of the current research interest on this pesticide. Of the 14 target pesticides, two were herbicides, seven were insecticides, and five were fungicides. Moreover, a recovery test using 5 μg/L nominal concentration was carried out on the target pesticides as a dissolved state by the analytical method used in this study. The recoveries ranged from 66.1% to 104% as shown in Table 2. Mefenacet had the highest recovery recorded, while flutolanil had the lowest.

## Chemicals

A gas chromatography–mass spectrometry pesticides standard dissolved in acetone was purchased from Cica Reagent (Pesticide Standard Solution 26; Kanto Chemical Co., Inc., Tokyo). Internal standards (naphthalene-$d_8$, anthracene-$d_{10}$, pyrene-$d_{10}$, and chrysene-$d_{12}$) were purchased from Cambridge Isotope Laboratories, Inc. (USA) or Wako Pure Chemical Industries, Ltd. (Japan). Dichloromethane, hexane, and acetone used were all pesticide grades, while silica gel (Wakogel, C100), sodium chloride, and anhydrous sodium sulfate were all analytical grades. These chemicals were purchased from Wako.

## Pesticide analysis

Extraction of pesticides was performed within 24 h upon arrival in the laboratory. A liquid–liquid extraction was conducted using 800 mL of glass fiber cartridge-filtered sample. Forty grams of sodium chloride was added followed by 60 mL of dichloromethane as extracting solvent. Sample was subjected to a vigorous mechanical shaking for 15 min. Aqueous and solvent portions were allowed to completely separate after shaking and then the dichloromethane portion was collected. A second extraction was performed on the

**Table 1** List of target pesticides with their usage, chemical composition, and mode of actions

| Pesticide name | Usage | Chemical composition | Mode of action |
|---|---|---|---|
| Chloroneb | Fungicide | Substituted benzene | Inhibition of lipid and membrane synthesis (lipid peroxidation)[a] |
| Diazinon | Insecticide | Organophosphorus | Inhibition of acetylcholinesterase[b] |
| Etofenprox | Insecticide | Pyrethroid | Modulation of sodium channel[b] |
| Fenobucarb | Insecticide | *N*-methyl carbamate | Inhibition of acetylcholinesterase[b] |
| Flutolanil | Fungicide | Carboxamide | Inhibition of respiration (complex II: succinate-hydrogenase)[a] |
| Iprobenfos | Fungicide | Phosphorothiolate | Inhibition of lipid and membrane synthesis (phospholipid biosynthesis, methyltransferase)[a] |
| Isoprocarb | Insecticide | *N*-methyl carbamate | Inhibition of acetylcholinesterase[b] |
| Malathion | Insecticide | Organophosphorus | Inhibition of acetylcholinesterase[b] |
| Mefenacet | Herbicide | Anilide (oxyacetamide) | Inhibition of very-long fatty acid synthesis (inhibition of cell division)[c] |
| MEP (fenitrothion) | Insecticide | Organophosphorus | Inhibition of acetylcholinesterase[b] |
| Mepronil | Fungicide | Carboxamide | Inhibition of respiration (complex II: succinate-hydrogenase)[a] |
| Phthalide | Fungicide | Isobenzofuranone | Inhibition of melanin biosynthesis in cell wall (reductase in melanin biosynthesis)[a] |
| Pyributicarb | Herbicide | Thiocarbamate | Inhibition of sterol biosynthesis in membranes (squalene-epoxidase in sterol biosynthesis)[c] |
| Pyriproxyfen | Insecticide | Juvenile hormone mimics | Mimics juvenile hormone[b] |

[a]*Source*: Fungicide Resistance Action Committee (http://www.frac.info/frac/index.htm)
[b]*Source*: Insecticide Resistance Action Committee (http://www.irac-online.org)
[c]*Source*: Herbicide Resistance Action Committee (http://www.plantprotection.org/hrac)

aqueous portion using similar conditions as above. Dichloromethane portion of the second extract were added to the first extract. Anhydrous sodium sulfate was added to the combined extract until a complete dehydration was achieved. Sample was concentrated to about 5 mL using a rotating evaporator with the water bath set at about 40°C. Concentrated sample was transferred immediately into a test tube for changing of solvent from dichloromethane to hexane and was further concentrated to 1 mL by gentle flow of nitrogen gas. Cleanup was performed in a 5-mL glass pipette (6 mm i.d. × 17 cm) filled with silica gel containing 3% moisture as adsorbent material. Pesticides were eluted with 20 mL of a 20% acetone–hexane mixture. The four internal standards were added before final concentration to 0.1 mL by nitrogen gas.

**Table 2** Recovery (%) of the target pesticides ($n = 3$)

| Pesticide name | *m*/*z* | Mean | SD |
|---|---|---|---|
| Chloroneb | 191; 206 | 78.9 | 6.09 |
| Diazinon | 179; 304 | 99.0 | 7.19 |
| Etofenprox | 135; 163 | 98.5 | 4.73 |
| Flutolanil | 173; 145 | 66.1 | 2.00 |
| Fenobucarb | 121; 150 | 92.6 | 7.21 |
| Iprobenfos | 204; 91 | 84.5 | 3.51 |
| Isoprocarb | 121; 136 | 85.2 | 6.62 |
| Malathion | 125; 173 | 84.3 | 7.17 |
| Mefenacet | 192; 136 | 104 | 16.4 |
| MEP (fenitrothion) | 277; 125 | 89.3 | 7.56 |
| Mepronil | 119; 269 | 93.4 | 3.20 |
| Phthalide | 243; 241 | 70.3 | 2.29 |
| Pyributicarb | 165; 108 | 70.9 | 1.74 |
| Pyriproxyfen | 136; 226 | 66.5 | 2.95 |

Tested concentration for all pesticides—5 μg/L

Sample was finally injected into a gas chromatograph (Agilent Technologies 6890N, USA) with mass spectrometry detector (Agilent Technologies 5973N) in splitless mode. Analytical conditions were as follows: (1) injection volume, 2 μL; (2) injector temperature, 250°C; (3) detector temperature, 280°C; (4) oven temperature, initially at 60°C (held for 1 min) then ramped to 180°C at 20°C/min (held for 5 min) then finally increased to 290°C at 3°C/min (held for 3 min); and (5) column, DB-5MS (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm; J & W Scientific, USA).

Data analyses

Most of the data processing was performed using the Microsoft Excel software. Comparison of temporal patterns was conducted on SPSS version 10.1 using a one-way analysis of variance.

## Results and discussion

Of the 14 target pesticides examined, 11 pesticides were detected at any station during the 2005 rice planting season. Of these, one was herbicide, seven were insecticides, and three were fungicides. Eight pesticides were detected in the wastewater reservoir, nine in the rice paddy canal, eight in Amori River, 11 in Sudo River, and eight in Nagaida River as shown in Table 3. Mefenacet had the highest maximum concentration recorded at 13.4 μg/L, which was detected in the rice paddy canal. It was also recorded highest in wastewater reservoir, Amori River, Sudo River, and Nagaida River. Flutolanil had the second highest maximum concentration at 1.64 μg/L, which was also detected in the rice paddy canal. Fenobucarb, on the other hand, was ranked third with regards to the maximum concentration recorded at 1.36 μg/L, which, however, was detected in Nagaida River. Five pesticides (fenobucarb, flutolanil, phthalide, iprobenfos, and mefenacet) were detected in all five stations, while the remaining pesticides (malathion, MEP, diazinon, isoprocarb, pyriproxyfen, and etofenprox) were detected only in four, three, or two stations. Table 3 also shows that generally, the frequencies of detection for fenobucarb, mefenacet, and flutolanil in all stations were greater than 90% except in Nagaida River where their frequencies of detection ranged only from 25% to 50%.

The appearance of six pesticides (diazinon, fenobucarb, iprobenfos, malathion, mefenacet, and MEP) in some freshwater areas of Kagoshima Prefecture, especially those that receive effluents from rice paddy fields, is somewhat related to the usage of these pesticides in the study area based

**Table 3** Maximum concentrations (μg/L) and frequencies of detection (%) of pesticides residues in the five sampling sites during the 2005 rice planting season

| Pesticide name | Wastewater reservoir | | Rice paddy canal | | Amori River | | Sudo River | | Nagaida River | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Max conc[a] | Freq det[b] | Max conc | Freq det | Max conc | Freq det | Max conc | Freq det | Max conc | Freq det |
| Diazinon | < 0.01[c] | 0.0 | < 0.01 | 0.0 | 0.02 | 28.6 | 0.01 | 14.3 | 0.02 | 3.6 |
| Etofenprox | < 0.01 | 0.0 | 0.11 | 8.3 | < 0.01 | 0.0 | 0.04 | 28.6 | < 0.01 | 0.0 |
| Fenobucarb | 0.55 | 100 | 0.35 | 100 | 0.17 | 100 | 0.47 | 100 | 1.36 | 46.4 |
| Flutolanil | 0.37 | 100 | 1.64 | 100 | 0.03 | 71.4 | 0.31 | 92.9 | 0.33 | 46.4 |
| Iprobenfos | 0.91 | 85.7 | 0.06 | 83.3 | 0.10 | 78.6 | 0.98 | 85.7 | 1.00 | 10.7 |
| Isoprocarb | < 0.01 | 0.0 | 0.03 | 33.3 | < 0.01 | 0.0 | 0.07 | 7.1 | 0.08 | 3.6 |
| Malathion | 0.03 | 57.1 | 0.01 | 25.0 | 0.04 | 50.0 | 0.02 | 35.7 | < 0.01 | 0.0 |
| Mefenacet | 3.31 | 100 | 13.4 | 100 | 0.58 | 92.9 | 5.64 | 92.9 | 2.77 | 25.0 |
| MEP (fenitrothion) | 0.01 | 21.4 | 0.01 | 8.3 | < 0.01 | 0.0 | 0.03 | 28.6 | 0.02 | 7.1 |
| Phthalide | 0.02 | 28.6 | 0.05 | 41.7 | 0.01 | 35.7 | 0.12 | 57.1 | 0.01 | 10.7 |
| Pyriproxyfen | 0.02 | 14.3 | < 0.1 | 0.0 | 0.04 | 14.3 | 0.05 | 7.1 | < 0.01 | 0.0 |

[a]Maximum concentration
[b]Frequency of detection
[c]Less than detection limit of 0.01 μg/L

on the PRTR data (ORCERC 2007). For instance, the probable reason for the high concentrations of mefenacet in the stations within Kirishima City is its high usage in the area. In 2005, mefenacet ranked fourth among 125 pesticides being monitored based on its application rate within the city, which was 721 kg/year. Fenobucarb, being another important pesticide detected in the study area based on the maximum concentration and frequency of occurrence, also ranked ninth in the same PRTR list with an application rate of 390 kg/year.

Like most rice paddy fields in Japan, irrigation and drainage canals in Kirishima City are entirely separate. The irrigation canals are built higher than the drainage canals and they are normally constructed on the opposite sides of the paddy fields (Sato 2001). As such, the pesticides that are carried with the effluents of the paddy fields as surface runoffs or adsorbed on suspended solids would end up first in the drainage canal. It is at this point when the pesticides begin to move out of their target area and travel towards larger tributaries. Small drainage canals would flow toward larger canals that eventually drain into rivers. For this study, in particular, the drainage canals studied lead toward the wastewater reservoir, which receives effluents from paddy fields that are located very near the sea. As expected, the concentrations of all pesticides except for iprobenfos are either the same or lower in the wastewater reservoir than in the rice paddy canal (Table 3). In particular, the concentrations of mefenacet and flutolanil in the drainage canal (13.4 and 1.64 μg/L, respectively) are about four times higher than in the wastewater reservoir (3.31 and 0.37 μg/L, respectively). It seems that degradation of some kind or dilution with other effluent water caused the decrease of measured concentrations as the pesticides flowed from the canal to the wastewater reservoir. This is in agreement with the findings of Nakano et al. (2004) where concentrations in a drainage connected directly to rice paddy fields ranged from 10 to 90 μg/L, while for the river water ranged only from 1 to 8 μg/L. The wastewater reservoir is like a freshwater lake or a marsh that acted as a sink for pesticide residues from rice paddy fields. Like Kawakami et al. (2005) who clearly found lower concentrations of pesticides in the marsh water than in the irrigation canals leading to Sugao Marsh (Ibaraki Prefecture), if the degradation contributes to the reduction of concentration, then the wastewater reservoir seems to be a useful option to remove pesticide residues before paddy effluent is released to the sea. Consequently, the wastewater reservoir, as temporary sink for effluents of rice paddy fields located near coastal areas, is effective in controlling the outflow of pesticide residues into the sea.

The riverine stations in Kirishima (Amori and Sudo) receive effluents from the rice paddy fields entirely different from the ones draining into the wastewater reservoir. However, together with Nagaida River, it seems that the rice farmers are applying the same kind and amount of pesticides. Most pesticides identified in the wastewater reservoir were also detected in the three rivers. In general, the concentrations of pesticides in Sudo River are higher compared to Amori and Nagaida rivers. For instance, the concentrations of mefenacet and flutolanil in the Sudo River (5.64 and 0.31 μg/L, respectively) are about onefold higher than in Amori River (0.58 and 0.03 μg/L, respectively). This can be explained by the nearness of the rice paddy fields to Sudo River sampling site, while the rice paddy fields that discharge their effluents into Amori River are located more upstream and far away from the sampling site. The difference between the Sudo and Nagaida rivers could be due to the larger area of rice paddy fields emptying into the Sudo River in comparison to the Nagaida River. Interestingly, concentration of fenobucarb in the Nagaida River (1.36 μg/L) is about three to eight times higher than in the Sudo and Amori rivers (0.47 and 0.17 μg/L, respectively), which could be due to differences in the application rates.

Results of the temporal variation of pesticide residues and its corresponding discussion were limited to pesticides with the three highest frequency of detection, and these were fenobucarb, mefenacet, and flutolanil. Line graphs shown in Fig. 3 illustrate that mefenacet concentrations in the wastewater reservoir started to increase from second week of June and immediately peaked by third week of this month. Concentrations gradually decreased until about last week of July. Similar patterns were observed in the rice paddy canal,

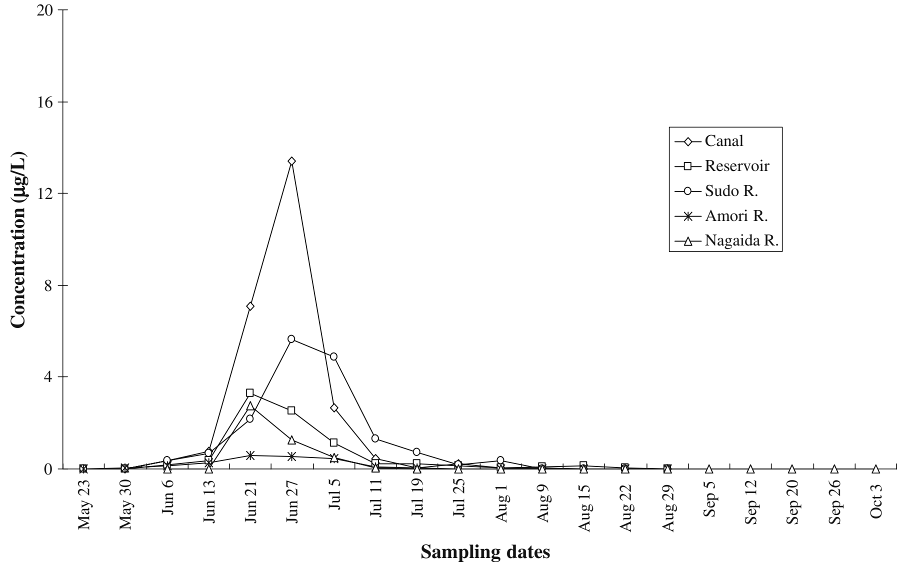



**Fig. 3** Temporal pattern of mefenacet concentrations (µg/L) during the 2005 rice planting season

Sudo River, and Amori River. The peaks of the distribution lasted between June 21 and July 5 or about 3 weeks for all stations. For fenobucarb, concentrations in the wastewater reservoir started to increase from second week of July and peaked by second week of August, as detailed in Fig. 4. Concentrations of fenobucarb also decreased but were still detected up to the end of August. The peaks of the distribution for fenobucarb were not very clear, but concentrations were generally higher starting from the middle of July. Similarly, relatively higher concentrations of flutolanil were observed in the later stages of the rice planting season, as shown in Fig. 5. A statistical comparison made to determine whether the temporal variations of the three pesticides were similar among the five stations studied showed that there is no significant difference among stations ($p > 0.01$).

Generally, herbicides had higher concentrations in the earlier stages of the rice planting season, while insecticides and fungicides had higher concentrations during the later stages. These

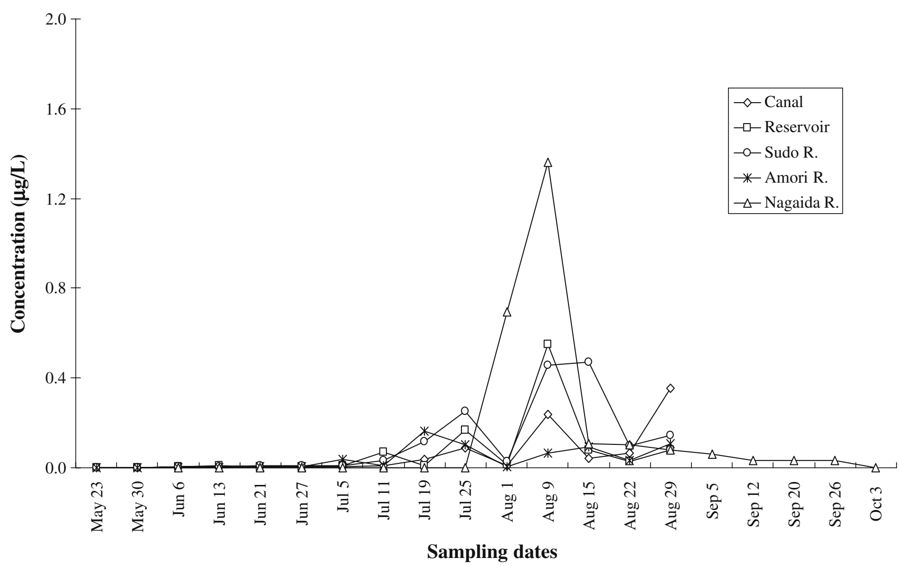



**Fig. 4** Temporal pattern of fenobucarb concentrations (µg/L) during the 2005 rice planting season

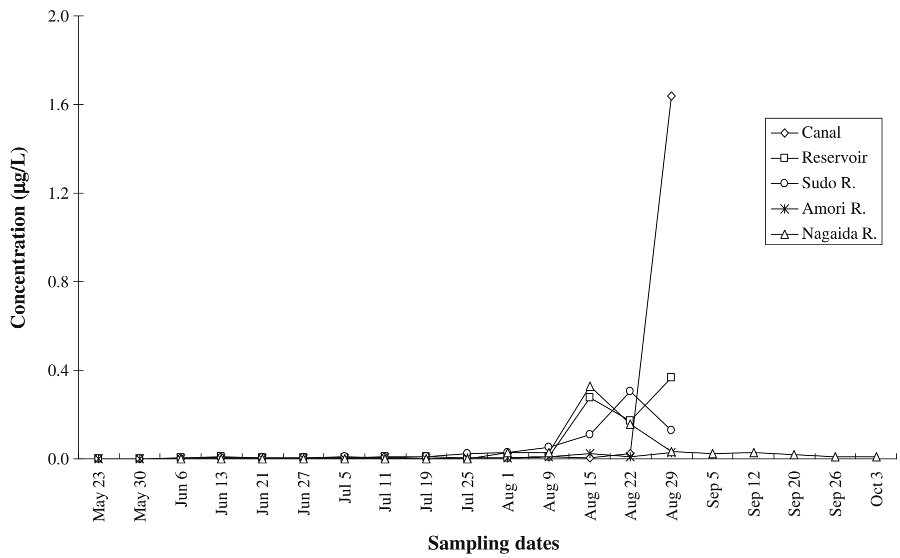



**Fig. 5** Temporal pattern of flutolanil concentrations (μg/L) during the 2005 rice planting season

findings coincided with the normal practice of farmers wherein application of herbicides is done during transplantation of rice, while insecticides and fungicides are applied when the rice is about to mature. It is interesting to note that pesticide application patterns seem to change in a short time, as illustrated by this study. This is in agreement with Nakano et al. (2004) who noticed that the concentrations of herbicides in the river water began to increase immediately after the application of herbicides and that most herbicides were hardly detected in the river after about 1 month of the transplantation, although the rainfall occurred many times. Moreover, this is in accordance to what was observed by Ueji and Inao (2001) that herbicides are generally detected in rivers and other water systems in concentrations on the nanograms per liter level for 2–3 months after use because concentration of herbicides in river water is correlated to the state of application on rice paddies. In addition, it seems that the concentrations and temporal patterns of the top three pesticides do not vary among the sampling sites. This has important implications on the effects of these rice pesticides to coastal organisms, since concentrations of pesticide residues in the wastewater reservoir, which directly flows out to sea, is not so significantly different from the three riverine stations.

To compare the appearance of rice pesticides between southern and northern–central Japan, pesticide residue concentrations in freshwater areas around Japan is summarized in Table 4. Comparison can only be done on pesticides that are detected in this study and in the previous studies. For this purpose, four pesticides are chosen to carry on with the comparison, and these are mefenacet, flutolanil, fenobucarb, and diazinon. In general, the concentrations of the four pesticides in the freshwater areas of Kagoshima Prefecture are lower compared to other areas of northern–central Japan. For example, the maximum concentration of fenobucarb detected in Kagoshima Prefecture (1.36 μg/L) was ten times lower in comparison to Kokai River in Ibaraki Prefecture (11.7 μg/L). The warmer weather conditions in southern Japan during the rice planting season possibly enhanced or hastened the degradation of volatile pesticides, as similarly observed in tropical regions. Meanwhile, the maximum concentrations of mefenacet in Sudo River, the Nagaida River, and wastewater reservoir (5.64, 2.77, and 3.31 μg/L, respectively) are approximately the same as the concentrations detected in other areas (1.9–11.0 μg/L), but Amori River has the lowest concentration (0.58 μg/L), while rice paddy drainage canal has the highest concentration (13.4 μg/L). Although this observation can be

**Table 4** A comparison of the concentrations (μg/L) of rice pesticide residues in some freshwater areas around Japan

| Prefecture | Body of water | Maximum concentrations of pesticides detected (μg/L) | | | | Reference |
|---|---|---|---|---|---|---|
| | | Mefenacet | Flutolanil | Fenobucarb | Diazinon | |
| Niigata | Shinano River | 1.90 | 0.02 | – | 0.02 | Tanabe et al. (2001) |
| Ibaraki | Kokai River | 7.83 | – | 11.7 | – | Hatakeyama and Shiraishi (1998) |
| | Sakura River | 6.00 | – | – | – | Hatakeyama et al. 1999 (as mentioned in Ueji and Inao 2001) |
| | Kozakura River | 11.0 | – | – | – | Nakano et al. (2004) |
| Shiga | Lake Biwa | – | – | – | 1.81 | Sudo et al. (2002) |
| Okayama | Lake Kojima | 6.20 | 30.3 | – | – | Okamura et al. (1999) |
| *not known* | Drainage canal | 4.40 | 234 | – | – | Kanazawa 1994 (as mentioned in Okamura et al. 1999) |
| Hiroshima | Kurose River | – | 0.11 | – | 0.09 | Derbalah et al. (2003) |
| Kagoshima | Amori River | 0.58 | 0.03 | 0.17 | 0.02 | This study |
| | Sudo River | 5.64 | 0.31 | 0.47 | 0.01 | This study |
| | Nagaida River | 2.77 | 0.33 | 1.36 | 0.02 | This study |
| | Drainage canal | 13.4 | 1.64 | 0.35 | < 0.01 | This study |
| | Wastewater reservoir | 3.31 | 0.37 | 0.55 | < 0.01 | This study |

attributed mostly to the application rate of mefenacet (ORCERC 2007) in the surrounding rice paddy fields, it can also be ascribed to the findings of Kibe et al. (2000) that the mefenacet was less adsorbable and hence was expected to translocate easily from the soils. This can cause rapid disappearance of mefenacet in the flowing waters, but the nearer the sampling point is to the paddy outflow, the higher the detected concentration.

Environmental risks of pesticides detected in the freshwater areas of southern Japan were assessed using the toxic units for each pesticide. The toxic units, which represents the simplest way of assessing environmental risk of hazardous chemicals, were calculated by dividing the maximum concentrations of pesticides detected in the freshwater sampling stations with the lowest toxic concentration recorded for all freshwater

**Table 5** Risk (as toxic units) of rice pesticides detected in southern Japan to some freshwater organisms

| Pesticide name | Lowest toxic concentration[a] (μg/L) | Organism showing lowest toxic concentration[a] | Toxic units (TU)[b] | | | |
|---|---|---|---|---|---|---|
| | | | Wastewater reservoir | Amori River | Sudo River | Nagaida River |
| Diazinon | 0.46 | *Ceriodaphnia dubia* | 0.02 | 0.05 | 0.01 | 0.05 |
| Etofenprox | 1,740.00 | *Tilapia mossambica* | 0.00 | 0.00 | 0.00 | 0.00 |
| Fenobucarb | 5.05 | *Paratya compressa improvisa* | 0.11 | 0.03 | 0.09 | 0.27 |
| Flutolanil | 1,100.00 | *Daphnia magna* | 0.00 | 0.00 | 0.00 | 0.00 |
| Iprobenfos | 500.00 | *Daphnia ambigua* | 0.00 | 0.00 | 0.00 | 0.00 |
| Isoprocarb | 8.00 | *Daphnia pulex* | 0.00 | 0.00 | 0.01 | 0.01 |
| Malathion | 2.15 | *Ceriodaphnia dubia* | 0.01 | 0.02 | 0.01 | 0.00 |
| Mefenacet | 8.60 | *Chlorella pyrenoidosa* | 0.39 | 0.07 | 0.66 | 0.32 |
| MEP (fenitrothion) | 0.36 | *Paratya compressa improvisa* | 0.04 | 0.03 | 0.07 | 0.04 |
| Phthalide | 40,000.00 | *Daphnia pulex* | 0.00 | 0.00 | 0.00 | 0.00 |
| Pyriproxyfen | 10.00 | *Daphnia carinata* | 0.00 | 0.00 | 0.00 | 0.00 |

[a]Source: Kegley et al. (2008)
[b]TU = environmental concentration/lowest toxic concentration; 0.01 was used for pesticides with detected environmental concentrations of <0.01 μg/L

organisms found in an online database on pesticide toxicity (Kegley et al. 2008). The calculated toxic units are summarized in Table 5. Although environmental risks of rice pesticides detected were generally low (toxic units were <1.0), relatively higher toxic units were calculated for fenobucarb and mefenacet. Risk of fenobucarb to a freshwater shrimp (*Paratya compressa improvisa*) was comparatively higher in Nagaida River, while risk of mefenacet to a green algae (*Chlorella pyrenoidosa*) was greater in the Sudo River. However, in contrast to the risk posed by pesticide concentrations detected in other freshwater areas of northern and central Japan (Table 4) where mefenacet and fenobucarb poses higher risk (toxic unit >1.0) in Kozakura and Kokai rivers, respectively, our assessment in freshwater areas of southern Japan showed lower or negligible environmental risk.

## Conclusions

Eleven pesticides were detected in a drainage canal, wastewater reservoir, and three rivers in Kagoshima Prefecture that are directly affected by paddy effluents during the 2005 rice planting season. Mefenacet, flutolanil, and fenobucarb had relatively higher maximum concentrations and were frequently detected. Herbicides had higher concentrations in the earlier stages of the rice planting season, while the insecticides and fungicides had higher concentrations in the later stages. The concentrations and temporal patterns of pesticides detected in the wastewater reservoir is comparable to that of the Amori, Sudo, and Nagaida rivers. As such, although the wastewater reservoir effectively reduced the concentrations of pesticide residues from the drainage canals, there is still a need to determine the occurrence and concentrations of these less persistent pesticides in the coastal waters immediately adjacent to the reservoir. Although toxic units were less than 1, implying low environmental risk, some rice pesticides with relatively high concentrations may still end up in the sea, as they are detected frequently and may pose some threat to the marine organisms since these pesticides were known to be accumulated by freshwater animals (Uno et al. 2001). Moreover, as pesticide residues were detected even in freshwater areas of southern Japan where environmental management and protection is highly regarded, this study showed the importance of continuous monitoring and assessment of pesticide residues in freshwater areas that receive effluents from rice paddy fields especially in the developing Asian countries where environmental regulations are not strictly followed or implemented.

**Acknowledgements** The authors are grateful to the members of the Education and Research Center for Marine Resources and Environment, Kagoshima University Faculty of Fisheries for their assistance during the conduct of this study.

## References

Anderson, B. S., Hunt, J. W., Phillips, B. M., Nicely, P. A., de Vlaming, V., Connor, V., et al. (2003). Integrated assessment of the impacts of agricultural drainwater in the Salinas River (California, USA). *Environmental Pollution, 124*, 523–532. doi:10.1016/S0269-7491(03)00012-5.

Belfroid, A. C., van Drunen, M., Beek, M. A., Schrap, S. M., VanGestel, C. A. M., & Van Hattum, B. (1998). Relative risks of transformation products of pesticides for aquatic ecosystems. *The Science of the Total Environment, 222*, 167–183. doi:10.1016/S0048-9697(98)00298-8.

Cedergreen, N., & Streibig, J. C. (2005). The toxicity of herbicides to non-target aquatic plants and algae: Assessment of predictive factors and hazard. *Pest Management Science, 61*, 1152–1160. doi:10.1002/ps.1117.

Comoretto, L., Arfib, B., & Chiron, S. (2007). Pesticides in the Rhone river delta (France): Basic data for a field-based exposure assessment. *The Science of the Total Environment, 380*, 124–132. doi:10.1016/j.scitotenv.2006.11.046.

Derbalah, A. S. H., Nakatani, N., & Sakugawa, H. (2003). Distribution, seasonal pattern, flux and contamination source of pesticides and nonylphenol residues in Kurose River water, Higashi-Hiroshima, Japan. *Geochemical Journal, 37*, 217–232.

Fushiwaki, Y., Tase, N., Kotoda, K., & Urano, K. (1994). Behavior of fungicide pentachloronitrobenzene and intermediates in an intensive farming area in Japan. *Japanese Journal of Toxicology and Environmental Health, 40*, 39–48.

GeNii National Institute of Informatics Scholarly and Academic Information Portal (2007). http://ge.nii.ac.jp/genii/jsp/index-e.jsp.

Gil, Y., & Sinfort, C. (2005). Emission of pesticides to the air during sprayer application: A bibliographic review. *Atmospheric Environment, 39*, 5183–5193. doi:10.1016/j.atmosenv.2005.05.019.

Hatakeyama, S., & Shiraishi, H. (1998). Biomonitoring with shrimp to detect seasonal change in river water toxicity. *Environmental Toxicology and Chemistry, 17*, 687–694. doi:10.1897/1551-5028(1998)017<0687:BWSTDS>2.3.CO;2.

Hatakeyama, S., Fukushima, S., Kasai, F., & Shiraishi, H. (1994). Assessment of herbicide effects on algal production in the Kokai River (Japan) using a model stream and *Selenastrum* bioassay. *Ecotoxicology (London, England), 3*, 143–156. doi:10.1007/BF00143411.

Hatakeyama, S., Inoue, T., Suzuki, K., Sugaya, Y., & Kasuga, S. (1999). Assessment of overall herbicide effects on growth of duckweed in a flow through aquarium carrying pesticide polluted river water. *Japanese Journal of Environmental Toxicology, 2*, 65–75.

Inoue, T., Ebise, S., Numabe, A., Nagafuchi, O., & Matsui, Y. (2002). Runoff characteristics of particulate pesticides in a river from paddy fields. *Water Science and Technology, 45*, 121–126.

Itagaki, N., Nagafuchi, O., Takimoto, K., & Okada, M. (2000). Fate of pesticides in a shallow reservoir. *Water Science and Technology, 42*, 217–222.

Japan Statistical Bureau (2007). http://www.stat.go.jp.

Kanazawa, J. (1994). *Environmental science of pesticides* [in Japanese] (pp. 141–156). Japan: Godo-Shuppan.

Kawakami, T., Eun, H., Arao, T., Endo, S., Ueji, M., Tamura, K., et al. (2006). Concentration and loading of several pesticides in water, suspended solids and sediment during ordinary water discharge in Sugao Marsh, Ibaraki Prefecture, Japan. *Journal of Pesticide Science, 31*, 6–13. doi:10.1584/jpestics.31.6.

Kawakami, T., Ishizaka, M., Ishii, Y., Eun, H., Miyazaki, J., Tamura, K., et al. (2005). Concentration and distribution of several pesticides applied to paddy fields in water and sediment, from Sugao Marsh, Japan. *Bulletin of Environmental Contamination and Toxicology, 74*, 954–961. doi:10.1007/s00128-005-0672-5.

Kegley, S. E., Hill, B. R., Orme, S., & Choi, A. H. (2008). PAN Pesticide Database, Pesticide Action Network, North America (San Francisco, CA). http://www.pesticideinfo.org.

Kibe, K., Takahashi, M., Kameya, T., & Urano, K. (2000). Adsorption equilibriums of principal herbicides on paddy soils in Japan. *The Science of the Total Environment, 263*, 115–125. doi:10.1016/S0048-9697(00)00671-9.

Nakano, Y., Miyazaki, A., Yoshida, T., Ono, K., & Inoue, T. (2004). A study on pesticide runoff from paddy fields to a river in rural region—1: Field survey of pesticide runoff in the Kozakura River, Japan. *Water Research, 38*, 3017–3022. doi:10.1016/j.watres.2004.02.013.

Nohara, S., & Iwakuma, T. (1996a). Pesticide residues in water and an aquatic plant, *Nelumbo* nucifera, in a river mouth at Lake Kasumigaura, Japan. *Chemosphere, 33*, 1409–1416. doi:10.1016/0045-6535(96)00258-5.

Nohara, S., & Iwakuma, T. (1996b). Residual pesticides and their toxicity to freshwater shrimp in the littoral and pelagic zone of Lake Kasumigaura, Japan. *Chemosphere, 33*, 1417–1424. doi:10.1016/0045-6535(96)00259-7.

Ntiamoah, A., & Afrane, G. (2008). Environmental impacts of cocoa production and processing in Ghana: Life cycle assessment approach. *Journal of Cleaner Production, 16*, 1735–1740. doi:10.1016/j.jclepro.2007.11.004.

Numabe, A., & Nagahora, S. (2006). Estimation of pesticide runoff from paddy fields to rural rivers. *Water Science and Technology, 53*, 139–146. doi:10.2166/wst.2006.047 .

Okamura, H., Omori, M., Luo, R., Aoyama, I., & Liu, D. (1999). Application of short-term bioassay guided chemical analysis for water quality of agricultural land run-off. *The Science of the Total Environment, 234*, 223–231. doi:10.1016/S0048-9697(99)00263-6.

Okamura, H., Piao, M., Aoyama, I., Sudo, M., Okubo, T., & Nakamura, M. (2002). Algal growth inhibition by river water pollutants in the agricultural area around Lake Biwa, Japan. *Environmental Pollution, 117*, 411–419. doi:10.1016/S0269-7491(01)00196-8.

Organization for Research and Communication on Environmental Risk of Chemicals (2007). http://env.safetyeng.bsk.ynu.ac.jp/ecochemi/.

Parveen, S., Kohguchi, T., Biswas, M., & Nakagoshi, N. (2005a). Predicting herbicide concentrations in paddy water and runoff to the river basin. *Journal of Environmental Sciences (China), 17*, 631–636.

Parveen, S., Kohguchi, T., Shimazawa, H., & Nakagoshi, N. (2005b). Measuring of some selected herbicides in paddy surface waters in the Saijo Basin, Western Japan. *Agronomy Sustainable and Development, 25*, 55–61. doi:10.1051/agro:2004055.

Sakai, M. (2003). Investigation of pesticides in rainwater at Isogo Ward of Yokohama. *Journal of Health Science, 49*, 221–225. doi:10.1248/jhs.49.221.

Sato, H. (2001). The current state of paddy agriculture in Japan. *Irrigation and Drainage, 50*, 91–99. doi:10.1002/ird.10.

Scholz, N. L., & Hopkins, W. A. (2006). Ecotoxicology of anticholinesterase pesticides: Data gaps and research challenges. *Environmental Toxicology and Chemistry, 25*, 1185–1186. doi:10.1897/05-699.1.

Steen, R. J. C. A., van der Vaart, J., Hiep, M., VanHattum, B., Cofino, W. P., & Brinkman, U. A. T. (2001). Gross fluxes and estuarine behavior of pesticides in the Scheldt Estuary (1995–1997). *Environmental Pollution, 115*, 65–79. doi:10.1016/S0269-7491(01)00085-9 .

Sudo, M., Kawachi, T., Hida, Y., & Kunimatsu, T. (2004). Spatial distribution and seasonal changes of pesticides in Lake Biwa, Japan. *Limnology, 5*, 77–86. doi:10.1007/s10201-003-0115-0.

Sudo, M., Kunimatsu, T., & Okubo, T. (2002). Concentration and loading of pesticide residues in Lake

Biwa basin (Japan). *Water Research, 36*, 315–329. doi:10.1016/S0043-1354(01)00196-8.

Sudo, M., Okubo, T., & Kaneki, R. (2005). Paddy herbicide inputs in the entire river inflow reaching Lake Biwa, Japan. *Limnology, 6*, 91–99. doi:10.1007/s10201-005-0145-x.

Sudo, M., Nishino, M., & Okubo, T. (2006). Decrease in herbicide concentrations and affected factors in lagoons located around Lake Biwa. *Water Science and Technology, 53*, 131–138. doi:10.2166/wst.2006.046.

Suzuki, S., Otani, T., Iwasaki, S., Ito, K., Omura, H., & Tanaka, Y. (2003). Monitoring of 15 pesticides in rainwater in Utsunomiya, eastern Japan, 1999–2000. *Journal of Pesticide Science, 28*, 1–7. doi:10.1584/jpestics.28.1.

Tada, M., & Hatakeyama, S. (2000). Chronic effects of an insecticide, fenobucarb, on the larvae of two mayflies, Epeorus latifolium and Baetis thermicus, in model streams. *Ecotoxicology (London, England), 9*, 187–195. doi:10.1023/A:1008990604166.

Tanabe, A., Mitobe, H., Kawata, K., Yasuhara, A., & Shibamoto, T. (2001). Seasonal and spatial studies on pesticide residues in surface waters of the Shinano River in Japan. *Journal of Agricultural and Food Chemistry, 49*, 3847–3852. doi:10.1021/jf010025x.

Thomson Scientific ISI Web of Knowledge (2007). http://www.isiwebofknowledge.com.

Ueji, M., & Inao, K. (2001). Rice paddy field herbicides and their effects on the environment and ecosystems. *Weed Biology and Management, 1*, 71–79. doi:10.1046/j.1445-6664.2001.00002.x.

Uno, S., Shiraishi, H., Hatakeyama, S., Otsuki, A., & Koyama, J. (2001). Accumulative characteristics of pesticide residues in organs of bivalves (*Anodonta woodiana* and *Corbicula leana*) under natural conditions. *Archives of Environmental Contamination and Toxicology, 40*, 35–47. doi:10.1007/s002440010146.

Yamaguchi, Y., Fukushima, M., Fujita, T., Yamamoto, T., & Yamada, A. (1992). Distribution and seasonal variation of pesticide residues in Yodo River basin, Japan. *Water Science and Technology, 25*, 61–68.

Zhang, X. Y., Liu, X. M., Lou, Y. Z., & Zhang, M. H. (2008). Evaluation of water quality in an agricultural watershed as affected by almond pest management practices. *Water Research, 42*, 3685–3696. doi:10.1016/j.watres.2008.05.018.