Selecting pesticides for inclusion in drinking water quality guidelines on the basis of detection probability and ranking

Paper published in Environment International Vol. 63, 2014.

Selecting pesticides for inclusion in drinking water quality guidelines on the basis of detection probability and ranking

Kentaro Narita[a], Yoshihiko Matsui[b,]*, Kensuke Iwao[a], Motoyuki Kamata[c], Taku Matsushita[b], and Nobutaka Shirasaki[b]

[a] Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[b] Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[c] College of Engineering, Kanto Gakuin University, Mutsuurahigashi 1-50-1, Kanazawa-ku, Yokohama 236-8501, Japan
* Corresponding author: Phone & Fax: +81-11-706-7280, Email: matsui@eng.hokudai.ac.jp

Research highlights

Indicators were tested for pesticide selection in water quality regulation.

Detection rate was defined to judge which indicators were the best.

The aspects incorporated into the best indicator are the following:

Local pesticide application rate according to rice-farming/upland-field applications

Degradation and adsorption properties as quantified by score values

Abstract

Pesticides released into the environment may pose both ecological and human health risks. Governments set the regulations and guidelines for the allowable levels of active components of pesticides in various exposure sources, including drinking water. Several pesticide risk indicators have been developed using various methodologies, but such indicators are seldom used for the selection of pesticides to be included in national regulations and guidelines. The aim of the current study was to use risk indicators for the selection of pesticides to be included in regulations and guidelines. Twenty-four risk indicators were created, and a detection rate was defined to judge which indicators were the best for selection. The combination of two indicators (local sales of a pesticide for the purposes of either rice farming or other farming, divided by the guideline value and annual precipitation, and amended with the scores from the physical and chemical properties of the pesticide) gave the highest detection rates. In this case study, this procedure was used to evaluate 134 pesticides that are currently unregulated in the Japanese Drinking Water Quality Guidelines, from which 44 were selected as pesticides to be added to the primary group in the guidelines. The detection probability of the 44 pesticides was more than 72%. Among the 102 pesticides currently in the primary group, 17 were selected for withdrawal from the group.

Keywords: drinking water quality standards, ranking, risk assessment, index

1. INTRODUCTION

Pesticides are considered to be an integral part of modern agriculture. The annual global consumption of 900 active chemical ingredients is estimated to be 2.4 billion kilograms, with a market value of US$39 billion (World Resources Institute, 1998; USEPA, 2011). The release of pesticides from agricultural fields and the resulting contamination of the environment may pose both ecological and human health risks (Capri and Karpouzas, 2007). Governments and nongovernmental organizations select certain pesticides and regulate their concentrations in drinking water. For example, the World Health Organization (2011) lists 48 active pesticide ingredients in its Drinking Water Quality Guidelines. In the United States, the Environmental Protection Agency (USEPA) lists 21 pesticides and related products in the National Primary Drinking Water Regulations (USEPA, 2009). “The USEPA uses the Unregulated Contaminant Monitoring program to collect data for contaminants that are suspected to be present in drinking water but for which health-based standards have not been set,” and the agency also periodically reviews the contaminants listed in the National Primary Drinking Water Regulations (USEPA, 2009). In Japan, no pesticides are listed in the Drinking Water Quality Standards (DWQS), but pesticides are included in a category referred to as “Complementary Items to Set the Target for Water Quality Management” (hereafter called the Japanese Drinking Water Quality Guidelines, JDWQG), for which analysis is recommended in line with DWQS (MHLWJ, 2003a). The JDWQG adopted the concept of a hazard index (e.g., Reffstrup et al., 2010), otherwise known as the *DI* value, for the purpose of assessing the total risk associated with exposure to multiple pesticides (MHLWJ, 2003a). The *DI* value is defined as

$$DI = \sum_i \frac{DV_i}{GV_i} \qquad (1)$$

where DV_i is the observed concentration of pesticide i, and GV_i is the reference concentration of pesticide i, which is determined in the JDWQG based on the acceptable daily intake (ADI) of the pesticide. Pesticide monitoring should be conducted with the minimum detection limit equal to 1% of each GV_i value, the summation should include monitored pesticides, and the DI should be 1.0 or less. For inclusion in the primary group of pesticides regulated by the JDWQG, the Ministry of Health, Labour and Welfare selected 102 pesticides from approximately 550 registered pesticides (MHLWJ, 2003a). The selection was based on the annual sales and the ADI values of pesticides because actual data on their presence in drinking water sources were limited at the time of the selection, particularly for pesticides that were unregulated at that time. The selected 102 pesticides were suspected to be present in water sources at concentrations greater than 1% of each GV_i value, but the reasoning behind this was scarce. Every a few years, pesticides are newly developed and the pesticides applied to fields are steadily changing. Therefore, regulatory authorities collect data for pesticides that are suspected to be present in drinking water in order to update the list of regulated pesticides. Monitoring authorities must determine which pesticides are likely to be present in a given water supply.

The European Union Drinking Water Directive (1998) specifies acceptable concentrations of pesticides (and related products) both separately (0.1 μg/L) and in total (0.5 μg/L). However, the target pesticides are not defined by the directive; instead, the monitoring authority must determine which pesticides are likely to be present in a given water supply. Under these circumstances, a rationale and methodology for reviewing unregulated/regulated pesticides and monitoring pesticides based on available but limited data are needed. Several pesticide risk indicators have been developed through various methodologies and with various objectives (Finizio et al., 2001; Reus et al., 2002; Gramatica and Guardo, 2002; Verro et al., 2009a, 2009b). The objectives include the assessment of toxicity to a particular organism and the assessment of human health risks associated with occupational exposure and exposure to contaminated water or food. Ranking and comparing the relative risks of pesticides according to risk indicator scores is expected to serve as a tool in decision making and policy formulation, such as the identification of more environmentally friendly pesticides and application practices (Reus and Leendertse, 2000; Juraske et al., 2007; Trevisan et al., 2009).

The score values for some pesticide risk indicators are directly related to the potential for surface water contamination, pesticide concentration in surface water, or the ratio between concentration and toxicity. The score values are then used to assist in the prioritization or selection of pesticides to be targeted in monitoring programs in local catchment areas (Papa et al., 2004; Kookana et al., 2005; Tani et al., 2012). The results of the pesticide ranking approach have been validated against measured concentrations (Kookana et al., 2005; Peterson, 2006; Tani et al., 2012). However, ranking and scoring methods have not yet been used to select pesticides to be regulated in national drinking water guidelines or standards, partly because ranking methods represent a relative risk rating for which the cutoff value for selection is rather arbitrary. Simulation by means of a hydrological diffuse pollution model may directly predict pesticide concentrations and provide absolute risks (Holvoet et al., 2007; Yang and Wang, 2010); however, such simulation requires the input of precise data sets, and the application of such a method is limited to the catchment scale (Matsui et al., 2007).

In the current study, our aim was to develop a procedure for selecting suspected pesticides to be included in regulation and to screen out the inessential pesticides from the regulation by applying a ranking method involving score values for pesticide risk indicators. While the procedure was applied to pesticide selection in the revision of the primary group of pesticides in the JDWQG, the concept and the fundamental structure of the procedure can be applied to other situations.

2. MATERIALS AND METHODS

2.1. Risk Indicators

We created and tested 24 risk indicators for pesticides in this study (Table 1). We tested the indicator A1 on the assumption that the occurrence of a pesticide in environmental waters is related to its annual application rate. We also used indicator A2, which is A1 divided by the guideline value (here, the GV_i value (MHLWJ, 2003a)) so the probability of detection would be taken into consideration. For the pesticides that are not assigned official GV_i values, GV_i values were calculated from their ADI value using the normal procedure, with the assumption of a water consumption of 2 L/day, a body weight of 50-kg, and a 10% allocation factor (MHLWJ, 2003b).

The pesticides applied for rice farming enter river water at high rates because of the large amount of natural freshwater required during the cropping season (Matsui et al., 2002). As shown in Fig. 1S (supporting material), the current study also confirmed that the concentrations of pesticides used in rice farming are higher than the concentrations of pesticides applied to upland fields, although the pesticides applied to upland fields are, nevertheless, detected in river water. Pesticides applied to rice paddies may therefore have a greater potential to contaminate river water than pesticides applied to upland fields. To account for these tendencies, we also used indicators A3 and A4, which are upland-field modifications of A1 and A2, respectively. Indicators A5 and A6 are rice-specific modifications of A1 and A2, respectively.

Runoff of a pesticide to surface water is affected by the properties of the pesticide. In a previous study (Tani et al., 2010), we used the diffuse pollution hydrologic model to conduct sensitivity analyses for the purpose of evaluating the influence of various pesticide properties on runoff, and our results indicated that pesticide adsorption and degradation in soil are the most influential properties and that water solubility also affects pesticide runoff to a certain extent. In a subsequent sensitivity analysis (Tani et al., 2012), we quantitatively evaluated the influence of three pesticide properties (the soil adsorption coefficient normalized by the organic-carbon content of the soil (K_{oc}), the half-life in soil and half-life in water) on the concentrations of rice-farming pesticides in river water. Using the results of the analyses, we systematically designed score tables for the pesticide properties in such a way that the sum of the scores for a particular pesticide was proportional to the logarithm of the predicted concentration of that pesticide in river water. Scores for soil adsorption and soil degradation, defined as Score *Y*, are given in a matrix table as a function of log K_{oc} and half-life with respect to degradation in soil (Table 1S, supporting material). Scores for degradation in water, defined as Score *Z*, are given in a table as a function of half-life with respect to degradation in water.

Indicators A7 and A8 correspond to A5 and A6, respectively, modified by incorporation of scores to account for the effects of soil adsorption and half-life. Because score tables have not yet been developed for upland-field pesticides, indicators that reflect the effects of pesticide properties cannot be used for upland-field pesticides.

Pesticide use varies regionally. For example, approximately 43% of the fenobucarb sold in Japan is sold in the Kyushu region in Japan, and 34% and 23% of phenthoate are sold in the Hokkaido and Tohoku regions, respectively (Fig. 2S, supporting material). Therefore, these pesticides can be expected to be detected at high concentrations in the surface waters of these regions, even if the national sales quantities are not large. Indicators A1–A8 do not reflect the possible regional differences. Therefore, we divided Japan into 10 geographical regions and used indicators similar to A1–A8 for each region. For example, B1 is the regional version of A1 and is the maximum value of (quantity of sales)/(regional area) among the values for the 10 regions. Indicators C1–C8 are modifications of B1–B8, respectively, in which regional land area is replaced by regional precipitation, in order to account for possible dilution effects.

2.2. Pesticides

In 2011, the number of registered pesticides in Japan was approximately 530 (FAMIC, 2011). The primary group of JDWQG consisted of 102 pesticides. The secondary and tertiary groups had 26 and 77 pesticides, respectively (Table 2). In addition to the currently listed pesticides, we selected 31 pesticides from among the following three categories: (1) pesticides listed in the “Provisional guidance relating to prevention of water contamination with pesticides used on golf courses” (MOEJ, 2010), (2) pesticides studied in survey research in Japan (Matsui, 2011), and (3) the top 30 herbicides, 30 insecticides, and 30 fungicides in terms of sales (JPPA, 2008–2011; FAMIC, 2011) and sales/ADI. The total number of pesticides included in the study was 236. Pesticide concentrations in raw water samples from water treatment plants were obtained from *Statistics on Water Supply* for fiscal years 2007–2010 (JWWA, 2009–2012). Each monitoring authority measured the concentration of each pesticide on average two times per year. Therefore, if we had judged detection/no-detection of a pesticide by using data from a single year, we would likely have missed pesticide concentrations that exceeded the detection level and would have incorrectly judged the detection/no-detection of some pesticides. Therefore, for each pesticide, we pooled the data for the 4 years from 2007 to 2010 into a single data point and used that data point to judge detection/no-detection (Table 2). Any clerical mistakes in the data were corrected after email inquiries regarding data that were deemed critical for determining whether the pesticides were detected or not detected. Additionally, inquiries were made for critical data that were deemed suspect, that is, data for pesticides that were detected at a few water authorities but at measured concentrations exactly equal to the reference concentration or the minimum detection limit. Data that were not included in these statistics were obtained directly from nine water supply authorities that conducted frequent measurements (see Acknowledgments). The concentrations of the 102 pesticides in the primary group of JDWQG were measured by 404 water authorities in Japan. Among the 102 pesticides, 78 were detected at concentrations of >1% of the corresponding GV_i value. The remaining 24 pesticides were either not detected within the minimum detection limit or were detected at a concentration of <1% of the GV_i value. Because the quantification of a pesticide concentration >1% of the GV_i value is recommended for evaluation of the *DI* value in JDWQG (MHLWJ, 2003b), the 24 pesticides were treated as pesticides that were not detected at significant concentrations (hereafter referred to as undetected pesticides). Nine water authorities also measured the concentrations of some of the pesticides in the secondary and tertiary groups and reported the detection of three pesticides from these groups. Finally, among the 236 pesticides for which we collected concentration data, 81 pesticides (hereafter referred as detected pesticides) were recorded as detected. The detected pesticides plus undetected pesticides were 105, and these were used as the index pesticides. For the remaining 131 pesticides (unmeasured pesticides), sufficient measurement data were not available.

2.3. Data for Calculating Risk Indicator Values

Annual prefectural pesticide sales of commercial product bases were obtained from pesticide sales data books (JPPA, 2008–2011) and were averaged for the years 2007–2010. Because detection/no-detection of each pesticide was judged on the basis of pooled data for the years 2007–2010, the pesticide sales for those years were also treated as a single data point for each pesticide. From these data, the quantities of pesticides sold specifically for rice farming were estimated by referring to the uses indicated on the product labels. For pesticides that can be used for several crops, the percentages used for rice farming were estimated from data for planted areas of crops, including rice (MAFFJ, 2011), and recommended pesticide application rates (Matsui et al., 2006; Kamata et al., 2008; FAMIC, 2011); and then the quantities of pesticides applied for rice farming were calculated. The quantities of a pesticide applied in upland fields were calculated by subtracting the quantities of the pesticide applied for rice farming from the total sale of the pesticide. Quantities of pesticides in terms of the amounts of active chemical ingredients were calculated from the amounts of the chemical ingredient in the product bases (FAMIC, 2011). The ADI values were obtained from a pesticide ADI database (Sugita et al., 2006; NIHS, 2011). For annual precipitation, we used the average values for the period, from were years 1976 to 2005 (MLITJ, 2011); the latest data including the target years of 2007-2010 was not available. K_{oc} values and half-lives of pesticides for evaluation of the score values (Tani et al., 2012) were obtained from the literature (Tomlin, 2006; FSC, 2011; MOEJ, 2011).

3. RESULTS AND DISCUSSION

3.1. Detection Rates of Pesticide Indicators

We scored the 236 pesticides by using each indicator, and then we ranked the pesticides according to the scores. A good indicator is one in which the detected pesticides are scored with high values but the undetected pesticides are scored with low values, so that the pesticides that will actually be detected can be selected. We used 105 pesticides (81 detected, 24 undetected, see Table 2) as index pesticides. To judge whether indicators were good for pesticide selection, we used a detection rate for each indicator, which was defined as

$$\text{Detection rate} = \frac{\text{The number of detected pesticides in the selected pesticides}}{\text{The number of index pesticides in the selected pesticides}} \quad (2)$$

A good indicator was one that gave a high detection rate. When the 236 pesticides were ranked according to indicator A1 and the pesticides with the 50 highest A1 values were selected, the number of index pesticides in the selection was 35 and the number of detected pesticides in the selection was 28 (selectively rate = 28/35 = 80%). As the number of selected pesticides increased, the selectively rate slightly decreased, although there were some ups and downs (dashed gray line, Fig. 1). Detection rates by A2 were higher than those by A1, but the results are not surprising because the detection/no-detection of pesticides is dependent on the GV_i value of the pesticide in consideration.

Indicators A5–A8 (and B5–B8, etc.) consider only rice-farming pesticides, which have a high tendency to run off into surface water. Moreover, A7 and A8 (and B7 and B8, etc.) account for pesticide properties that could affect runoff rates. Therefore, A5–A8 can be expected to show better detection rates than A1 and A2. However, the former cannot be used to select for upland-field pesticides. Therefore, we used A5–A8 in combination with A1– A4. For example, to use the combination of A4 and A6 (hereafter referred to as A4A6) to select 50 pesticides, we first selected a certain number of pesticides by using A6 (regarding paddy-field pesticides) and then selected the remaining pesticides by using A4 (regarding upland-field pesticides). The detection rate depended on the numbers in the first and second selections. In the case of selecting 50 pesticides by using A4A6, for example, the detection rate was maximized when 49 pesticides were selected with A6 and 1 pesticide was selected with A4. We defined this type of high detection rate as the single unique detection rate for each combination of indicators at a given total number of selected pesticides (e.g., 50), and this high detection rate is hereafter referred to simply as the detection rate. The detection rates for A4A6 depended on the number of selected pesticides (solid gray line, Fig. 1). The detection rates were 100% when selected pesticides were less than 82, and the rate gradually decreased as the number of selected pesticides was increased. Overall, the detection rates by A4A6 were higher than those by A2, proving that dividing pesticides according to rice-paddy and upland-field applications and then using the combination of two indicators was successful.

Among the four indicators shown in Fig. 1, C4C8 yielded the highest detection rate most of the time when the number of selected pesticides ranged from 50 to 150. The detection rate was 100% until 91 pesticides were selected, at which point the rate began to decrease gradually with increasing pesticide selections.

We actually tested 48 indicator combinations: 16 combinations of indicators based on national pesticide usage [(A1–A4) × (A5–A8)], 16 combinations of indicators based on regional pesticide usage [(B1–B4) × (B5–B8)], and 16 combinations of indicators based on regional pesticide usage and precipitation [(C1–C4) × (C5–C8)] (Table 3). Among these 48 combinations, C4C8 gave the highest detection rate 82 times when the number of selected pesticides ranged from 50 to 150. B4B8 gave the highest rate 78 times. Overall, the indicators in the B series and the C series showed better detection rates than those in the A series. This result indicates the importance of regional differences in pesticide applications: pesticides applied regionally and pesticides applied locally but intensively are detected more often than pesticides applied nationwide. The indicators in the C series were slightly better overall than the B series; this result suggests that precipitation would have a dilution effect on pesticide concentrations, rather than triggering pesticide runoff. Somewhat better detection rates were achieved by the series of “8” (e.g., A8) relative to those achieved by the series of “6” (e.g., A6), proving that the incorporation of pesticide properties, such as soil-adsorbability, in the indicator of the 8-series plays a certain role in better selecting pesticides. On the basis of these results, we used C4C8 to select pesticides in the case study.

3.2. Selecting Pesticides for Addition to the Primary Group

When the number of pesticides selected with C4C8 was ≤ 91, the detection rate was 100% (Fig. 1). The 91 pesticides included 56 index pesticides, all of which were detected pesticides. This cutoff level was designated as the first selection level. We changed the selection level stepwise for each by adding approximately 10 index pesticides and then calculating the detection rates. When 108 pesticides (including 11 additional index pesticides) were selected, the detection rate decreased to 95.5%. This cutoff level was designated as the second selection level. Of the 11 additional index pesticides, eight were detected pesticides (detection rate 72.7% for the 11 additional index pesticides, Fig. 2). When 143 pesticides were selected (including 10 additional index pesticides; third selection level), only four of the 10 index pesticides were detected pesticides (detection rate 40%). That is, there was a substantial decrease in the detection rate below the second selection level. When 12 index pesticides were added (fourth selection level), the detection rate remained low (41.7%). On the basis of these results, we determined that the second selection level was a reasonable cutoff level.

A scatter plot of C8 versus C4 for the index pesticides (Fig. 3) clearly indicated that the first selection level screened out all the undetected pesticides, the second selection level screened out all but three of the undetected pesticides, and the undetected pesticides clustered at the lower left of the plot. A scatter plot of C8 versus C4 for the unmeasured pesticides showed that 35 unmeasured pesticides fell on the right or upper side of the area to the right of or above the first selection level (Fig. 4). Because the index pesticides in this area were all detected, these 35 unmeasured pesticides in the same area would likely be detected if they were measured. Nine unmeasured pesticides were added between the first and second selection levels. Because the detection rate at the second level was 72.7%, these nine unmeasured pesticides would likely be detected at a similarly high percentage if they were measured. Thus, our results suggest that 44 (= 35 + 9) among the 131 unmeasured pesticides should be included in the primary group being revised. Collecting data on whether these 44 pesticides are detected or not is of high importance, but collecting those data will take time. In the meantime, standard methods for the determination of these pesticides should be developed. Once the primary group of JDWQG has been revised, water supply authorities will be officially directed to monitor these pesticides.

3.3. Selecting Pesticides to Be Withdrawn from the Primary Group

C4C8 was chosen because this combination maximized the detection rate, which is equivalent to minimizing the detection rate for undetected pesticides and in turn is equivalent to maximizing the undetection rate, which is defined as

$$\text{Undetection rate} = \frac{\text{Number of undetected pesticides in the unselected pesticides}}{\text{The number of index pesticides in the unselected pesticides}} \qquad (3)$$

We therefore used C4C8 to choose pesticides that should be withdrawn from the current primary group. For eight detected pesticides among the 105 index pesticides in the group (Table 2), no sales records were available; these are pesticides for which pesticide registration was cancelled. The reason that these pesticides were detected is unknown; the statistics may be incorrect, or these pesticides may be extremely persistent in the environment. Our selection method, which is based on pesticide sales, cannot be used to evaluate the probability of detection of these eight pesticides. When they were omitted from the calculation, the undetection rate was 100% (Fig. 5) for the left side of the dashed line (designated as the first withdrawal level; Fig. 6). The 11 pesticides in the first withdrawal level were all undetected pesticides. Withdrawal levels were changed stepwise for each by adding approximately 10 withdrawal candidate pesticides. Until the second withdrawal level, another nine pesticides were identified as candidates for withdrawal, and six out of the nine were undetected pesticides (undetection rate 66.7%). When the cutoff level was further relaxed (third withdrawal level), the undetection rate decreased to 40.0%. The undetected and detected pesticides were mixed between the second and third withdrawal levels. If we take the second withdrawal level as the cutoff level, 17 undetected pesticides should be withdrawn from the primary group because of the very low probability of their detection and the fact that there are no records of their detection.

4. CONCLUSIONS AND FUTURE WORK

Twenty-four indicators were created (Table 1) and tested using the detection rate defined by equation (1) in order to efficiently select pesticides that would likely be detected if monitored. The combination of indicators C4 and C8 maximized the detection rate, suggesting that this combination was the best for selecting the pesticides of probable detection. This result reflected the importance of local pesticide consumption according to rice-farming/upland-field application, guideline value, degradation and adsorption properties as quantified by score values, and annual precipitation.

The application of the indicators suggests that the primary group of JDWQG should be amended with the addition of 44 pesticides, as well as the removal of 17 pesticides. The probability of detection of the 44 pesticides was more than 72%. Whether these 44 pesticides can actually be detected is an important question, and a long-term, follow-up study is needed to answer this question. Before nationwide monitoring of these pesticides can be implemented, several tasks will have to be completed, including the establishment of standard analytical methods and official revision of the primary group. Furthermore, our results suggest that local variations in pesticide use are an important aspect of predicting the probability of pesticide detection. Additional studies may allow the prediction of pesticide detection locations. In this study, we used binary statistical data: pesticides were either detected or not detected. However, the probability of detection or no-detection could also be predicted from quantitative data for measured pesticide concentrations. Further study will provide additional data for the selection of regulated pesticides.

ACKNOWLEDGMENTS

We thank Hachinohe Regional Water Supply Authority, Sendai City Waterworks, Ibaraki Prefectural Waterworks Bureau, Chiba Prefecture Waterworks Bureau, Kanagawa Water Supply Authority, Niigata Municipal Bureau of Waterworks, Waterworks Bureau of Nara Prefectural Government, Waterworks Bureau of the City of Hiroshima, and Southern Fukuoka Water Supply Authority for providing pesticide concentration data. Thanks are also due to Dr. T. Aizawa, Dr. M. Asami, Dr. T. Nishimura, Dr. N. Sugimoto, Mr. T. Ogawa, and Dr. T. Ikemoto, whose expertise was very helpful. This study was supported by the Health and Labour Sciences Research Grant (H25-Kenki-Ippan-007) from the Ministry of Health, Labour, and Welfare, Japan. The results of this work contributed to the revision of JDWQG. However, this work has not been evaluated by these entities and does not necessarily reflect their opinion; therefore, no official endorsement should be inferred.

APPENDIX. SUPPORTING INFORMATION

Table 1S, Fig. 1S and Fig. 2S are available online at ######.

REFERENCES

Capri E., Karpouzas D., 2007. Pesticide risk assessment in rice paddies: theory and practice. Elsevier Science, Amsterdam, pp. 255.

Drinking Water Directive. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal of the European Communities L330, 05/12/1998 P.0032-0054; http://eur-lex.europa.eu/LexUriServ/site/en/oj/1998/l_330/l_33019981205en00320054.pdf. [accessed on 5 Mar. 2012].

FAMIC (Food and Agricultural Materials Inspection Center), 2011; http://www.acis.famic.go.jp/searchF/vtllm001.html. [accessed on 16 June 2012, in Japanese].

Finizio A., Calliera M., Vighi M., 2001. Rating systems for pesticide risk classification on different ecosystems. Ecotoxicol. Environ. Saf. 49(3), 262–74.

FSC (Food Safety Commission). Risk Assessment Reports of Pesticides, 2011; http://www.fsc.go.jp/fsciis/evaluationDocument/list?itemCategory=001. [accessed on 16 June 2012, in Japanese].

Gramatica P., Guardo A.D., 2002. Screening of pesticides for environmental partitioning tendency. Chemosphere 47(9), 947–956.

Holvoet K.M.A., Seuntjens P., Vanrolleghem P.A., 2007. Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecol. Modelling. 209(1), 53–64.

JPPA (Japan Plant Protection Association), 2008-2011. *Pesticide directory 2007-2010*. Tokyo, Japan. (in Japanese)

JWWA (Japan Water Works Association), 2009-2012. *Statistics on Water Supply 2007-2010*. Vol. 90-93. Tokyo, Japan. (in Japanese)

Juraske R., Antón A., Castells F., Huijbregts M.A.J., 2007. PestScreen: A screening approach for scoring and ranking pesticides by their environmental and toxicological concern. Environ. Int. 33(7), 886–893.

Kamata M., Aizawa T., Ikegai T., Magara Y., 2008. Estimation of pesticide runoff to evaluate the monitoring priority of pesticide on water quality management. Proceedings 7th IWA World Water Congress, Vienna, Austria, CD-ROM.

Kookana R.S., Correll R.L., Miller R.B., 2005. Pesticide Impact Rating Index – A Pesticide Risk Indicator for Water Quality. Wat. Air Soil Poll. 5(1), 45–65.

MAFFJ (Ministry of Agriculture, Forestry and Fisheries, Government of Japan). Crop Statistics, 2011; http://www.maff.go.jp/j/tokei/kouhyou/sakumotu/index.html. [accessed on 16 June 2012, in Japanese].

Matsui Y., Itoshiro S., Buma M., Hosogoe K., Yuasa A., Shinoda S., Matsushita T., Inoue T., 2002. Predicting pesticide concentrations in river water by hydrologically calibrated basin-scale runoff model. Wat. Sci. Tech. 45(9), 141–148.

Matsui Y., Narita K., Inoue T., Matsushita T., 2006. Investigating rice-farming pesticide concentrations in river water using a basin-scale runoff model with uncertain inputs. Trans ASABE. 49(6), 1723–1735.

Matsui Y., Narita K., Inoue T., Matsushita T., 2007. Using precise data set on farming and pesticide properties to verify a diffuse pollution hydrological model for predicting pesticide concentration. Wat. Sci. Tech. 56(1), 71–80.

Matsui Y., 2011. The FY2010 Report of Health and Labour Sciences Research Grant (Research on Health Security Control): Multidisciplinary research on risk assessment and control for drinking-water quality. Ministry of Health, Labour and Welfare, Government of Japan. (in Japanese)

MHLWJ (Ministry of Health, Labor and Welfare, Government of Japan). Revision of drinking water quality standard. The 4th meeting of Health Sciences Council, document 3-III, 2003a; http://www.nilim.go.jp/lab/bcg/siryou/tnn/tnn0264pdf/ks0264011.pdf. [accessed on 12 July 2012].

MHLWJ (Ministry of Health, Labor and Welfare, Government of Japan). Analytical method for the guideline values in the drinking water quality standard, 2003b; http://wwwhourei.mhlw.go.jp/hourei/doc/tsuchi/151014-h.pdf. [accessed on 16 June 2012, in Japanese].

MLITJ (Ministry of Land, Infrastructure, Transport and Tourism, Government of Japan). Outline of water resources in Japan (water resources white paper), 2011; http://www.mlit.go.jp/common/000160795.pdf. [accessed on16 June. 2012, in Japanese].

MOEJ (Ministry of the Environment, Government of Japan). Provisional guidance relating prevention of water contamination with pesticides used in golf courses, 2010; http://www.env.go.jp/water/dojo/noyaku/law_data/f402kansuido0077_kaisei.pdf. [accessed on 16 June 2012, in Japanese].

MOEJ (Ministry of the Environment, Government of Japan). Standards to Withhold Agricultural Chemicals Registration, 2011; http://www.env.go.jp/water/sui-kaitei/kijun.html. [accessed on 16 June 2012, in Japanese].

NIHS (Japan National Institute of Health Sciences). The databases for ADI and relevant information on pesticides, 2011; http://www.nihs.go.jp/hse/food-info/pest_res/index.html. [accessed on 27 Dec. 2011, in Japanese].

Papa E., Castiglioni S., Gramatica P., Nikolayenko V., Kayumov O., Calamari D., 2004. Screening the leaching tendency of pesticides applied in the Amu Darya Basin (Uzbekistan). Wat. Res. 38(16), 3485–3494.

Peterson R.K.D., 2006. Comparing ecological risks of pesticides: the utility of a Risk Quotient ranking approach across refinements of exposure. Pest Manag. Sci. 62(1), 46–56.

Reffstrup T.K., Larsen J.C., Meyer O., 2010. Risk assessment of mixtures of pesticides. Current approaches and future strategies. Regul. Toxicol. Pharmacol. 56(2), 174–192.

Reus J., Leendertse P., 2000. The environmental yardstick for pesticides: a practical indicator used in the Netherlands. Crop Prot. 19(8), 637–641.

Reus J., Leendertse P., Bockstaller C., Fomsgaard I., Gutsche V., Lewis K., Nilsson C., Pussemier L., Trevisan M., van der Werf H., Alfarroba F., Blümel S., Isart J., McGrath D., Seppälä T., 2002. Comparison and evaluation of eight pesticide environmental risk indicators developed in Europe and recommendations for future use. Agr. Ecosyst. Environ. 90(2), 177–187.

Sugita T., Sasaki S., Tanaka K., Toda M., Uneyama C., Yamamoto M., Morikawa K., 2006. Development of the databases for ADI and relevant information on food additives, pesticides and veterinary drugs. Bulletin of National Institute of Health Sciences. 124, pp.69–73 (in Japanese).

Tani K., Matsui Y., Narita K., Ohno K., Matsushita T., 2010. Sensitivity analysis using a diffuse pollution hydrologic model to assess factors affecting pesticide concentrations in river water. Wat. Sci. Tech. 62(11), 2579–2589.

Tani K., Matsui Y., Iwao K., Kamata M., Matsushita T., 2012. Selecting analytical target pesticides in monitoring: sensitivity analysis and scoring. Wat. Res. 46(3), 741–749.

Tomlin C.D.S., 2006. The e-Pesticide Manual, Version 4.0. The British Crop Production Council, Surrey, UK.

Trevisan M., Guardo A.D., Balderacchi M., 2009. An environmental indicator to drive sustainable pest management practices. Environ. Modelling & Software. 24(8), 994–1002.

USEPA. National Primary Drinking Water Regulations, 2009; http://water.epa.gov/drink/contaminants/index.cfm. [accessed on 23 March 2012].

USEPA. Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates, 2011; www.epa.gov/opp00001/pestsales/07pestsales/market_estimates2007.pdf. [accessed on 3 June 2012].

Verro R., Finizio A., Otto S., Vighi M., 2009a. Predicting pesticide environmental risk in intensive agricultural areas. I: screening level risk assessment of individual chemicals in surface waters. Environ. Sci. Technol. 43(2), 522–529.

Verro R., Finizio A., Otto S., Vighi M., 2009b. Predicting pesticide environmental risk in intensive agricultural areas. II: screening level risk assessment of complex mixtures in surface waters. Environ. Sci. Technol. 43(2), 530–537.

World Health Organization, 2011. Guidelines for Drinking-Water Quality, 4th ed. Geneva, Switzerland, pp. 541.

World Resources Institute. World pesticide use, 1998. http://www.wri.org/publication/content/8660. [accessed on 3 June 2012].

Yang Y., Wang L., 2010. A review of modelling tools for implementation of the EU Water Framework Directive in handling diffuse water pollution. Wat. Resour. Manag. 24(9), 1819–1843.

Table 1. Indicators used for pesticide selection

Indicator	Definition	Unit
A1	(Quantity of sales)/(national land area)	(ton year^{-1}) km^{-2}
A2	[(Quantity of sales)/GV$_i$]/(national land area)	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
A3	(Quantity of sales for upland field)/(national land area)	(ton year^{-1}) km^{-2}
A4	[(Quantity of sales for upland field)/GV$_i$]/(national land area)	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
A5	(Quantity of sales for rice-farming)/(national land area)	(ton year^{-1}) km^{-2}
A6	[(Quantity of sales for rice-farming)/GV$_i$]/(national land area)	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
A7	(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})}$/(national land area)	(ton year^{-1}) km^{-2}
A8	[(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})/}GV_i$]/(national land area)	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
B1	Max [(Quantity of sales)/(regional land area)]$_i$	(ton year^{-1}) km^{-2}
B2	Max {[(Quantity of sales)/GV$_i$/](regional land area)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
B3	Max [(Quantity of sales for upland field)/(regional land area)]$_i$	(ton year^{-1}) km^{-2}
B4	Max {[(Quantity of sales for upland field)/GV$_i$]/(regional land area)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
B5	Max [(Quantity of sales for rice-farming)/(regional land area)]$_i$	(ton year^{-1}) km^{-2}
B6	Max {[(Quantity of sales for rice-farming)/GV$_i$]/(regional land area)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
B7	Max [(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})}$/(regional land area)]$_i$	(ton year^{-1}) km^{-2}
B8	Max {[(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})}$/GV$_i$]/(regional land area)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ km^{-2}
C1	Max [(Quantity of sales)/(regional precipitation)]$_i$	(ton year^{-1}) (km^3 year^{-1})$^{-1}$
C2	Max {[(Quantity of sales)/GV$_i$]/(regional precipitation)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ (km^3 year^{-1})$^{-1}$
C3	Max [(Quantity of sales for upland field)/(regional precipitation)]$_i$	(ton year^{-1}) (km^3 year^{-1})$^{-1}$
C4	Max {[(Quantity of sales for upland field)/GV$_i$]/(regional precipitation)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ (km^3 year^{-1})$^{-1}$
C5	Max [(Quantity of sales for rice-farming)/(regional precipitation)]$_i$	(ton year^{-1}) (km^3 year^{-1})$^{-1}$
C6	Max {[(Quantity of sales for rice-farming)/GV$_i$]/(regional precipitation)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ (km^3 year^{-1})$^{-1}$
C7	Max [(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})}$/(regional precipitation)]$_i$	(ton year^{-1}) (km^3 year^{-1})$^{-1}$
C8	Max {[(Quantity of sales for rice-farming) × 10$^{(\text{Score Y + Score Z - 6})}$/GV$_i$]/(regional precipitation)}$_i$	(ton year^{-1}) (μg L^{-1})$^{-1}$ (km^3 year^{-1})$^{-1}$

Table 2. Pesticides included in this study

Designation	Category of the current JDWQG	No. in primary group	No. in secondary group	No. in tertiary group	No. of others	Total no.	
Detected pesticides	Detected in the 4 years (2007–2010)	78	1	2	0	81	105 (used as index pesticides)
Undetected pesticides	Measured but not detected in the 4 years (2007–2010)	24	0	0	0	24	
Unmeasured pesticides	No data or insufficient data	0	25	75	31	131	
Total no.		102	26	77	31	236	

Table 3. Number of times maximum (including ties) detection rate was recorded

A series	A5	A6	A7	A8
A1	0	7	0	16
A2	24	42	23	48
A3	0	8	0	17
A4	4	45	7	53

B series	B5	B6	B7	B8
B1	0	12	0	3
B2	39	67	36	67
B3	0	13	0	4
B4	19	76	20	<u>78</u>

C series	C5	C6	C7	C8
C1	0	12	0	9
C2	40	63	34	74
C3	0	13	0	10
C4	20	76	20	<u>82</u>

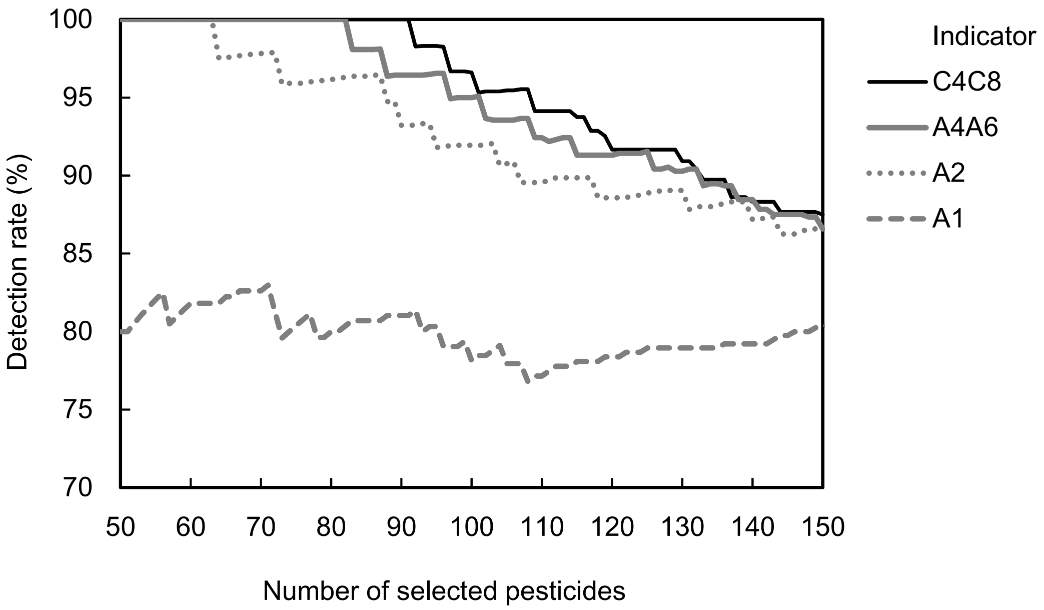

Figure 1. Variation of detection rate with number of selected pesticides.

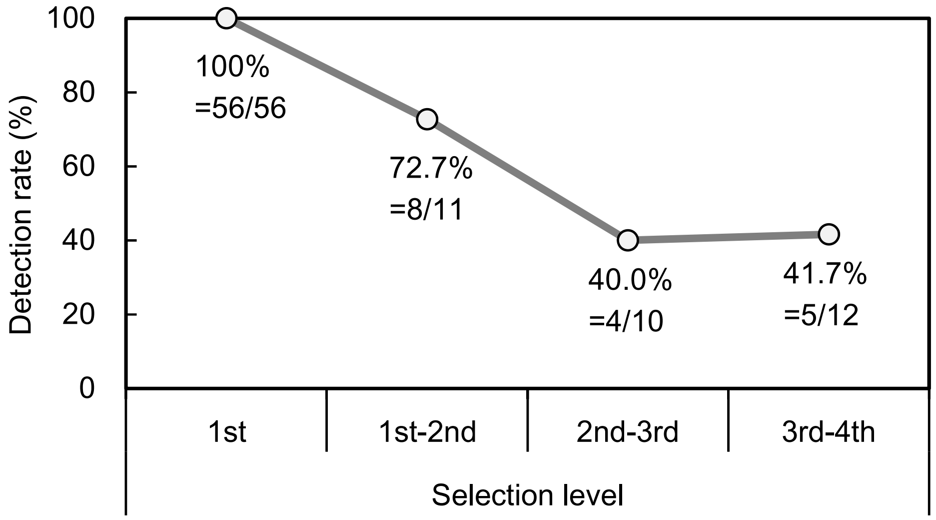

Figure 2. Variation of detection rate with selection level.

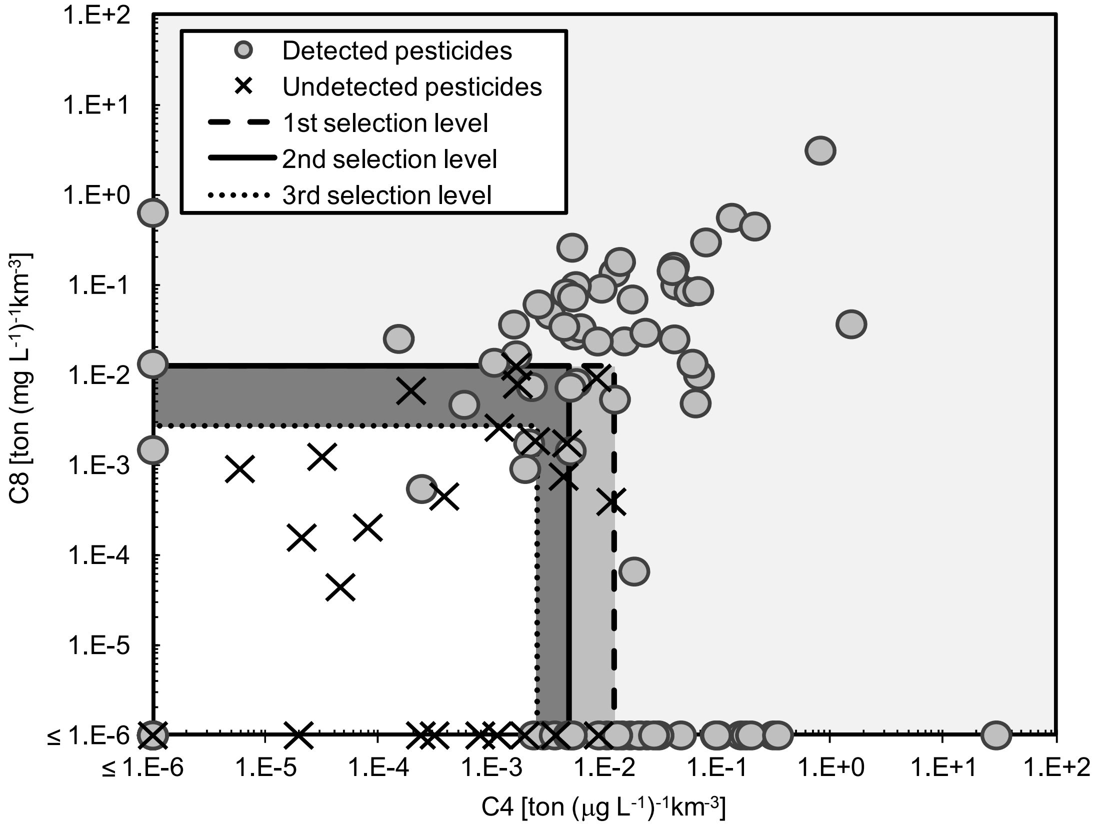

Figure 3. Scatter plot of C8 versus C4 for the index pesticides.

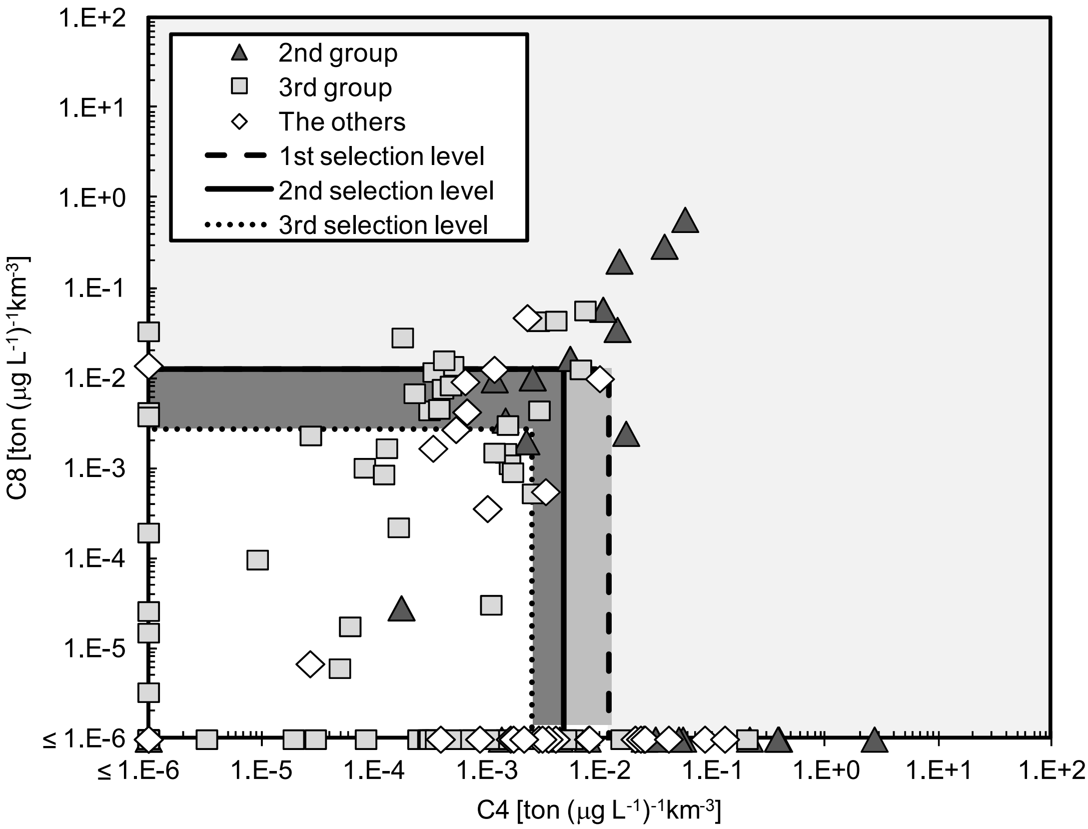

Figure 4. Scatter plot of C8 versus C4 for the unmeasured pesticides.

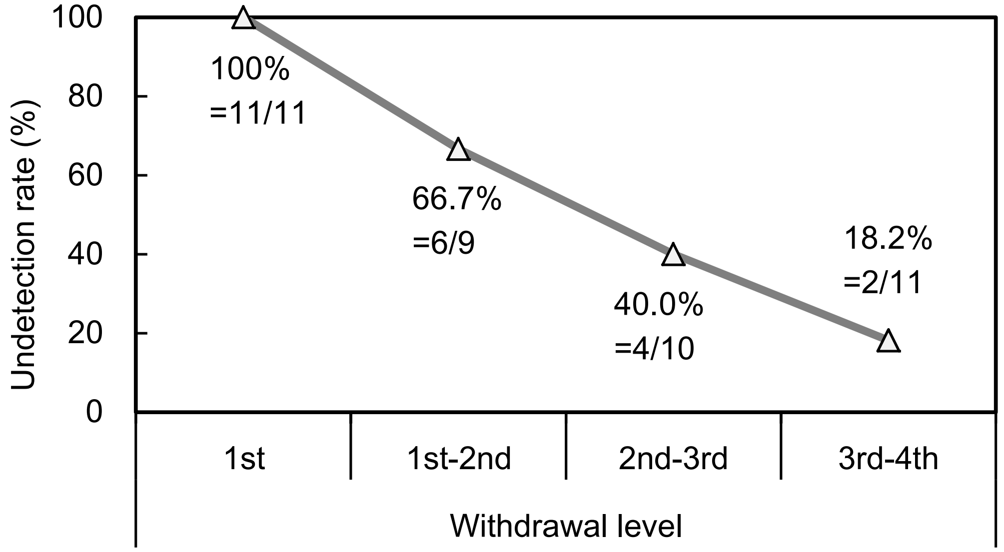

Figure 5. Variation of undetection rate with withdrawal level.

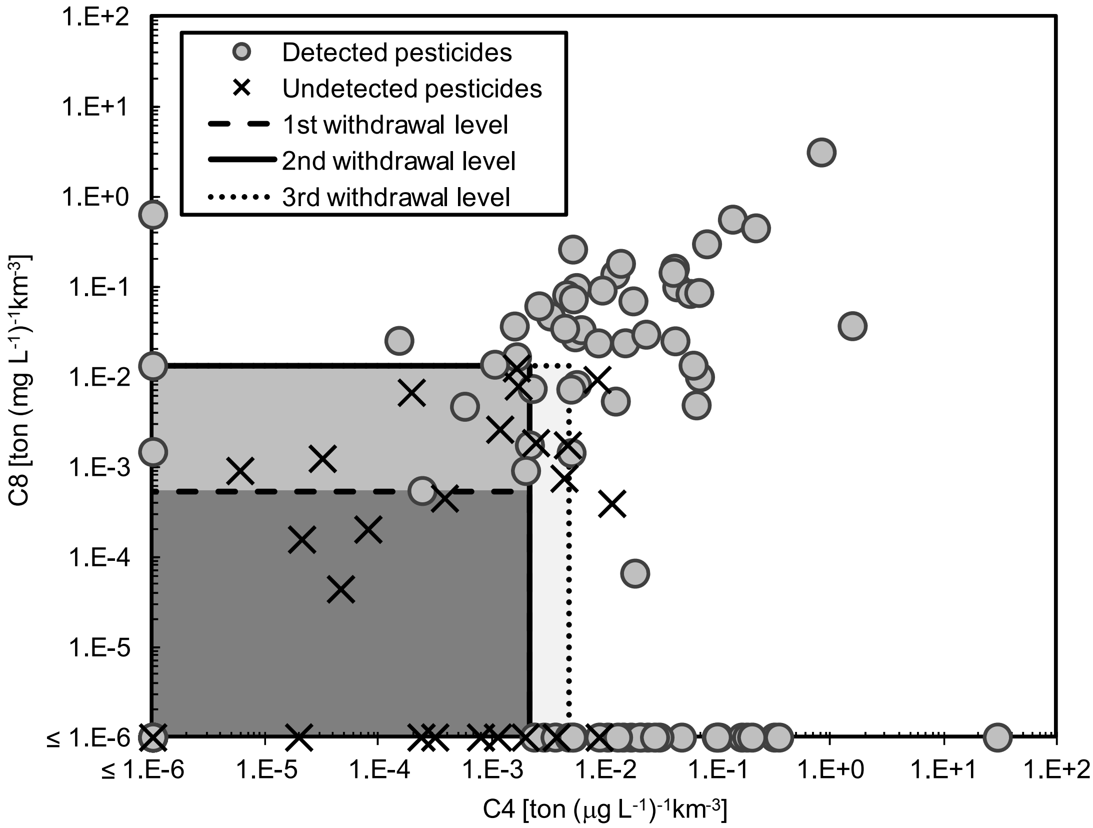

Figure 6. Scatter plot of C8 versus C4 for the pesticides in the primary group.

Supporting Material

Selecting pesticides for inclusion in drinking water quality guidelines on the basis of detection probability and ranking

Kentaro Narita[a], Yoshihiko Matsui[b,*], Kensuke Iwao[a], Motoyuki Kamata[c], Taku Matsushita[b], and Nobutaka Shirasaki[b]

[a] Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[b] Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[c] College of Engineering, Kanto Gakuin University, Mutsuurahigashi 1-50-1, Kanazawa-ku, Yokohama 236-8501, Japan
* Corresponding author: Phone & Fax: +81-11-706-7280, Email: matsui@eng.hokudai.ac.jp

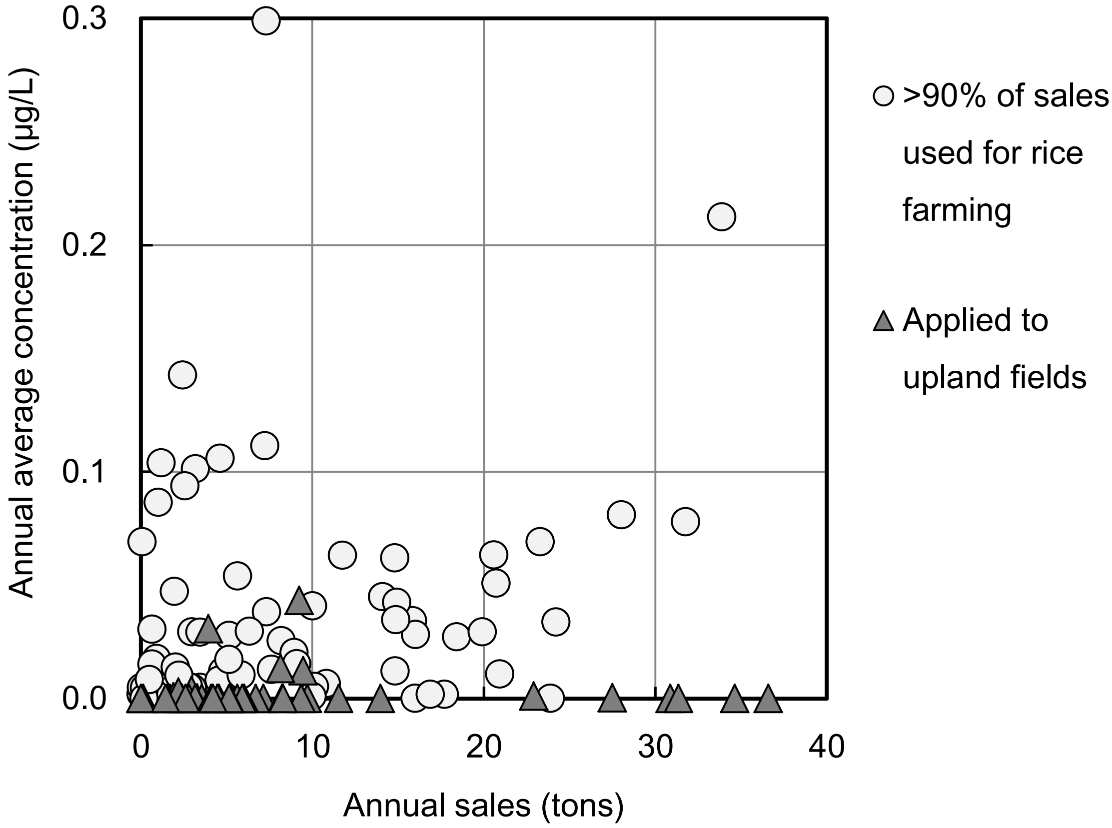

Figure 1S. Annual average pesticide concentration versus annual sales in the Chikugo River basin, 2004–2007.

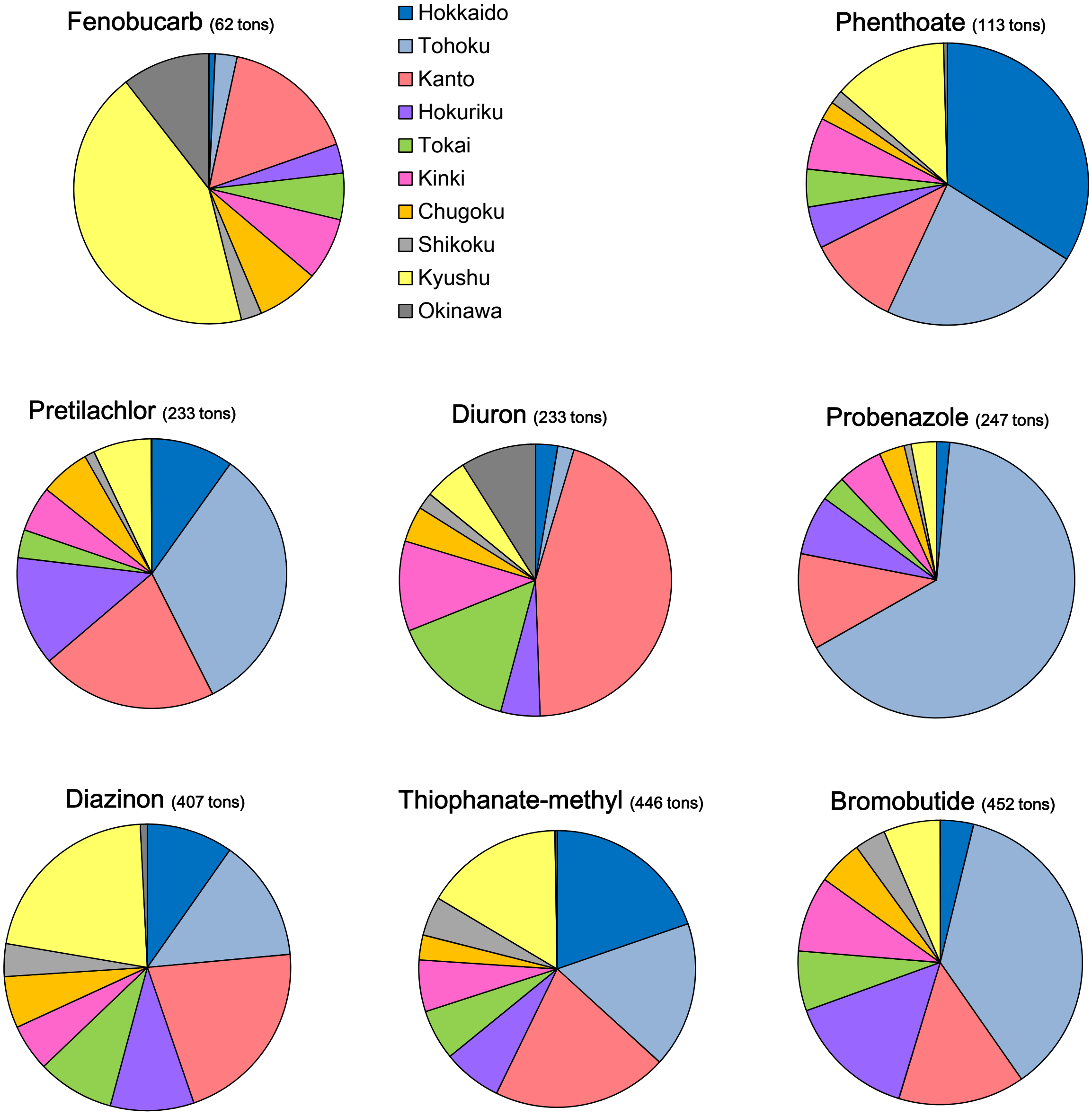

Figure 2S. Pesticide sales by region in 2008.

Table 1S. Score tables for soil adsorption, soil degradation, and water degradation of fungicides and herbicides. K_{OC} is the organic-carbon-based soil adsorption coefficient (mL/g), and HLS is the half-life (day) with respect to degradation in soil. HLW is the half-life (day) with respect to degradation in water (Tani et al. 2012).

A. Values of Score *Y* for fungicides

log HLS \ log K_{OC}	6.0 ≥ & > 5.5	5.5 ≥ & > 5.0	5.0 ≥ & >4.5	4.5 ≥ & >4.0	4.0 ≥ & >3.5	3.5 ≥ & >3.0	3.0 ≥ & >2.5	2.5 ≥ & >2.0	2.0 ≥ & >1.5	1.5 ≥ & >1.0	1.0 ≥ & >0.5	0.5 ≥ & >0.0
3.0 ≥ & > 2.5	0.4	1.1	1.5	1.6	1.7	1.8	1.8	1.8	1.9	2.1	2.2	2.5
2.5 ≥ & > 2.0	0.4	1.1	1.5	1.6	1.7	1.7	1.8	1.8	1.9	2.0	2.2	2.5
2.0 ≥ & > 1.5	0.4	1.1	1.5	1.6	1.7	1.7	1.7	1.8	1.8	2.0	2.1	2.3
1.5 ≥ & > 1.0	0.5	1.1	1.5	1.6	1.6	1.6	1.6	1.7	1.8	1.9	2.0	2.1
1.0 ≥ & > 0.5	0.4	1.1	1.5	1.6	1.6	1.5	1.4	1.5	1.6	1.7	1.8	1.9
0.5 ≥ & > 0.0	0.4	1.1	1.5	1.6	1.6	1.4	1.3	1.3	1.4	1.5	1.6	1.7
0.0 ≥ & > –0.5	0.4	1.1	1.5	1.6	1.5	1.3	1.2	1.2	1.3	1.4	1.4	1.5
–0.5 ≥ & > –1.0	0.3	1.0	1.5	1.6	1.5	1.3	1.2	1.1	1.2	1.2	1.3	1.3
–1.0 ≥ & > –1.5	0.3	1.0	1.5	1.6	1.5	1.3	1.1	1.1	1.1	1.1	1.1	1.2
–1.5 ≥ & > –2.0	0.4	1.1	1.5	1.6	1.5	1.3	1.1	1.1	1.0	1.1	1.1	1.1

B. Values of Score *Y* for herbicides

log HLS \ log K_{OC}	6.0 ≥ & > 5.5	5.5 ≥ & > 5.0	5.0 ≥ & >4.5	4.5 ≥ & >4.0	4.0 ≥ & >3.5	3.5 ≥ & >3.0	3.0 ≥ & >2.5	2.5 ≥ & >2.0	2.0 ≥ & >1.5	1.5 ≥ & >1.0	1.0 ≥ & >0.5	0.5 ≥ & >0.0
3.0 ≥ & > 2.5	0.4	1.1	1.5	1.7	1.7	1.8	1.8	1.8	1.9	2.0	2.1	2.3
2.5 ≥ & > 2.0	0.3	1.1	1.5	1.6	1.7	1.7	1.8	1.8	1.9	2.0	2.1	2.2
2.0 ≥ & > 1.5	0.3	1.1	1.5	1.6	1.7	1.7	1.7	1.7	1.8	1.9	2.0	2.1
1.5 ≥ & > 1.0	0.3	1.0	1.5	1.6	1.6	1.6	1.6	1.7	1.7	1.8	1.9	2.0
1.0 ≥ & > 0.5	0.3	1.0	1.5	1.6	1.6	1.5	1.5	1.5	1.6	1.7	1.7	1.8
0.5 ≥ & > 0.0	0.3	1.0	1.5	1.6	1.5	1.4	1.3	1.4	1.5	1.5	1.6	1.7
0.0 ≥ & > –0.5	0.3	1.0	1.5	1.5	1.5	1.3	1.3	1.3	1.3	1.4	1.5	1.5
–0.5 ≥ & > –1.0	0.3	1.0	1.5	1.5	1.5	1.3	1.2	1.2	1.3	1.3	1.3	1.4
–1.0 ≥ & > –1.5	0.3	1.1	1.5	1.5	1.5	1.3	1.2	1.2	1.2	1.2	1.3	1.3
–1.5 ≥ & > –2.0	0.3	1.0	1.5	1.6	1.5	1.3	1.2	1.2	1.2	1.2	1.2	1.2

C. Values of Score *Z* for fungicides and herbicides

Log HLW of fungicides	Log HLW of herbicide	Score *Z*
> 1.59	> 1.38	3.0
1.59 ≥ & > 0.87	1.38 ≥ & > 0.86	2.9
0.87 ≥ & > 0.55	0.86 ≥ & > 0.62	2.8
0.55 ≥ & > 0.32	0.62 ≥ & > 0.43	2.7
0.32 ≥ & > 0.14	0.43 ≥ & > 0.29	2.6
0.14 ≥ & > –0.02	0.29 ≥ & > 0.16	2.5
–0.02 ≥ & > –0.15	0.16 ≥ & > 0.05	2.4
–0.15 ≥ & > –0.27	0.05 ≥ & > –0.05	2.3
–0.27 ≥ & > –0.38	–0.05 ≥ & > –0.14	2.2
–0.38 ≥ & > –0.48	–0.14 ≥ & > –0.23	2.1
–0.48 ≥ & > –0.57	–0.23 ≥ & > –0.31	2.0
–0.57 ≥ & > –0.66	–0.31 ≥ & > –0.38	1.9
–0.66 ≥ & > –0.74	–0.38 ≥ & > –0.45	1.8
–0.74 ≥ & > –0.82	–0.45 ≥ & > –0.52	1.7
–0.82 ≥ & > –0.89	–0.52 ≥ & > –0.59	1.6
–0.89 ≥ & > –0.97	–0.59 ≥ & > –0.65	1.5

Log HLW of fungicides	Log HLW of herbicide	Score *Z*
–0.97 ≥ & > –1.03	–0.65 ≥ & > –0.71	1.4
–1.03 ≥ & > –1.10	–0.71 ≥ & > –0.77	1.3
–1.10 ≥ & > –1.16	–0.77 ≥ & > –0.83	1.2
–1.16 ≥ & > –1.22	–0.83 ≥ & > –0.88	1.1
–1.22 ≥ & > –1.28	–0.88 ≥ & > –0.94	1.0
–1.28 ≥ & > –1.34	–0.94 ≥ & > –0.99	0.9
–1.34 ≥ & > –1.39	–0.99 ≥ & > –1.04	0.8
–1.39 ≥ & > –1.44	–1.04 ≥ & > –1.09	0.7
–1.44 ≥ & > –1.49	–1.09 ≥ & > –1.14	0.6
–1.49 ≥ & > –1.55	–1.14 ≥ & > –1.19	0.5
–1.55 ≥ & > –1.59	–1.19 ≥ & > –1.24	0.4
–1.59 ≥ & > –1.64	–1.24 ≥ & > –1.28	0.3
–1.64 ≥ & > –1.69	–1.28 ≥ & > –1.33	0.2
–1.69 ≥ & > –1.74	–1.33 ≥ & > –1.38	0.1
–1.74 ≥	–1.38 ≥	0.0

Tani, K., Matsui, Y., Iwao, K., Kamata, M. and Matsushita, T. (2012) Selecting analytical target pesticides in monitoring: Sensitivity analysis and scoring. Water Research 46(3), 741-749.