Selecting analytical target pesticides in monitoring: sensitivity analysis and scoring

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Abstract

Measuring river water concentrations of all pesticides applied in a catchment area is a daunting task. In this study, we conducted sensitivity analyses using a diffuse pollution hydrologic model to quantitatively evaluate the influence of pesticide properties (e.g., log K_{OC}, degradability [half-life]) on concentrations of rice-farming pesticides in river water. Using the results of the analyses, score tables were systematically designed for the pesticide properties such that the sum of the scores for a particular pesticide, designated as the contamination index, was proportional to the expected/predicted concentration of that pesticide in river water. The contamination indexes for pesticides applied in three river basins were calculated and compared with the corresponding observed pesticide concentrations. Correlations between contamination indexes and observed concentrations were fairly good. Pesticides were ranked according to the quotients obtained by dividing the pesticide concentrations predicted from the contamination indexes by the corresponding drinking-water quality guideline values, and pesticide candidates to be monitored were successfully selected on the basis of a threshold quotient.

Keywords: pesticide runoff, index, ranking, risk assessment

1. Introduction

Pesticides have markedly enhanced agricultural productivity and crop yields (e.g. Bolognesi, 2003). However, pesticide releases from agricultural fields and the resulting contamination of surface water threaten human health, as well as the local ecosystem in many regions, because surface water is a primary source of drinking water (Gilliom et al., 1999; Hildebrandt et al., 2008; Vryzas et al., 2009; Wittmer et al., 2010). Governments regulate pesticide concentrations in drinking water. For example, the European Union Drinking Water Directive specifies a maximum acceptable concentration of 0.1 μg/L for individual pesticides and a maximum total acceptable concentration of 0.5 μg/L for all pesticides and their metabolites, degradation products, and reaction products (Drinking Water Directive, 1998). The analytical target pesticides are not defined by the Directive, but those pesticides which are likely to be present in a given supply need be monitored by the monitoring authority. In order to select the analytical target pesticides, therefore, a risk assessment is required which takes into account the pesticide usage and the local circumstances, but this process is not defined in the Directive. A hundred and two pesticides are listed in the Japanese drinking water quality guideline (JDWQG) on the basis of the quantities sold and the availability of quantification methods, but the monitoring authority is required to further select the analytical target pesticides depending on its local circumstances [MHLWJ (Ministry of Health, Labor and Welfare of Japan), 2003a]. Chemical scoring and ranking methods are developed as a screening tool for risk assessment of chemicals (Swanson et al., 1997; Finizio et al., 2001; Gramatica and Guardo, 2002; Juraske et al., 2007). A score table that ranks pesticides has been proposed for the selection of analytical target pesticides for JDWQG (Kamata et al., 2007). In this score table (hereafter referred as the old score table), a pesticide is scored between 1 and 5 for each of the following properties: quantity sold, octanol–water partition coefficient (log K_{OW}), degradability, and acceptable daily intake (ADI), as shown in Table 1S in the supplementary information. Ideally, the sum of the first three scores (Scores A–C in Table 1S, which are related to pesticide runoff from rice paddies), should be well correlated with the concentrations of a particular pesticide in river water, but the score table has not been validated. Generally, the results of chemical ranking approach have seldom been validated against measured concentrations, while the approach is applied for screening pesticides in surface water (Altenburger et al., 1993; Papa et al., 2004). In addition, the score table does not include any criteria for selecting which pesticides should be monitored. For example, even if a list of pesticides was sorted and prioritized by means of the score table, the table does not specify an absolute threshold value above which a pesticide should be selected for monitoring. Consequently, the score table is hardly accepted as a screening tool by monitoring authorities.

In the current study our aim was to develop and test new score tables for (1) selecting pesticides with the potential to contaminate river water and (2) facilitating the development of a program for monitoring water quality. Rice-farming pesticides were investigated in this study. Rice-farming pesticides enter river water at high rates but other pesticides used in upland fields do not because rice cropping on paddy fields requires a large amount of fresh natural water and rice-paddy water is discharged directly by artificial drainage into rivers or percolates into the ground (Matsui et al., 2002). Therefore, pesticides applied to rice paddy fields have a greater potential to contaminate river water, some of which is the source of drinking water.

2. Materials and Methods

2.1. Diffuse pollution hydrologic model

Although many models and their applications have been reported, few are designed to predict runoff of rice-farming pesticides from rice-paddy fields (Inao and Kitamura, 1999; Miao et al., 2003; Nakano et al., 2004, Inao et al., 2008). Moreover, very few studies have attempted to develop a model applicable to basin-scale catchments and able to predict rice-farming pesticide concentrations in river water (Matsui et al., 2002). The diffuse pollution hydrologic model applied in this study is described in detail elsewhere (Matsui et al., 2006a, b). In the model, briefly, river basins were divided into a grid of 1-km^2 cells and then each grid cell was subdivided into 12 compartments: a rice-paddy compartment et al. (Matsui et al., 2006a, Tani et al., 2010). It is assumed that applied pesticides reach the paddy fields (the loss due to the drift of pesticide, the effect of application mode, the effect of spray formulation, and the effect of adjuvants were not accounted). A set of differential mass-balance equations was defined to describe the dynamics of the pesticide and water in each compartment. The equations are solved as a system of ordinary differential equations by Gear's stiff method (backward differentiation formulas) from the IMSL MATH/LIBRARY (Visual Fortran Versions 6.6, Compaq). The Chikugo River (33.18°N, 130.28°E, length: 143 km, basin area: 2860 km^2) and Sagami River basins (35.25°N, 139.22°E, length 109 km, basin area 1680 km^2) were selected as the model river basins.

2.2. Pesticides

Pesticide concentrations observed in 2004–2008 in the Mabechi River (40.47°N, 141.42°E, length 142 km, basin area 2050 km^2) and in 2004–2007 in the Chikugo and Sagami Rivers were used for evaluating the score tables. Pesticide concentration data were obtained from the local water supply authorities (see Acknowledgements), who routinely measured pesticide concentrations according to the JDWQG standard methods (MHLWJ, 2003b). Pesticide property data were obtained by PCKOCWIN, KOWWIN and BIOWIN program in the EPI Suite (Aronson et al., 2006), Tomlin (2006), Kamrin (1997), and Ministry of the Environment of Japan (2010). The quantities of pesticides sold in the basins were estimated from pesticide sale data books (Japan Plant Protection Association, 2005–2009) after allocation of the pesticide sales to the river basins on the basis of land-use data (Matsui et al., 2006a; Kamata et al., 2008).

2.3 Sensitivity analyses for constructing the new score tables

2.3.1. Score for quantity of pesticide sold

Pesticides applied in fields reach the river after having been diluted. Given a pesticide, therefore, the basic potential for the pesticide concentration in river water should be proportional to the quantity of pesticide sold divided by the river flow rate. In the current study, the score for the quantity of pesticide sold, defined as Score X, is given by

$$\text{Score } X = \log\left(\frac{M}{Q}\right) \tag{1}$$

where M is the quantity of pesticide sold (mg/year), Q is the annual river flow rate (km^3/year).

2.3.2. Score for pesticide degradation and adsorption

Of the pesticide properties that affect runoff rates and river water concentrations (e.g., Capri and Karpouzas, 2007) adsorption in soil is one of the most importants (Kreuger and Törnqvist, 1998). Sensitivity analyses (Tani et al., 2010) indicate that adsorption and degradation in soil are the most influential properties. Water solubility somewhat affects pesticide runoff, but highly soluble compounds tend to have low soil adsorption coefficients and vice versa; that is, soil adsorption coefficient and water solubility are related. The following regression equation for the relationship between K_{OC}, the organic-carbon-based soil adsorption coefficient (mL/g), and water solubility (S, mg/L) has been proposed to be applicable for most pesticides (Lyman et al., 1990):

$$0.55\log S = -\log K_{OC} + 3.64 \quad (2)$$

Therefore, we considered two parameters [K_{OC} for adsorption and half-life in soil (HLS) for degradation] in our sensitivity analyses, and water solubility was treated as a sub-parameter represented by the soil adsorption coefficient according to equation (2). Input values of HLS, which is an index of soil degradation, were varied between 10^{-2} and 10^{3} day, and K_{OC}, an index of organic-carbon-based soil adsorption in soil, was varied between 1 and 10^{6} mL/g. Because the runoff rates of herbicides and fungicides differ owing to differences in application dates (Tani et al., 2010), sensitivity analyses for herbicides and fungicides were conducted separately.

Figure 1 shows a graph of the results of the fungicide sensitivity analysis for adsorption and degradation in soil of the Sagami River basin; the vertical axis is the dimensionless simulated pesticide concentration (C/M_V), where C is the average simulated concentration (μg/L) for the

4-month period starting with the date of fungicide application, and M_V is a parameter determined by the quantity of the applied fungicide (mg) divided by the total river flow volume (L) for the 4 months starting from the date of application. Another fungicide sensitivity analysis was conducted for Chikugo River basin. Because Score X is designed as such that a score increment of 1 corresponds to a 10-fold increased in pesticide concentration, scores for soil adsorption and soil degradation, defined as Score *Y* (view A in Table 1), were also designed similarly as equation (3) after the C/M_V values for the two rivers were averaged geometrically.

$$\text{Score } Y = \log\left(\frac{C}{M_V}\right) \qquad (3)$$

Because the concentration is normalized by the quantity of the applied pesticide in equation (3), Score *Y* value is not affected by the quantity of the applied fungicide but it is reflected by HLS and K_{OC} values. A score table for herbicides (view B in Table 1) was determined by means of a process similar to that used for fungicides.

With regard to degradation in water, Tani et al. (2010) reported that pesticide concentrations are influenced and decreased only when the rate constant of degradation in water was large. Similar results were obtained in the sensitivity analyses for degradation in water of the Sagami and Chikugo River basins in the current study. Using the results of the sensitivity analyses, the score tables for values of half-life in water (HLW) were determined in the same way as that of Score Y (Score Z in view C of Table 1).

3. Results and Discussion

3.1. Correlation between contamination index and pesticide concentration

Pesticide concentrations observed from 2004 to 2008 in the Mabechi River as well as from 2004 to 2007 in the Chikugo and Sagami Rivers were used for the evaluation of the score tables. Contamination index values, defined as the sum of the scores, were calculated for each of the pesticides used in the Mabechi, Chikugo, and Sagami River basins by means of the new score tables (Score X was calculated from equation (1), and Scores Y and Z were obtained from Table 1) and the old score table (Scores A–C, Table 1S in the supplementary information). Figure 1S in the supplementary information shows an example of the correlation between the contamination index values and average measured concentrations (sum of the measured concentrations divided by the number of water samples) of pesticides in the Chikugo River in 2004. Higher correlations were obtained with the new score tables than with the old score table. The coefficient of determination R^2 increased from 0.18 to 0.52 when the new score tables were applied (compare views A and B in Figure 1S). However, the concentrations for any given contamination index value were scattered in a range around the logarithm of 2. The data scattering may have been due to the uncertainty for the application dates and application methods (including drift and adjuvant) for the pesticides; the acquisition of accurate application dates and the accurate evaluation for the effects of application methods were hard (Matsui et al., 2006a) and therefore these factors were not considered in the calculation of the contamination index. It may also be due to the accuracy of Score X values. In evaluating Score X value it is assumed that the quantity of pesticide applied was equal to the amount of the sales in that year. This assumption may, however, not be very accurate because all the purchased pesticides may not necessarily be applied in the agricultural field in a year after the purchase.

Figure 2 summarizes the R^2 values for the plots of the average concentrations of pesticides against the contamination index values for the three rivers. Overall, the contamination index values calculated with the new score tables were better correlated with pesticide concentrations than the values calculated with the old score table, indicating that the new score tables are effective tools for preliminary ranking or prioritizing pesticides to be monitored.

3.2. Use of the tables to select pesticides to be monitored

3.2.1. Estimating maximum pesticide concentration with the new score tables

Figure 3 shows the relationship between the highest observed pesticide concentrations and contamination index values. Since score is defined such that a score increase of 1 corresponds to a 10-fold increase in the pesticide concentration in river water, the relationship between highest observed concentration and contamination index, which is given by a sum of scores, is described, in the ideal situation, by the following equation:

$$\log C_{\mathrm{H}} = \text{Contamination Index} - A \qquad (4)$$

where C_{H} is the highest observed pesticide concentration (μg/L) and A is a constant. The mean A value was 11.6. The A value for the one-sided 95% upper confidence limit was 10.7.

Therefore, C_U, the one-sided 95% upper confidence limit of the maximum pesticide concentration (μg/L), is predicted by the following equation:

$$\log C_{\mathrm{U}} = \text{Contamination Index} - 10.7 \qquad (5)$$

3.2.2. Use of possible maximum concentration to select pesticides to be monitored

JDWQG specifies that *DI* value should not exceed 1; *DI* is the sum of the DV_i/GV_i quotients for monitored pesticides:

$$DI = \sum_i \frac{DV_i}{GV_i} \qquad (6)$$

where DV_i is the observed concentration of pesticide *i* and GV_i is the reference concentration of pesticide *i* and is determined in JDWQG by MHLWJ (2003a) based on the acceptable daily intake of the pesticide. However, the calculation of *DI* value still has a potential problem that the value is heavily dependent on the number of monitored pesticides. In the current study, we predicted the maximum possible concentration of pesticide *i*, PV_i, in river water by using equation (5), and we then calculated PV_i/GV_i values. The PV_i/GV_i values were compared with the DV_i/GV_i values for the highest observed concentration.

Figure 4 shows the DV_i/GV_i and PV_i/GV_i quotients of pesticides applied in the Sagami River basin in 2004. Because the quantification of pesticide concentrations above 1/100 of each GV_i value is recommended in evaluating *DI* value in JDWQG (MHLWJ, 2003b), a PV_i/GV_i quotient of 0.01 can be regarded as a threshold limit in selecting pesticides to be monitored and used for *DI* value calculation. That is, if the PV_i/GV_i value of pesticide *i* is less than 0.01, nonnecessity for monitoring that pesticide is suggested. By applying this threshold limit, we selected 16 pesticides from the 34 pesticides applied in the Sagami River basin for monitoring in the year 2004, as shown in Figure 4. Among the 16 selected pesticides the seven pesticides were for which DV_i/GV_i actually exceeded 0.01 (iprobenfos, molinate, mefenacet, benthiocarb, esprocarb, simetryn, and bromobutide). However, other seven pesticides had DV_i/GV_i values of <0.01 although their PV_i/GV_i values were ≥0.01. This is understandable because PV_i is the maximum possible pesticide concentration predicted by the one-sided 95% upper confidence limit, and PV_i can be regarded as a conservative estimate. Two pesticides (diquat monohydrate and cafenstrole) were selected as pesticide candidates, but their concentrations were not actually measured.

The numbers of pesticide candidates for monitoring selected by this method are summarized in Table 2: 16–21 pesticide candidates among the 30–34 in the Mabechi River, 16–18 among the 31–34 in the Sagami River, and 22–25 among the 32–33 in the Chikugo River. The success of the selection method was evaluated by comparison with pesticide monitoring data (columns E–H in Table 2). For all the data in the table, the groups of selected pesticides for which the PV_i/GV_i values were >0.01 included all the pesticide with DV_i/GV_i values of ≥0.01. There was no pesticide with a PV_i/GV_i value of <0.01 and a DV_i/GV_i value of ≥0.01. As shown in Column H of Table 2, 26–75% of the selected pesticides with PV_i/GV_i values of ≥0.01 had DV_i/GV_i values of ≥0.01 (the success rate in selecting pesticide candidates for monitoring was 26–75%). We feel these percentages constitute successful first efforts. It is notable that the pesticides with PV_i/GV_i values of <0.01 were all (100% in Column H of Table 2) with DV_i/GV_i values of <0.01 (the success rate in removing pesticides unnecessary for monitoring was 100%).

The three rivers we evaluated in the current study are currently monitored for pesticides selected on the basis of previous experience by the local water supply authorities rather than by means of our proposed method. However, for rivers where pesticides are not monitored or have no basis for determining the necessity of monitoring, our proposed method could save time and expense in identifying monitoring needs. A considerable number of water supply authorities in Japan also monitor all or most of the 102 pesticides that are listed in JDWQG without conducting any risk assessment to properly select the mentoring pesticides. Under such circumstances, our proposed new score tables and method could assist in the selection of pesticides to be monitored and the determination of which pesticides require no monitoring. No such decision could be reached by means of any other ranking tool, such as the old score table, which prioritizes pesticides but does not have an absolute criterion for selection. Pesticide compounds with a similar property can be analyzed with the same multi-residue method. The monitoring costs thus do not simply depend on the mere number of compounds to analyze, but on the number of analytical methods to run and the individual costs of these methods. However, the analysis requires the standard solution and the accuracy control of analysis for each compound, and therefore the proper selection of monitoring pesticides has a strong merit.

4. Conclusions

1) New, improved score tables designed for selecting pesticides on the basis of their properties were prepared by restructuring and refinement based on sensitivity analyses conducted with a pesticide diffuse pollution model. The correlations between observed pesticide concentrations and contamination index values calculated with the new score tables

were greatly improved over correlations obtained with the old score table.

2) Possible maximum concentrations of pesticides (PV_i) were estimated from the one-sided 95% upper confidence limit for the regression line for the contamination index. The number of pesticide candidates for monitoring selected on the basis of the threshold PV_i/GV_i quotient of 0.01 was roughly two-thirds of the number of pesticides applied. All the pesticides that actually detected in the river waters with DV_i/GV_i quotients larger than 0.01 were included in the list of selected pesticide candidates. The new score tables give contamination index values and then PV_i/GV_i values, which can be expected to be useful criteria for determining whether or not a pesticide should be monitored on the basis of a threshold value of 0.01.

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Appendix. Supplementary Information

Tables 1S and Figures 1S are available in the online version at ######.

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Figure and table captions

Figure 1. Plot of results of sensitivity analysis for adsorption and degradation in soil for fungicides in the Sagami River basin. Dimensionless pesticide concentrations (C/M_V), where C is the average simulated concentration for the 4-month period starting from the date of pesticide application (μg/L), and M_V is the fictive concentration determined by assuming that the quantity of applied pesticide was dissolved uniformly in the total river flow volume for the 4 months starting from the date of application, are plotted against K_{OC} and HLS (half-life with regard to degradation in soil).

Figure 2. Comparison of the coefficients of determination (R^2) for plots of average pesticide concentrations versus contamination index values calculated with the new score tables and the old score table.

Figure 3. Relationship between the highest observed concentrations of pesticides and the contamination index values calculated with the new score tables. The solid line is a plot of the equation log C_H = Contamination index - 11.4. The dashed lines indicate one-sided 95% upper and lower confidence limits.

Figure 4. PV_i/GV_i (open bars) and DV_i/GV_i (solid bars) values for pesticides in the Sagami River basin in 2004. [a)] The concentrations were not measured (PV_i is the possible maximum predicted concentrations of pesticide *i*, GV_i is the reference concentration of pesticide *i* in JDWQG, and DVi is the observed concentration of pesticide *i*).

Table 1. New 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.

Table 2. Performance of new score tables for selecting pesticides (PV_i is the possible maximum predicted concentrations of pesticide *i*, GV_i is the reference concentration of pesticide *i* in JDWQG, and DV_i is the observed concentration of pesticide *i*).

Table 1. New 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.

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

Table 2. Performance of new score tables for selected pesticides (PV_i is the possible maximum predicted concentrations of pesticide i, GV_i is the reference concentration of pesticide i in JDWQG, and DV_i is the observed concentration of pesticide i).

Column A	Column B Year	Column C	Column D Applied in rice paddy	Column E With measured concentration	Column F With DVi/GVi < 0.01	Column G With DVi/GVi ≥ 0.01	Column H Success ratio (%)
Mabechi River	2004	Number of pesticides	34	18	13	5	
		with $PV_i/GV_i \geq 0.01$	21	14	9	5	36 [a)]
		with $PV_i/GV_i < 0.01$	13	4	4	0	100 [b)]
	2005	Number of pesticides	34	22	17	5	
		with $PV_i/GV_i \geq 0.01$	20	16	11	5	31 [a)]
		with $PV_i/GV_i < 0.01$	14	6	6	0	100 [b)]
	2006	Number of pesticides	33	18	12	6	
		with $PV_i/GV_i \geq 0.01$	19	14	8	6	43 [a)]
		with $PV_i/GV_i < 0.01$	14	4	4	0	100 [b)]
	2007	Number of pesticides	30	18	12	6	
		with $PV_i/GV_i \geq 0.01$	18	13	7	6	46 [a)]
		with $PV_i/GV_i < 0.01$	12	5	5	0	100 [b)]
	2008	Number of pesticides	30	18	9	9	
		with $PV_i/GV_i \geq 0.01$	16	12	3	9	75 [a)]
		with $PV_i/GV_i < 0.01$	14	6	6	0	100 [b)]
Sagami River	2004	Number of pesticides	34	23	16	7	
		with $PV_i/GV_i \geq 0.01$	16	14	7	7	50 [a)]
		with $PV_i/GV_i < 0.01$	18	9	9	0	100 [b)]
	2005	Number of pesticides	31	26	20	6	
		with $PV_i/GV_i \geq 0.01$	17	15	9	6	40 [a)]
		with $PV_i/GV_i < 0.01$	14	11	11	0	100 [b)]
	2006	Number of pesticides	32	30	23	7	
		with $PV_i/GV_i \geq 0.01$	18	17	10	7	41 [a)]
		with $PV_i/GV_i < 0.01$	14	13	13	0	100 [b)]
	2007	Number of pesticides	31	28	22	6	
		with $PV_i/GV_i \geq 0.01$	17	16	10	6	38 [a)]
		with $PV_i/GV_i < 0.01$	14	12	12	0	100 [b)]
Chikugo River	2004	Number of pesticides	32	23	16	7	
		with $PV_i/GV_i \geq 0.01$	23	20	13	7	35 [a)]
		with $PV_i/GV_i < 0.01$	9	3	3	0	100 [b)]
	2005	Number of pesticides	32	29	23	6	
		with $PV_i/GV_i \geq 0.01$	24	23	17	6	26 [a)]
		with $PV_i/GV_i < 0.01$	8	6	6	0	100 [b)]
	2006	Number of pesticides	33	29	23	6	
		with $PV_i/GV_i \geq 0.01$	22	21	15	6	29 [a)]
		with $PV_i/GV_i < 0.01$	11	8	8	0	100 [b)]
	2007	Number of pesticides	32	28	21	7	
		with $PV_i/GV_i \geq 0.01$	25	22	15	7	32 [a)]
		with $PV_i/GV_i < 0.01$	7	6	6	0	100 [b)]

[a)] Number of pesticides with $DV_i/GV_i \geq 0.01$/number of pesticides with $PV_i/GV_i \geq 0.01$

[b)] Number of pesticides with $DV_i/GV_i < 0.01$/number of pesticides with $PV_i/GV_i < 0.01$

Figure

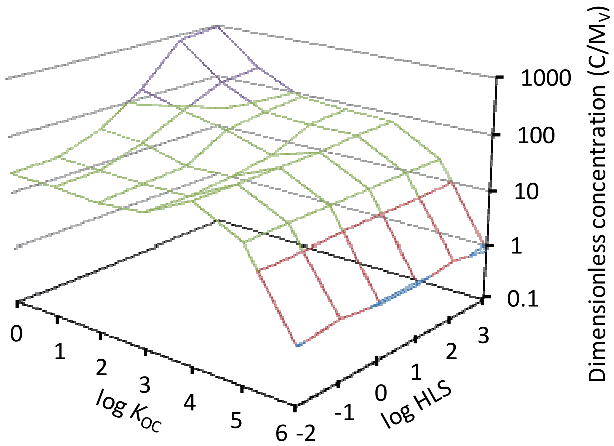

Figure 1. Plot of results of sensitivity analysis for adsorption and degradation in soil for fungicides in the Sagami River basin. Dimensionless pesticide concentrations (C/M_V), where C is the average simulated concentration for the 4-month period starting from the date of pesticide application (μg/L), and M_V is a parameter determined by the quantity of the applied fungicide (mg) divided by the total river flow volume (L) for the 4 months starting from the date of application, are plotted against K_{OC} and HLS (half-life with regard to degradation in soil).

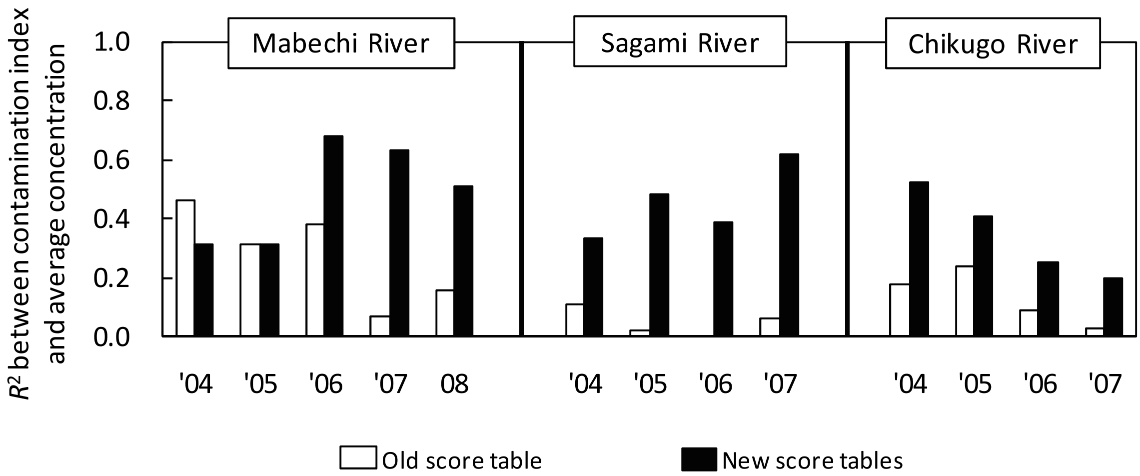

Figure 2. Comparison of the coefficients of determination (R^2) for plots of average pesticide concentrations versus contamination index values calculated with the new score tables and the Aizawa score table.

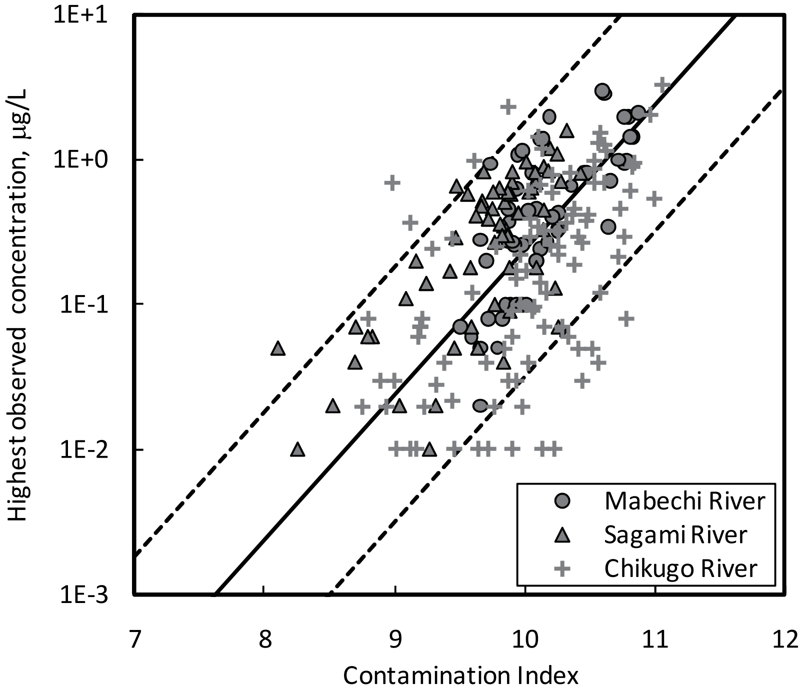

Figure 3. Relationship between the highest observed concentrations of pesticides and the contamination index values calculated with the new score tables. The solid line is a plot of the equation log C_H = Contamination index - 11.4. The dashed lines indicate one-sided 95% upper and lower confidence limits.

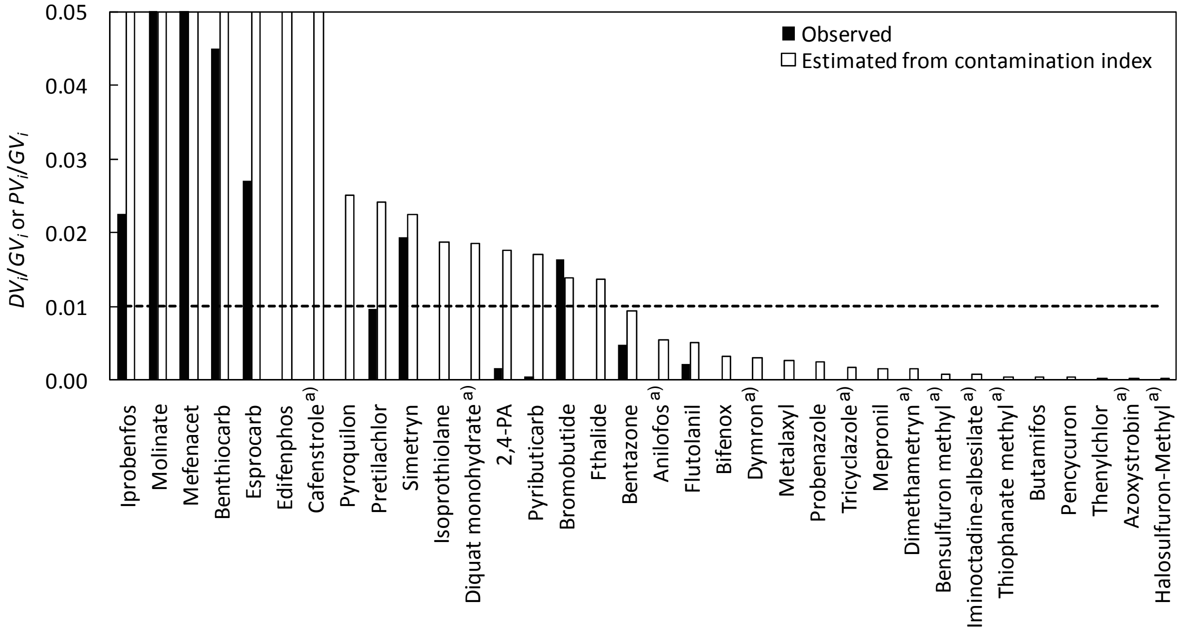

Figure 4. PV_i/GV_i (open bars) and DV_i/GV_i (solid bars) values for pesticides applied in rice paddies in the Sagami River basin in 2004. [a] The concentrations were not measured (PV_i is the possible maximum predicted concentrations of pesticide *i*, GV_i is the reference concentration of pesticide *i* in JDWQG, and DVi is the observed concentration of pesticide *i*).

Supplementary Information

Selecting analytical target pesticides in monitoring: sensitivity analysis and scoring

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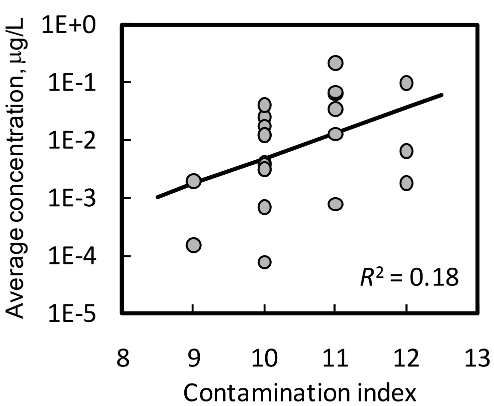
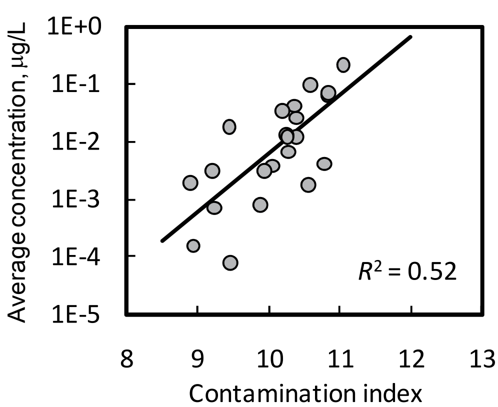
Table 1S. Old score table (Kamata et al., 2008)

Quantity sold (t/year)	Score A	logK_{OW}	Score B	Degradability (half life)	Score C	ADI ($mg \cdot kg^{-1} \cdot d^{-1}$)	Score D
1000 <	5	6 <	1	hours	1	1 <	1
100 < & ≤ 1000	4	4 < & ≤ 6	2	days	2	0.1 < & ≤ 1	2
10 < & ≤ 100	3	2 < & ≤ 4	3	weeks	3	0.01 < & ≤ 0.1	3
1 < & ≤ 10	2	0 < & ≤ 2	4	months	4	0.001 < & ≤ 0.01	4
≤ 1	1	≤ 0	5	longer than the above	5	≤ 0.001	5



A. Old score table



B. New score tables

Figure 1S. Correlations between the average concentrations of pesticides in the Chikugo River and the contamination index values (2004).