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

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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.

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 (USEPA, 2011; World Resources Institute, 1998). 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

$$DI = \sum_i \frac{DV_i}{GV_i} \tag{1}$$

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

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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; Gramatica and Guardo, 2002; Reus et al., 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 (Juraske et al., 2007; Reus and Leendertse, 2000; 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 (Kookana et al., 2005; Papa et al., 2004; 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 (supplementary data), 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, supplementary data). 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, supplementary data). 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