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Selection of Priority Pesticides in Japanese Drinking Water Quality Regulation: Validity, Limitations, and Evolution of a Risk Prediction Method

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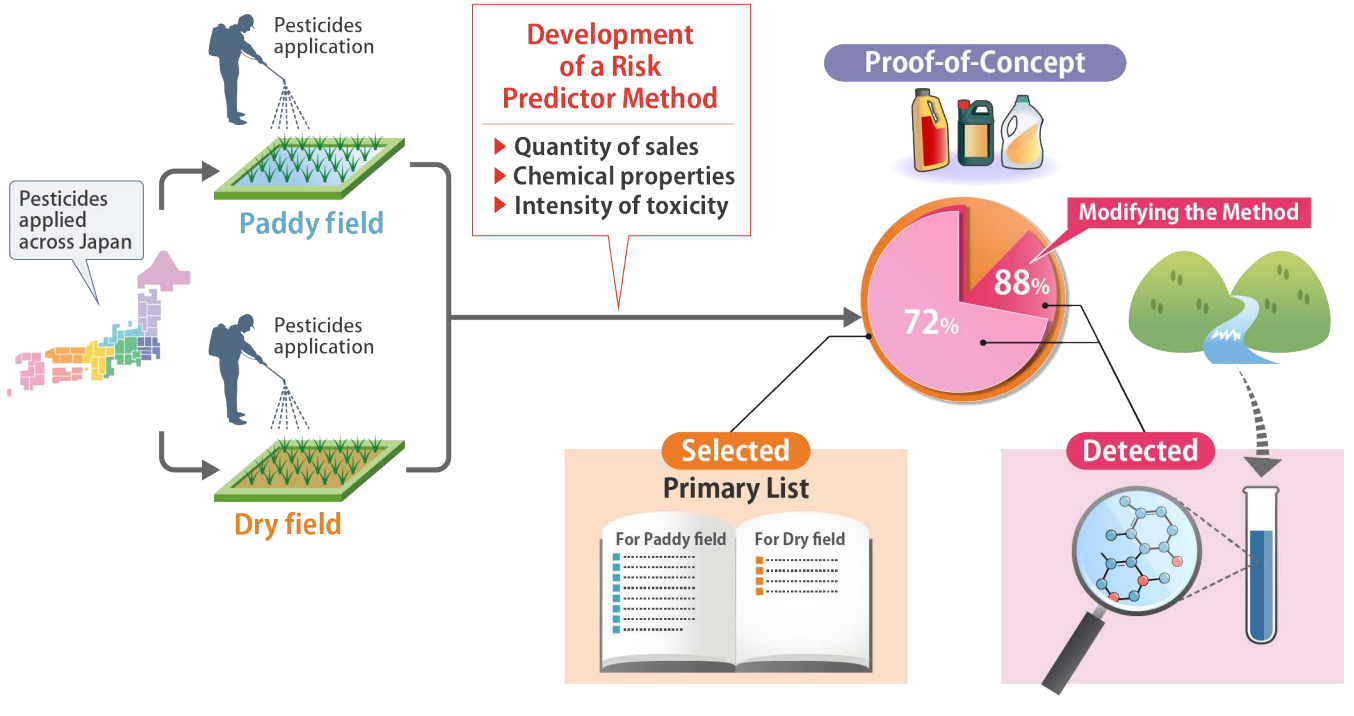
Research Highlights

- Validity of risk prediction method was assessed using pesticide monitoring data
- The method successfully selected pesticides with a high risk of detection
- Most of pesticides selected by the method were detected in drinking water sources
- Inclusion of latest sales figures and degradability improved selection accuracy
- Low monitoring frequency is correlated with low detection rates in regional areas


Pesticides application
Paddy field
Pesticides applied across Japan
Pesticides application
Dry field
Development of a Risk Predictor Method
Quantity of sales
Chemical properties
Intensity of toxicity
Proof-of-Concept
Modifying the Method
88%
72%
Selected
Primary List
For Paddy field
For Dry field
Detected

Abstract

Several risk scoring and ranking methods have been applied for the prioritization of micropollutants, including pesticides, and in the selection of pesticides to be regulated regionally and nationally. However, the effectiveness of these methods has not been evaluated in Japan. We developed a risk prediction method to select pesticides that have a high probability of being detected in drinking water sources where no monitoring data is available. The risk prediction method was used to select new pesticides for the 2013 Primary List in the Japanese Drinking Water Quality Guidelines. Here, we examined the effectiveness of the method on the basis of the results of water quality examinations conducted by water supply authorities across Japan, and studied ways to improve the risk prediction method. Of the 120 pesticides in the 2013 Primary List, 80 were detected in drinking water sources (raw water entering water treatment plants). The rates of detection of the newly selected pesticides and previously listed pesticides were not significantly different: 64% and 68%, respectively. When the risk predictor was revised to incorporate degradability of dry-field pesticides and current pesticide sales data, the rate of detection of pesticides selected as having a high risk of detection improved from 72% to 88%. We prepared regional versions of the Primary List using the revised risk predictors and verified their utility. The number of listed pesticides varied greatly by region, ranging from 32 to 73; all regional lists were much shorter than the national Primary List. In addition, 55% to 100% of the pesticides detected in each region were included in a Regional Primary List. This work verifies the ability of the risk prediction method to screen pesticides and select those with a high risk of detection.

Keywords: Drinking water quality standards; Prioritization; Risk assessment; Risk predictor; Risk ranking

1. Introduction

Pesticides are used worldwide to eliminate or control agricultural pests and weeds, thereby increasing crop yields. However, pesticides also pose environmental risks, especially when used inappropriately, being toxic substances intentionally released into the environment. Their inappropriate use may result in widespread release to the environment, with potential adverse effects on both human health and ecosystems (de O. Gomes et al., 2020; Md Meftaul et al., 2020; Vryzas et al., 2020; Zhang et al., 2019). To protect human health and ecosystem, environmental regulations of pesticides are developed and enforced by regulatory authorities. However, pesticides vary greatly in environmental fate, toxicity, and application, and regulation and monitoring of pesticides in the environment needs to take into account the complexity and variability of these factors (de Souza et al., 2020; Rathore and Nollet, 2012; Reichenberger et al., 2007; Vrana et al., 2005). An appropriate risk assessment process that evaluates pesticides for their potential risk is needed in order to provide the necessary scientific support for regulatory procedures and monitoring programs (Bu et al., 2013; Kortenkamp et al., 2019).

In risk assessment processes, environmental exposure concentrations are traditionally based on environmental monitoring data, which are obtained by sampling and analytical measurement (Carazo-Rojas et al., 2018; Iturburu et al., 2019; Johnson et al., 2008). Risk ranking and scoring methods based on actual environmental data have been proposed to identify priority substances for regulation and monitoring (Kuzmanović et al., 2015; Papadakis et al., 2015a; Papadakis et al., 2015b; Skinner et al., 2016; Slobodnik et al., 2012; Sugeng et al., 2013; Tsaboula et al., 2019a; Tsaboula et al., 2016; Tsaboula et al., 2019b; von der Ohe et al., 2011; Zheng et al., 2016). However, environmental data are not easily obtainable for all hazardous contaminants. Since routine monitoring generally targets substances regulated by monitoring programs, new environmental contaminants may be omitted, in conflict with the risk management objective of screening for unknown but potentially high-risk contaminants (Bu et al., 2013). Risk

assessment based on sampling and analytical measurement is flawed if it focuses only on certain pre-selected compounds (Guillén et al., 2012).

Model-based risk ranking and scoring methods are important screening tools in identifying priority substances when data are scarce (Kools et al., 2008; Swanson et al., 1997). Risk assessment based on model-predicted concentrations can cover a wider range of compounds and has a greater chance of identifying new and potentially harmful compounds in the environment. Many predictive risk assessment methods have been proposed to prioritize and select high-risk pesticides (Bu et al., 2013; Casado-Martinez et al., 2018; Daginnus et al., 2011; Juraske et al., 2007; Mitchell et al., 2002), and some of these methods have been extended to target environmental transformation products of pesticides (Sinclair et al., 2006). Some methods have been applied to regulatory procedures and monitoring programs (USEPA, 2001; USEPA, 2017). However, to the best of our knowledge, follow-up studies that validate the risk ranking and scoring methods have yet to be conducted.

Narita et al. (2014) proposed a risk prediction method that is suitable for selecting pesticides with high risk of detection in surface water used as a drinking water source. A combination of two risk predictors was used to select new pesticides to be included in the 2013 Primary List of pesticides in the Japanese Drinking Water Quality Guidelines (JDWQG). However, the appropriateness of the method for the selection of new pesticides has not been validated. After the Primary List was amended to include new pesticides, mostly identified by the method, and took effect in the JDWQG (MHLWJ, 2013), many municipal and regional water supply authorities implemented monitoring of these pesticides and began collecting occurrence data thereby providing an opportunity to conduct a follow-up study on the risk prediction method and to validate the two risk predictors.

On the other hand, approximately half of Japanese water supply authorities do not monitor

75 pesticides (Kosaka et al., 2017). The primary reason is that the pesticides are listed in the non-
76 enforceable JDWQG but not in the national enforceable standard (Drinking Water Quality
77 Standard). Another reason is that authorities do not have sufficient data on which pesticides
78 have a high risk of detection in their region and which have not. In this study, we examine
79 pesticide monitoring and detection records and determine whether the appropriate pesticides
80 were selected for monitoring. We discuss the efficacy of the risk prediction method (Narita et
81 al., 2014) and investigate why some of the selected pesticides were not detected. Lastly, we
82 propose revised risk predictors and use them to select pesticides with a high risk of detection
83 nationally and regionally, as a proof-of-concept.

84

85 **2. Material and methods**

86 **2.1. Target pesticides and their measurement**

87 Table S1 in the Supplementary Information lists the 120 pesticides targeted in this study. These
88 are the pesticides listed in the Primary List of the JDWQG, which was revised in 2013 mostly
89 on the basis of our research (Narita et al., 2014). The pesticides comprise 56 herbicides, 34
90 insecticides, 28 fungicides, 1 insecticide–fungicide combination, and 1 soil fumigant. The
91 previous Primary List, effective until 2012, comprised 102 pesticides. Of the 120 pesticides on
92 the 2013 list, 87 were on the old Primary List. The remaining 33 were added in 2013.

93 We obtained data on the concentrations of these 120 pesticides in raw water entering water
94 treatment plants for the fiscal years (FY) 2013 and 2014, after the 2013 Primary List was
95 implemented, from *Statistics on Water Supply* (JWWA, 2015; JWWA, 2016), which
96 summarizes the results of water quality examinations conducted by all water supply utilities in
97 Japan (Table S1). The water quality examinations were conducted under strict accuracy control

98 according to the standard methods associated with the JDWQG (MHLWJ, 2013). In FY 2014,
99 614 of the approximately 1400 water utilities in Japan examined raw water for pesticides
100 (Kosaka et al., 2017). In addition, we obtained data for FY 2015 from 10 water supply
101 authorities that conducted frequent pesticide measurements (Matsui, 2016). At each water
102 treatment plant, raw water was sampled 0 to 13 times a year and analyzed for pesticide
103 concentrations. Of the 120 pesticides, 81 were detected by gas chromatography-mass
104 spectrometry and 39 were detected by liquid chromatography-mass spectrometry, according to
105 the official analytical methods (MHLWJ, 2003). Pesticide detection is defined as detection of
106 that pesticide with a concentration ≥1% of the corresponding guideline value (*GV*), and non-
107 detection is defined in the opposite case. This is because the quantification limit for each
108 pesticide is 1% of the *GV* for the pesticide in the JDWQG (MHLWJ, 2013) (see the
109 Supplementary Information).

110

111 **2.2. Risk predictors**

112 The details of the risk predictors and the selection process are described by Narita et al. (2014).
113 In brief, there are two risk predictors: one for rice paddy pesticides and one for dry-field
114 pesticides, including wheat, corn, vegetables, and orchard fields. Since runoff rates of rice
115 paddy pesticides are especially high compared to those of dry-field pesticides (Kamata et al.,
116 2020; Watanabe et al., 2007), rice-paddy pesticides are treated separately. The point source
117 pollution of pesticides is not assumed because its impact is not large in Japan (Matsui et al.,
118 2006). Runoff of a pesticide to surface water is also affected by other factors such as spray drift
119 and drainage, but these local factors were not able to be taken into account in the risk predictors
120 being applied in a nationwide scale (Narita et al., 2014). The risk predictor for dry-field
121 pesticides (URI_i) is based on parameters for pesticide sales quantity [t year^{-1}], *GV* [μg L^{-1}], and

annual precipitation [km^3 $year^{-1}$], while that for rice paddy pesticides (PRI_i) is based on the same parameters plus scores reflecting the sorption and degradation characteristics of the pesticide. No sorption and degradation scores in URI_i were due to the lack of a proper quantitative assessment (Narita et al., 2014).

$$URI_i = \mathrm{Max}(u_{i,1}, u_{i,2},,,,,, u_{i,10}) \qquad (1)$$

$$u_{i,j} = \frac{(\text{Sales quantity for dry fields})_j}{(GV_i)(\text{Annual precipitation})_j} \qquad (2)$$

$$PRI_i = \mathrm{Max}(p_{i,1}, p_{i,2},,,,,, p_{i,10}) \qquad (3)$$

$$p_{i,j} = \frac{(\text{Sales quantity for paddy fields})_j}{(GV_i)(\text{Annual precipitation})_j} \times 10^{(\text{Score } Y_i + \text{Score } Z_i)} \qquad (4)$$

where URI_i is the risk predictor of pesticide i applied to dry fields [ton (μg L^{-1})$^{-1}$ km^{-3}] and PRI_i is that of pesticide i applied to paddy fields [ton (μg L^{-1})$^{-1}$ km^{-3}]. In the paper of Narita et al. (2014), URI_i was denoted as C4 and PRI_i as C8. The territory of Japan was divided into 9 regions, and the $u_{i,j}$ and $p_{i,j}$ values of each pesticide i were calculated for each region j (as a whole). Score Y is a parameter for pesticide degradability, and Score Z is a parameter for pesticide sorption. If either the URI_i or PRI_i value was larger than the detection threshold, predetermined empirically by the detection/non-detection of pesticides (Narita et al., 2014), that pesticide was identified as having a potentially high risk of detection and added to the 2013 Primary List.

2.3. Data acquisition and analysis

Data used to calculate the URI_i and PRI_i values in this study came from the following sources. Annual sales of commercial formulated pesticide products in each region were obtained from

143 pesticide sales data books (JPPA, 2014-2016). From the sales data, the amount of active
144 ingredient applied to each field in each region was calculated by the method of Narita et al.
145 (2014). GV_i values were obtained from the ministry notification (MHLWJ, 2013). The 10-year
146 average precipitation data for the period 2005–2014 obtained from statistics (MICJ, 2017) were
147 used in equations (2) and (4). The soil adsorption coefficient normalized by the organic-carbon
148 content (K_{oc}) and half-lives in soil, water, and sunlight were obtained from the literature (FSC,
149 2017; MAFFJ, 2017; MOEJ, 2017; Tomlin, 2006), and were used for calculating Score Y and
150 Score Z in equation (2) (Tani et al., 2012). When there was no report of K_{oc} in the literature,
151 values were estimated by using the EPI Suite K_{oc}-win software (EPI Suite, 2012).

152 Regression analyses were performed using the R Statistical Package (R Core Team, 2019).
153 Coefficients of determination (R^2) were determined from 1-SSreg/SStot , where SSreg is the
154 sum of squares of the residuals around the regression line, and SStot is the sum of squares of
155 the residuals around a horizontal line representing the mean value. R^2 in the case of the
156 regression line with an intercept of 0 was calculated using the Microsoft excel without using R
157 (Motulsky and Christopoulos, 2004).

158

159 **3. Results and discussion**

160

161 **3.1. Validity of the risk prediction method**

162 The new Primary List was implemented in 2013, and monitoring of the 120 listed pesticides
163 began in FY 2013. Of the 120 pesticides, 80 (detection rate = 67%) were detected in 2013 to
164 2015 (Fig. 1). Of the 33 pesticides new to the list, the detection rate was 64%. Of the remaining
165 87 pesticides, it was 68%. The detection rate did not differ significantly between new and

166 continuously listed pesticides (p-value = 0.83).

167 Following the revision of the Primary List according to the risk predictors, 90 of 120 listed
168 pesticides had a high risk of potential detection (Narita et al., 2014). Of these 90 pesticides, 65
169 were detected (72%) (Panel A of Fig. 1). Major pesticides that were detected were bromobutide,
170 molinate and iminoctadine-albesilate (Table S1). The remaining 30 pesticides were included in
171 the 2013 Primary List according to administrative decisions made by the Ministry of Health,
172 Labor and Welfare because of their record of detection or because the predictor values were not
173 sufficiently low enough for exclusion from the list. Of these 30 pesticides, 15 were detected
174 (50%). Thus, the detection ratio of the 90 pesticides selected on the basis of the risk predictors
175 was significantly higher than that of the remaining 30 pesticides (p-value = 0.047). Among the
176 120 listed pesticides, 40 were not detected at any location (dividing 40 by 120, the no-detection
177 rate is 33%), although they were included in the monitoring. The no-detection rate of 33 % was
178 higher than the no-detection rate from 2007 to 2010 (23%), before the 2013 Primary List was
179 implemented (Narita et al., 2014).

180 We looked for ways to improve the risk prediction method. Both risk predictors (URI_i and PRI_i)
181 include pesticide sales quantity, among other factors. However, the pesticides added to the
182 Primary List in 2013 were selected after the calculation of risk predictor values based on
183 pesticide sales of 2007–2010. Therefore, if sales quantities of pesticides had declined greatly
184 from 2007–2010 to 2013–2015, the likelihood of detecting these pesticides would be much
185 lower. For 20 pesticides (half of the 40 that were not detected, Category A in Table 1 and Panel
186 B of Fig. 1), the sales quantities were lower in 2013–2015 than in 2007–2010 or remained low
187 from 2007–2010 to 2013–2015. For the 6 pesticides in Category A-1 (Table 1), sales declined
188 between these two periods, and when the URI_i and PRI_i values were recalculated on the basis
189 of the sales quantity for 2013–2015, the values were low enough for exclusion from the Primary
190 List. Therefore, the decrease in sales appears to explain why these pesticides were not detected.

191 Since the sales quantity can change from year to year, periodic review of sales is required for
192 accurate risk assessment. For the remaining 14 of the 20 pesticides (Category A-2 in Table 1),
193 sales quantity was low in both 2007–2010 and 2013–2015, making the risk of detection low in
194 both periods. These pesticides remained in the 2013 Primary List because the risk was not low
195 enough for them to be excluded when the Primary List was revised.

196 In addition to changes in pesticide sales quantity, degradability was considered as another
197 potential cause of non-detection. Some of the 40 undetected pesticides have short half-lives.
198 Excluding pesticides in Category A (Table 1), 11 pesticides had half-lives < 2 days in soil,
199 water, or sunlight (Category B in Table 1). Thus, the non-detection of these 11 pesticides was
200 likely due to decomposition following application to the field. Ten of these pesticides were
201 applied to dry fields, and degradability was not included in the URI_i (because no data are
202 available to estimate Score *Y* values), whereas it was included (as Score *Y*) in the PRI_i (Tani et
203 al., 2012; Tani et al., 2010). The one remaining pesticide (pyrazolynate) of the 11 was applied
204 to paddy fields. At the time of risk evaluation for revision of the Primary List in 2013, however,
205 the degradability of pyrazolynate was unknown, and it was assumed to be non-degradable by
206 default. Its degradability has since been determined (MOEJ, 2016). When it is used to calculate
207 the PRI_i value, the pesticide is flagged as unlikely to be detected. Thus, for 31 of the 40
208 undetected pesticides, we were able to determine why they were not detected. However, for the
209 remaining 9 (Category C in Table 1), we were not able to determine any clear reason why they
210 were not detected. For very stable pesticides such as glufosinate, however, they might be
211 detected even after they are no longer shipped and no longer in use. We also surmise that they
212 might have been detected if they had been monitored more frequently.

213

214 **3.2. Improvement of the risk predictors**

215 **3.2.1 New risk predictor (*$URIM_i$*) for dry-field pesticides**

216 Examining the possible causes for non-detection of pesticides (Section 3.1) confirmed that
217 degradability is a key factor for dry-field pesticides. To introduce degradability into the URI_i,
218 we turned to previous studies of the relationship between degradability of pesticides applied to
219 dry fields and their runoff (Dabrowski and Balderacchi, 2013; Daginnus et al., 2011). We
220 focused on the study by Chen et al. (2002) because their approach could be mathematically
221 incorporated into the risk predictor. They proposed a Surface Water Mobility Index (SWMI) to
222 quantify the movement of dry-field pesticides into surface water via overland runoff and erosion
223 on various catchment scales. The SWMI incorporates pesticides' soil sorption coefficients and
224 half-lives in soil. Chen et al. (2002) applied the SWMI to several catchments of various sizes,
225 and found that values were well correlated with the relative concentrations of pesticides
226 (concentration per pesticide application rate), indicating that the runoff potential of a dry-field
227 pesticide can be predicted from the SWMI, the amount of pesticide applied, and basin area. We
228 applied SWMI to the 10 geographical regions in Japan, but we found no correlation between
229 SWMI values and relative concentrations of dry-field pesticides (R^2 = 0.027 in Kanto and 0.044
230 in Kyushu; Fig. S1). Thus, SWMI values could not be used to quantify the effects of soil
231 sorption coefficients and half-life in soil on pesticide concentrations in river water. Each of the
232 fields used by Chen et al. (2002) for verification of the SWMI is a single river basin: even the
233 largest one is approximately 1 to 1/5 times the sizes of our research areas (the 9 geographical
234 regions in Japan). Each of our research areas is a geographical region consisting of many river
235 basins. Moreover, pesticide application quantity per basin area in their study was an order of
236 magnitude larger than the values used in our study. The SWMI was well correlated with
237 pesticide concentration in their study, but our target is the prediction of detection/non-detection.
238 These methodological differences might explain the failure of SWMI to accurately account for
239 non-detection of dry-field pesticides due to the rates of pesticide degradation.

Assuming that the minimum half-life (m_{HL}) is a dominant factor in the presence of a pesticide in surface water, we plotted detected pesticides (•) and undetected pesticides (△) in a two-dimensional plane: m_{HL} values on the *x*-axis and URI_i values on the *y*-axis (Fig. 2). All detected pesticides had large URI_i values and/or large m_{HL} values (>1.7 days). Therefore, we developed $URIM_i$ as an improved risk predictor for pesticides applied to dry fields:

$$URIM_i = \mathrm{Max}\left(um_{i,1}, um_{i,2}, , , , , , um_{i,10}\right) \tag{5}$$

$$um_{i,j} = \frac{(\text{Sales quantity for dry fields})_j}{(GV_i)(\text{Annual precipitation})_j} \times u(m_{HL} - 1.7\ \text{d}) \tag{6}$$

where $u(m_{HL} - 1.7\ \text{d})$ is a step function, where $u = 0$ when the value ($m_{HL} - 1.7$ d) is negative and $u = 1$ when it is positive, and m_H is the minimum value of half-lives in soil, water, and sunlight.

3.2.2 Effectiveness of new risk predictor ($URIM_i$)

Of the 40 pesticides that were not detected in 2013–2015, 20 were not detected owing to low or decreased sales quantity. Therefore, we recalculated URI_i and PRI_i using 2013–2015 sales data, then we verified whether $URIM_i$ could predict the probability of detection of a pesticide better than URI_i. As shown in Table 2 and Fig. S2, when URI_i and PRI_i and 2007–2010 pesticide sales data were used, 90 pesticides were selected for monitoring. Of the 90 pesticides, 65 were detected in 2013–2015. When URI_i and PRI_i and pesticide sales data from 2013–2015 were used, 79 pesticides were selected for monitoring, and the detection rate improved to 78%. However, it should be noted that 3 detected pesticides were omitted due to the decreased sale quantity, while the number of selected pesticides decreased from 90 to 79. Using PRI_i and $URIM_i$ instead of URI_i improved the detection rate to 88%, better predicting pesticide detection.

262 Again, it should be noted that 3 detected pesticides were omitted, while the number of selected
263 pesticides decreased from 79 to 67. Furthermore, when the potential detection threshold was
264 optimized, as described by Narita et al. (2014), the detection rate was further improved to 91%
265 (Table 2; Fig. S3). Our detection rate of 91% was much higher than the 84% obtained by Narita
266 et al. (2014), indicating that our new risk predictor provides improved risk assessment.

267

268 **3.3. Design of regional Primary Lists**

269 **3.3.1 Regional pesticide sales quantities and detected pesticides**

270 Since the main crops produced differ with regional characteristics such as climate and
271 topography, types and amounts of pesticides used will also vary by region. As shown in Fig.
272 S4, the coefficient of determination (R^2) for the correlations between pesticide sales at the
273 national and regional scales varied greatly from 0.18 (Hokkaido region) to 0.90 (Tokai region),
274 which indicates the diversity of pesticides applied by region. Thus, pesticides with a high risk
275 of detection should also vary by region. All 120 pesticides in the 2013 Primary List were
276 monitored in all regions, but the number detected ranged from 6 to 51 (Table S2).

277 Some pesticides were detected only in few regions, and no pesticides were detected in all
278 regions (Fig. S5). Four pesticides were detected in 8 of the 9 regions: cafenstrole, bromobutide,
279 fipronil, and fenitrothion. Of the 80 detected pesticides, only 13 (16%) were detected in ≥5 of
280 the 9 regions, and 67 (84%) were detected in fewer than half of the regions (Fig. 3). Eleven
281 pesticides were detected in the Hokkaido region, 4 of these in the Tohoku region, so the overlap
282 detection rate in Tohoku/Hokkaido was 36% (4/11). As shown in Table S3, the overlap
283 detection rate ranged from 0% to 95%, and the average value for each region ranged from 30%
284 to 63%. These data clearly indicate that pesticides with a high risk of detection vary from region

285 to region.

286 **3.3.2 Regional Primary Lists**

287 Priority pesticides to be monitored will differ between water utilities because the pesticides that
288 are likely to be detected also vary by region. However, the JDWQG presents a single Primary
289 List, and recommends that each water utility select pesticides from the list for monitoring. In
290 practice, however, almost all water utilities monitor all listed pesticides. To improve regional
291 monitoring efficiency, we prepared regional versions of the Primary List and tested their utility.
292 To create Regional Primary Lists (Fig. S6), we calculated regional risk predictor values and
293 selected pesticides with a high risk of detection in each region on the basis of the modified
294 detection threshold (Section 3.2.2). Between 30 and 62 pesticides were selected per region,
295 making each list less than half of the Primary List. Moreover, they included fewer than 66
296 pesticides, the number selected nationally by the improved risk predictors (Table 2). Five to
297 43% of the pesticides included in the current national Primary List were detected in each region
298 (Fig. 4). Of the 66 pesticides selected nationally by the improved risk predictors (Table 2),
299 regional detection rates ranged from 9% to 64%. Detection rates of regionally selected
300 pesticides were higher: 18% to 65%. Moreover, all detected pesticides were included in the
301 Regional Primary List. In other regions, however, fewer pesticides were detected, some non-
302 selected pesticides were detected, and fewer pesticides were still detected when the regional
303 selection was used. This may be due to the lack of pesticide sales data. The regional selections
304 were based on risk predictor values calculated by using pesticide sales for each region. Since
305 distribution channels are complex, however, pesticides are not always applied in the region in
306 which they were purchased, with the result that their use is not recorded in the correct regional
307 sales data. Pesticide selection for monitoring could be improved if the threshold level of
308 potential detection was optimized for each region with more measurement data. Overall, the
309 improvement of detection rates by regional pesticide selection indicates that Regional Primary

310 Lists can be expected to enhance the efficiency of pesticide monitoring by more accurately
311 selecting pesticides with high detection risk, and Regional Primary Lists are recommended for
312 water utilities to accurately select pesticides.

313 However, the use of Regional Primary Lists did not guarantee very high detection rates yet,
314 though their detection rates were higher than those by the national Primary List. In 8 regions
315 (all except Kanto and Kinki), detection rates were <50%, i.e., more than half of the pesticides
316 in the list were not detected. To examine the cause of the low detection rates, we performed a
317 regression analysis to determine whether catchment area, precipitation, or the annual average
318 number of pesticide measurements could be related. Neither watershed area nor annual
319 precipitation was correlated with detection rate (R^2= 0.0022 and 0.0083, respectively; Panels A
320 and B of Fig. 5). The detection rate was moderately correlated (R^2 = 0.71) with the average
321 number of measurements (Panel C of Fig. 5). The two regions where detection rates exceeded
322 50% had the highest measurement frequencies. In contrast, in regions where detection rates
323 were <30%, concentrations were measured fewer than 100 times a year. Recently, Asami et al.
324 (2020) detected pesticides in raw water in areas not monitored by the utilities. Therefore, we
325 consider that the low detection rates observed in some regions could be due to a low monitoring
326 frequency.

327

328 **4. Conclusion**

329 Of the 120 pesticides listed in the 2013 Primary List, 80 were detected in raw water to be treated
330 for use as drinking water. Detection rates of pesticides added to the list in 2013 and previously
331 listed pesticides were similar: 64% and 68%, respectively. The similar detection rates indicate
332 that the risk prediction method is a valid method to select new pesticides for addition to the
333 Primary List. We verified that pesticides with a high risk of detection could be predicted by

using an index based on sales quantity, degradability, and soil sorption.

Of the 40 pesticides that were not detected, 20 had low or decreased sales quantities. When we re-evaluated the risk of detection using risk predictor values based on updated sales quantities, 10 of the 20 were found to have small detection risk, explaining why they were not detected. Of the remaining 20 pesticides, 10 were applied in dry fields, and the URI_i does not consider pesticide degradability. When the risk predictor was calculated using updated sales quantity data and the URI_i was modified to include degradability, the detection rate improved from 73% to 88%. When the detection threshold was optimized, the detection rate of pesticides selected as having a high risk of detection was improved to 91%.

Pesticide sales and detected pesticides varied regionally. Although the national Primary List contains 120 pesticides, only 5% to 43% of pesticides were detected in each region. Although the development and use of Regional Primary Lists instead of the national Primary List improved the detection rate, it remained low, at 18% to 65% per region. A low monitoring frequency may explain the low detection rates.

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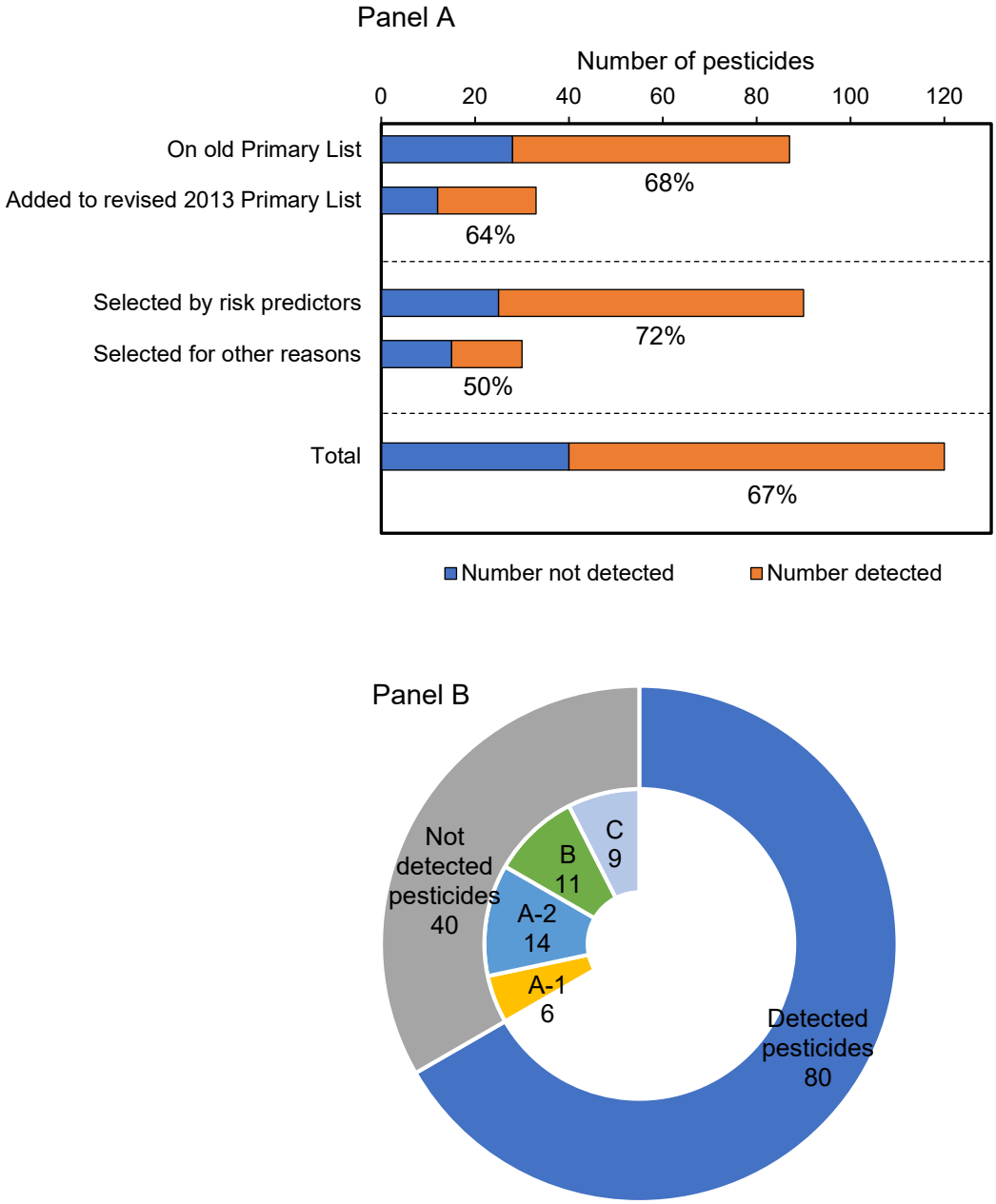

Fig. 1 Number and rate of detection of pesticides in the new Primary List (Panel A) and a breakdown by the cause of non-detection (Panel B) (fiscal years 2013–2015). A-1: low sales volume (selected by the old risk predictor), A-2: low sales volume (not selected by the old risk predictor, but selected by committee), B: pesticides with a half-life of <2 days, C: reason for non-detection unclear.

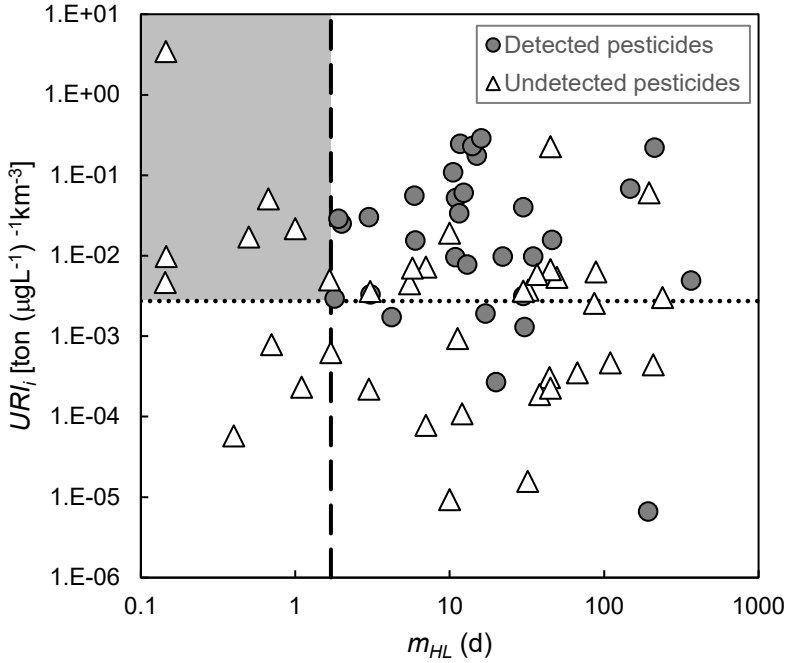

Fig. 2 Scatter plot of URI_i values versus m_{HL} values of the detected (closed circles) and not detected (open triangles) pesticides. Dotted line indicates the threshold level of the old risk predictor for upland-field pesticides; Dashed line indicates m_{HL} of 1.7 d.

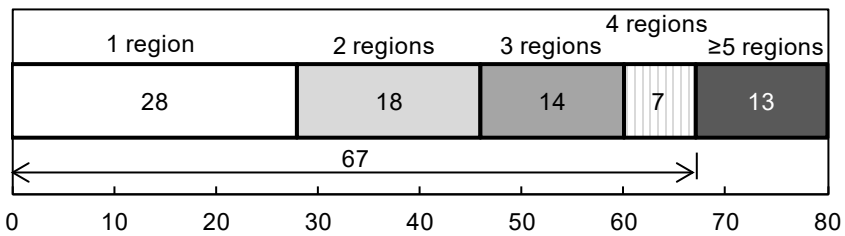

Fig. 3 Number of pesticides detected in single and multiple regions.

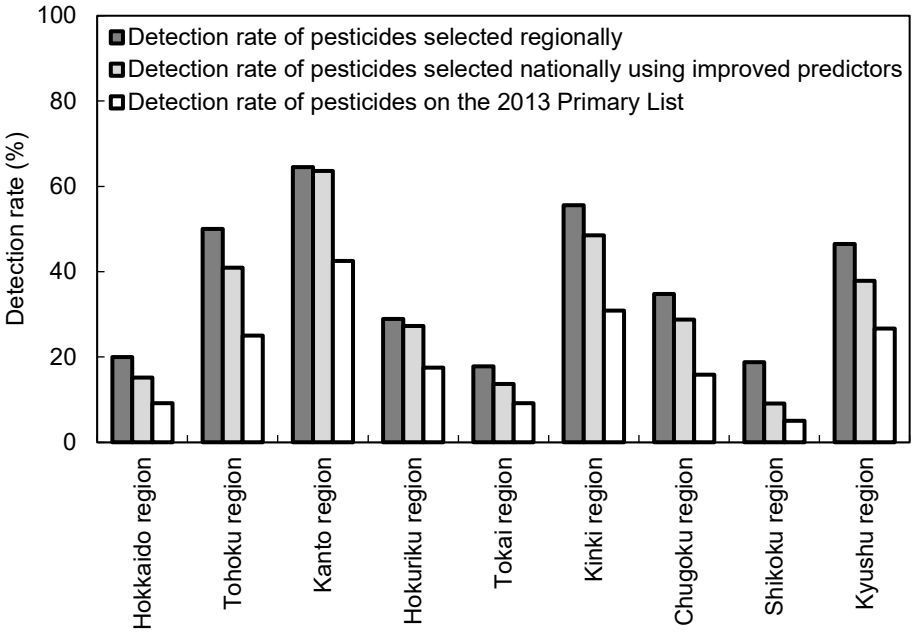

Fig. 4 Comparison of detection rates between the Regional Primary Lists and the national Primary List.

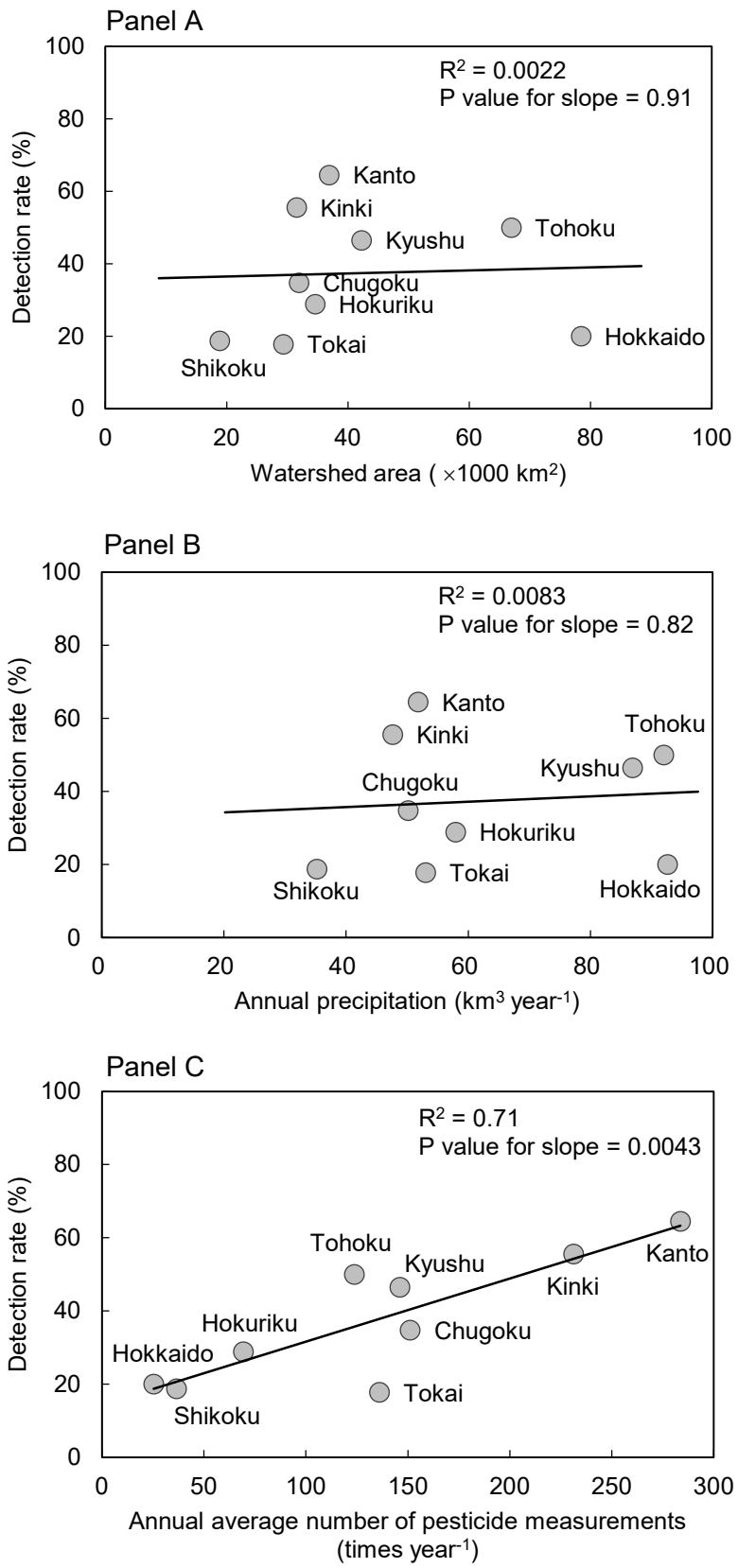

Fig. 5 Regression analyses of detection rate against watershed area (Panel A) / annual precipitation (Panel B) / frequency of pesticide monitoring (Panel C).

1 Table 1 Pesticides in the revised 2013 Primary List that were not detected and their characteristics.

Category	Use	Pesticide name	Old Primary List	Half-life in soil (days)	Half-life in water (days)	Half-life in sunlight (days)	Sales in 2013–2015 (t/year)	Percentage of sales for dry field application (%)	Percentage of sales for rice paddy application (%)	Suggestion by indicator value based on sales 2007–2010	Suggestion by indicator value based on sales 2013–2015
A-1	Fungicide	Edifenphos	Listed	194	ND	ND	0	0	0	SU & SP	NS
(6)		Etridiazole	Listed	7.0	103	ND	0	0	0	SU	NS
		Fthalide	Listed	200	2.8	0.6	146	0	100	SU	NS
	Herbicide	Bethrodine	Listed	32	Stable	0.2	4	100	0	SU	NS
		Dithiopyr	Listed	947	Stable	37	5	100	0	SU	NS
	Insecticide	Isoprocarb	Listed	12	353	41	0	0	0	SP	NS
A-2	Fungicide	Carpropamid	Listed	170	Stable	167	0	0	0	NS	NS
(14)		Isoprothiolane	Listed	66	Stable	Stable	90	4	96	NS	NS
		Mepronil	Listed	44	Stable	6.6	30	50	50	NS	NS
		Metalaxyl	Listed	38	Stable	100	26	59	41	NS	NS
		Thiophanate methyl	Listed	25	41	0.7	390	93	7	NS	NS
	Herbicide	Dimepiperate	Listed	7.0	ND	ND	0	0	0	NS	NS
		Dymron	Listed	50	Stable	3.3	244	0	100	NS	NS
		Methyldymron	Listed	175	ND	ND	0	0	0	NS	NS
		Pendimethalin	Listed	239	Stable	3.8	131	100	0	NS	NS
		Propyzamide	Listed	30	42	174	24	100	0	NS	NS
		Terbucarb	Listed	146	ND	ND	0	0	0	NS	NS
	Insecticide	Dimethoate	Listed	3.1	68	144	30	100	0	NS	NS
		Etofenprox	Listed	11	Stable	2.0	93	48	52	NS	NS
		Thiodicarb	Listed	5.5	32	16	35	100	0	NS	NS
B	Fungicide	Benomyl	Listed	0.44	0.06	ND	106	65	35	SU	SU

(11)		Chlorothalonil	Listed	14	Stable	0.1	300	90	10	SU	SU
		Dazomet	Not listed	1.0	0.1	0.3	2,999	100	0	SU	SU
		Dithianon	Not listed	13	0.6	0.1	71	100	0	SU	SU
	Herbicide	Butamifos	Listed	17	Stable	0.1	30	92	8	SU	SU
		Metribuzin	Not listed	45	Stable	0.3	33	100	0	SU & SP	SU
		Pyrazolynate	Not listed	9.0	0.7	0.04	198	0	100	SU & SP	NS
		Trifluralin	Listed	115	14	1.1	154	78	22	SU	SU
	Insecticide	Amitraz	Not listed	0.5	0.9	5.1	8	100	0	SU	SU
		Carbam sodium	Not listed	212	0.1	ND	250	100	0	SU	SU
		Carbaryl	Listed	14	12	1.7	57	100	0	SU	SU
C	Fungicide	Propiconazole	Listed	50	Stable	58	29	100	0	SU	SU
(9)	Herbicide	Cyhalofop butyl	Not listed	0.3	97	5.3	62	0	100	SU & SP	SP
		Glufosinate	Not listed	5.7	Stable	1187	355	53	47	SU & SP	SU & SP
		Mecoprop	Listed	10	31	3.2	115	100	0	SU	SU
		Napropamide	Listed	89	ND	ND	8	100	0	SU	SU
		Paraquat	Not listed	7.0	30	ND	88	61	39	SU & SP	SU & SP
	Insecticide	Cartap	Not listed	3.0	ND	0.2	149	38	62	NS	NS
		Cyanophos	Not listed	196	ND	ND	36	100	0	SU	SU
		Prothiofos	Not listed	45	234	17	60	100	0	SU	SU

Category A: Low sales volume
A-1: Selected by the old risk indicator
A-2: Not selected by the old risk indicator (selected by committee)
Category B: Pesticides with a half-life of <2 days
Category C: Reason for non-detection unclear
ND: No data
NS: Not selected
SU: Selected by URI_i
SP: Selected by PRI_i

Table 2 Detection rate with the improved risk indicators.

Risk indicators	Number of selected pesticides	Number of pesticides detected in 2013–2015	Detection rate
(1) URI_i, PRI_i and 2007–2010 pesticide sales	90	65	72%
(2) URI_i, PRI_i and 2013–2015 pesticide sales	79	62	78%
(3) $URIM_i$, PRI_i and 2013–2015 pesticide sales	67	59	88%
(4) Detection threshold optimized per Narita et al. (2014)	66	60	91%

Supplementary Material

Selection of Priority Pesticides in Japanese Drinking Water Quality Regulation: Validity, Limitations, and Evolution of a Risk Prediction Method

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Table S1 Pesticides in the new Primary List of the Japanese Drinking Water Quality Guideline.

Name of pesticide	Use	Number of water supply authorities monitoring this pesticide	Number of examinations per authority per year [a]	GV [b] (μg/L)	Maximum DV (μg/L)	mDI [c]	Included in the old Primary List	Selected based on risk predictors (RPs)/or for other reasons (OTH)	Examination methods
1,3-Dichloropropene	Soil fumigant	389	7	50	0.5	0.01	Y	RPs	GC-MS
2,4-PA	Herbicide	377	6	30	1.2	0.04	Y	RPs	GC-MS
Acephate	Insecticide	412	6	6	0.84	0.14	Y	RPs	LC-MS (P)
Alachlor	Herbicide	366	7	30	0.6	0.02	Y	RPs	GC-MS
Asulam	Herbicide	377	5	200	2.0	0.01	Y	RPs	LC-MS (P)
Atrazine	Herbicide	354	6	10	8.2	0.82	Y	RPs	GC-MS
Benfuracarb	Insecticide	353	5	40	9.2	0.23	Y	RPs	LC-MS (P)
Bentazone	Herbicide	434	6	200	10	0.05	Y	RPs	LC-MS (N)
Benthiocarb	Herbicide	392	7	20	4.0	0.20	Y	RPs	GC-MS
Bromobutide	Herbicide	451	6	100	160	1.60	Y	RPs	GC-MS
Buprofezin	Insecticide	383	6	20	2.0	0.10	Y	RPs	GC-MS
Cafenstrole	Herbicide	429	6	8	2.96	0.37	Y	RPs	GC-MS
Carbofuran	Insecticide	350	5	5	0.50	0.10	Y	RPs	LC-MS (P)
Chlorpyriphos	Insecticide	389	6	3	0.09	0.03	Y	RPs	GC-MS
Diazinon	Insecticide	458	6	5	0.15	0.03	Y	RPs	GC-MS
Dichlobenil	Herbicide	364	7	10	0.5	0.05	Y	RPs	GC-MS
Dichlorvos	Insecticide	403	6	8	0.16	0.02	Y	RPs	GC-MS
Dimethametryn	Herbicide	399	6	20	0.4	0.02	Y	RPs	GC-MS
Diquat monohydrate	Herbicide	343	5	5	4.0	0.80	Y	RPs	LC-MS
Dithiocarbamate peticides	Insect–fungicide	131	4	5	1.0	0.20	Y	RPs	GC-MS
Diuron	Herbicide	342	6	20	0.2	0.01	Y	RPs	LC-MS (P)
EPN	Insecticide	374	6	4	0.12	0.03	Y	RPs	GC-MS
Esprocarb	Herbicide	395	6	30	2.1	0.07	Y	RPs	GC-MS
Ethylthiometon	Insecticide	380	7	4	0.12	0.03	Y	RPs	GC-MS
Fenitrothion	Insecticide	495	6	3	0.45	0.15	Y	RPs	GC-MS
Fenobucarb	Insecticide	426	6	30	1.5	0.05	Y	RPs	GC-MS
Fenthion	Insecticide	379	6	6	1.92	0.32	Y	RPs	GC-MS
Fipronil	Insecticide	399	6	0.5	0.16	0.31	Y	RPs	LC-MS (N)
Glyphosate	Herbicide	387	5	2000	60	0.03	Y	RPs	LC-MS
Iminoctadine-albesilate	Fungicide	318	5	6	4.98	0.83	Y	RPs	LC-MS
Iprobenfos	Fungicide	381	7	90	1.8	0.02	Y	RPs	GC-MS
Isoxathion	Insecticide	408	6	8	0.48	0.06	Y	RPs	GC-MS
Malathion	Insecticide	400	7	50	0.5	0.01	Y	RPs	GC-MS
Mefenacet	Herbicide	433	6	20	2.4	0.12	Y	RPs	GC-MS
Methidathion	Insecticide	402	7	4	1.0	0.25	Y	RPs	GC-MS
Methomyl	Insecticide	376	6	30	2.1	0.07	Y	RPs	LC-MS (P)
Molinate	Herbicide	404	7	5	4.3	0.86	Y	RPs	GC-MS
Oxine-copper	Fungicide	350	6	30	0.6	0.02	Y	RPs	LC-MS (P)
Pencycuron	Fungicide	405	6	100	1	0.01	Y	RPs	GC-MS
Phenthoate	Insecticide	377	6	7	0.49	0.07	Y	RPs	GC-MS
Pretilachlor	Herbicide	438	6	50	1.5	0.03	Y	RPs	GC-MS
Probenazole	Fungicide	417	5	50	19.5	0.39	Y	RPs	LC-MS (P)
Pyributicarb	Herbicide	385	6	20	0.6	0.03	Y	RPs	GC-MS
Pyroquilon	Fungicide	410	6	40	7.2	0.18	Y	RPs	GC-MS
Simazine	Herbicide	389	6	3	0.15	0.05	Y	RPs	GC-MS
Simetryn	Herbicide	403	7	30	1.5	0.05	Y	RPs	GC-MS
Thiram	Fungicide	386	6	20	4.2	0.21	Y	RPs	LC-MS (P)
Trichlorphon	Insecticide	379	6	5	0.35	0.07	Y	RPs	GC-MS
Triclopyr	Herbicide	357	6	6	0.12	0.02	Y	RPs	GC-MS
Benomyl [d]	Fungicide	383	5	20	N.D.	N.D.	Y	RPs	LC-MS (P)
Bethrodine	Herbicide	347	6	10	N.D.	N.D.	Y	RPs	GC-MS
Butamifos	Herbicide	372	6	20	N.D.	N.D.	Y	RPs	GC-MS
Carbaryl	Insecticide	364	6	50	N.D.	N.D.	Y	RPs	LC-MS (P)
Chlorothalonil	Fungicide	451	6	50	N.D.	N.D.	Y	RPs	GC-MS
Dithiopyr	Herbicide	351	6	9	N.D.	N.D.	Y	RPs	GC-MS
Edifenphos	Fungicide	364	6	6	N.D.	N.D.	Y	RPs	GC-MS
Etridiazole	Fungicide	346	6	4	N.D.	N.D.	Y	RPs	GC-MS
Fthalide	Fungicide	432	6	100	N.D.	N.D.	Y	RPs	GC-MS
Isoprocarb	Insecticide	335	6	10	N.D.	N.D.	Y	RPs	GC-MS
Mecoprop	Herbicide	371	6	50	N.D.	N.D.	Y	RPs	LC-MS (N)
Napropamide	Herbicide	343	6	30	N.D.	N.D.	Y	RPs	GC-MS
Propiconazol	Fungicide	354	6	50	N.D.	N.D.	Y	RPs	GC-MS
Trifluralin	Herbicide	392	7	60	N.D.	N.D.	Y	RPs	GC-MS
Anilofos	Herbicide	327	6	3	0.57	0.19	Y	OTH	GC-MS
Captan	Fungicide	399	6	300	75	0.25	Y	OTH	GC-MS
Chlornitrofen	Herbicide	327	6	0.1	0.06	0.60	Y	OTH	GC-MS
Dalapon	Herbicide	298	5	80	12	0.15	Y	OTH	LC-MS (N)
Endosulfan	Insecticide	328	6	10	0.3	0.03	Y	OTH	GC-MS
Isofenphos	Insecticide	341	6	1	0.05	0.05	Y	OTH	GC-MS
Piperophos	Herbicide	321	6	0.9	0.06	0.07	Y	OTH	GC-MS
Procymidon	Fungicide	352	6	90	0.9	0.01	Y	OTH	GC-MS

Name of pesticide	Use	Number of water supply authorities monitoring this pesticide	Number of examinations per authority per year [a]	GV [b] (μg/L)	Maximum DV (μg/L)	mDI [c]	Included in the old Primary List	Selected based on risk predictors (RPs)/or for other reasons (OTH)	Examination methods
Pyridaphenthion	Insecticide	342	6	2	0.64	0.32	Y	OTH	GC-MS
Tricyclazole	Fungicide	382	6	80	2.4	0.03	Y	OTH	LC-MS (P)
Carpropamid	Fungicide	338	6	40	N.D.	N.D.	Y	OTH	LC-MS (P)
Dimepiperate	Herbicide	332	6	3	N.D.	N.D.	Y	OTH	GC-MS
Dimethoate	Insecticide	368	6	50	N.D.	N.D.	Y	OTH	GC-MS
Dymron	Herbicide	415	6	800	N.D.	N.D.	Y	OTH	LC-MS (P)
Etofenprox	Insecticide	450	6	80	N.D.	N.D.	Y	OTH	GC-MS
Isoprothiolane	Fungicide	416	6	300	N.D.	N.D.	Y	OTH	GC-MS
Mepronil	Fungicide	396	6	100	N.D.	N.D.	Y	OTH	GC-MS
Metalaxyl	Fungicide	422	6	60	N.D.	N.D.	Y	OTH	GC-MS
Methyldymron	Herbicide	343	6	30	N.D.	N.D.	Y	OTH	GC-MS
Pendimethalin	Herbicide	407	6	300	N.D.	N.D.	Y	OTH	GC-MS
Propyzamide	Herbicide	371	6	50	N.D.	N.D.	Y	OTH	GC-MS
Terbucarb	Herbicide	332	6	20	N.D.	N.D.	Y	OTH	GC-MS
Thiodicarb	Insecticide	343	6	80	N.D.	N.D.	Y	OTH	LC-MS (P)
Thiophanate methyl	Fungicide	396	6	300	N.D.	N.D.	Y	OTH	LC-MS (P)
Benfuresate	Herbicide	232	7	70	0.7	0.01	N	RPs	GC-MS
Benzofenap	Herbicide	223	6	4	0.2	0.05	N	RPs	LC-MS (P)
Butachlor	Herbicide	244	7	30	2.1	0.07	N	RPs	GC-MS
Cadusafos	Insecticide	230	6	0.6	0.02	0.04	N	RPs	GC-MS
Clomeprop	Herbicide	250	6	20	5.0	0.25	N	RPs	LC-MS (P)
Cyanazine	Herbicide	232	7	4	0.28	0.07	N	RPs	GC-MS
Fentrazamide	Herbicide	237	6	10	1.0	0.10	N	RPs	LC-MS (P)
Ferimzone	Fungicide	136	4	50	3.0	0.06	N	RPs	LC-MS (P)
Fluazinam	Fungicide	221	6	30	0.6	0.02	N	RPs	LC-MS (N)
Fosthiazate	Insecticide	229	7	3	0.03	0.01	N	RPs	GC-MS
MCP	Herbicide	229	6	5	0.45	0.09	N	RPs	LC-MS (N)
Metominostrobin	Fungicide	247	7	40	3.2	0.08	N	RPs	GC-MS
Orysastrobin	Fungicide	248	7	100	2	0.02	N	RPs	GC-MS
Oxaziclomefone	Herbicide	255	6	20	1.0	0.05	N	RPs	LC-MS (P)
Pyrazoxyfen	Herbicide	210	6	4	0.04	0.01	N	RPs	GC-MS
Quinoclamine	Herbicide	234	7	5	0.2	0.04	N	RPs	GC-MS
Amitraz	Insecticide	207	5	6	N.D.	N.D.	N	RPs	LC-MS (P)
Carbam sodium	Insecticide	117	4	10	N.D.	N.D.	N	RPs	GC-MS
Cyanophos	Insecticide	225	7	3	N.D.	N.D.	N	RPs	GC-MS
Cyhalofop butyl	Herbicide	251	6	6	N.D.	N.D.	N	RPs	GC-MS
Dazomet	Fungicide	127	4	6	N.D.	N.D.	N	RPs	GC-MS
Dithianon	Fungicide	119	4	30	N.D.	N.D.	N	RPs	LC-MS
Glufosinate	Herbicide	152	4	20	N.D.	N.D.	N	RPs	LC-MS
Metribuzin	Herbicide	229	7	30	N.D.	N.D.	N	RPs	GC-MS
Paraquat	Herbicide	134	4	5	N.D.	N.D.	N	RPs	LC-MS
Prothiofos	Insecticide	128	4	4	N.D.	N.D.	N	RPs	GC-MS
Pyrazolynate	Herbicide	225	6	20	N.D.	N.D.	N	RPs	LC-MS (P)
Benzobicyclon	Herbicide	240	5	90	4.5	0.05	N	OTH	LC-MS (P)
Cumyluron	Herbicide	231	7	30	1.2	0.04	N	OTH	GC-MS
Indanofan	Herbicide	230	7	9	0.09	0.01	N	OTH	GC-MS
Pyraclonil	Herbicide	144	4	10	0.8	0.08	N	OTH	LC-MS (P)
Tiadinil	Fungicide	223	6	100	1	0.01	N	OTH	LC-MS (N)
Cartap	Insecticide	132	4	300	N.D.	N.D.	N	OTH	LC-MS (P)

a Number of pesticide examinations per year per water supply utility.

b Guideline Value.

c maximum DVi/ GVi values for raw water. N.D. denotes no detection.

d Benomyl, the active ingredient, was determined to be undetectable because the metabolite was measured instead of the active ingredient.

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. The JDWQG uses the concept of a hazard index, known as the *DI* value, for the purpose of assessing the total risk associated with exposure to multiple pesticides. 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 from the acceptable daily intake 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. Although JDWQG is a guideline for drinking water, many water supply authorities also measure pesticides in raw water to determine the presence of pesticides in water sources and the necessity of water treatment operations such as injection of powdered activated carbon.

Table S2 Detection rate in each region.

Region	Regional area (km^2)	Monitored pesticides	Detected pesticides
Hokkaido	78,421	120	11
Tohoku	66,927	120	30
Kanto	36,891	120	51
Hokuriku	34,579	120	21
Tokai	29,344	120	11
Kinki	31,533	120	37
Chugoku	31,921	120	19
Shikoku	18,806	120	6
Kyushu	42,192	120	32

Table S3 Overlap detection rate (%) between regions. The vertical axis represents the denominator, and the horizontal axis represents the numerator.

Region	Pesticides detected		A	B	C	D	E	F	G	H	I	Avg.
Hokkaido	11	A		36	45	45	0	55	36	9	55	35
Tohoku	30	B	13		80	37	27	60	53	13	57	43
Kanto	51	C	10	47		27	16	49	35	10	43	30
Hokuriku	21	D	24	52	67		29	62	38	19	48	42
Tokai	11	E	0	73	73	55		64	55	27	45	49
Kinki	37	F	16	49	68	35	19		41	11	51	36
Chugoku	19	G	21	84	95	42	32	79		26	58	55
Shikoku	6	H	17	67	83	67	50	67	83		67	63
Kyushu	32	I	19	53	69	31	16	59	34	13		37

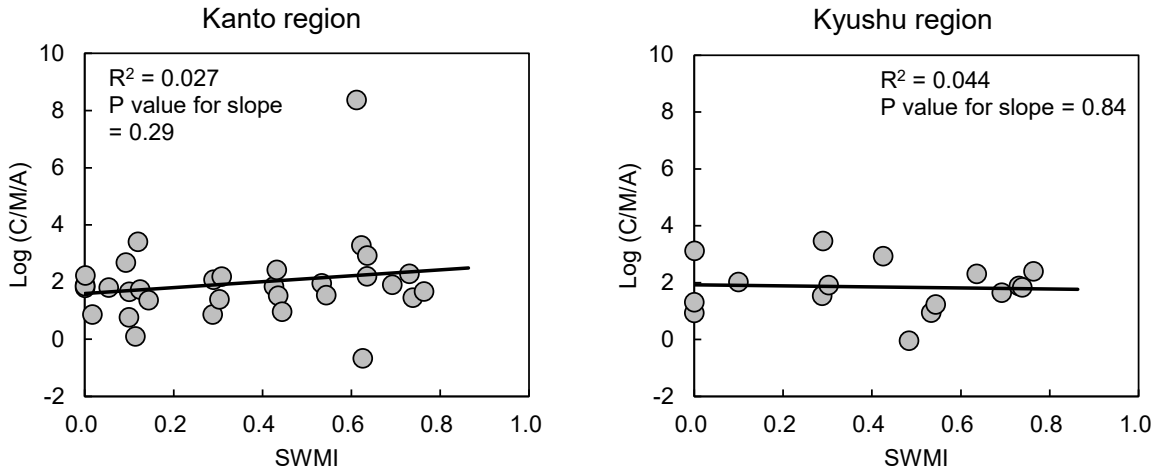

Fig. S1 Plots of relative pesticide concentrations against SWMI values (Kanto and Kyushu regions are shown as examples).

The SWMI values were obtained according to the following equation (Chen et al., 2002):

$$SWMI = \mathrm{EXP}\left(-\frac{3.466}{HLS}\right) \cdot \left[\frac{(1 + 0.00026 \cdot K_{OC})}{(1 + 0.00348 \cdot K_{OC})}\right] \quad (2)$$

where K_{oc} is soil adsorption coefficient normalized by the organic-carbon content (L/kg), and *HLS* is half-lives in soil (d).

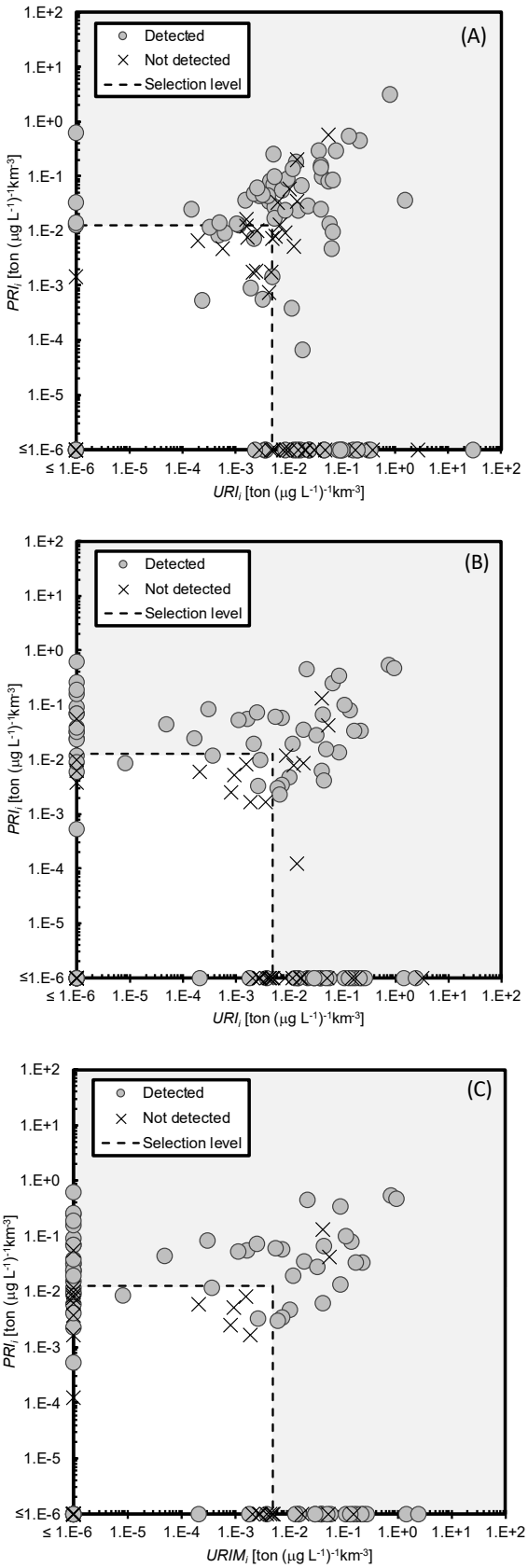

Fig. S2 Scatter plot of PRI_i versus URI_i ($URIM_i$) for the 2013 Primary List pesticides. (A) The old risk predictors (average pesticide sales quantity for 2007–2010). (B) Pesticide sales quantity updated to 2013–2015. (C) Pesticide sales quantity for 2013–2015 combined with the new risk predictor for upland-field pesticides, $URIM_i$.

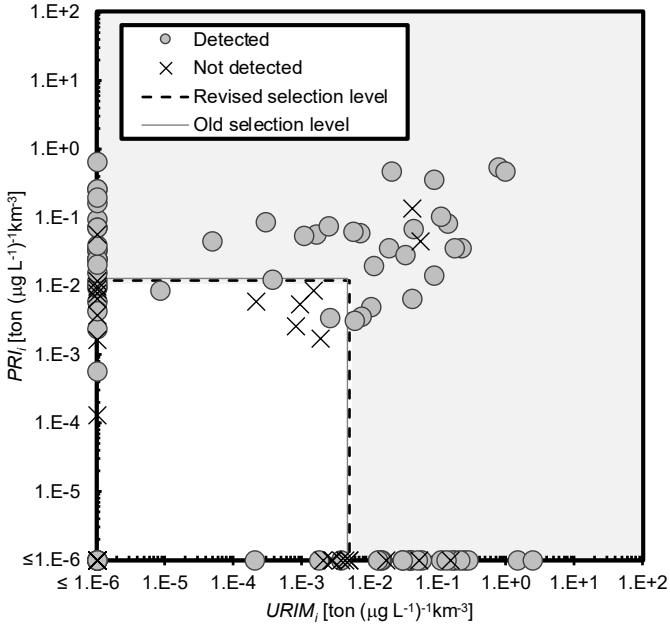

Fig. S3 Setting of the new selection level for the new risk predictor.

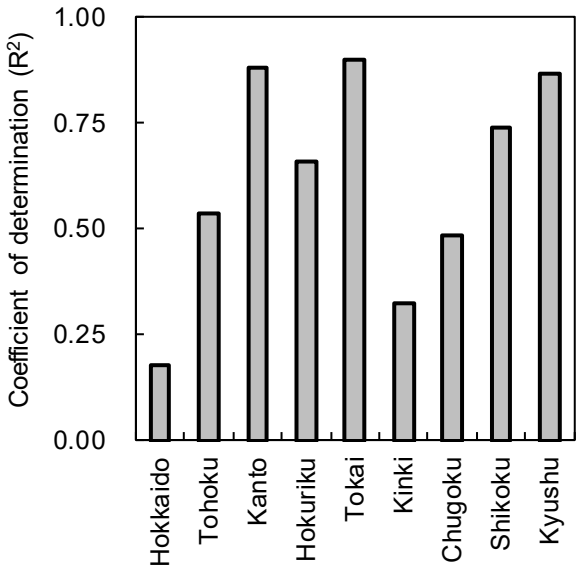

Fig. S4 Coefficient of determination (R^2) between national and regional pesticide sales quantities in Japan. R^2 values were determined for the regression lines with an intercept of zero.

Use	Name	Hokkai-do	To-hoku	Kanto	Hoku-riku	Tokai	Kinki	Chu-goku	Shi-koku	Kyu-shu	#
Herbicide	Dalapon									■	1
	2,4-PA			■							1
	MCP			■	■		■			■	4
	Asulam						■				1
	Atrazine	■			■						2
	Anilofos			■							1
	Alachlor			■							1
	Indanofan						■			■	2
	Esprocarb			■	■						2
	Oxaziclomefone			■		■				■	3
	Cafenstrole		■	■	■	■	■	■	■	■	8
	Quinoclamine		■	■			■			■	4
	Cumyluron	■		■			■				3
	Glyphosate			■							1
	Glufosinate										0
	Clomeprop		■								1
	Chlornitrofen					■					1
	Cyanazine		■	■		■	■	■			5
	Diuron	■									1
	Dichlobenil	■								■	2
	Diquat monohydrate							■	■		2
	Dithiopyr										0
	Cyhalofop butyl										0
	Simazine			■			■			■	3
	Dimethametryn		■	■			■	■			4
	Simetryn		■	■							2
	Dimepiperate										0
	Dymron										0
	Benthiocarb			■				■		■	3
	Terbucarb										0
	Triclopyr			■	■						2
	Trifluralin										0
	Napropamide										0
	Paraquat										0
	Piperophos						■				1
	Pyraclonil		■	■			■	■		■	5
	Pyrazoxyfen		■							■	2
	pyrazolynate										0
	Pyributicarb									■	1
	Fentrazamide		■	■	■	■				■	5
	Butachlor		■	■	■		■	■		■	6
	Butamifos										0
	Pretilachlor	■	■	■			■	■		■	6
	Propyzamide										0
	Bromobutide		■	■	■	■	■	■	■	■	8
	Benzobicyclon			■							1
	Benzofenap		■	■			■	■			4
	Bentazone		■	■		■		■			4
	Pendimethalin										0
	Bethrodine										0
	Benfuresate		■	■							2
	Mecoprop										0
	Methyldymron										0
	Metribuzin										0
	Mefenacet	■	■	■	■		■	■		■	7
	Molinate		■	■	■	■	■	■			6
Insect-fungicide	Dithiocarbamate peticides			■							1
Soil fumigant	1,3-Dichloropropene						■				1

Use	Name	Hokkai-do	To-hoku	Kanto	Hoku-riku	Tokai	Kinki	Chu-goku	Shi-koku	Kyu-shu	#
Insecticide	EPN				■		■				2
	Acephate			■			■				2
	Amitraz										0
	Isoxathion		■	■				■			3
	Isofenphos		■	■	■						3
	Isoprocarb										0
	Etofenprox										0
	Endosulfan						■				1
	Cadusafos		■	■						■	3
	Cartap										0
	Carbaryl										0
	Carbofuran		■	■			■	■		■	5
	Chlorpyriphos	■			■		■				3
	Cyanophos										0
	Dichlorvos			■							1
	Ethylthiometon			■							1
	Dimethoate										0
	Diazinon			■	■		■			■	4
	Thiodicarb										0
	Trichlorphon			■							1
	Pyridaphenthion				■						1
	Fipronil		■	■		■	■	■	■	■	8
	Fenitrothion	■	■	■	■		■	■	■	■	8
	Fenobucarb			■			■			■	3
	Fenthion			■			■	■			3
	Phenthoate			■							1
	Buprofezin		■				■			■	3
	Prothiofos										0
	Benfuracarb			■			■				2
	Fosthiazate						■				1
	Malathion				■						1
	Methomyl		■	■						■	3
	Carbam sodium										0
	Methidathion					■	■				2
Fungicide	Isoprothiolane										0
	Iprobenfos			■			■			■	3
	Iminoctadine-albesilate			■					■		2
	Edifenphos										0
	Etridiazole										0
	Oxine-copper			■							1
	Orysastrobin			■						■	2
	Carpropamid										0
	Captan				■						1
	Chlorothalonil										0
	Dithianon										0
	Dazomet										0
	Tiadinil						■			■	2
	Thiram		■	■			■				3
	Thiophanate methyl										0
	Tricyclazole		■							■	2
	Pyroquilon	■	■	■	■		■	■		■	7
	Ferimzone	■								■	2
	Fthalide										0
	Fluazinam			■							1
	Procymidon	■									1
	Propiconazol										0
	Probenazole		■								1
	Benomyl										0
	Pencycuron									■	1
	Metalaxyl										0
	Metominostrobin		■		■	■	■				4
	Mepronil										0

■ Detected ■ Undetected

Fig. S5 Detection of pesticides by region (2013–2015).

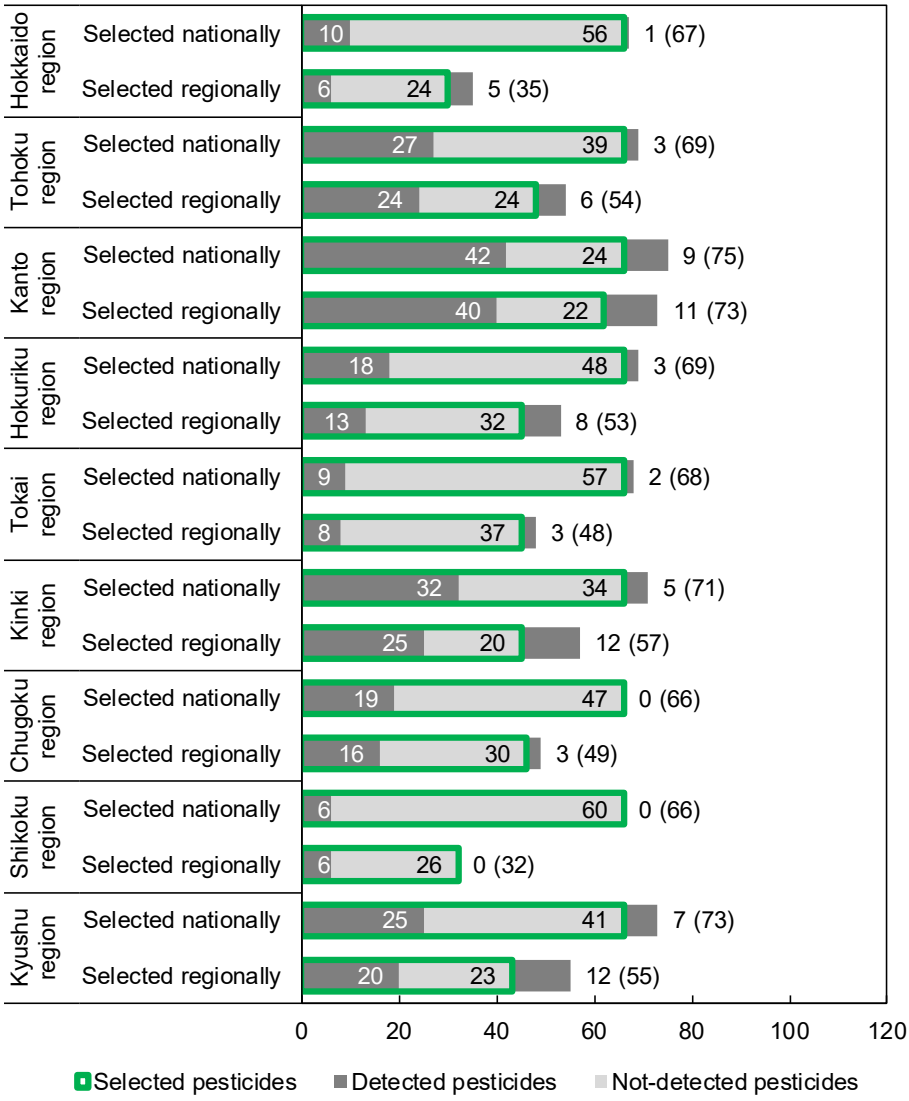

Fig. S6 Numbers of pesticides selected/not selected nationally/regionally and pesticides detected regionally. The numbers in parentheses indicate subtotals. Green boxes: pesticides selected using the risk predictors. Dark gray bars: detected pesticides. Dark gray bars in green boxes: pesticides that were both selected and detected. Light gray bars in green boxes: pesticides selected by the risk predictors but not detected. Dark gray bars with no borders: pesticides that were not selected but were detected.