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**National trends in pesticides in drinking water and water sources in Japan**

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1

2 **Highlights**

3

- 4
- Over 14,000 drinking and source water samples were tested for 162 pesticides.
  - 5
  - Bromobutide and bentazone were detected at  $> 0.1 \mu\text{g/L}$  in  $>30\%$  of samples.
  - 6
  - Tefuryltrione and dymron were detected at  $> 0.1 \mu\text{g/L}$  in  $>10\%$  of samples.
  - 7
  - Many of the frequently detected pesticides are used for paddy rice farming.
  - 8
  - Since the 1970s, use of herbicides with higher ADIs and lower *Kow* is increasing.

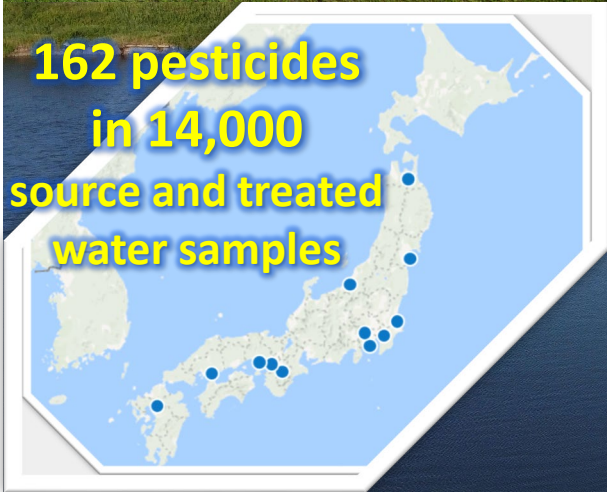
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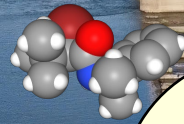
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**Rice-farming  
herbicides detected  
at high concentrations**

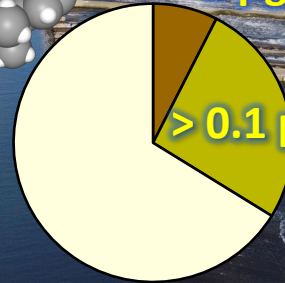
**162 pesticides  
in 14,000  
source and treated  
water samples**



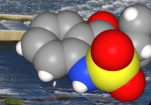
**Bromobutide**



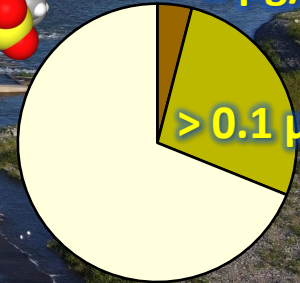
**> 1 µg/L**



**Bentazone**



**> 1 µg/L**



1 **Abstract**

2 Although agricultural activities—especially paddy rice cultivation—are prominent in watersheds in  
3 Asian countries, few comprehensive studies have examined pesticide concentrations in water in these  
4 areas. Here, we report the concentrations of 162 pesticides in treated drinking water and source water  
5 (14,076 samples) in Japan, where rice cultivation is common, along with trends in sales of herbicides,  
6 fungicides, and insecticides from 1963 to 2016. Herbicides and fungicides—especially those used in  
7 rice farming were frequently detected in drinking water sources.

8 The herbicide bromobutide, which is not listed in drinking water quality standards or guidelines except  
9 in Japan, as well as the widely used-and-detected bentazone, were frequently detected in source water  
10 (bromobutide and bentazone were detected at concentrations  $> 0.1 \mu\text{g/L}$  in 31.1% and 33.8% of  
11 samples, respectively). Dymron and tefuryltrione were also detected in over 10% of samples at  
12 concentrations  $> 0.1 \mu\text{g/L}$ . The highest observed concentration of bromobutide was  $10 \mu\text{g/L}$ , and 7.5%  
13 of samples had concentrations  $> 1 \mu\text{g/L}$ . High concentrations were also observed for halosulfuron  
14 methyl ( $7.9 \mu\text{g/L}$ ), pyroquilon (7.0), molinate (6.8), and metominostrobin (4.6). Some of the pesticides  
15 frequently detected in source water were not detected at all in drinking water, but the main cause of  
16 the non-detection appeared to be degradation by chlorine. From the 1970s onward, sales of herbicides  
17 and fungicides with higher acceptable daily intakes (ADIs; i.e., with lower toxicity) have increased.  
18 However, the percentage of herbicides with very low ADIs ( $< 10^{-2.5} \text{ mg kg}^{-1} \text{ d}^{-1}$ ) being shipped has  
19 also increased. Tefuryltrione, which was detected at normalized concentrations  $> 0.1$  in 8% of samples,  
20 is an example of this type of herbicide. The average  $\log\text{-}K_{ow}$  of herbicides has decreased from the  
21 1970s to the present, due to the strong trend towards the application of hydrophilic herbicides, such  
22 glyphosate. The need for increased monitoring of pesticides used in rice paddy farming is highlighted.

23

24

25 **Keywords:** pesticide concentration, occurrence, rice farming, ADI,  $K_{ow}$

26

27 **1. Introduction**

28 Globally, about 900 chemical substances are registered as pesticides, with sales of \$56 billion in 2012  
29 (USEPA, 2016). Approximately 50% of these are used as herbicides, followed by fumigants,  
30 insecticides, and fungicides (USEPA, 2003). However, there is concern about the environmental  
31 contamination from pesticide use, because their application involves release into the environment.  
32 Countries in East and Southeast Asia, including Japan, have warm or mild weather with heavy rainfall,  
33 and the pesticide quantities used per agricultural area are larger than those in the United States of  
34 America (USA) and in European countries. For example, the average pesticide application rate (by  
35 active ingredient) per cultivated area is 2.3 kg/ha in 28 EU countries and 2.4 kg/ha in the USA, whereas  
36 that in Japan is 14.8 kg/ha—about six times those in the EU and the USA (FAO, 2016). As paddy rice  
37 is commonly cultivated in East and Southeast Asia and pesticides applied to paddy fields can more  
38 easily leach into the surrounding environment than those applied to dry fields, pesticides may pose a  
39 great risk to the aquatic environment in East and Southeast Asia. In addition, many countries in East  
40 and Southeast Asia, such as Japan, depend on surface water as the major source of drinking water. The  
41 quality of source water for drinking water is strongly affected by pesticides in the environment.

42

43 To estimate the risks posed by pesticides in surface water, the amounts of pesticides used must be  
44 determined, and these should closely correspond to total sales quantities. Some countries report  
45 pesticide sales as part of national statistical data (USEPA, 2016) (eurostat, 2018). In the USA,  
46 concentrations of pesticides detected in each area, long-term changes, and relations to shipping  
47 amounts are reported by the U.S. Geological Survey National Water-Quality Assessment Program, for  
48 which Stone et al. (2014) have published an analysis. The most frequently detected pesticides included  
49 11 herbicides (including atrazine and its degradates, diethylatrazine, metolachlor, simazine, and  
50 prometon), four insecticides (including diazinon), and one fungicide (metalaxyl) (Stone et al., 2014).  
51 For pesticides primarily used for agriculture (cyanazine, alachlor, atrazine and its degradates,  
52 metolachlor, and carbofuran), concentration trends in major rivers show wide agreement with trends  
53 in usage in the connected basins (Ryberg and Gilliom, 2015). However, except in these counties, the

54 quantities used, the types of pesticides, and long-term trends are seldom reported, except in  
55 information on pesticide formulations themselves. In Japan, data are available on the sales volumes of  
56 commercial pesticide formulations by prefecture. Additionally, the contents of agricultural chemicals  
57 (active ingredients) in all pesticide formulations are publicly available through the Food and  
58 Agricultural Material Inspection Centre. However, these data have not been used to determine long-  
59 term trends in types of pesticide applications (Narita et al., 2014).

60

61 On the other hand, occurrence of pesticides in environmental water is reported in many countries. In  
62 France, and England and Wales, the pesticides detected most often are atrazine and two of its  
63 transformation products; although atrazine was withdrawn in 2003, they have been found in  
64 groundwater (Lopez et al., 2015; Manamsa et al., 2016). Atrazine, acetochlor, diazinon, prometryn,  
65 and terbutryn have been detected in the surface waters of rivers in Hungary at concentrations of  
66 approximately 0.1 to 1 µg/L (Maloschik et al., 2007). Pesticides frequently detected in Greece were  
67 the herbicides atrazine, simazine, alachlor, metolachlor and trifluralin, the insecticides diazinon and  
68 parathion methyl and the organochlorine pesticides lindane, endosulfan and aldrin (Konstantinou et  
69 al., 2006; Papadakis et al., 2015). In many cases, concentrations in surface waters were in the low parts  
70 per billion (ppb) range (Albuquerque et al., 2016; Konstantinou et al., 2006). Li and Jennings (2017)  
71 identified a total of 5,474 maximum contaminant levels (MCLs) for 415 different pesticides in  
72 drinking water in 103 nations and discussed the range of MCLs of the 25 most commonly regulated  
73 pesticides. Thus, many studies have been published on pesticide monitoring in areas with dry-field  
74 cropping.

75

76 However, few have been published for areas of paddy rice cultivation. Studies of persistent organic  
77 pollutants in surface waters in China examined only organochlorine insecticides (Han and Currell,  
78 2017; Li et al., 2015). Monitoring of four major rivers in Korea detected only two organophosphorus  
79 insecticides (Cho et al., 2014), but their target pesticides did not include herbicides commonly used  
80 for paddy rice cultivation. Qi et al. (2014) quantified 51 pesticides in the Yangtze River, but the water

81 was sampled only once at one location, and eight of the compounds were detected at very low  
82 concentrations (1 to 10 ng/L). An analysis of the trends in herbicide use for paddy rice farming in  
83 Japan (Hamamura, 2018) suggested that the pesticides associated with paddy rice cultivation differ  
84 from those detected in the USA and European countries. Narushima et al. (2014) reported the detection  
85 of pesticides in drinking water and its source water in Niigata prefecture in Japan, an area with a high  
86 level of paddy rice cultivation. The pesticides detected differed according to the weather conditions  
87 and seasons, but most were herbicides—especially those used in paddy rice cultivation. Therefore, the  
88 risk of effluence of pesticides from paddy fields into rivers is probably higher than that of dry-field  
89 pesticides. To summarize the above, little information is available about the quantity and trends in use,  
90 or about detected concentrations, particularly in East and Southeast Asian countries where paddy rice  
91 cultivation is common.

92

93 Based on the above, we set the research objectives as follows: these are to identify 1) pesticides with  
94 high concentrations and frequency of detection from the nation-wide occurrence results of pesticide  
95 (herbicides, fungicides, and insecticides) monitoring in Japan, where pesticides have been used for  
96 long periods and 2) the trends in sales and physical properties of pesticides used in Japan, where  
97 statistical data are available.

98

## 99 **2. Materials and methods**

100

### 101 **2.1 Detection of pesticides in water supplies**

102

103 Monitoring of the 162 pesticides was conducted by the 12 main water supply utilities in Japan (Figure  
104 1S, Supplementary Information, SI) from 2012 to 2017. The study period was from April to October  
105 each year. At most facilities, monitoring was performed once per month, but five facilities conducted  
106 monitoring weekly in May and June. Pesticides are detected in river water, but rarely in groundwater  
107 (Asami et al., 2020). Thus, the research areas were rivers supplying source water for water treatment

108 plants, together with their upstream areas (hereinafter referred to collectively as source water), and  
109 water treated in treatment plants (hereinafter referred to as treated water). The target pesticides,  
110 measurement season, measurement time, and water treatment process at each water supply utility are  
111 summarized in Table 1S (SI). All analyses were conducted under strict accuracy control according to  
112 the official analytical methods (MHLWJ, 2003). Because the water supply utilities do not all use the  
113 same analytical instruments, measurement methods were not identical across facilities for each  
114 pesticide. Therefore, LOQ (limit of quantification) was not the same for every pesticide. Although  
115 uniform measurement accuracy is desirable, we could not achieve this in the national survey. However,  
116 the minimum required measurement accuracy was 1% of the guideline value, and the accuracy of all  
117 examinations exceeded this value. The analytical methods are summarized in Table 2S (SI).

118

## 119 **2.2 Physical properties and sales of pesticides**

120

121 To understand trends in sales of pesticides, historical data were analyzed. Data for commercially  
122 formulated pesticide products were obtained from the directory of pesticides (JPPA, 1963-2013),  
123 which contains detailed information on domestic sales of formulated pesticides. Data were compiled  
124 for the amount of each active ingredient in commercially formulated pesticide products and by year  
125 from 1963 to 2016. The active ingredients of pesticides were categorized as herbicides, insecticides,  
126 or fungicides. We used the octanol-water partition coefficient ( $K_{ow}$ ) and acceptable daily intake (ADI)  
127 to characterize pesticides. Log  $K_{ow}$ , which is a hydrophobicity parameter that affects the movement  
128 of a pesticide in soil, was determined by using the Estimation Programs Interface Suite (USEPA, 2018).  
129 ADI is a strong index of the toxicity of pesticides, with smaller values indicating greater toxicity. The  
130 ADI values in the database of the National Institute of Health Science were used (NIHS, 2018). These  
131 data were used to determine trends in sales quantities of pesticides classified according to log  $K_{ow}$   
132 and ADI.

133

## 134 **3. Results and discussion**

135

### 136 **3.1 Detected concentrations of pesticides**

137

138 A total of 14,076 samples were tested during the 6-year sampling period, with an average of 2,346  
139 measurements per pesticide and an average of 400 measurements per pesticide per year. Of the 162  
140 pesticides monitored, 31 were frequently detected (>100 times); the number of tests conducted for  
141 each of these pesticides during the investigation period ranged from 634 to 3,095. The concentrations  
142 of the 31 pesticides frequently detected in source waters are shown in Fig. 1. Two herbicides  
143 (bentazone and bromobutide) were detected >1,000 times in source waters. The detection rates of these  
144 two herbicides exceeded 40%, with bentazone at 52% (1,468 detections per 2,830 measurements) and  
145 bromobutide at 41% (1,280 per 3,095).

146 Fifteen pesticides had maximum detected concentrations of  $\geq 1 \mu\text{g/L}$  (Fig.1). In particular, 7 pesticides  
147 were detected at high concentrations (>3  $\mu\text{g/L}$ ): four herbicides (bromobutide 10  $\mu\text{g/L}$ , halosulfuron  
148 methyl 7.9  $\mu\text{g/L}$ , molinate 6.8, and bentazone 4.1  $\mu\text{g/L}$ ), two fungicides (pyroquilon 7.0  $\mu\text{g/L}$  and  
149 metominostrobin 4.6  $\mu\text{g/L}$ ), and one insecticide (dinotefuran 3.7  $\mu\text{g/L}$ ). All of these pesticides are  
150 commonly used in paddy rice cultivation. According to the data of Narita et al. (2014), the ratio of  
151 paddy-field application to overall application was molinate 100%, bentazone 100%, metominostrobin  
152 100%, bromobutide 76%, dinotefuran 72% halosulfuron methyl 65%, and pyroquilon 61%. Molinate,  
153 bentazone, and metominostrobin are applied mostly in paddy rice cultivation in Japan. For the other  
154 pesticides, more than 50% are used in paddy fields. For the 5 pesticides (bromobutide, halosulfuron  
155 methyl, pyroquilon, metominostrobin, and dinotefuran) among these 7 pesticides, no drinking water  
156 quality standards or guidelines are provided by the WHO (World Health Organization) or in countries  
157 other than Japan (see Table 2S, SI, for their guideline values of Japan).

158

159 Figure 2 shows the concentrations in treated water of the 31 pesticides that were frequently detected  
160 in source water. Twenty-one of these pesticides were also detected in treated water. Bentazone and  
161 bromobutide were detected at especially high frequencies, in treated water. Bromobutide (2.7  $\mu\text{g/L}$ ),

162 bentazone (2.2 µg/L), dinotefuran (2.2 µg/L), metominostrobin (4.6 µg/L) and pyroquilon (1.1 µg/L)  
163 were detected at high concentrations in treated water. Although the concentrations are all below the  
164 WHO and Japanese guideline values, the maximum detected concentrations of 16 pesticides including  
165 bromobutide-debromo (a decomposition product of bromobutide) exceeded 0.1 µg/L, which is the EU  
166 standard for individual chemicals.

167

168 Eight of the 31 pesticides were not detected in treated water, although they were frequently detected  
169 in source water. Seven of these 8 pesticides (molinate, simetryn, tefuryltrione, fipronil, fenitrothion,  
170 bensulfuron methyl, and halosulfuron methyl) are decomposed by chlorine treatment, as outlined  
171 below. Molinate decomposes to ketomolinate and molinate sulfoxide (Imai and Kuwatsuka, 1984).  
172 Simetryn is decomposed by chlorine treatment (Watanabe et al., 2007b). Tefuryltrione decomposes to  
173 form 2-chloro-4-(methylsulfonyl)-3-[(tetrahydrofuran-2-ylmethoxy) methyl] benzoic acid (CMTBA)  
174 upon chlorine treatment, at a high conversion rate, and CMTBA was frequently detected in treated  
175 water and tap water. (Kamata et al., 2017). Fipronil yields its sulfone or additional forms in chlorine  
176 treatment (Teerlink et al., 2017). Fenitrothion is transformed into its oxon form and other fragments  
177 by chlorine treatment (Takanashi et al., 2012). Chlorine treatment also decomposes bensulfuron  
178 methyl (Hu et al., 2015) and halosulfuron methyl (Wang et al., 2015). Therefore, these seven pesticides  
179 may not have been detected here because they were transformed into other compounds by chlorine  
180 treatment. Because of the unknown toxicity of the transformed compounds, no detection of these  
181 pesticides in treated water does not necessarily mean the reduction of risk. However, toxicity  
182 evaluation and monitoring have been insufficient to date in Japan. No information was available for  
183 the remaining pesticide (esprocarb) to determine their behavior during the treatment process.

184

### 185 **3.2 Frequency of detection**

186

187 The cumulative frequency distributions of the concentrations of the 31 frequently detected pesticides  
188 (16 herbicides, 9 fungicides, and 6 insecticides) are shown in Figures 3, 4, and 5. Bentazone,

189 bromobutide, and tefuryltrione were detected in >30% of source water samples, and the concentrations  
190 of these pesticides were higher than those of other pesticides. The percentages of samples with a  
191 concentration > 1, 0.1 and > 0.01 µg/L (percentages in excess of 1, 0.1 and 0.01 µg/L) as well as the  
192 overall detection rates and log *Kow* values, are summarized in Table 1. Below, in Sections 3.2.1 to  
193 3.2.3, we discuss the detection ratios and concentrations for herbicides, fungicides, and insecticides.

194

### 195 **3.2.1 Herbicides**

196 Among the 16 herbicides, bentazone and bromobutide had higher cumulative frequency distributions  
197 than other herbicides (Fig. 3). For bromobutide, the percentage in excess of 1 µg/L was 7.5%. The  
198 percentage in excess of 0.1 µg/L was >10% for bentazone, bromobutide, tefuryltrione, and dymron.  
199 The percentages in excess of 0.1 µg/L were very high for bentazone (33.8%) and bromobutide (31.1%).  
200 In Japan, these four pesticides are mostly applied in rice farming, confirming the high risk of detection  
201 of excessive residues of rice-farming pesticides (Luo et al., 2011; Watanabe et al., 2007a). The ratio  
202 of paddy-field application to overall application was 100% for bentazone, 76% for bromobutide, 100%  
203 for tefuryltrione, and 85% for dymron. Measurement of herbicide concentrations in river waters in  
204 small catchment areas found high runoff ratios of bromobutide and dymron, at 25%–31% and 26%–  
205 37%, respectively (Kawasaki et al., 2008; Morohashi et al., 2012; Sudo and Kawachi, 2006), which is  
206 consistent with the high frequency of detection of paddy pesticides of our study. Bentazone is famous  
207 for its occurrence in groundwater at very high concentrations up to 120 µg/L owing to its high mobility,  
208 and high concentrations were also reported in river waters (WHO, 2016). The WHO provides a health-  
209 based value for bentazone in drinking water, but the other three abovementioned pesticides  
210 (bromobutide, tefuryltrione, and dymron) have no drinking water quality standards or guidelines,  
211 except in Japan. These three herbicides are not monitored in other Asian countries, where paddy rice  
212 farming is common. The 15 herbicides that were frequently detected in source waters (Fig. 3) all had  
213 log *Kow* values ≤ 4 except esprocarb, which has less solubility in water than the other herbicides (Table  
214 1). However, the correlation between log *Kow* and the percentage in excess of 0.1 µg/L was weak (Fig.  
215 2S, SI). Further research on the amount, purpose, and timing of pesticide application is needed.

216

### 217 **3.2.2 Fungicides and insecticides**

218

219 Among the nine fungicides, isoprothiolane and iprobenfos showed percentages in excess of 1 µg/L of  
220 >1% (Figs. 4 and 5, and Table 1). Isoprothiolane, iprobenfos, and metominostrobin showed relatively  
221 high percentage in excess of > 0.1 µg/L (8.2%, 7.5%, and 4.4%, respectively). These compounds are  
222 primarily used for rice farming, with the high ratio of paddy-field application to overall application:  
223 97%, 100%, and 100% for isoprothiolane, iprobenfos, and metominostrobin, respectively.

224

225 Among the insecticides, dinotefuran and imidaclopride showed high percentages in excess of 0.1 µg/L:  
226 these were 3.9% and 3.3%, respectively. Dinotefuran is primarily used for rice farming (72%), and  
227 62% of imidaclopride was applied for rice farming. Both have recently attracted much attention as a  
228 neonicotinoid pesticide and have been measured in Asia (Hladik et al., 2018; Lamers et al., 2011; Lu  
229 et al., 2020; Yi et al., 2019; Zhang et al., 2020; Zhang et al., 2019).

230

### 231 **3.2.3 Comparison of herbicides, fungicides, and insecticides**

232

233 Herbicides had the highest detection percentages and detected concentrations, followed by fungicides,  
234 whereas those for insecticides were lowest: the percentages in excess of 0.1 µg/L were >1% for 14  
235 herbicides, 7 fungicides, and 3 insecticides. Among pesticides with percentages in excess of 1 µg/L,  
236 herbicides exhibited the highest frequency of detection, followed by fungicides.

237

238 The high concentrations and excess percentages of herbicides and fungicides may be related to the  
239 quantity, objective, period, and method of their application. Total annual application quantity was large  
240 for herbicides and fungicides, and substantially lower for insecticides (Fig. 7), as discussed in Section  
241 3.3. As described in Section 3.3.2, herbicides and fungicides are generally more hydrophilic than  
242 insecticides, as indicated by their log *K<sub>ow</sub>* values, suggesting a greater tendency to reach aquatic

243 environments. It should be noted, however, that log  $K_{ow}$  is not the sole determinant of detection  
244 frequency, as noted in Section 3.2.1. Twelve out of the 14 herbicides and 5 out of the 7 fungicides are  
245 applied only in rice farming, whereas the remaining 2 herbicides and 2 fungicides are applied in both  
246 rice farming and dryland farming. In rice farming, herbicides and fungicides are applied directly to  
247 paddy fields when the fields are full of water. Generally, insecticides are applied only when the water  
248 level in rice fields is low, or occasionally during a pest outbreak. Therefore, we concluded that  
249 herbicides and fungicides were detected more frequently and at higher concentrations than insecticides  
250 because they are used in large quantities, are applied when the field is covered with ponded water that  
251 can easily overflow or leach into river water, and are more hydrophilic (Deknock et al., 2019; Wagner  
252 et al., 2019; Watanabe et al., 2007a).

253

#### 254 **3.2.4 Comparison between source water and treated water**

255

256 Concentrations of pesticides in source water and treated water were compared by using cumulative  
257 distributions. We selected bentazone, bromobutide, and pyroquilonone for this analysis because they  
258 were detected at high levels in terms of both concentration and frequency. The results are shown in  
259 Figure 6. The percentage in excess of 0.01- $\mu\text{g/L}$  for bentazone was 51% in source water and 24% in  
260 treated water. That for bromobutide was 41% in source water and 20% in treated water, and that for  
261 pyroquilonone was 20% in source water and 9% in treated water. These results show that, for each  
262 pesticide, the percentage in excess of 0.01- $\mu\text{g/L}$  in treated water was about half that in source water.  
263 Similarly, the percentage in excess of 0.1- $\mu\text{g/L}$  in treated water was about half that in source water.  
264 Although it is unclear which treated water samples were made from which source water, these data  
265 suggest that the removal rates of bentazone, bromobutide, and pyroquilonone in water treatment plants  
266 were not high.

267

#### 268 **3.2.5 Normalized concentrations**

269

270 Normalized concentration (NC), which is the concentration divided by the guideline value of each  
271 pesticide, is used in place of the absolute concentration value to depict the cumulative distribution of  
272 a pesticide. We used the guideline values in the Japanese Drinking Water Quality regulations, because  
273 these are the only standards that cover all 31 frequently detected pesticides. The guideline values are  
274 derived from the conversion of ADI to drinking water concentration using 50 kg as body weight, 2 L  
275 as drinking water volume per day, and 10% as an allocation factor; an  $NC < 1$  indicates that the  
276 concentration does not exceed the guideline value. Cumulative distributions for normalized  
277 concentrations of herbicides in source water are shown in Figure 3S (SI). Except in the case of molinate,  
278 NC did not exceed 1. Only tefuryltrione, molinate, and carbofuran had NC values  $> 0.1$ ; the pesticide  
279 with the highest NC value was molinate, followed by tefuryltrione. Tefuryltrione had the highest  
280 percentage in excess of NC 0.1: 8% of its total measurements had an  $NC > 0.1$ . Twelve herbicides had  
281 NC values  $> 0.01$ , and among these, tefuryltrione was again present at the highest percentage in excess  
282 of NC 0.1 (27%), followed by bromobutide (8%) and molinate (6%). The herbicides, fungicides, and  
283 insecticides with  $NC > 0.01$  in source water are summarized in Table 2. Eighteen pesticides are listed,  
284 and most (12) are herbicides. Eight pesticides had an  $NC > 0.1$ . These pesticides had low guideline  
285 values ( $\leq 40 \mu\text{g/L}$ ), which means low ADI values, except bromobutide. No pesticides with  $NC > 0.1$   
286 were detected in treated water. Of the 11 pesticides detected frequently in source water (dymron,  
287 bensulfuron methyl, diuron, isoprothiolane, tricyclazole, oryastrobin, flutolanil, carpropamid,  
288 imidacloprid, dinotefuran, and clothianidin) none had an  $NC > 0.01$  (e.g., clothianidin had  $NCs \leq$   
289  $0.001$ ). Therefore, these pesticides may not be high priority for frequent monitoring in drinking water  
290 sources, even though their detection rates were high.

291

### 292 **3.3 Sales of pesticides**

293

294 Analysis of data from 1963 to 2016 showed that the sales quantity of pesticides (based on active  
295 ingredients excluding inorganic components and oil) in Japan continuously increased until 1986,  
296 reaching a maximum of 70,000 t. After 1986, sales of pesticides decreased over the following 20 years,

297 owing to the large decrease in sales quantity of insecticides (Fig. 7). Since the 1990s, sales quantities  
298 of herbicides and fungicides have both been much larger than that of insecticides. Herbicides,  
299 fungicides, and insecticides accounted for 50%, 40%, and 10%, by mass, respectively, of the total sales  
300 quantity as of 2016. Sales quantity was largest for herbicides, followed by fungicides, and smallest for  
301 insecticides (Fig. 7). To date, approximately 600 active ingredients are registered as pesticides, and  
302 approximately 4,500 commercial products are available; these numbers are still gradually increasing  
303 (data not shown).

304

### 305 **3.3.1 Pesticide sales quantities by ADI**

306

307 Since 1963, a total of 922 active ingredients of pesticides have been applied in Japan, and ADI  
308 information is available for 290 of these. We calculated changes in sales quantity according to ADI  
309 values for the pesticides with known ADI values (Fig. 6S, SI). Figure 8 shows the results for  
310 herbicides, fungicide, and insecticides, respectively, along with changes in the percentage of pesticides  
311 with known ADI values

312

313 ADI values are available for half of the herbicides used before the mid-1970s [Fig. 8(A)]. ADI values  
314 are available for most (> 90%) herbicides applied after 1990. The percentage of herbicides with  
315 relatively low ADIs ( $10^{-2.0}$  to  $10^{-2.5}$  mg kg<sup>-1</sup> d<sup>-1</sup>), such as thiobencarb, decreased and the percentage of  
316 herbicides with high ADIs ( $> 10^{-0.5}$  mg kg<sup>-1</sup> d<sup>-1</sup>), such as glyphosate, increased strongly, accounting  
317 for 30% of the total as of 2016, causing the average ADI for all herbicides to increase (Fig. 7S, SI).

318 The arithmetic weighted mean ADI was about 30 times higher in 2016 than it was in the 1960s and  
319 1970s, indicating that the herbicides applied are becoming less toxic overall. However, since 2010, the  
320 sales percentage of herbicides with low ADIs ( $< 10^{-2.5}$  mg kg<sup>-1</sup> d<sup>-1</sup>) has remained almost constant at  
321 around 5%. Herbicides with very low ADIs ( $< 10^{-3.0}$  mg kg<sup>-1</sup> d<sup>-1</sup>), such as tefuryltrione, have emerged,  
322 although their percentage of the total herbicide sales remains very low (1% in 2016). Because it is  
323 difficult to develop active ingredients with high selectivity toward specific weeds, the need for such

324 pesticides with high toxicity (low ADI) remains. Tefuryltrione, with an ADI value of  $10^{-3.1}$  mg kg<sup>-1</sup> d<sup>-1</sup>  
325 (= 0.8 μg kg<sup>-1</sup> d<sup>-1</sup>), which was detected at normalized concentrations > 0.1 in 8% of samples, as  
326 described in the previous section, is an example of this type of herbicide.

327

328 ADI values are available for over 80% of the fungicides applied after 1970 [Fig. 8(B)]. The percentage  
329 of fungicides with ADI values from  $10^{-2}$  to  $10^{-3.5}$  mg kg<sup>-1</sup> d<sup>-1</sup>, such as chloropicrin and dazomet,  
330 increased beginning in the 1970s and leveled out in the 2000s. In contrast, the percentage of fungicides  
331 with higher ADI values ( $10^{-1}$  to  $10^{-2.0}$  mg kg<sup>-1</sup> d<sup>-1</sup>) was decreasing. The average ADI decreased for  
332 fungicides beginning in the mid-1980s (Fig. 8S, SI); before that, it was increasing, but it should be  
333 noted that the ADIs of many fungicides were unknown in that period, as shown in Fig. 8(B). For  
334 herbicides, the average ADI increased (Fig. 7S, SI). ADI values are available for > 80% of the  
335 insecticides in use at any point during the study period [Fig. 8(C)]. Until the mid-2000s, most of the  
336 insecticides had an ADI <  $10^{-2}$  mg kg<sup>-1</sup> d<sup>-1</sup>, and the ADI values of insecticides were generally lower  
337 than those of herbicides or fungicides. After the mid-2000s, however, the percentage of insecticides  
338 with ADI values >  $10^{-1.5}$  mg kg<sup>-1</sup> d<sup>-1</sup> increased, as did the average ADI (Fig. 9S, SI), indicating a trend  
339 towards the application of low-toxicity insecticides. As of 2016, the average ADI of herbicides is  
340 around one order of magnitude higher than those of fungicides or insecticides. For example, the  
341 arithmetic weighted means of the ADI values for herbicides, fungicides, and insecticides for 2016  
342 were 0.30, 0.022, and 0.038 mg kg<sup>-1</sup> d<sup>-1</sup>, respectively.

343

### 344 **3.3.2 Sales of pesticides by log *Kow***

345

346 Log *Kow* values are available for most of the pesticides that have been applied in Japan (Fig. 10S, SI).  
347 Changes in shipping rates are shown in Fig. 9 and 10S (SI) for herbicides, fungicides, insecticides,  
348 and all pesticides, respectively.

349

350 Until the 1980s most herbicides [Fig. 9(A)] were hydrophobic, with log *Kow* values > 2. After that,

351 the use of very hydrophobic pesticides with  $\log K_{ow} > 4$  [mostly CNP (chlornitrofen): its registration  
352 was expired in 1996] decreased, and the use of hydrophilic herbicides (mostly an ionicity herbicide,  
353 glyphosate) with  $\log K_{ow} < -2$  increased. The most commonly used pesticides with  $\log K_{ow} > 4$  are  
354 bromobutide and dymron. The pesticides with  $4 > \log K_{ow} > 2$  occupy majority ( $> 65\%$ ), and the  
355 representatives is 1,3-dichloropropene. The average  $\log K_{ow}$  was found to have declined significantly,  
356 from 3.5 to 0.5, in the last 50 years (Fig. 14) due to the decrease of CNP and the increase of glyphosate.

357

358 Before 1970, most fungicides [Fig. 9(B)] were hydrophobic, with  $\log K_{ow} > 2$ : a typical example of  
359 this is sodium pentachlorophenol-hydrate. However, the use of less hydrophobic fungicides with  $\log$   
360  $K_{ow}$  from 2 to 0 increased until 1980, and it still accounts for  $\sim 40\%$  of current fungicide use: most of  
361 these pesticides are dazomet and mancozeb of dithiocarbamate pesticides. Since 1980, the use of  
362 hydrophilic fungicides with  $\log K_{ow}$  from 0 to  $-2$  represented by chloropicrin has been increasing,  
363 suggesting increasing use of hydrophilic fungicides. On average, the  $\log K_{ow}$  values of fungicides are  
364 lower than those of insecticides, indicating that fungicides are more hydrophilic than insecticides.  
365 They were also lower than those of herbicides until 2005 (Fig. 10). After 2005, however, herbicides  
366 were more hydrophilic than fungicides, and insecticides were the least hydrophilic.

367

368 Most of the insecticides used in Japan have been hydrophobic, with  $\log K_{ow}$  from 4 to 0 [Fig. 9(C)],  
369 although the percentage of insecticides with  $\log K_{ow}$  from 4 to 2 decreased (60%) during the 1980s  
370 and the percentage of less hydrophobic substances increased. It should be noted that the percentages  
371 of hydrophilic insecticides with low  $\log K_{ow}$  values (0 to  $-2$ ) and hydrophobic insecticides with high  
372  $\log K_{ow}$  ( $>4$ ) are increasing. Since the use of all insecticides is decreasing (Fig. 7), however, the use  
373 of pesticides in all categories is decreasing.

374

#### 375 **4. Conclusions**

376

377 We analyzed pesticide occurrence data (14,076 samples) collected from 2012 to 2017 by 12 major

378 water supply authorities all over Japan, where rice cultivation is common. We identified 4 herbicides  
379 that occurred frequently in source waters: bromobutide, bentazone, tefuryltrione, and dymron. For  
380 these 4 herbicides, more than 10% of source water samples exceeded concentrations of 0.1 µg/L; in  
381 particular, the percentages in excess of 0.1 µg/L were > 40% for bentazone and bromobutide. For  
382 tefuryltrione, 8% of source water samples had NCs that exceeded 0.1. These pesticides are applied  
383 mostly in rice farming. In addition to these 4 herbicides, the herbicides molinate and halosulfuron  
384 methyl, the fungicides pyroquilon and metominostrobin, and the insecticide dinotefuran occurred at  
385 high concentrations. For seven of them (bromobutide, tefuryltrione, dymron, halosulfuron methyl,  
386 pyroquilon, metominostrobin, and dinotefuran) no drinking water quality standards or guidelines are  
387 provided in countries other than Japan. Overall, herbicides exhibited the highest frequency of detection,  
388 followed by fungicides. Herbicides and fungicides used in rice farming deserve greater attention,  
389 especially in regions where ponding water in rice paddies is common. Further research into the  
390 monitoring of pesticides used in rice paddy farming could help to identify appropriate guidelines to  
391 ensure good water quality.

392

393 The average ADI of herbicides is around one order of magnitude higher than that of fungicides or  
394 insecticides. Use of herbicides and fungicides with higher ADIs, such as glyphosate, has been  
395 increasing since 1970. Since 2010, however, the sales percentage of herbicides with low ADIs (ADI  
396  $< 10^{-2.5}$  mg kg<sup>-1</sup> d<sup>-1</sup>) has been kept nearly constant (~10%). Herbicides with very low ADIs (log ADI  
397 from -3.0 to -3.5), such as tefuryltrione, have emerged, although their percentage of total herbicide  
398 sales quantity remains very low. Tefuryltrione, for which 8% of the total measurements had NC values  
399  $> 0.1$ , is typical of these low-ADI herbicides. The average log *K<sub>ow</sub>* of herbicides has decreased largely  
400 in the last 50 years, coinciding with a strong trend towards the use of more hydrophilic agents as  
401 herbicides and fungicides, such as glyphosate, and with the registration expiration of the hydrophobic  
402 herbicide, CNP. In this way, low-toxicity pesticides have been increasing in Japan. Besides, pesticides  
403 have changed from hydrophobic to hydrophilic, i.e., their solubility in water has increased, making  
404 them more challenging to be removed by water treatment. Some of the pesticides are readily

405 decomposed by chlorination and not detected in treated water. Because the chlorination may yield  
406 degradation products with higher toxicity, however, it does not necessarily mean the reduction of risk.  
407 The detection method and toxicity evaluation of degradation products are very limited, and further  
408 study is needed for their identification and monitoring.

409

410

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412

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421

422

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540

Table 1. Detection rates, concentration excess ratios, and log  $K_{ow}$  values of pesticides in source waters

Application	Name	Detection rate	$\geq 1 \mu\text{g/L}$	$\geq 0.1 \mu\text{g/L}$	$\geq 0.01 \mu\text{g/L}$	Log $K_{ow}$
Herbicide	bentazone	51.9%	4.5%	33.8%	51.7%	-0.94
	bromobutide	41.4%	7.5%	31.1%	40.5%	3.46
	pretilachlor	16.6%	0.065%	7.2%	16.4%	3.90
	dymron	19.7%	0.14%	10.6%	19.7%	2.70
	mefenacet	12.0%	0.065%	3.8%	11.8%	3.23
	bensulfuron methyl	17.9%		5.6%	17.9%	0.79
	molinate	10.6%	0.48%	2.8%	9.4%	2.88
	simetryn	11.8%	0.10%	3.1%	11.2%	2.14
	dimethametryn	9.9%		1.9%	9.8%	3.20
	cafenstrole	9.1%		2.2%	8.6%	3.21
	tefuryltrione	35.5%		15.8%	30.3%	1.90
	carbofuran	8.6%		2.8%	8.0%	2.30
	halosulfuron methyl	8.3%	0.55%	2.5%	5.1%	-0.02
	esprocarb	2.6%		0.38%	2.6%	4.62
diuron	4.6%		2.2%	3.8%	3.00	
Fungicide	isoprothiolane	20.1%	1.9%	8.2%	19.9%	2.80
	metominostrobin	14.7%	0.03%	4.4%	14.7%	2.32
	pyroquilon	15.7%		1.9%	12.2%	1.60
	flutolanil	11.2%		1.5%	11.2%	3.77
	iprobenfos	18.8%	1.3%	7.5%	18.5%	3.37
	benomyl	5.2%	0.14%	1.3%	4.6%	1.36
	tricyclazole	13.5%		0.44%	5.8%	1.41
	orysastrobin	5.6%	0.03%	1.8%	4.1%	2.36
	isoprothiolane	20.1%	1.9%	8.2%	19.9%	2.80
Insecticide	imidaclopride	25.7%		3.3%	20.5%	0.57
	fenobucarb	6.8%	0.07%	1.6%	6.8%	2.67
	dinotefuran	10.2%	0.73%	3.9%	7.2%	-0.55
	fenitrothion	5.4%		0.41%	4.9%	3.55
	fipronil	5.7%			2.1%	4.00
	clothianidin	19.9%			1.2%	0.70

Table 2. Detection rates and normalized concentration (NC) values exceeding 0.1, 0.01, and 0.01 in source waters

Pesticide	Application	Detection rate	NC $\geq 0.1$	NC $\geq 0.01$	NC $\geq 0.001$	Guideline value in Japan ( $\mu\text{g/L}$ )
tefuryltrione	herbicide	35.5%	8.4%	27.0%	35.5%	2
molinatate	herbicide	10.6%	0.84%	6.4%	9.4%	5
carbofuran	herbicide	8.6%	0.65%	4.3%	8.5%	5
metominostrobin	fungicide	20.0%	0.12%	3.7%	12.9%	40
fenitrothion	insecticide	5.4%	0.11%	3.1%	5.3%	3
fipronil	insecticide	5.7%	0.07%	4.4%	4.4%	0.5
bromobutide	herbicide	41.4%	0.06%	7.5%	31.1%	100
pyroquilon	fungicide	29.9%	0.06%	2.3%	7.8%	40
bentazone	herbicide	51.9%		0.7%	23.9%	200
pretilachlor	herbicide	16.6%		0.8%	12.2%	50
mefenacet	herbicide	12.0%		1.6%	10.7%	20
simetryn	herbicide	11.8%		1.1%	9.6%	30
dimethametryn	herbicide	9.9%		0.93%	8.3%	20
cafenstrole	herbicide	9.1%		3.0%	8.6%	8
halosulfuronmethyl	herbicide	8.3%		0.50%	2.2%	300
esprocarb	herbicide	2.6%		0.14%	1.5%	30
iprobefos	fungicide	6.0%		0.16%	1.6%	90
fenobucarb	insecticide	6.8%		0.42%	4.3%	30

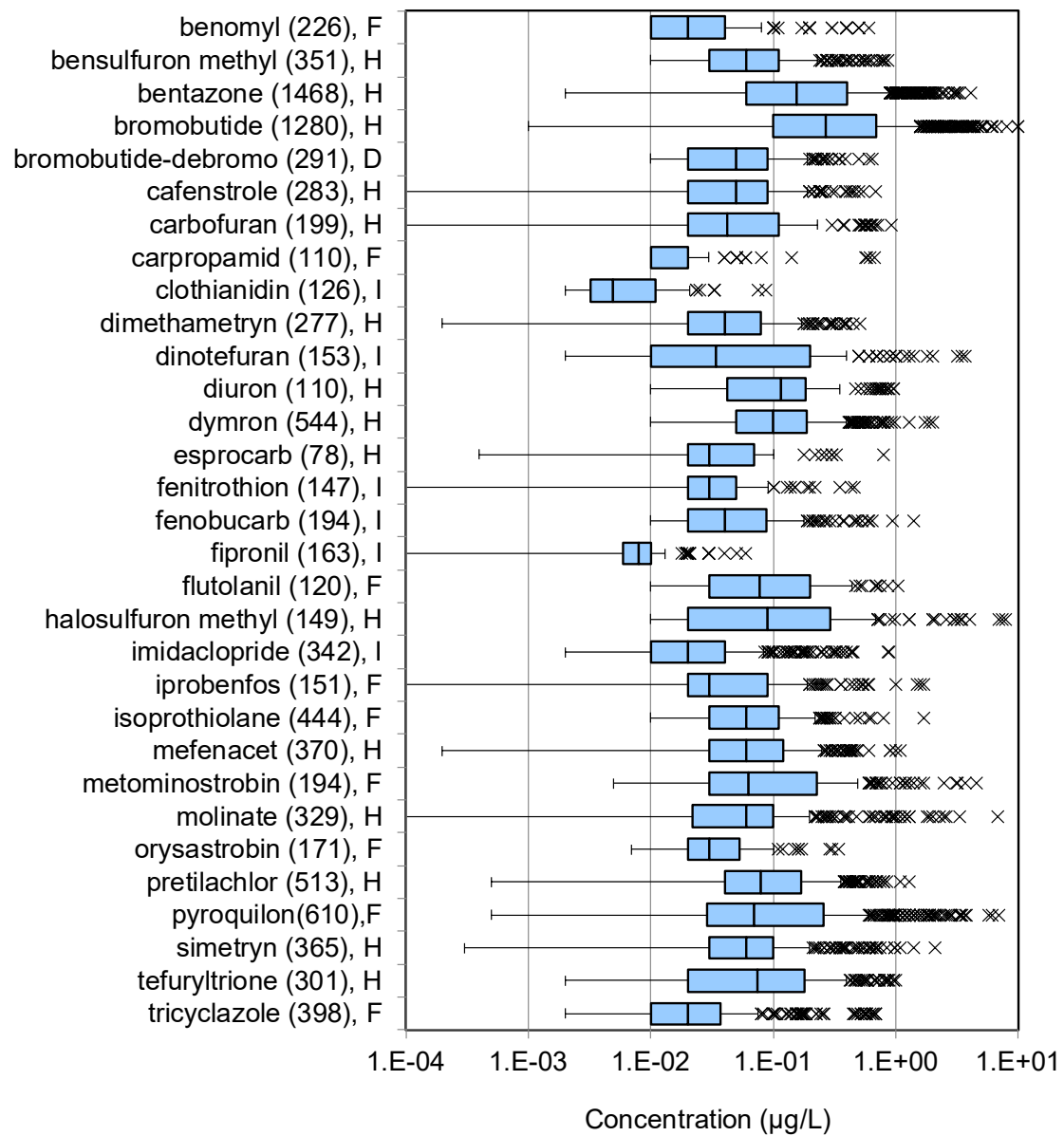


Fig. 1. Pesticide concentrations in drinking water sources (2012–2017). Data were collected from the 12 main water supply utilities in Japan. Pesticides are listed in alphabetical order. Bromobutide-debromo is a metabolite of bromobutide. Numbers in parentheses after pesticide names indicate the numbers of times detected. H, herbicide; F, fungicide; I, insecticide. The lower whisker is the lowest concentration larger than 1.5IQR (interquartile range) below the first quartile, while the upper whisker is the highest concentration than 1.5IQR above the third quartile. All other observed concentrations are plotted as outliers.

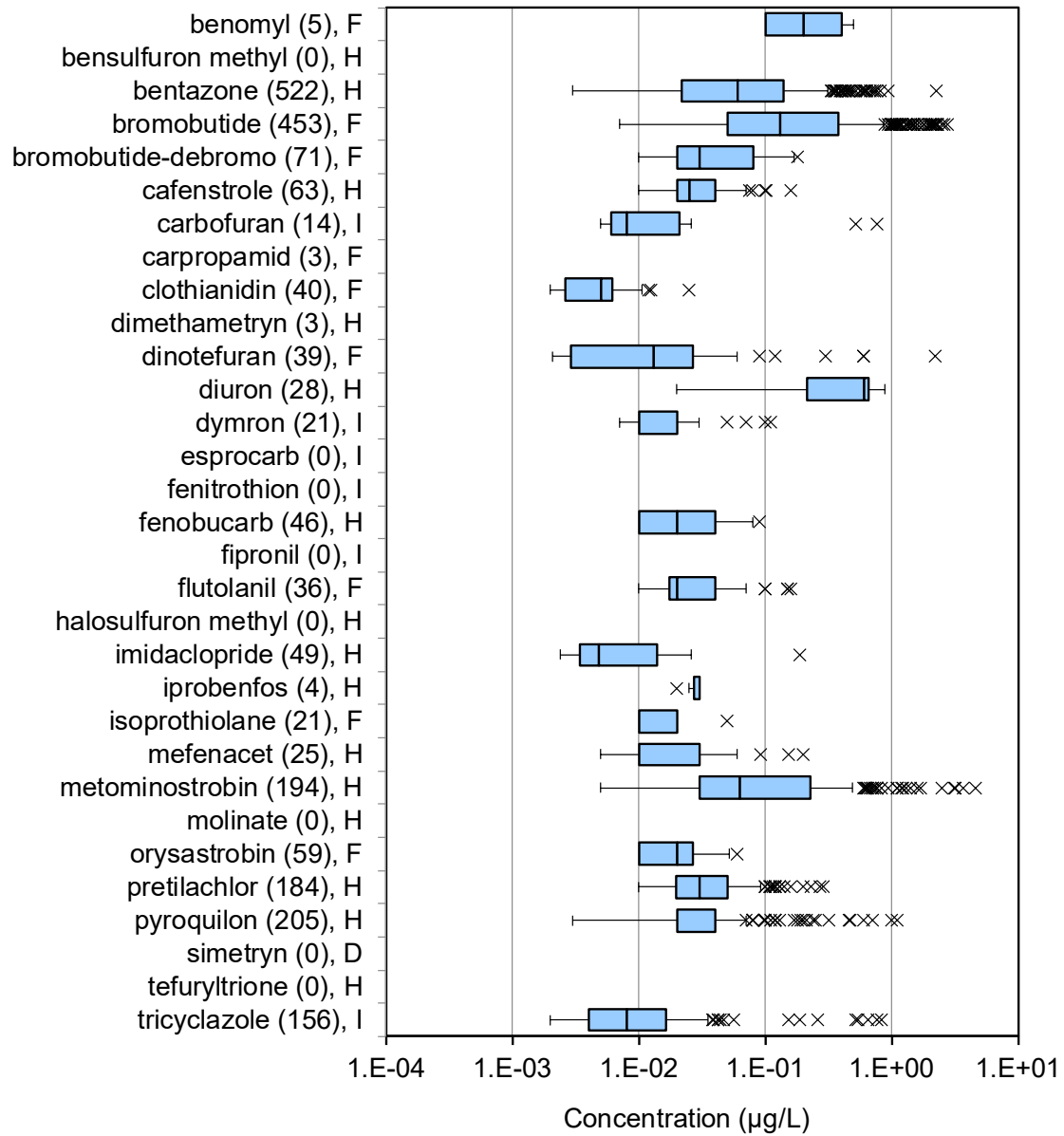


Fig. 2. Pesticide concentrations in treated water (drinking water) (2012–2017). Data were collected from the 12 main water supply utilities in Japan. Pesticides are listed in alphabetical order. Bromobutide-debromo is a metabolite of bromobutide. Numbers in parentheses after pesticide names indicate the number of times detected. H, herbicide; F, fungicide; I, insecticide. The lower whisker is the lowest concentration larger than 1.5IQR (interquartile range) below the first quartile, while the upper whisker is the highest concentration than 1.5IQR above the third quartile. All other observed concentrations are plotted as outliers. The lack of a box plot means that the pesticide was undetectable.

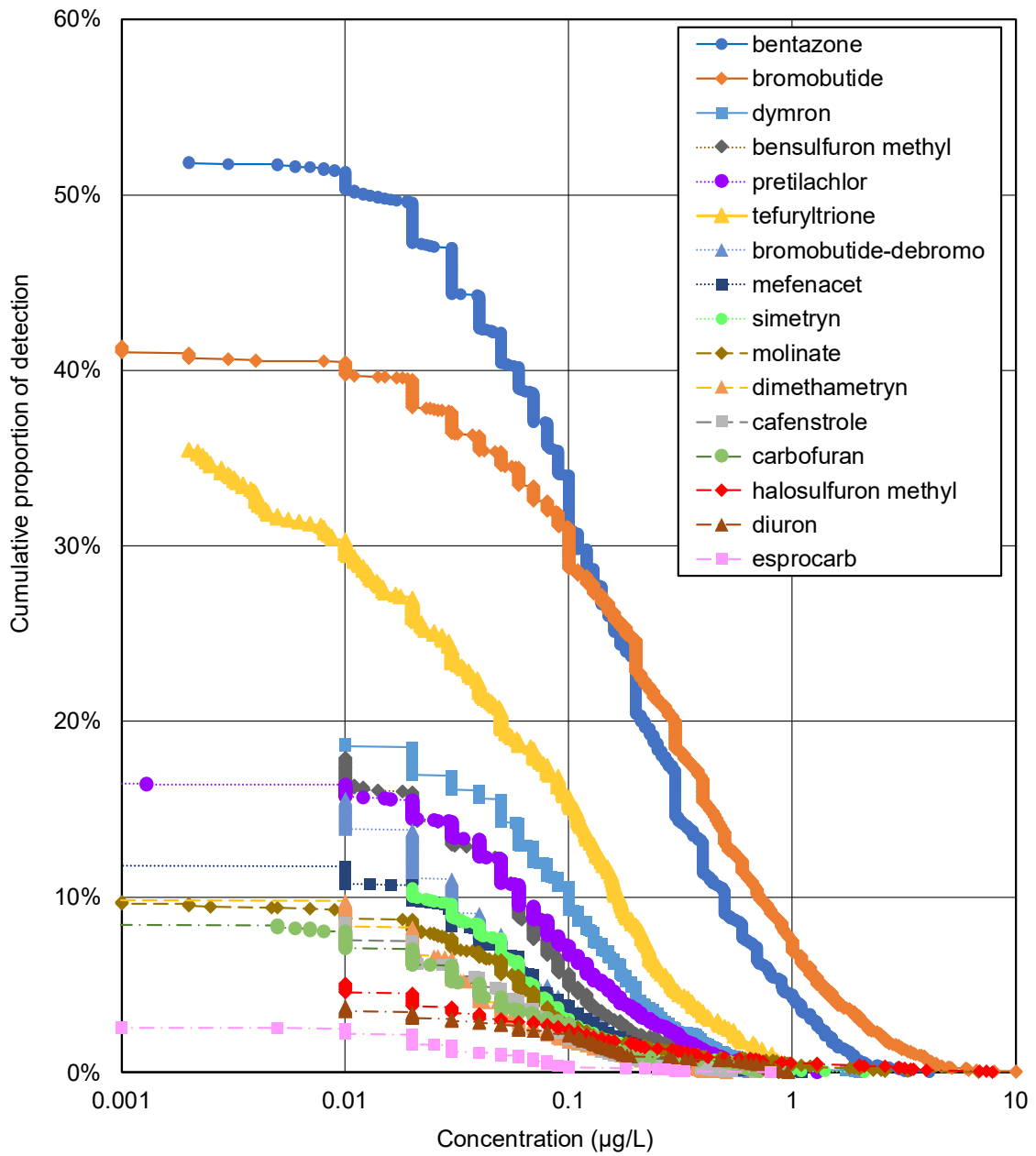


Fig. 3. Cumulative frequency distributions for herbicide concentrations in drinking water sources (2012–2017). Bromobutide-debromo is a metabolite of bromobutide.

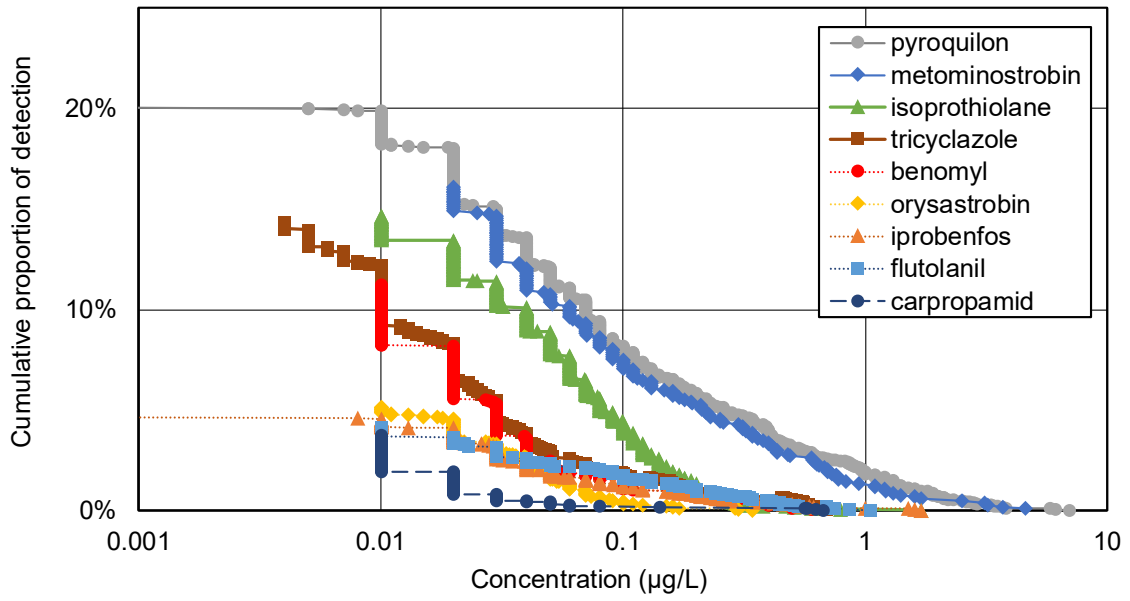


Fig. 4. Cumulative frequency distributions for concentrations of fungicides in drinking water sources (2012–2017).

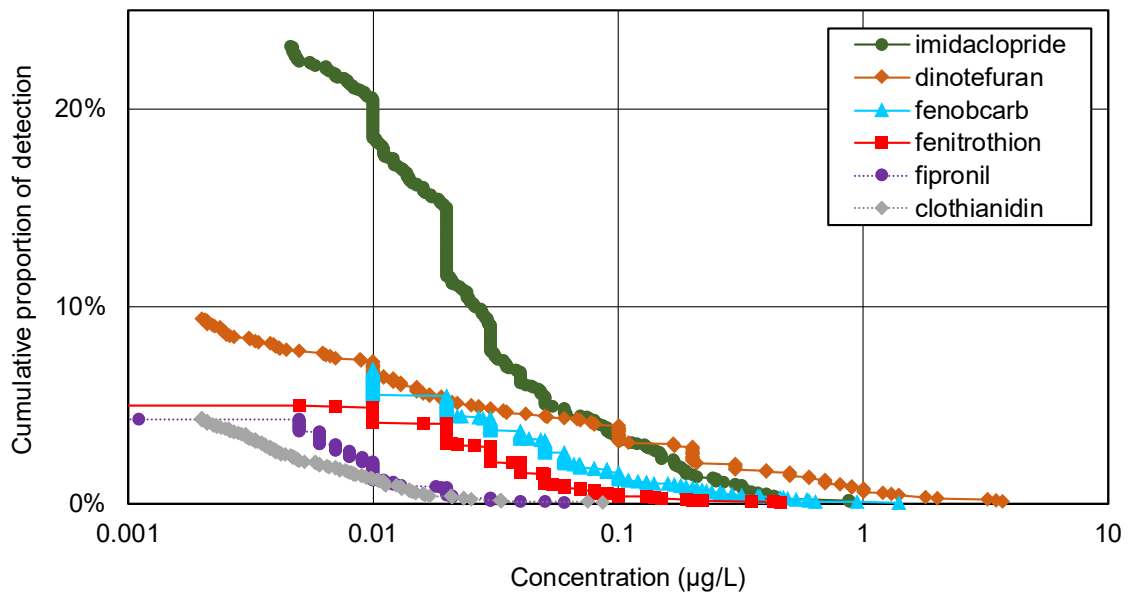


Fig. 5. Cumulative frequency distributions for concentrations of insecticides in drinking water sources (2012–2017).

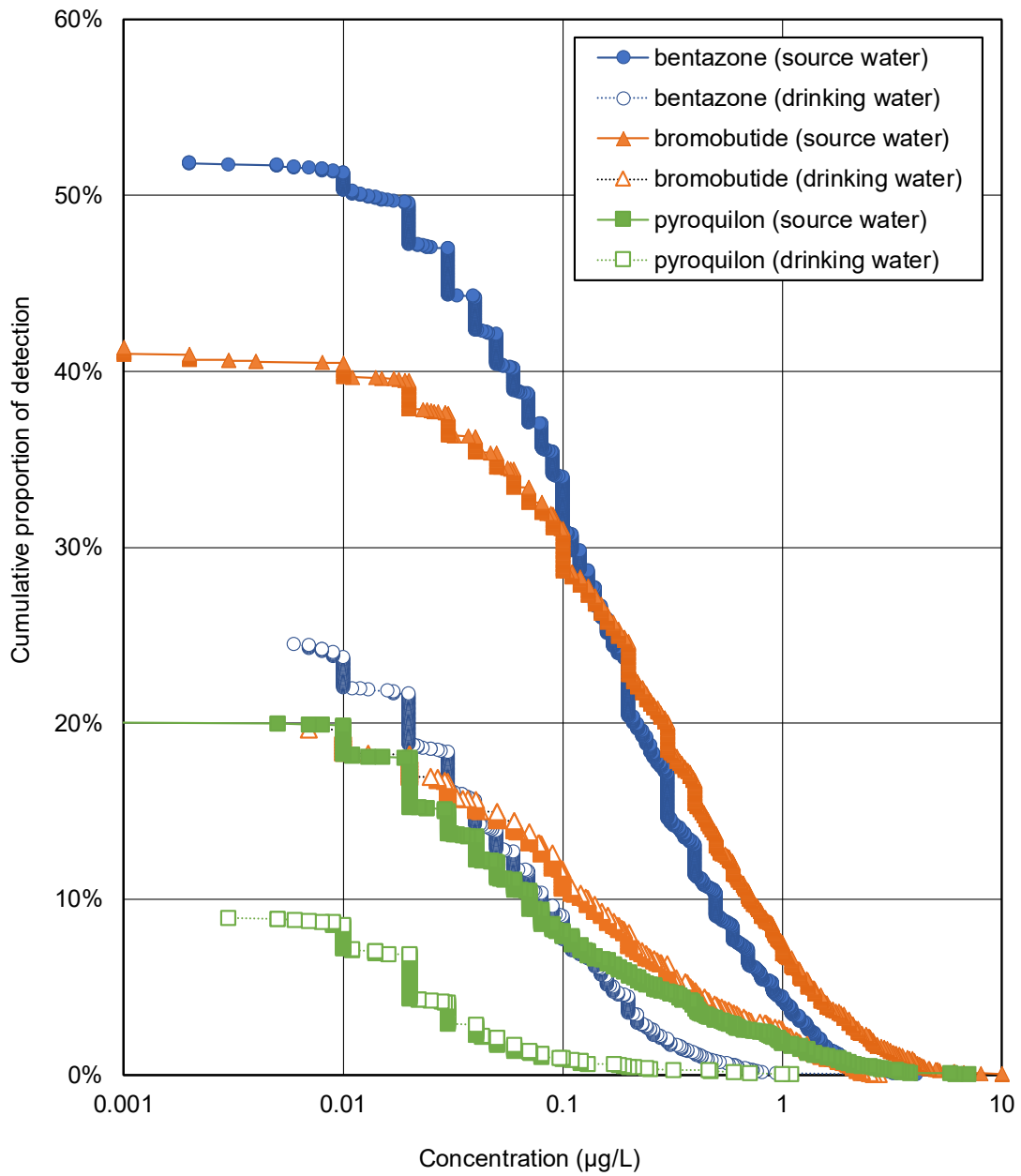


Fig. 6. Comparison of cumulative frequency distributions of pesticide concentrations between drinking water sources and treated water (drinking water) (2012–2017).

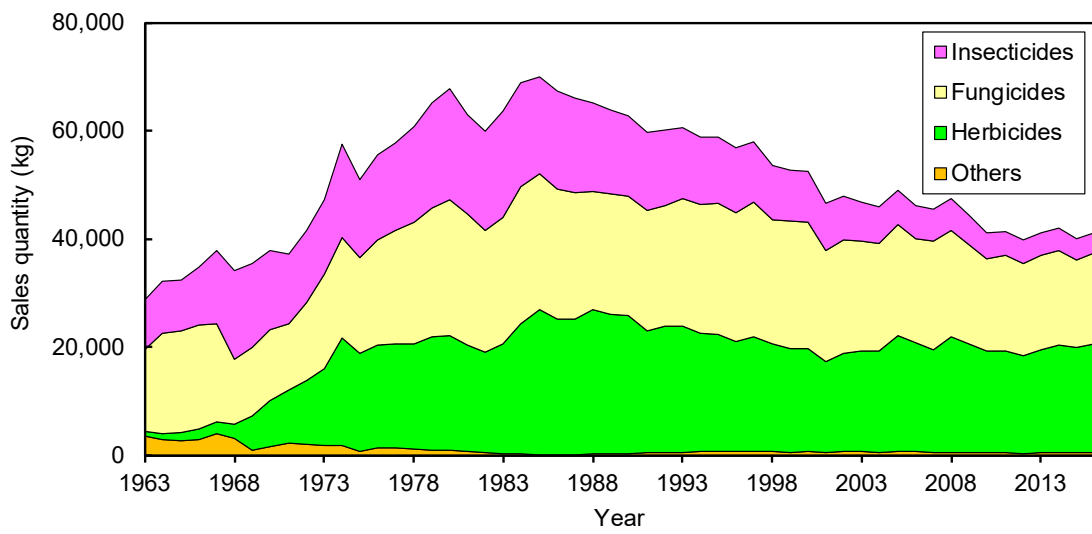


Fig. 7. Changes in pesticide (active ingredient) sales quantities

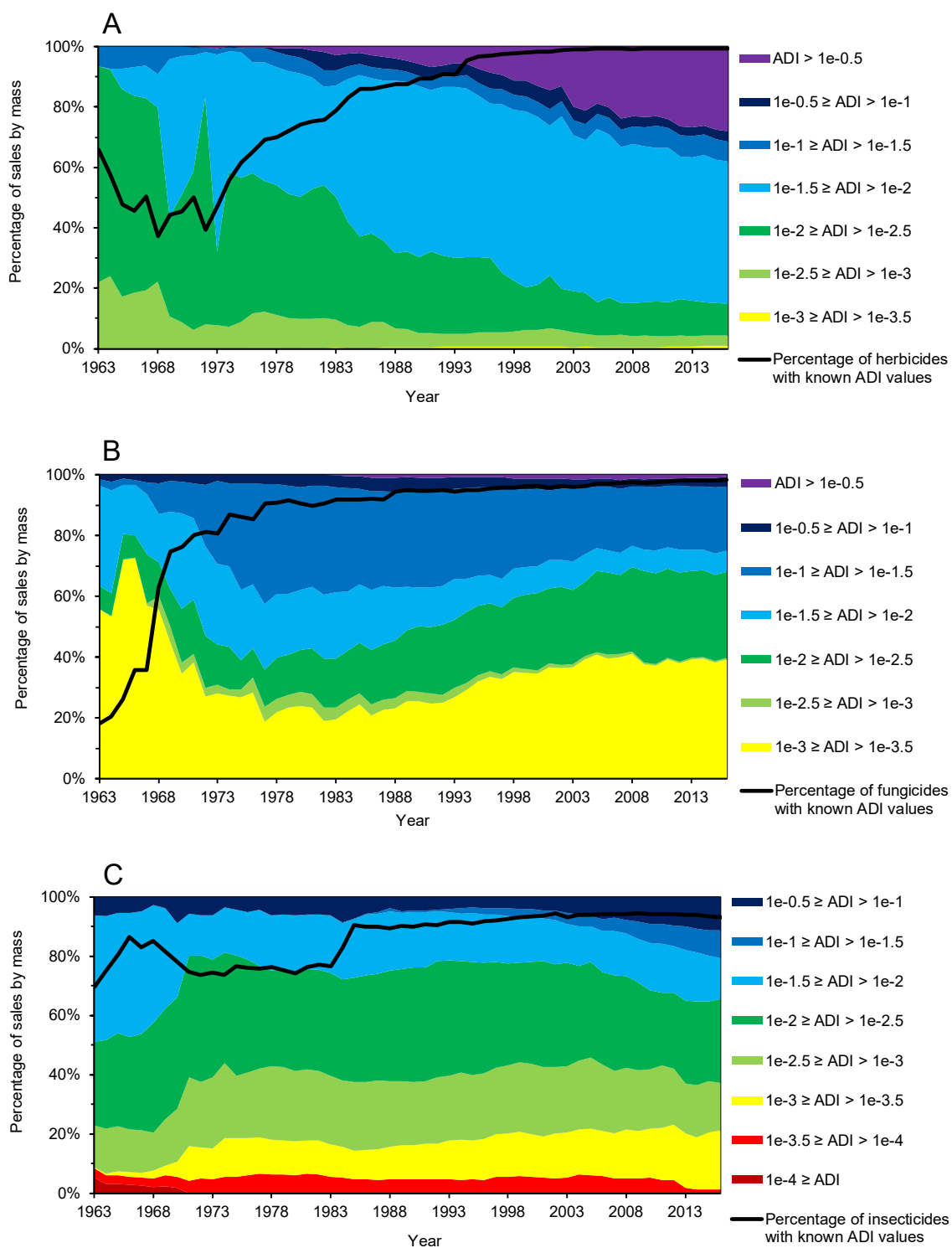


Fig. 8. Sales quantities of herbicide (Panel A), fungicide (Panel B), and insecticide (Panel C) categorized by acceptable daily intake (ADI) values ( $\text{mg kg}^{-1} \text{d}^{-1}$ ). The black line indicates the percentages of herbicides with known ADI values.

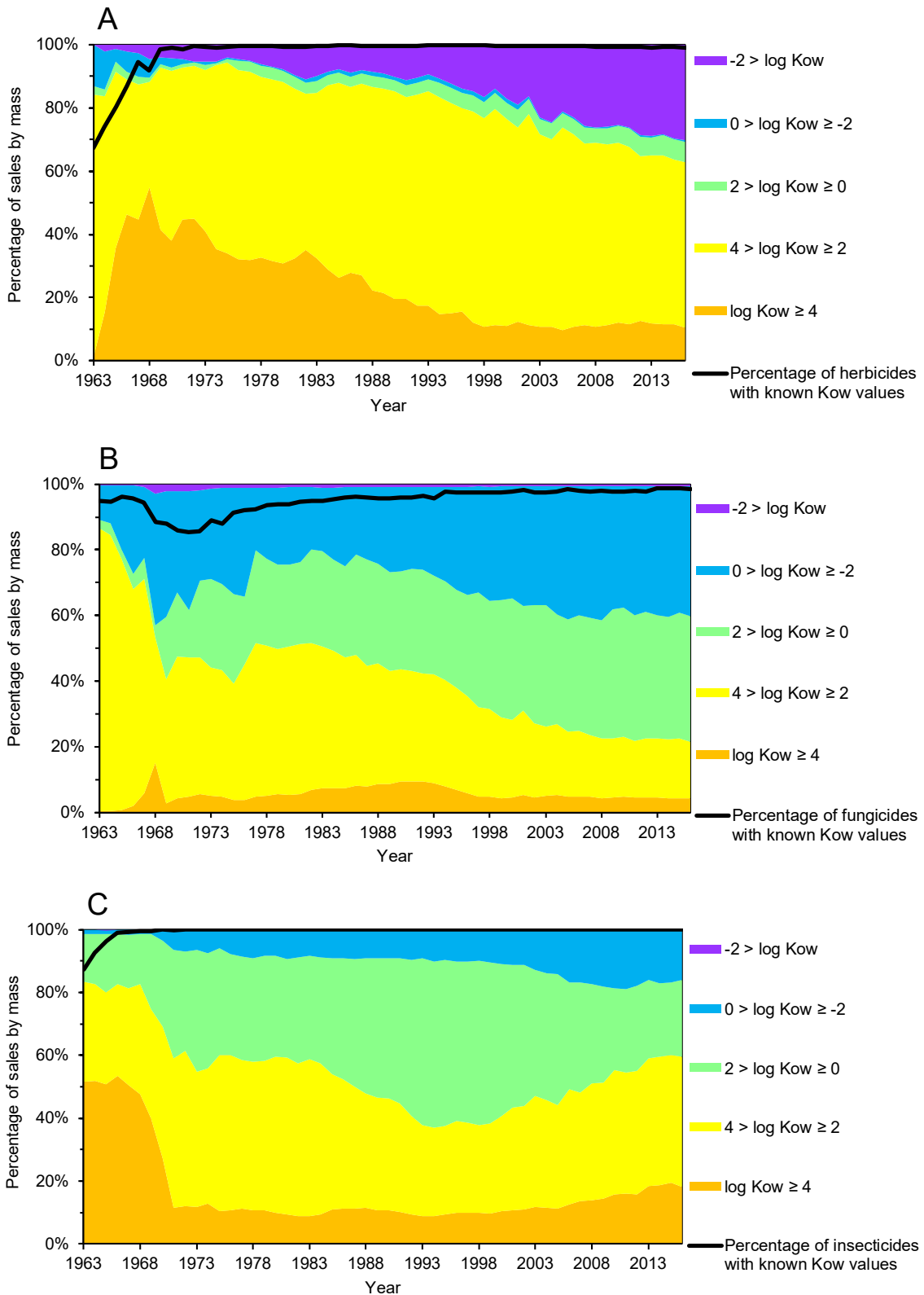


Fig. 9. Sales quantities of herbicide (Panel A), fungicide (Panel B), and insecticide (Panel C) categorized by log Kow values. The black line indicates the percentages of herbicides with known Kow values.

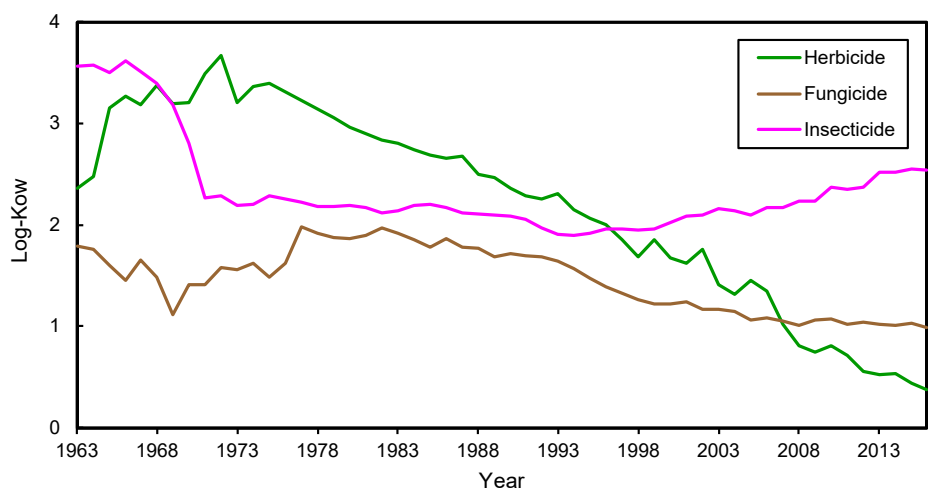


Fig. 10. Changes of arithmetic mean log-Kow values of herbicides, fungicides, and insecticides.

# Supplementary Information

Paper submitted to STOTEN

## National trends in pesticides in drinking water and water sources in Japan



Fig. 1S. Locations of the 12 main water supply utilities

Table 1S. Numbers of target pesticides, sampling frequencies and times, water sources, and water treatment processes

Water utility	Number of pesticides examined	Sampling frequency and time period	Raw water source	Water treatment processes
Hachinohe	97	Weekly from to early May to mid-September	Mabechi River and Nitta River	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Sendai	84	Monthly from May to August	Kamafusa Dam, Nanakitada River, and Miyadoko Dam	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Ibaraki	111	From April to September Ten times for 28 pesticides Twice for 83 pesticides	Tone River	Coagulation, sedimentation, sand filtration, ozonation, bioactivated carbon filtration, and chlorination
	111	From April to September Ten times for 28 pesticides Twice for 83 pesticides	Hinuma River	Coagulation, sedimentation, sand filtration, granular activated carbon, and chlorination
	111	From April to September Six times for 28 pesticides Twice for 83 pesticides	Lake Kasumigaura	Coagulation, sedimentation, sand filtration, granular activated carbon, and chlorination
Chiba	128	Once each in May and July for raw water Monthly from May to August for treated water	Tone River, Edo River, Lake Imba, and Takataki Dam	Powdered activated carbon, coagulation, sedimentation, sand filtration, (in some cases ozonation, granular activated carbon), and chlorination
Tokyo	160	Monthly from May to August	Tone River, Ara River	Powdered activated carbon, coagulation, sedimentation, sand filtration, ozonation, granular activated carbon, and chlorination
	160	Monthly from May to August	Tama River	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
	160	Monthly from May to August	Tama River	Sand filtration and chlorination
	160	Monthly from May to August	Sagami River	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Kanagawa Koiki	122	Weekly from May to October for 97	Sakawa River and Sagami River	Powdered activated carbon, coagulation, sedimentation,

Water utility	Number of pesticides examined	Sampling frequency and time period	Raw water source	Water treatment processes
		pesticides for raw water Monthly from November to April for 122 pesticides for raw water Monthly for treated water		sand filtration, and chlorination
Niigata	32	Once in April Four times in each of May and June Three times in July Twice in each of August and September	Sinano, Nakanokuchi, Nishikawa, Agano rivers	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Nara	133	Weekly from May to August Twice in each of September and October	Murou Dam	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Osaka	125	Monthly from May to September	Yodo River	Coagulation, sedimentation, ozonation, sand filtration, ozonation, granular activated carbon, and chlorination
Kobe	116	Four times a year	Sengari Reservoir	(Granular activated carbon in some cases), coagulation, sedimentation, sand filtration, and chlorination
Hiroshima	117	Twice a month from late April to October	Ohta River and Toshi Dam	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination
Fukuoka	99	Weekly from April to mid-October	Chikugo River	Powdered activated carbon, coagulation, sedimentation, sand filtration, and chlorination

Table 2S. Analytical methods used for detection of pesticides

No.	Name of pesticide	Use etc.	Examination methods	LOQ	Japanese Guideline value (µg/L)
1	2,4-D (2,4-dichlorophenoxyacetic acid)	Herbicide	LC/MS, SPE-LC/MS	0.01, 0.02, 0.05, 0.1	30
2	Acephate	Insecticide	LC/MS, SPE-LC/MS, LC/MS/MS	0.005, 0.06, 0.1, 0.8	6
3	Acetamiprid	Insecticide	LC/MS, SPE-LC/MS, SPE-LC/MS/MS	0.002, 0.005	NA
4	Alachlor	Herbicide	SPE-GC/MS	0.01, 0.02, 0.2	30
5	Ametryn	Herbicide	SPE-LC/MS	0.004	NA
6	Aminomethylphosphonic acid (AMPA)	Herbicide	der.HPLC	0.5	NA
7	Asulam	Herbicide	LC/MS, SPE-LC/MS	0.005, 0.01, 0.05, 0.1	200
8	Atrazine	Herbicide	SPE-GC/MS	0.005, 0.05	10
9	Azimsulfuron	Herbicide	SPE-LC/MS	0.02	NA
10	Azoxystrobin	Fungicide	LC/MS, SPE-LC/MS	0.01, 0.02, 0.1	NA
11	Benfluralin (bethrodine, benefin)	Herbicide	SPE-GC-MS	0.01	10
12	Benfuracarb	Insecticide	SPE-LC/MS, LC/MS	0.01, 0.04, 0.05, 0.1	40
13	Benfuresate	Herbicide	SPE-GC/MS	0.005, 0.01, 0.03, 0.05, 0.1	70
14	Benomyl	Fungicide	SPE-LC/MS, LC/MS, LC/MS/MS	0.01, 0.02, 0.1, 0.2	20
15	Bensulfuron-methyl	Herbicide	SPE-LC/MS, LC/MS	0.01, 0.05, 0.1	NA
16	Bentazone	Herbicide	SPE-LC/MS, SPE-der.GC/MS, LC/MS	0.002, 0.01, 0.02, 0.05, 0.1, 0.2	200
17	Benzobicyclon	Herbicide	LC/MS	0.01	90
18	Benzoepin sulfate (endosulfan)	Insecticide	SPE-GC/MS	0.005, 0.02	10
19	Benzofenap	Herbicide	SPE-LC/MS, SPE-GC/MS, LC/MS	0.005, 0.01, 0.04	4
20	Bifenox	Herbicide	SPE-GC/MS	0.005	NA
21	Bromacil	Herbicide	SPE-LC/MS, SPE-GC/MS	0.005, 0.004, 0.1	NA
22	Bromobutide	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1, 0.4, 1	100
23	Bromobutide-debromo	Degradation compound	SPE-GC/MS, LC/MS	0.01, 0.02, 0.05, 0.1	NA
24	Buprofezin	Insecticide	SPE-GC/MS	0.01	20
25	Butachlor	Herbicide	SPE-GC/MS	0.01, 0.02, 0.05, 0.1, 0.2, 0.3	30
26	Butamifos	Herbicide	SPE-GC/MS	0.02	20
27	Cadusafos	Insecticide	LC/MS	0.006	0.6
28	Cafenstrole	Herbicide	SPE-GC/MS, SPE-LC/MS	0.01, 0.02, 0.05, 0.08	8
29	Captan	Fungicide	SPE-GC/MS	0.1	300
30	Carbaryl	Insecticide	LC/MS, SPE-LC/MS	0.005, 0.01, 0.02, 0.05	50
31	Carbendazim (MBC)	Fungicide	LC/MS	0.1	NA
32	Carbofuran	Insecticide	SPE-LC/MS, LC/MS, SPE-GC/MS	0.005, 0.01, 0.02, 0.05, 0.1	5
33	Carpropamid	Fungicide	LC/MS, SPE-LC/MS	0.005, 0.01, 0.03, 0.05	40
34	Chlorantraniliprole	Insecticide	SPE-LC/MS	0.01	NA
35	Chloroneb	Fungicide	SPE-GC/MS,	0.005	NA
36	Chlorpyrifos-methyl	Insecticide	SPE-LC/MS, SPE-GC/MS	0.005, 0.01	NA
37	Chlorpyrifos	Insecticide	SPE-GC/MS	0.02, 0.03, 0.05	3
38	Chlortal dimethyl (TCTP)	Herbicide	SPE-GC/MS	0.005	NA
39	Clomeprop	Herbicide	SPE-LC/MS, LC/MS	0.01, 0.05	20
40	Clothianidin	Insecticide	SPE-LC/MS, SPE – LC/MS/MS	0.002, 0.004, 0.01	NA
41	CMTBA (2-chloro-4-methylsulfonyl-3-[(tetrahydrofuran-2-yl-methoxy) methyl] benzoic acid)	Degradation compound	LC-MS-MS, SPE-LC/MS, LC/MS	0.02, 0.04, 0.004	NA
42	Cumyluron	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.05, 0.2	30
43	Cyanazine	Herbicide	SPE-GC/MS, LC/MS, LC/MS/MS	0.02, 0.04, 0.05, 0.1	4
44	Cyanophos	Insecticide	LC/MS,	0.05	3
45	Dalapon (2,2-DPA)	Herbicide	LC/MS, SPE-LC/MS	0.1, 0.2	80
46	Diazinon	Insecticide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1	5
47	Diazinon Oxone	Degradation compound	SPE-GC/MS, LC/MS	0.005, 0.01, 0.03	NA
48	Dichlobenil	Herbicide	SPE-GC/MS	0.005, 0.01, 0.05, 0.1	10
49	Dichlorprop	Herbicide	SPE-LC/MS	0.01	NA
50	Dichlorvos	Insecticide	SPE-GC/MS	0.005, 0.01, 0.05, 0.08	8
51	Diclomezine	Fungicide	SPE-LC/MS	0.004	NA
52	Diffubenzuron	Insecticide	SPE-LC/MS	0.03	NA
53	Dimethametryn	Herbicide	SPE-GC/MS	0.005, 0.01, 0.02, 0.05, 0.1	20
54	Dimethoate	Insecticide	SPE-GC/MS	0.005, 0.02, 0.05	50
55	Dinotefuran	Insecticide	SPE-LC/MS, LC/MS, SPE – LC/MS/MS	0.002, 0.004, 0.01, 0.04, 0.1, 1, 2	NA
56	Dithiopyr	Herbicide	SPE-GC/MS	0.01	9
57	Diuron	Herbicide	SPE-LC/MS, LC/MS, SPE-LC/MS/MS	0.005, 0.01, 0.05, 0.1	20
58	Dymron	Herbicide	SPE-LC/MS, LC/MS	0.01, 0.05, 0.1	800

No.	Name of pesticide	Use etc.	Examination methods	LOQ	Japanese Guideline value (µg/L)
59	Edifenphos	Fungicide	LC/MS, SPE-GC/MS	0.01, 0.06	6
60	EPN	Insecticide	SPE-GC/MS	0.2	4
61	Esprocarb	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1	30
62	Ethiprole	Insecticide	SPE-LC/MS	0.01	NA
63	Ethylthiometon	Insecticide	LC/MS, SPE-GC/MS	0.005, 0.02, 0.05, 0.1	4
64	Etridiazole	Fungicide	SPE-GC/MS	0.1	4
65	Fenitrothion (MEP)	Insecticide	SPE-GC/MS	0.005, 0.01, 0.02, 0.03, 0.05	3
66	Fenitrothion oxon (MEP oxon)	Degradation compound	SPE-GC/MS	0.01, 0.1	NA
67	Fenobucarb	Insecticide	SPE-GC/MS, LC/MS	0.01, 0.02, 0.05, 0.1	30
68	Fenthion (MPP)	Insecticide	SPE-GC/MS, LC/MS	0.01, 0.02, 0.1, 0.2	6
69	Fenthion oxon (MPP oxon)	Degradation compound	LC/MS	0.01	6
70	Fenthion sulfone oxon (MPP sulfone oxon)	Degradation compound	LC/MS, SPE-LC/MS	0.02, 0.2	6
71	Fenthion sulfoxide oxon (MPP sulfoxide oxon)	Degradation compound	LC/MS	0.01	6
72	Fenthion sulfoxide (MPP sulfoxide)	Degradation compound	SPE-GC/MS, LC/MS	0.01, 0.05	6
73	Fenthion-sulfone (MPP sulfone)	Degradation compound	SPE-GC/MS	0.01	6
74	Fentrazamide	Herbicide	SPE-LC/MS, LC/MS/MS, LC/MS	0.01, 0.05, 0.1	10
75	Ferimzone	Fungicide	LC/MS	0.02	50
76	Fipronil	Insecticide	SPE-GC/MS, SPE-LC/MS, SPE-LCMSMS	0.005, 0.01	0.5
77	Flazasulfuron	Herbicide	SPE-LC/MS	0.002	NA
78	Fluazinam	Fungicide	LC/MS	0.02	30
79	Flutolanil	Fungicide	SPE-GC/MS, LC/MS	0.01, 0.02, 0.1	NA
80	Fosthiazate	Insecticide	LC/MS	0.03	3
81	Fthalide	Fungicide	SPE-GC/MS	0.01, 0.02	100
82	Furametpyr	Fungicide	SPE-LC/MS, LC/MS	0.004, 0.01	NA
83	Glyphosate	Herbicide	der.HPLC, Other	0.5, 1	2000
84	Halosulfuron-methyl	Herbicide	SPE-LC/MS, LC/MS, SPE-LCMSMS	0.005, 0.01, 0.05, 0.1	NA
85	Imazosulfuron	Herbicide	LC/MS, SPE-LC/MS	0.03, 0.04, 0.05, 0.1	NA
86	Imidacloprid	Insecticide	SPE-LC/MS, LC/MS, SPE-LC/MS/MS	0.002, 0.004, 0.01, 0.05, 0.1	NA
87	Indanofan	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01	9
88	Iprobenfos	Fungicide	SPE-GC/MS	0.01, 0.02, 0.03, 0.05, 0.08, 0.1, 0.2	90
89	Isofenphos oxon	Degradation compound	LC/MS	0.005, 0.03	1
90	Isoprocarb	Insecticide	SPE-GC/MS	0.02	10
91	Isoprothiolane	Fungicide	SPE-GC/MS	0.01, 0.02, 0.05, 0.1	300
92	Isoxathion	Insecticide	SPE-GC/MS	0.01, 0.2	8
93	Isoxathion oxon	Degradation compound	SPE-GC/MS	0.01, 0.05, 0.08	8
94	Kromprop decomposition product B	Degradation compound	LC/MS/MS	0.1	NA
95	Linuron	Herbicide	SPE-GC/MS, LC/MS	0.01, 0.05, 0.1	NA
96	Malathion	Insecticide	SPE-GC/MS	0.005, 0.01, 0.02, 0.05, 0.1	50
97	Malathion Oxon	Insecticide	SPE-GC/MS	0.005	50
98	Manzeb	Fungicide	SPE-LC/MS	0.005	5 (as CS2)
99	MCPA (2-methyl-4-chlorophenoxyacetic acid)	Herbicide	LC/MS, SPE-GC/MS, SPE-LC/MS	0.004, 0.01, 0.02, 0.05, 0.1	5
100	Mecoprop	Herbicide	SPE-LC/MS, SPE-LC/MS/MS, LC/MS	0.01, 0.02, 0.05, 0.1	50
101	Mefenacet	Herbicide	SPE-GC/MS, SPE-LC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.09, 0.1, 0.2	20
102	Mepronil	Fungicide	SPE-GC/MS	0.01, 0.02, 0.05	100
103	Mesotrione	Herbicide	SPE-LC/MS	0.01	NA
104	Metalaxyl	Fungicide	SPE-GC/MS	0.005, 0.01, 0.02, 0.04	60
105	Methidathion	Insecticide	SPE-GC/MS	0.01, 0.1	4
106	Methomyl	Insecticide	SPE-LC/MS, LC/MS	0.005, 0.01, 0.02, 0.1	30
107	Methyldymron	Herbicide	SPE-GC/MS	0.03, 0.05	30
108	Metominostrobin	Fungicide	SPE-GC/MS	0.01, 0.05	40
109	Metribuzin	Herbicide	LC/MS	0.05	30
110	Molinate	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1	5
111	Napropamide	Herbicide	SPE-GC-MS	0.01	30
112	Nitenpyram	Insecticide	SPE-LC/MS, SPE-LC/MS/MS	0.002, 0.004	NA
113	Oryastrobin	Fungicide	SPE-GC/MS	0.01, 0.02, 0.03, 0.05	100
114	Oxaziclomefone	Herbicide	SPE-GC/MS, SPE-LC/MS	0.004, 0.01	20
115	Oxine-copper	Fungicide	LC/MS	0.5	30
116	Paclobutrazol	Plant growth regulator	SPE-GC/MS	0.005	NA

No.	Name of pesticide	Use etc.	Examination methods	LOQ	Japanese Guideline value (µg/L)
117	Pencycuron	Fungicide	SPE-GC/MS, SPE-LC/MS	0.005, 0.01, 0.03, 0.05, 0.1	100
118	Pendimethalin	Herbicide	SPE-GC/MS	0.01, 0.02	300
119	Pensulide (SAP)	Herbicide	SPE-LC/MS	0.01, 0.03	NA
120	Pentoxazone	Herbicide	LC/MS	0.2	NA
121	Phenthoate	Insecticide	SPE-GC/MS	0.02, 0.05	7
122	Pretilachlor	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.4, 0.5	50
123	Probenazole	Fungicide	LC/MS, SPE-LC/MS, SPE-GC/MS	0.005, 0.1, 0.5	50
124	Procymidon	Fungicide	LC/MS, SPE-GC/MS	0.01, 0.05, 0.5	90
125	Prometryn	Herbicide	SPE-LC/MS,	0.004	NA
126	Propyrisulfuron	Herbicide	LC/MS,	0.04	NA
127	Propyzamide	Herbicide	LC/MS, SPE-GC/MS	0.01, 0.02, 0.05, 0.1	50
128	Prothiofos	Insecticide	SPE-GC/MS	0.04	4
129	Pyraclonil	Herbicide	LC/MS, SPE-LC/MS, LC/MS/MS	0.01, 0.02, 0.05, 0.1	10
130	Pyrazolynate	Herbicide	SPE-LC/MS, LC/MS	0.005, 0.01	20
131	Pyrazosulfuron-ethyl	Herbicide	SPE-LC/MS	0.01	NA
132	Pyrazoxyfen	Herbicide	SPE-GC/MS	0.02	4
133	Pyributicarb	Herbicide	SPE-GC/MS	0.01, 0.02	20
134	Pyridaphenthion	Insecticide	SPE-GC/MS	0.005	2
135	Pyriminobac-methyl	Herbicide	SPE-GC/MS, SPE-LC/MS	0.004, 0.05, 0.01	NA
136	Pyriproxyfen	Insecticide	SPE-GC/MS	0.01	NA
137	Pyroquilon	Fungicide	SPE-GC/MS	0.005, 0.01, 0.02, 0.05, 0.1, 0.4	40
138	Quinoclamine	Herbicide	SPE-GC/MS, LC/MS, SPE-LC/MS	0.01, 0.02, 0.05, 0.1	5
139	Quizalofop-ethyl	Herbicide	SPE-LC/MS	0.004	NA
140	Sidurone	Herbicide	SPE-LC/MS	0.01	NA
141	Simazine	Herbicide	SPE-GC/MS	0.01, 0.02, 0.03	3
142	Simetryn	Herbicide	SPE-GC/MS, LC/MS	0.01, 0.02, 0.03, 0.05, 0.1, 0.3	30
143	Tebuconazole	Fungicide	SPE-LC/MS, LC/MS, SPE – LC/MS/MS	0.002, 0.004, 0.005	NA
144	Tebufenozide	Insecticide	SPE-LC/MS,	0.004, 0.01	NA
145	Tefuryltrione	Herbicide	SPE-LC/MS, LC/MS, LC-MS-MS	0.002, 0.01, 0.02, 0.04, 0.05, 0.1	2
146	Terbucarb (MBPMC)	Herbicide	SPE-GC/MS	0.01, 0.02	20
147	Thenylchlor	Herbicide	SPE-GC/MS	0.01	NA
148	Thiamethoxam	Insecticide	SPE-GC/MS, SPE-LC/MS, SPE – LC/MS/MS	0.002, 0.004, 0.05	NA
149	Thifluzamide	Fungicide	SPE-GC/MS, SPE-LC/MS	0.004, 0.01	NA
150	Thiobencarb	Herbicide	SPE-GC/MS, LC/MS	0.005, 0.01, 0.02, 0.05, 0.1	20
151	Thiocyclam	Insecticide	SPE-LC/MS	0.03	NA
152	Thiodicarb	Insecticide	LC/MS	0.1	80
153	Thiophanate methyl	Fungicide	SPE-LC/MS	0.05	300
154	Thiuram	Fungicide	SPE-LC/MS	0.03, 0.2	20
155	Tiadimil	Fungicide	SPE-LC/MS	0.004, 0.01	100
156	Trichlorphon	Insecticide	SPE-GC/MS, SPE-LC/MS	0.01, 0.05, 0.2, 0.3	5
157	Triclofos methyl	Fungicide	SPE-GC/MS	0.01	NA
158	Triclopyr	Herbicide	SPE-LC/MS, LC/MS	0.01, 0.02, 0.06	6
159	Triclopyr-2-butoxyethyl	Herbicide	SPE-GC/MS	0.02, 0.06	NA
160	Tricyclazole	Fungicide	SPE-LC/MS, LC/MS	0.002, 0.008, 0.01, 0.05, 0.1	80
161	Trifluralin	Herbicide	SPE-GC/MS	0.005, 0.01	60
162	Zineb	Fungicide	SPE-LC/MS	0.01	5 (as CS2)

LC/MS: liquid chromatography – mass spectrometry

LC/MS/MS: liquid chromatography – tandem mass spectrometry

SPE-LC/MS/MS: solid phase extraction – liquid chromatography – tandem mass spectrometry

SPE-LC/MS: solid phase extraction-liquid chromatography – mass spectrometry

SPE-GC/MS: solid phase extraction – gas chromatography – mass spectrometry

SPE-der.GC/MS: solid phase extraction – derivatization – gas chromatography – mass spectrometry

der.HPLC: derivatization and high performance liquid chromatography

NA: not applicable

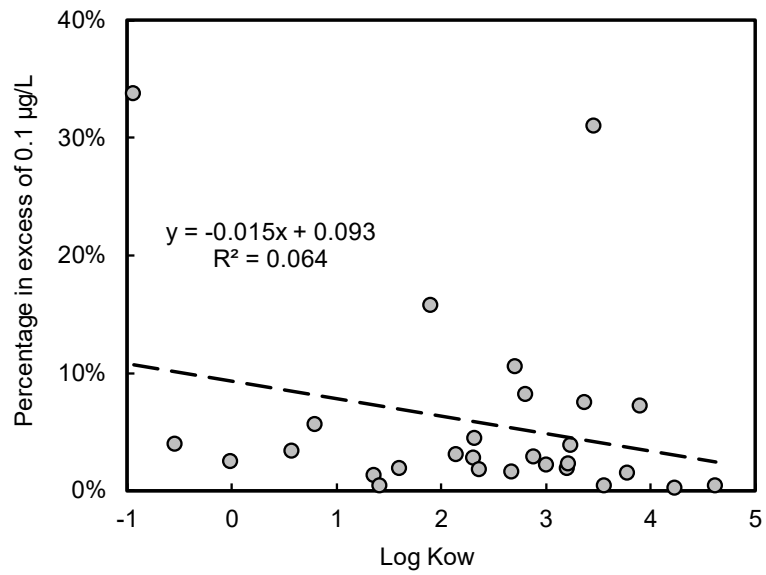
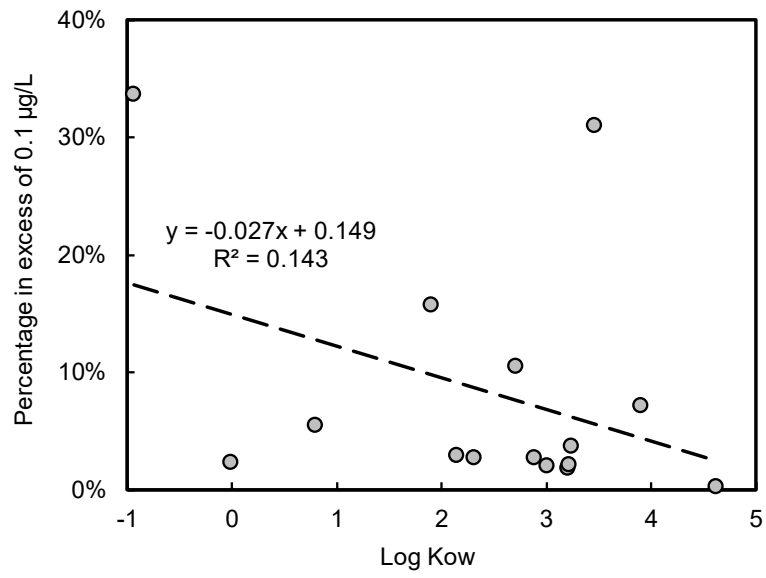


Fig. 2S. Detection rate vs. Log-Kow of herbicides (upper panel) and pesticides (lower panel).

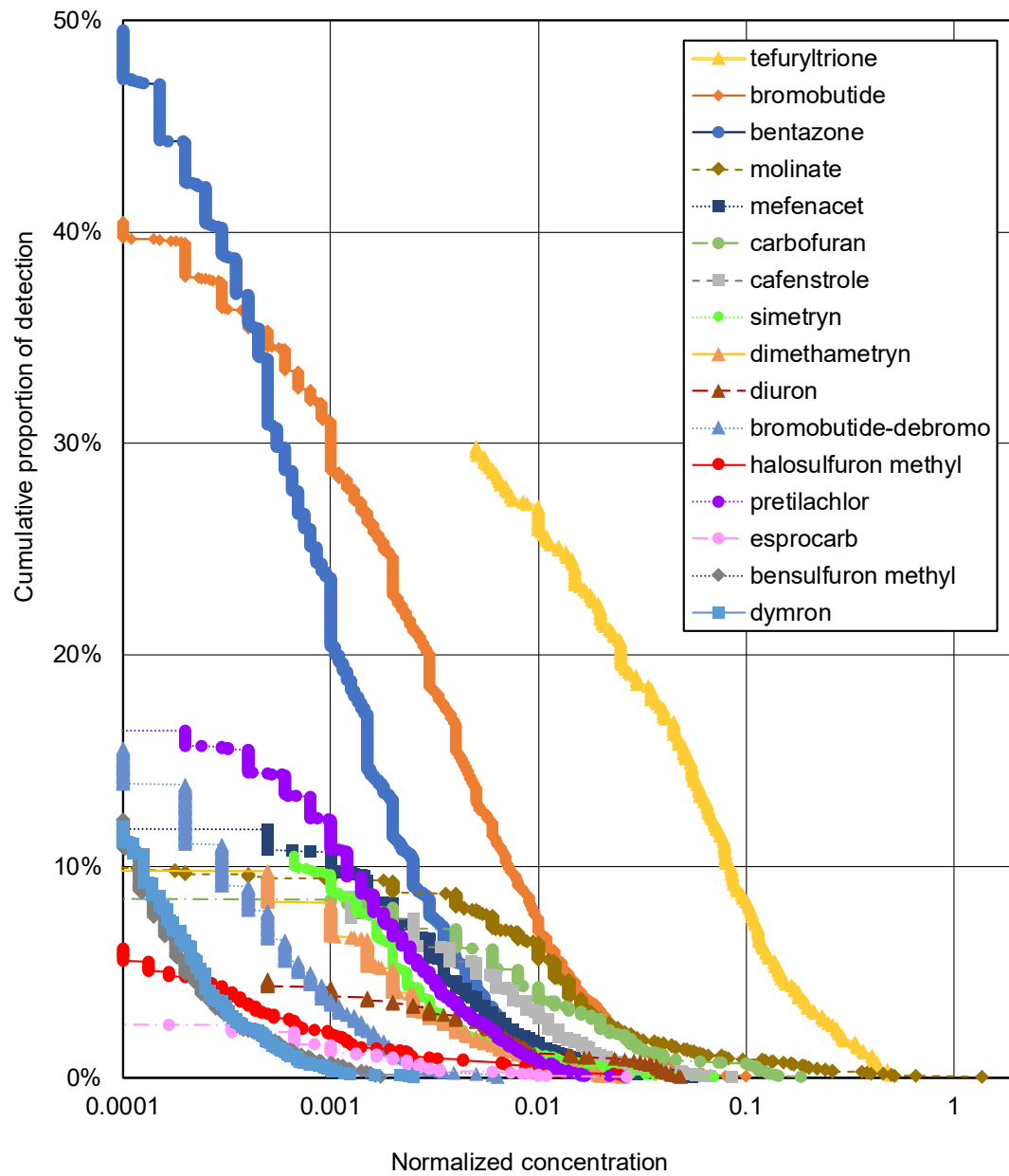


Fig. 3S. Cumulative frequency distributions for normalized concentrations (detected concentration divided by guideline value) of herbicides in drinking water sources (2012–2017). Bromobutide-debromo is a metabolite of bromobutide.

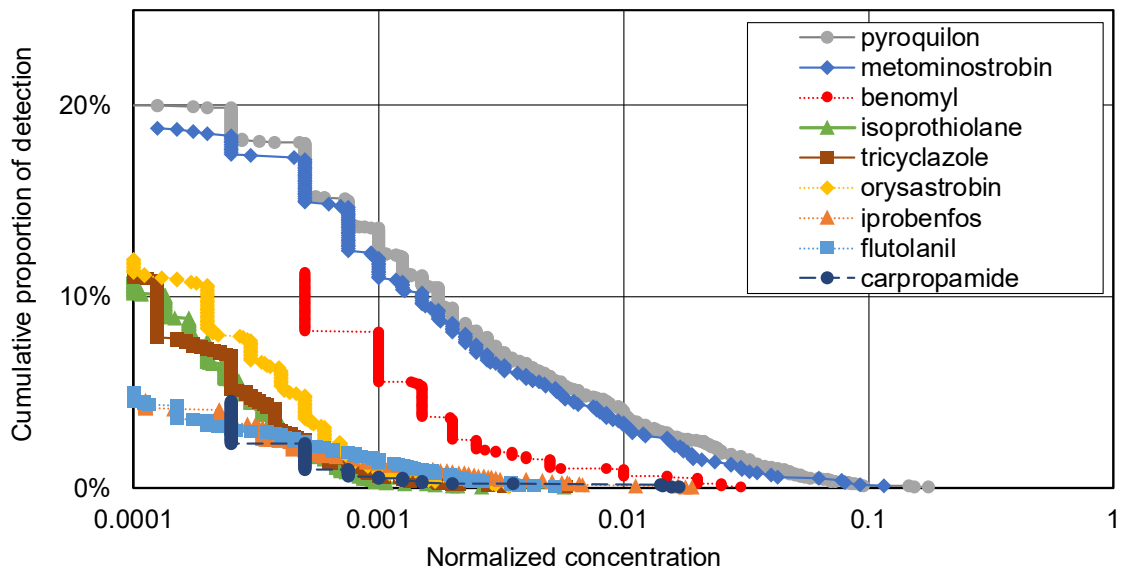


Fig. 4S. Cumulative frequency distributions for normalized concentrations (detected concentration divided by guideline value) of fungicides in drinking water sources (2012–2017).

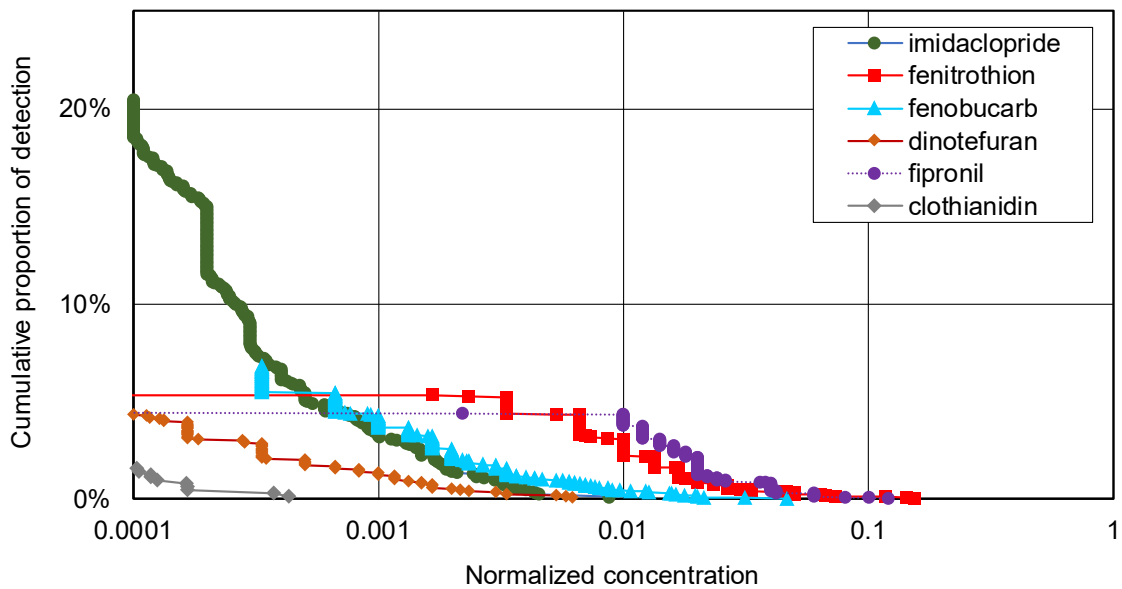


Fig. 5S. Cumulative frequency distributions for normalized concentrations (detected concentration divided by guideline value) of insecticides in drinking water sources (2012–2017).

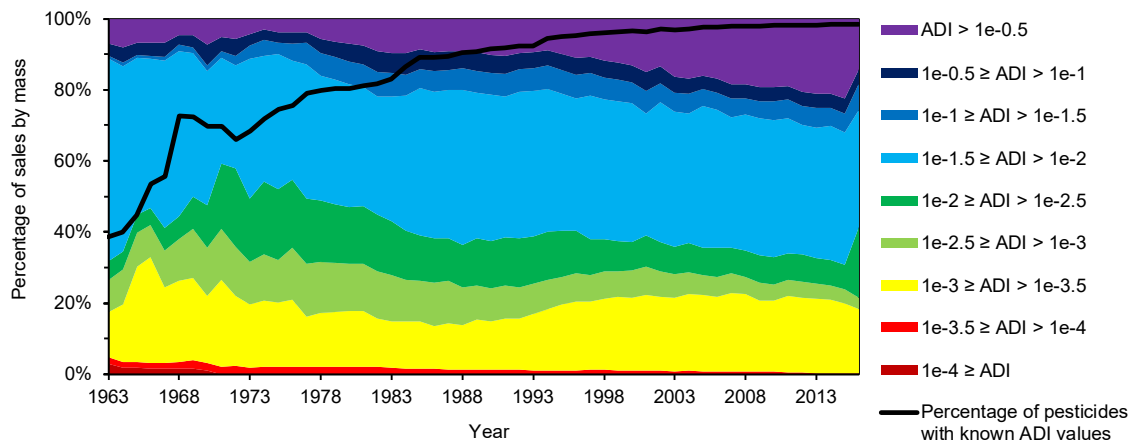


Fig. 6S. Pesticide sales quantities by acceptable daily intake (ADI) values ( $\text{mg kg}^{-1} \text{d}^{-1}$ ). The black line indicates the percentages of pesticides with known ADI values.

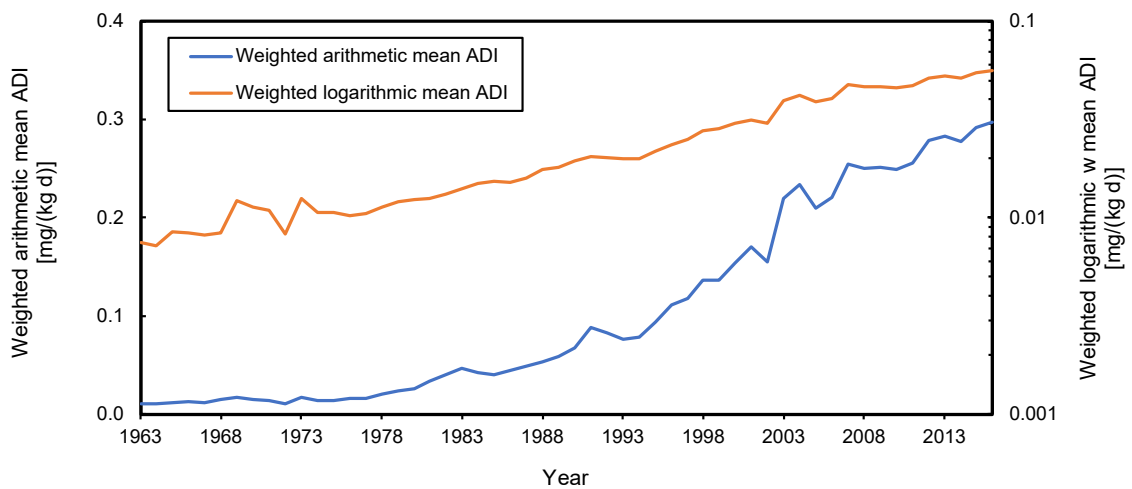


Fig. 7S. Average acceptable daily intake (ADI) values of herbicides

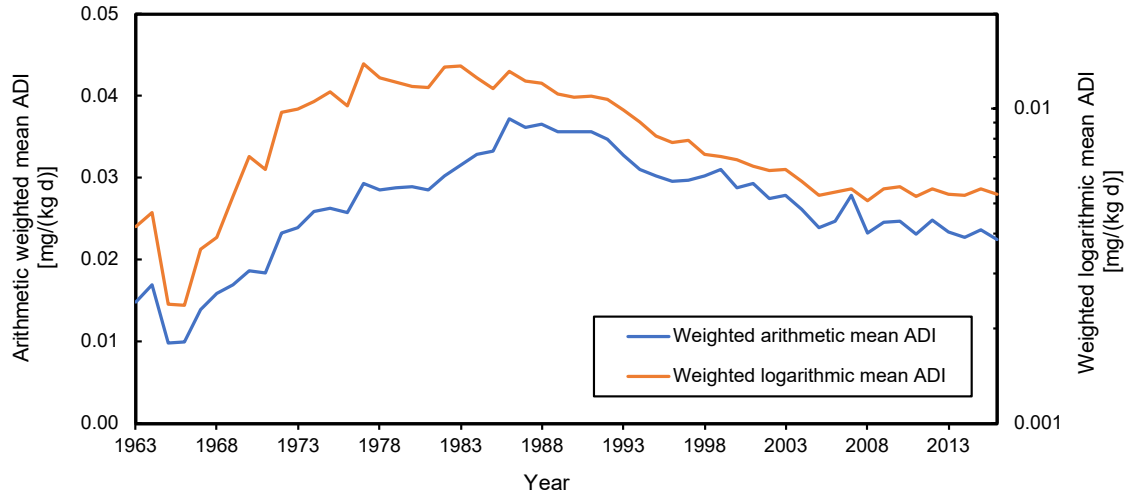


Fig. 8S. Average acceptable daily intake (ADI) values of fungicides

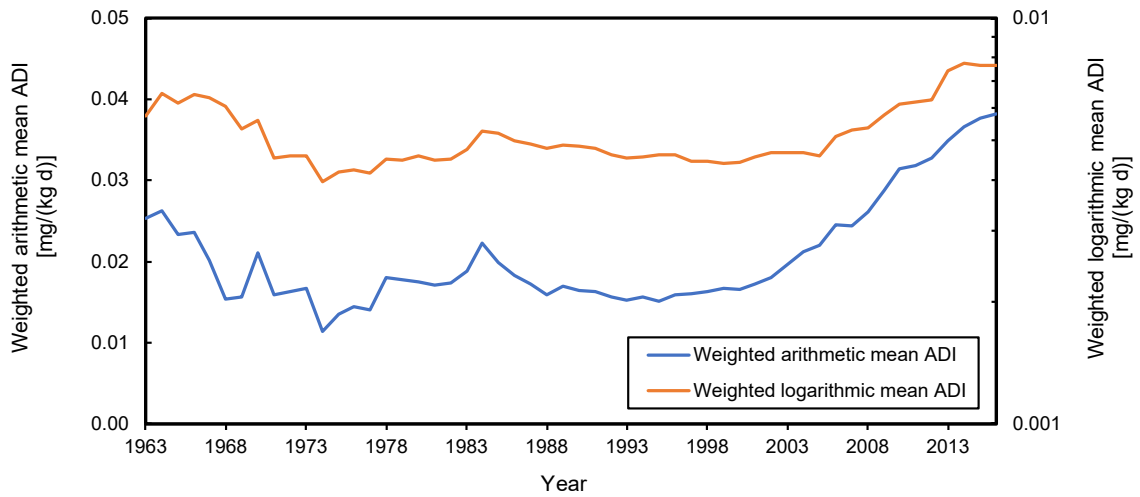


Fig. 9S. Average acceptable daily intake (ADI) values of insecticides

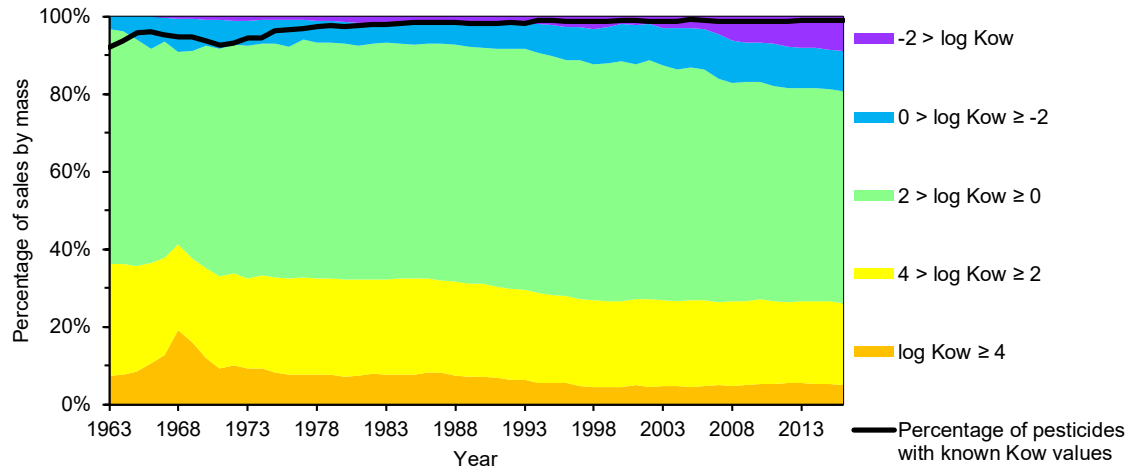


Fig. 10S. Pesticide sales quantities categorized by log Kow values. The black line indicates the percentages of pesticides with known Kow values.