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Review

Temporal trends in organophosphorus pesticides use and concentrations in river water in Japan, and risk assessment

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ABSTRACT

We reviewed organophosphorus pesticide use in Japan between 1982 and 2016 using data from the National Institute of Environmental Studies. Organophosphorus pesticide concentrations in river water throughout Japan were taken from the literature, and risk assessments were performed for some organophosphorus pesticides based on risk quotients and hazard quotients. Assessments were performed for 20 common pesticides, including insecticides, fungicides, and herbicides. The amounts used decreased in the order: insecticides > herbicides > fungicides. Organophosphorus insecticide and fungicide use have decreased over the last four decades, but organophosphorus herbicide use has increased. During this period, annual organophosphorus pesticide use was the highest for chlorpyrifos (105,263 tons/year) and the lowest for glyphosate-sodium (8 tons/year). The ecotoxicological risk assessment indicated that diazinon and fenitrothion posed strong risks to the Japanese aquatic environment, and chlorpyrifos and malathion have moderate risks. None of the pesticides that were assessed posed significant risks to humans. Continued use of organophosphorus pesticides in Japan may cause strong risks to aquatic environments. These risks should be reassessed periodically.

Contents

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Introduction

Pesticides help improve the quality and quantity of crops produced. However, pesticides can cause environmental problems (Spiewak, 2001). For example, humans are exposed to pesticide residues in food and other environmental media (Mnif et al., 2011). Approximately 600 kilotons of pesticide formulations are produced every year in Japan (Iwakuma et al., 1993), and large quantities are applied to farmland (including rice paddies) and gardens (Sakai, 2003). Pesticide application (as the active ingredient) to arable land in Japan in the 1990s was estimated to be 1.5 tons/km^2, which was much higher than inother members of the Organization for Economic Co-operation and Development (OECD) (0.29 tons/km^2 in Germany, 0.78 tons/km in Italy, and 0.21 tons/km^2 in the USA) (OECD, 2002). Pesticide residues have been detected in numerous water bodies in Japan (Hatakeyama et al., 1991; Tsuda et al., 1998; Sakai, 2001; Derbalah et al., 2003; Sudo et al., 2004; Tsuda et al., 2009; Tanabe and Kawata, 2009; Phong et al., 2012; Narushima et al., 2014; Chidya et al., 2018). Pesticide residues in surface water pose risks to humans and aquatic organisms.

Japan has a long history of pesticide use and laws governing its use (Ohta, 2013). Attention needs to be paid to the presence of pesticides in the environment, even though pesticide use in Japan is governed by agricultural laws (Chikushi et al., 2009). This is because large amounts of pesticides have been produced and released into the environment (Numabe et al., 1992; Tsuda et al., 2009, Tsuda et al., 1994, Tsuda et al., 1997; Itagaki et al., 2000; Tanabe et al., 2001; Sudo et al., 2002; Derbalah et al., 2003; Tahara, 2005; Kaonga et al., 2017; Chidya et al., 2018). Pesticide contamination in surface water, particularly through the agricultural use of pesticides, is a worldwide problem (Tsuda et al., 1997). The environment mainly becomes contaminated with pesticides through the application of the pesticides to crops (Abdullah et al., 1997), and surface water mainly becomes polluted by pesticides through runoff of precipitation, stormwater discharges from agricultural land, and runoff of irrigation water (Vryzas et al., 2011). There is a strong possibility that surface and ground water will become contaminated with pesticides in areas with high levels of agricultural activity, and this is especially important when the water is intended for use in either irrigation activities or human consumption (Herrero-Hernandez et al., 2013).

Human exposure to pesticides can be controlled and decreased by properly implementing pesticide application controls, such as by setting maximum pesticide residue limits for food (Japanese Ministry of Health, Labour and Welfare, 2006) and, in Japan, implementation of the Pollutant Release and Transfer Register Law (Japanese Ministry of the Environment and Ministry of Economy, Trade, and Industry, 2001) works efficiently to control and reduce human exposure to pesticides. The large amounts of pesticides used in Japan compared with other countries have caused concern about the exposure of pesticides to people applying them and to the general population.

Organophosphorus compounds (OPs) form one of the largest groups of chemical pesticides. OPs have been used for >60 years to protect crops, livestock, and human health. OPs are produced by reacting alcohols with phosphoric acid (Ghorab and Khalil, 2015), and are often used as fungicides, herbicides, and insecticides because they are cost-effective and have broad activity. However, OPs are very toxic (Costa, 2006). Excessive use of OPs has resulted in non-target organisms, including birds, fish, and humans, being exposed to and harmed by OPs (Salvi et al., 2003; Pazou et al., 2006; Reinecke and Reinecke, 2007; Revankar and Shyama, 2009; Jokanovic et al., 2011).

Various OPs may pose risks to aquatic organisms and humans (PPDB, 2017). It is therefore important to perform ecotoxicological and human health risk assessments of pesticide concentrations in environmental media such as river water and other types of fresh water to attempt to ensure the safety of aquatic organisms and humans (ECC, 2003). Numerous risk assessment approaches are available. The conventional method is to compare measured concentrations with permitted limits for drinking water or to environmental quality standards. Risk quotients are currently adopted for risk assessment (ECC, 2003; Palma et al., 2014).

Much research into various pesticide classes has been performed, but few reviews of organophosphorus herbicides, fungicides, and insecticides have been published, even though OPs are important and very toxic pesticides. The review presented here is therefore required. Trends in OP use in Japanese prefectures have not been fully evaluated, particularly in relation to sources of OPs in aquatic systems and the risks posed by OPs in aquatic systems to environmental and human health. Here, OP use in Japan between 1982 and 2016 was reviewed, and the potential risks posed by OPs to humans and other biota were assessed. Potential risks posed by OPs were estimated using OP concentrations from the literature and calculated risk quotients (RQs) and hazard quotients (HQs).

1. Materials and methods

1.1. *Data analyzed and study area*

The OP data used were obtained from the Japanese National Institute of Environmental Studies database (NIES, 2015). OP use data were available for all 47 Japanese prefectures. Particular interest was paid to the total amounts of OPs used each year in each prefecture. OPs were selected to represent each main use type (herbicide, fungicide, and insecticide). The chemical structures of the selected OPs are shown in Fig. 1 and the modes of action, CAS numbers, and classifications of the OPs are shown in Table 1. Data for the risk assessments for the OPs were obtained from previous publications (JACC, 2010; USEPA, 2016; PPDB, 2017). OP concentrations in the water of different rivers (location presented in Fig. 2) in Japan for use in the risk assessments were obtained from previous publications.

1.2. *Risk assessment for OPs*

1.2.1. *Ecotoxicological risk assessment*

The toxicity exposure ratio or RQ, defined as the measured environmental concentration divided by the predicted no-effect concentration (PNEC), is commonly used in risk assessments. Here, risk assessments for the selected pesticides were performed using RQs. The measured concentrations of the selected pesticides in different rivers in Japan (obtained from literature) are shown in Table 2. The chemical properties of the pesticides and ecotoxicological risk assessment data for the pesticides are shown in Table 3.

The RQ_i for pesticide i was calculated using Eq. (1):

$$RQ_i = \frac{MEC}{PNEC} \tag{1}$$

where, MEC (mg/L) is the measured environmental concentration and PNEC is the predicted no-effect concentration. Each PNEC (mg/L) was calculated from a critical concentration such as the concentration lethal to 50% of test organisms (LC_{50}), 50% effective concentration (EC_{50}), or no-observed-effect concentration (NOEC). The calculations were performed using previously published standards (ECC, 2003; Vryzas et al., 2009; Palma et al., 2014).

To account for uncertainty in the data and missing data when calculating the toxicity parameters, PNECs were estimated for three trophic levels (algae, crustaceans, and fish) using assessment factors (AFs). The equations used to calculate the critical concentrations (PNEC = NOEC/AF, PNEC = LC_{50}/AF, or PNEC = EC_{50}/AF) were selected depending on whether NOEC, LC_{50}, or EC_{50} data were available for algae, aquatic invertebrates, and fish. An AF of 1000 was used when at least one short-term assay result was available for one trophic level, an AF of 100 was used when data from one long-term assay were available for fish or zooplankton, and AFs of 50 and 10 were used when data from two and three long-term assays, respectively, were available (ECC, 2003). The NOEC, LC_{50}, EC_{50}, and log octanol–water partition coefficient data were taken from reputable databases (JACC, 2010; USEPA, 2016; PPDB, 2017). The RQs were used to classify the OPs as low risk ($0.01 \le RQ < 0.1$), medium risk ($0.1 \le RQ < 1$, or high risk ($RQ \ge 1$) (Sánchez-Bayo et al., 2002; Vryzas et al., 2011).

1.2.2. *Human health risk assessment*

Non-carcinogenic risks to humans posed by the selected OPs were estimated using HQs, as in previous studies (Hu et al., 2011; USEPA, 2010; Papadakis et al., 2015). The HQs were calculated assuming that surface water (as drinking water) is ingested directly (Hu et al., 2011; Papadakis et al., 2015) using Eq. (2):

$$HQ = \frac{CDI}{RfD} \tag{2}$$

where CDI (mg/kg body weight) is the chronic daily intake of the OP through ingestion per unit body weight, and RfD (mg/(kg·day)) is the reference dose for the pesticide through oral exposure only. The RfD was represented by the acceptable daily intake, as in a previous publication (USEPA, 2016). The CDI for each pesticide was calculated using Eq. (3):

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{3}$$

where, C (mg/L) is the measured concentration of a pesticide in river water, IR is the water ingestion rate (0.87 L/day for a 6-year-old child, 1.41 L/day for a 70-year-old adult), EF is the exposure frequency (365 days/year), ED is the exposure period (6 years for a child, 70 years for an adult), BW is the body weight (20 kg for a child, 70 kg for an adult), and AT is the average lifespan (2190 days for a child, 25,550 days for an adult) (USEPA, 2010). $HQ > 1$ was taken to indicate that adverse effects could occur and $HQ < 1$ to indicate that adverse effects were improbable (Papadakis et al., 2015).

2. Results and discussion

2.1. *Trends in use of selected OPs in Japan*

2.1.1. *Organophosphorus insecticides*

The organophosphorus insecticides considered here were acephate, chlorpyrifos, chlorpyrifos-methyl, diazinon, dimethoate, ebufos, fenitrothion, isoxathion, malathion, pirimiphos-methyl, and profenphos. These insecticides are generally used to protect crops, livestock, and humans from insects.

Acephate is an organophosphorus insecticide used to control insects such as aphids and leafminers that affect agricultural crops (PPDB, 2017). Acephate has recently become of concern because exposure to acephate adversely affects

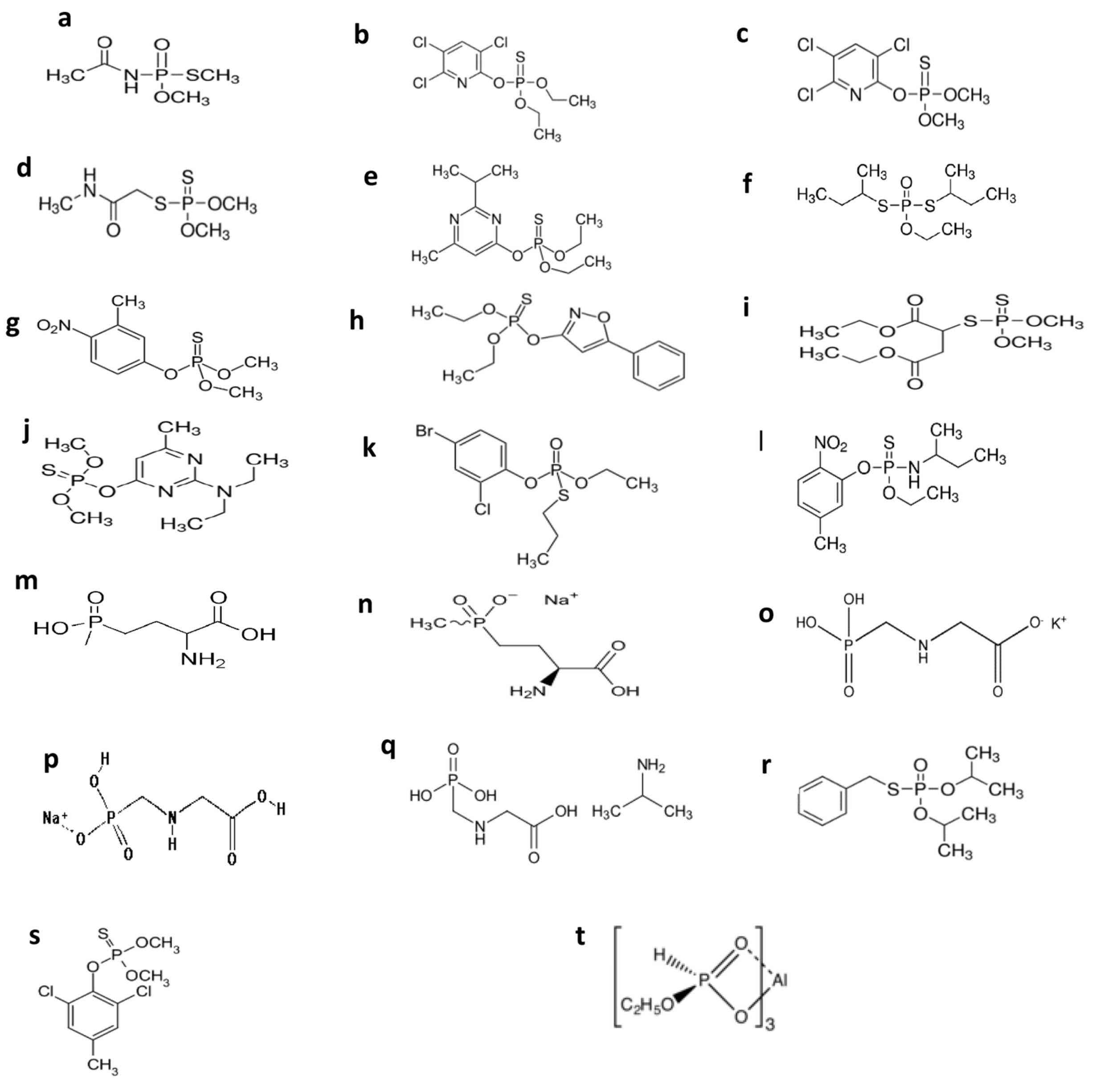

Fig. 1 – Chemical structures of reviewed organophosphorus pesticides: acephate (a); chlorpyrifos (b); chlorpyrifos-methyl (c); dimethoate (d); diazinon (e); ebufos (f); fenitrothion (g); isoxathion (h); malathion (i); pirimphos-methyl (j); profenphos (k); butamifos (l); glufosinate-ammonium (m); glufosinate-sodium (n); glyphosate-potassium (o); glyphosate-sodium (p); glyphosate-isopropyl ammonium (q); iprobenfos (r); tolclofos-methyl (s); and fosetyl-al (t).

metabolism (causing problems such as hyperglycemia) and causes DNA damage and cancer (Costa, 2006; Du et al., 2014). Acephate has been used in Japan since 1982, and its usage data for 1982–2016 are shown in Fig. 3a. Large quantities of acephate were used between 1986 and 2002 (maximum 795.33 tons in 1995, minimum 274.93 tons in 2016). Acephate use gradually increased between 1983 and 2000, then gradually decreased until 2016.

Chlorpyrifos, one of the most commonly used organophosphorus insecticides, is used around the world to control insects in agricultural and domestic settings (USEPA, 2002). Chlorpyrifos may adversely affect humans and the environment, so in 2001 its use to control domestic pests in the United States was banned and its use on certain crops was restricted. Chlorpyrifos has been used in Japan since 2001 (2001–2015 usage data are shown in Fig. 3b). Large quantities of chlorpyrifos were used in Japan between 2001 and 2002 (maximum 105,263 tons in 2001, minimum 74,279 tons in 2004). Chlorpyrifos use decreased between 2002 and 2004, increased until 2008, decreased until 2011, then increased slightly until 2015.

Chlorpyrifos-methyl is one of the most widely used organophosphorus insecticides for protecting agricultural crops (Munoz et al., 2011). Chlorpyrifos-methyl use in Japan between 1982 and 2011 is shown in Fig. 3c. Large quantities of chlorpyrifos-methyl were used in Japan between 1986 and 1991. Chlorpyrifos-methyl use increased between 1983 and 1987, then gradually decreased until 2011 (maximum 150.08 tons in 1987, minimum 0.6 tons in 2011).

Table 1 – Names, CAS numbers, classes, and modes of action of the pesticides that were assessed *.

Compound	CAS number	Class	Mode of action
Acephate	30560-19-1	Insecticide	Inhibition of ACHE
Chlorpyrifos	2921-88-2	Insecticide	Inhibition of ACHE
Chlorpyrifos-methyl	5598-13-0	Insecticide	Inhibition of ACHE
Dimethoate	60-51-5	Insecticide	Inhibition of ACHE
Diazinon	333-41-5	Insecticide	Inhibition of ACHE
Ebufos	95465-99-9	Insecticide	Inhibition of ACHE
Fenitrothion	22-14-5	Insecticide	Inhibition of ACHE
Isoxathion	18845-01-8	Insecticide	Inhibition of ACHE
Malathion	121-75-5	Insecticide	Inhibition of ACHE
Pirimiphos-methyl	29232-93-7	Insecticide	Inhibition of ACHE
Profenphos	41198-08-7	Insecticide	Inhibition of ACHE
Butamifos	36335-67-8	Herbicide	Microtubule assembly inhibition
Glufosinate- ammonium	77182-82-2	Herbicide	Inhibition of glutamine synthetase
Glufosinate-P-sodium	70033-13-5	Herbicide	Inhibition of glutamine synthetase
Glyphosate-isopropylammonium	96639-11-1	Herbicide	Inhibition of EPSP synthase
Glyphosate-potassium	39600-42-5	Herbicide	Inhibition of EPSP synthase
Glyphosate-sodium	70393-85-0	Herbicide	Inhibition of EPSP synthase
Iprobenfos	26087-47-8	Fungicide	Phospholipid biosynthesis inhibitor
Tolclofos-methyl	57018-04-9	Fungicide	Lipid peroxidation inhibitor
Fosteyl-Aluminum	39148-24-8	Fungicide	Inhibits spore germination

ACHE: acetylcholinesterase; EPSP: enolpyruvylshikimate-3-phosphate synthase.
* Source of all OPs pesticides data in this table obtained from PPBD, 2018.

Diazinon is widely applied to fruits, vegetables, and other commercially produced plants (e.g., tea and tobacco) to control insects and mites (Cycoń et al., 2009). Diazinon has also been used to control insects in gardens and domestic buildings (Bailey et al., 2000). Diazinon use in Japan between 1982 and 2016 is shown in Fig. 3d. Diazinon reached a maximum in 1983, then gradually decreased until 2016 (maximum 924.07 tons in 1983, minimum 329.95 tons in 2016).

Dimethoate is used to control mites and insects both systemically and on contact. Dimethoate has been used to control a wide range of insects affecting many crops (including vegetables) and flowers. Dimethoate has also been used to control domestic flies and some insects that affect livestock. Dimethoate has been used in Japan since 2001, and usage data for 2001–2015 are shown in Fig. 3e. Large quantities of dimethoate were used between 2001 and 2002 (maximum 73,218 tons in 2001, minimum 7356 tons in 2015).

Ebufos (cadusafos) is used to control a wide range of soil insects and nematodes in many fruit and vegetable crops (Zheng et al., 1994). Ebufos has been used in Japan since 2001, and use between 2001 and 2016 is shown in Fig. 3f. Ebufos use in Japan gradually increased from 2002 to 2016, and large

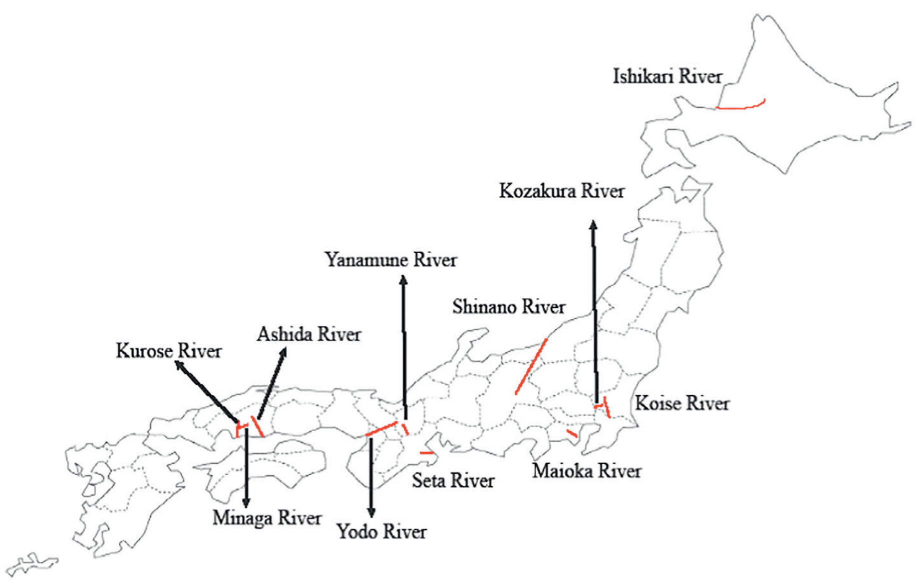

Fig. 2 – River locations (red lines) in Japan.

Table 2 – Concentrations of the selected organophosphorus pesticides found in river water in Japan.

River	Compound	Year	Concentration (ng/L)			Reference
			Minimum	Maximum	Average	
Ashida River	Diazinon	2004	–	250	56	Tahara, 2005
	Fenitrothion	2004	–	1100	210	Tahara, 2005
	Iprobenfos	2004	–	540	110	Tahara, 2005
Ishikari River	Diazinon	2004	–	–	16	Kondoh et al., 2001
	Isoxathion	2001		10	3	Kondoh et al., 2001
Koise River	Iprobenfos	1993	4300	17,500	10,400	Iwakuma et al., 1993
Kozakura River	Fenitrothion	1992	–	–	25	Numabe et al., 1992
Kurose River	Diazinon	2004	–	30	23	Tahara, 2005
		2016	12	1194	348	Chidya et al., 2018
	Fenitrothion	2001	21	304	35	Derbalah et al., 2003
		2004	–	250	82	Tahara, 2005
		2013	2.2	107	54	Kaonga et al., 2017
	Iprobenfos	2003	–	68	21	Tahara, 2005
	Isoxathion	2001	9	20	10	Derbalah et al., 2003
	Butamifos	2001	7	82	9	Derbalah et al., 2003
		2004	–	15	4.7	Tahara, 2005
	Tolclofos-methyl	2001	6	25	9	Derbalah et al., 2003
Maioka River	Tolclofos-methyl	2001	–	7	7	Sakai, 2002
Minaga River	Fenitrothion	2000	–	–	8	Itagaki et al., 2000
Seta River	Diazinon	2002	19	33	23	Sudo et al., 2002
	Fenitrothion	2002	ND	18	6	Sudo et al., 2002
Shinano River	Diazinon	1996	14	320	38	Tanabe et al., 2001
	Fenitrothion	1996	14	1700	89	Tanabe et al., 2001
	Iprobenfos	1996	12	870	180	Tanabe et al., 2001
	Butamifos	1996	18	34	28	Tanabe et al., 2001
	Chlorpyrifos	1996	4	10	7	Tanabe et al., 2001
	Malathion	1996	28	38	33	Tanabe et al., 2001
	Dimethoate	1996	26	200	113	Tanabe et al., 2001
Yanamune River	Diazinon	2009	10	20	10	Tsuda et al., 2009
	Fenitrothion	2009	–	20	10	Tsuda et al., 2009
	Iprobenfos	2009	10	10	10	Tsuda et al., 2009
Yodo River	Diazinon	1987	380	2500	1390	Fukushima, 1987
	Fenitrothion	1987	10	280	142	Fukushima, 1987

ND, not detected; –, no data available.

Table 3 – Chemical properties of the organophosphorus pesticides and ecotoxicological risk assessment data for the organophosphorus pesticides in Japanese river water*.

Compound	$\log K_{OW}$ (solubility in mg/L)	Trophic levels (mg/L) (NOEC except indicated)			Critical concentration	Assessment factor
		Algae	Aquatic invertebrates	Fish		
Butamifos	4.62 (6.19)	0.025 (EC_{50})	NA	4.10 (LC_{50})	0.025 (EC_{50})	1000
Chlorpyrifos	4.7 (1.05)	0.43	0.0046	0.00014	0.00014 (NOEC)	50
Diazinon	3.81 (60)	6.4 (EC_{50})	0.00056	0.7	0.00056 (NOEC)	50
Dimethoate	0.75 (25900)	32	0.04	0.4	0.04 (NOEC)	50
Fenitrothion	3.3 (19)	0.1	0.000078	0.088	0.000078 (NOEC)	10
Iprobenfos	3.37 (540)	6.05 (EC_{50})	1.2 (EC_{50})	14.7 (LC_{50})	1.2 (EC_{50})	1000
Isoxathion	3.88 (1.9)	NA	0.0052 (EC_{50})	1.7 (LC_{50})	0.0052 (EC_{50})	1000
Malathion	2.75 (148)	13 (EC_{50})	0.00006	0.091	0.00006 (NOEC)	50
Tolclofos-methyl	4.56 (0.70)	0.032	0.026	0.012	0.012 (NOEC)	10

NOEC: no-observed-effect-concentration, risk assessment parameter that represents the concentration of a pollutant that will not show harm effect to the species involved, with respect to the effect that is studied.
NA: not available.
* Data Sources: PPBD, 2018; USEPA, 2016.

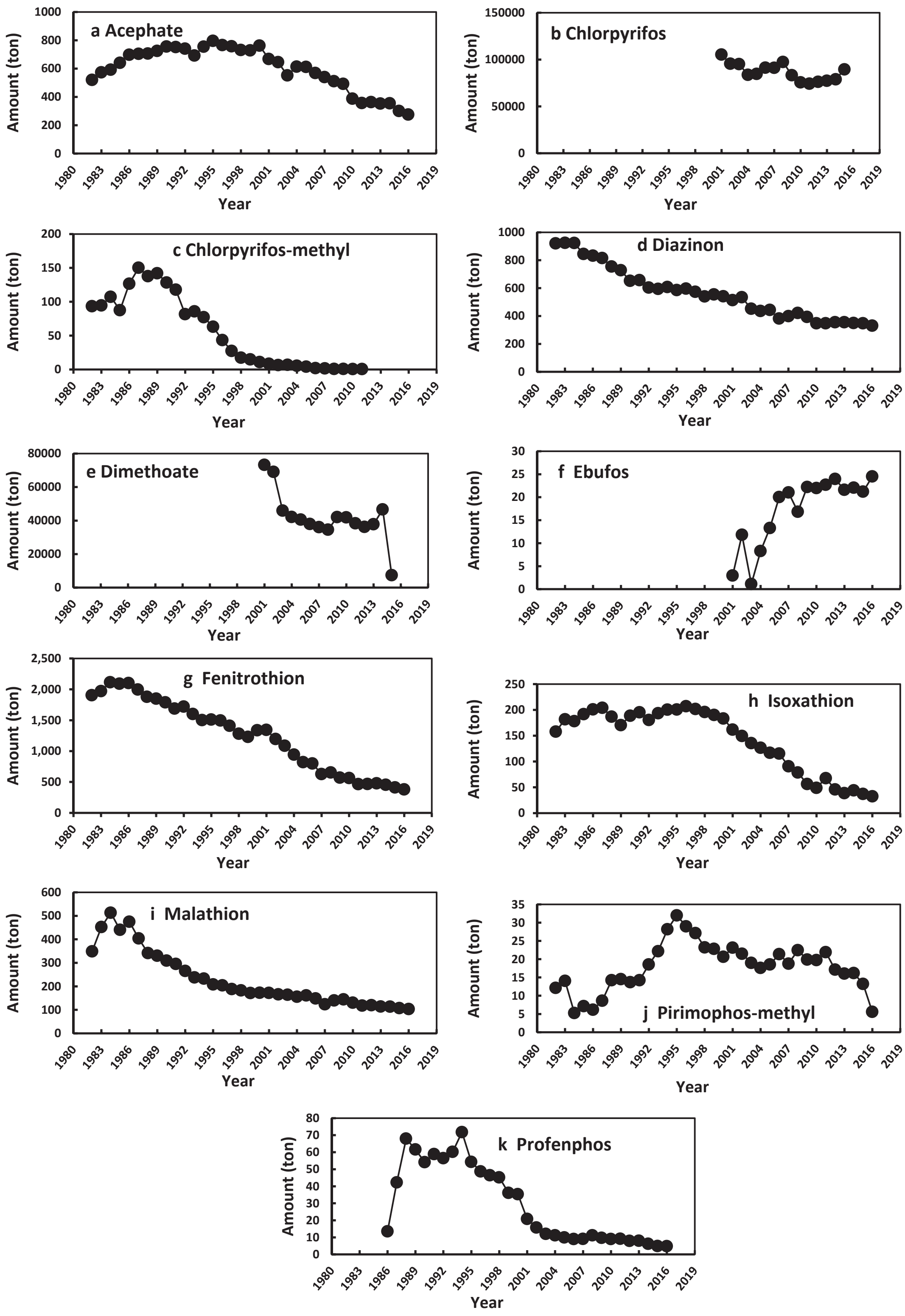

Fig. 3 – Temporal trends in organophosphate insecticide use in Japan (1982–2016).

quantities were used between 2009 and 2016 (maximum 24.51 tons in 2016, minimum 1.107 tons in 2003).

Fenitrothion is commonly used in Japan, primarily to control rice-stem borers. Fenitrothion is effective but acutely toxic to non-target organisms (Derbalah et al., 2004). Fenitrothion use in Japan between 1982 and 2016 is shown in Fig. 3g. Large quantities of fenitrothion were used between 1983 and 2000. Fenitrothion use gradually increased between 1983 and 2000, then gradually decreased until 2016 (maximum 2114.10 tons in 1984, minimum 379.124 tons in 2016).

Isoxathion is used to control many sucking and chewing insects (e.g., aphids, coccidae, and scale insects) on various fruit, vegetable, and ornamental crops. Isoxathion also has non-food applications (Robert et al., 1998). Isoxathion use in Japan between 1982 and 2016 is shown in Fig. 3h. Large quantities of isoxathion were used between 1983 and 2000, then use decreased until 2016 (maximum 206.99 tons in 1996, minimum 32.46 tons in 2016).

Malathion is used to control insects affecting agricultural crops, insects in residential areas, and pests such as head and body lice (Gao et al., 2018). Malathion is also used to control mosquitoes in water bodies, meaning it can be found at high concentrations in water and can affect non-target organisms (Karmakar et al., 2016). Malathion can disrupt the endocrine system (McKinlay et al., 2008; Mnif et al., 2011). Malathion has been used in Japan since 1982, and use between 1982 and 2016 is shown in Fig. 3i. Large quantities of malathion were used between 1983 and 1986. Malathion use increased between 1983 and 1984, then continually decreased until 2016 (maximum 513.35 tons in 1984, minimum 103.25 tons in 2016).

Pirimiphos-methyl (Silman and Futerman, 1987; Taylor, 1990) is used to control a wide range of insects affecting stored products (Huang and Subramanyam, 2005; Kljajić and Perić, 2006). Pirimiphos-methyl has been used in Japan since 1982, and use between 1982 and 2016 is shown in Fig. 3j. Large quantities of pirimiphos-methyl were used between 1994 and 1997. Pirimiphos-methyl use decreased in 1984, increased between 1985 and 1995, then gradually decreased until 2016 (maximum 31.99 tons in 1995, minimum 5.58 tons in 2016).

Profenphos (curacron) is widely used to control caterpillars, whiteflies, and mites on vegetables (Habiba et al., 1992). Profenphos has been used in Japan since 1986, and use between 1986 and 2016 is shown in Fig. 2k. Large quantities of profenphos were used between 1988 and 1994. Profenphos use increased dramatically between 1987 and 1988, gradually decreased until 1990, increased between 1991 and 1994, and decreased until 2016 (maximum 71.8 tons in 1994, minimum 4.8 tons in 2016).

2.1.2. Organophosphorus fungicides

The organophosphorus fungicides considered in this review were fosetyl-Al, iprobenfos, and tolclofos-methyl. These compounds are commonly used to control fungi that affect agricultural crops.

Fosetyl-Al is a systemic fungicide used to control fungal diseases in many agricultural crops (FAO, 2013). Fosetyl-Al inhibits spore germination or blocks mycelium development and causes sporulation induction in the host-plant defenses (Urban and Lebeda, 2007). Fosetyl-Al has been found to cause crustacean and fish mortality, intoxicate mollusks and zooplankton, and severely irritate the eyes in humans (Kaonga et al., 2017). Fosetyl-Al has been used in Japan since 1983, and use between 1983 and 2016 is shown in Fig. 4a. Large quantities of fosetyl-Al were used between 1986 and 2000. Fosetyl-Al use increased between 1984 and 1999, then gradually decreased until 2016 (maximum 223.47 tons in 1999, minimum 24.08 tons in 1983).

Iprobenfos is an organic thiophosphate fungicide that is the S-benzyl O,O-diisopropyl ester of phosphorothioic acid. Iprobenfos is used to control leaf and ear blast, stem rot, and sheath blight in rice (Uesugi, 2001). Iprobenfos is one of the most commonly used fungicides in Japan and is often detected in freshwater (Nohara and Iwakuma, 1996). Iprobenfos has been used in Japan since 1982, and use between 1984 and 2016 is shown in Fig. 4b. Large quantities of iprobenfos were used between 1982 and 1984, then use gradually decreased until 2016 (maximum 2314.46 tons in 1982, minimum 11.18 tons in 2016).

Tolclofos-methyl is used to control fungal diseases that affect many crops. Tolclofos-methyl is very toxic to many aquatic organisms (USEPA, 2013). Tolclofos-methyl has been used in Japan since 1984, and use between 1984 and 2016 is shown in Fig. 4c. Large quantities of tolclofos-methyl were used between 1992 and 1999. Tolclofos-methyl use increased between 1984 and 1995, gradually decreased until 2008, then increased slightly until 2016 (maximum 203.53 tons in 1995, minimum 0.675 tons in 1984).

2.1.3. Organophosphorus herbicides

The organophosphorus herbicides studied here were butamifos, glufosinate-ammonium, glufosinate-sodium, glyphosate-isopropyl ammonium, glyphosate-potassium, and glyphosate-sodium. These compounds are used to control weeds.

Butamifos is used to control annual and graminaceous weeds in rice and various vegetable crops including beans, beets, cereals, onions, strawberries, and wheat. In Japan, pesticides such as butamifos are classed as ‘management items’ in drinking water regulations (Kamoshita et al., 2010). Butamifos has been used in Japan since 1982, and use between 1982 and 2016 is shown in Fig. 5a. Large quantities of butamifos were used between 1985 and 1999. Butamifos use increased between 1983 and 1996, then gradually decreased until 2016 (maximum 47.66 tons in 1996, minimum 11.28 tons in 1982).

Glufosinate is a non-selective, post-emergence, broad-spectrum herbicide that is widely used to control weeds (Royer et al., 2000; Ibáñez et al., 2005). Glufosinate kills weeds by competitively inhibiting glutamine enzyme synthesis (Kataoka et al., 1996; Rojano-Delgado et al., 2014). Glufosinate was registered as a pesticide in Japan in 1984, and other glufosinate-based herbicides, such as glufosinate-ammonium and glufosinate-sodium, came into use later. There have been numerous accidental and suicidal deaths caused by ingestion of glufosinate herbicides (Tanaka et al., 1998). Glufosinate is not persistent in the environment but may pose risks to human health because it is used widely and intensively in agriculture (Druart et al., 2011; Lin et al., 2012).

Glufosinate-ammonium has been used in Japan since 1984, and use between 1984 and 2016 is shown in Fig. 5b. Large quantities of glufosinate-ammonium were used between 1993 and 1999. Glufosinate-ammonium use increased between 1985 and 1995, gradually decreased until 2002, increased until 2003, then remained relatively stable until 2016 (maximum 448.12 tons in 1995, minimum 0.869 tons in 1984).

Glufosinate-sodium has been used in Japan since 2011, and use between 2011 and 2016 is shown in Fig. 5c. Glufosinate-sodium use increased between 2011 and 2016 (maximum 41.71 tons in 2016, minimum 10.70 tons in 2011).

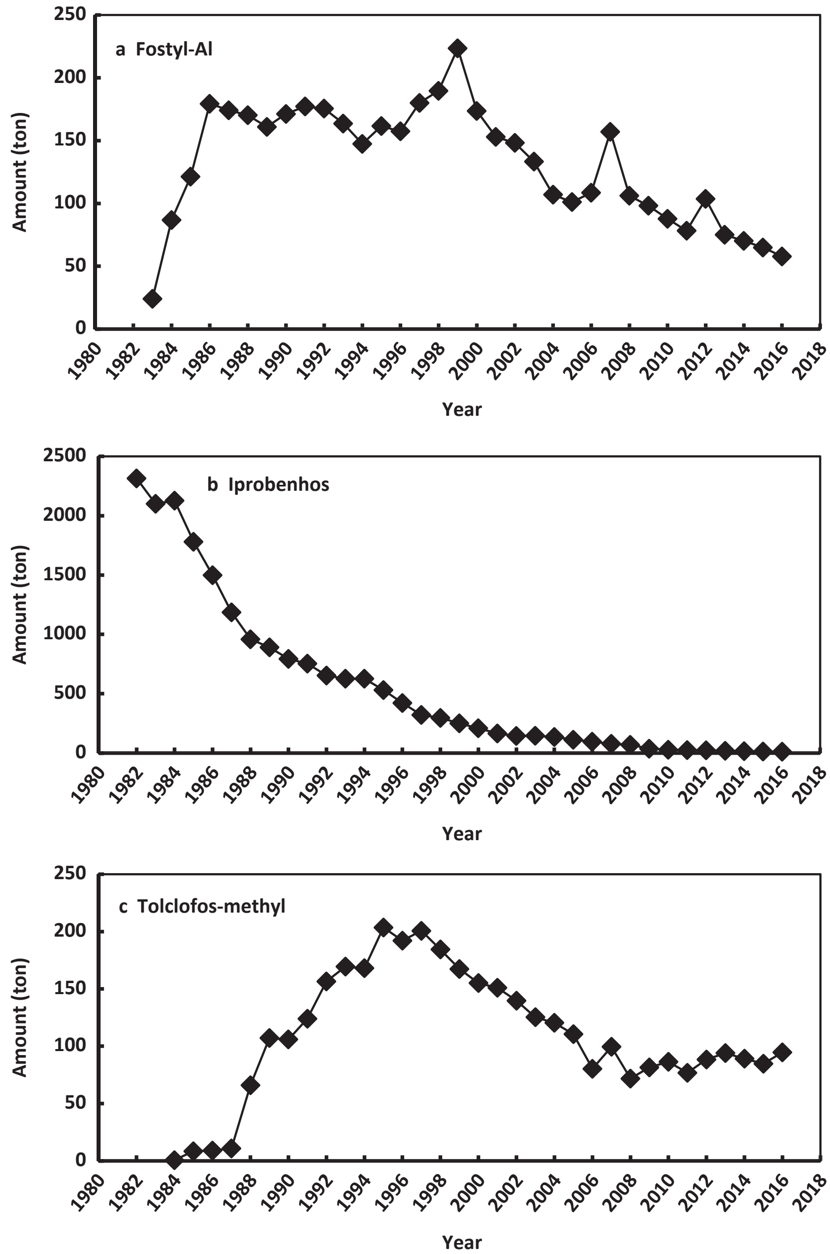

Fig. 4 – Temporal trends in organophosphate fungicide use in Japan (1982–2016).

Glyphosate-based herbicides such as glyphosate, glyphosate-potassium, glyphosate-ammonium, and glyphosate-isopropyl ammonium are systemic broad-spectrum herbicides. Glyphosate sales in 2010 were worth approximately US\$ 6.5 × 10^9, which was more than sales of all other herbicides combined (Sansom, 2012). In 2011, 650,000 tons of glyphosate products were used around the world (CCM International, 2011).

Glyphosate-isopropyl ammonium has been used in Japan since 1989, and use between 1989 and 2016 is shown in Fig. 5d. Glyphosate-isopropyl ammonium use in Japan increased markedly in two specific periods, 1997–1999 and 2003–2016. Glyphosate-isopropyl ammonium use increased between 1990 and 1998, gradually decreased until 2002, then increased until 2016 (maximum 2313.88 tons in 2016, minimum 45.94 tons in 1989).

Glyphosate-potassium has been used in Japan since 2005, and use between 2005 and 2016 is shown in Fig. 5e. Large quantities of glyphosate-potassium were used between 2009 and 2016. Glyphosate-potassium use increased between 2006 and 2016 (maximum 3106.26 tons in 2016, minimum 1.333 tons in 2005).

Glyphosate-sodium has been used in Japan since 1992, and use between 1992 and 2016 is shown in Fig. 5f. Large quantities of glyphosate-potassium were used between 1995 and 1996, then use gradually decreased until 2005 and then increased until 2016 (maximum 6.94 tons in 1996, minimum 0.81 tons in 2010).

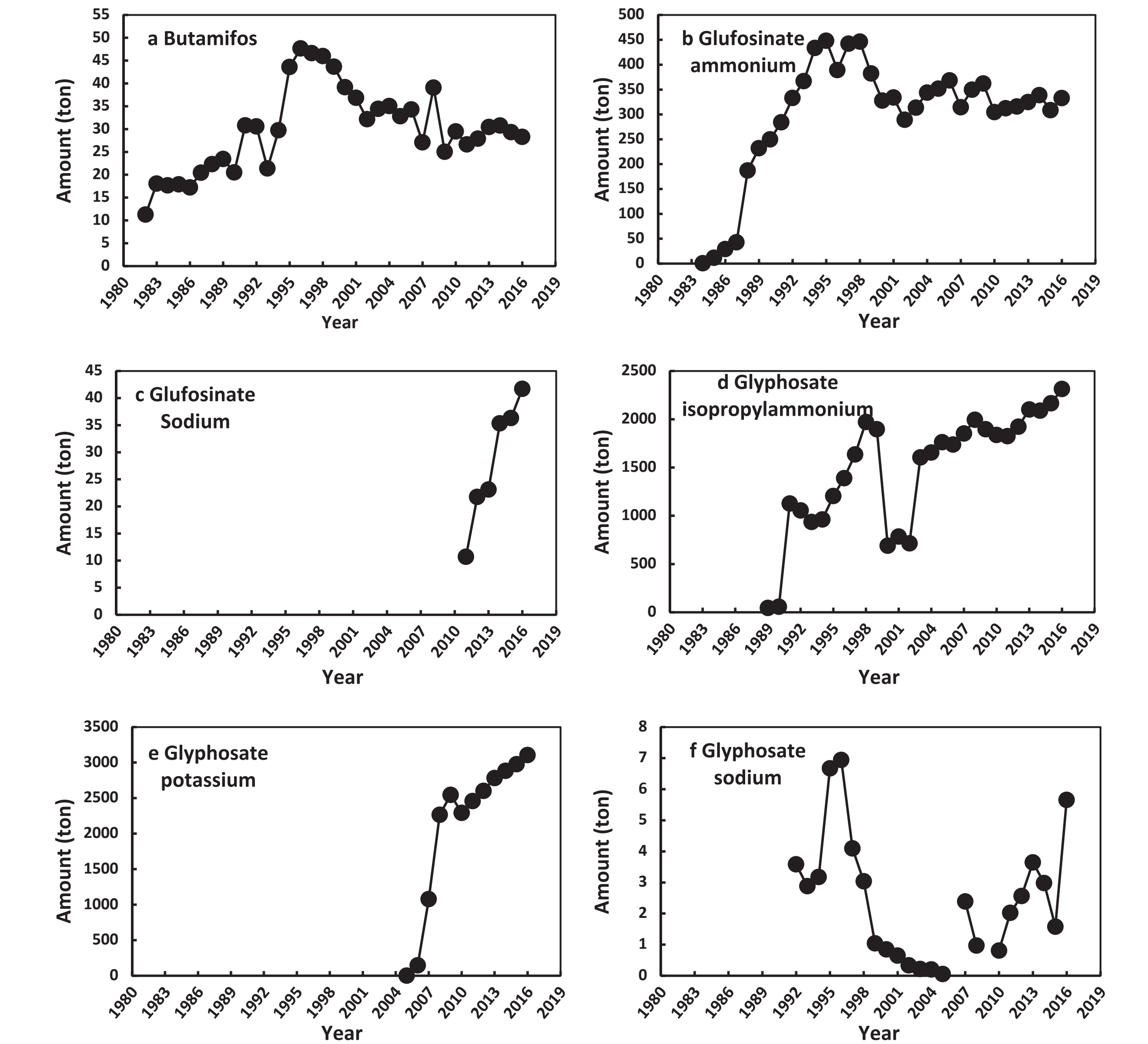

Fig. 5 – Temporal trends in organophosphate herbicide use in Japan (1982–2016).

2.2. General overview of OP uses in Japan

As shown in Fig. 6, organophosphorus herbicide use increased and organophosphorus insecticides and fungicides decreased over the study period (Fig. 6). The maximum total quantities of each OPs class used in a year were 2214.62 tonsfor organophosphorus fungicides in 1984, 5828.7 tons oforganophosphorus herbicides in 2016, and 180,145 tonsoforganophosphorus insecticides in 2001. Glyphosate-potassium and glyphosate-sodium were the most- and least-used organophosphorus herbicides, respectively. Iprobenfos and tolclofos-methyl were the most- and least-used organophosphorus fungicides, respectively. Chlorpyrifos and ebufos were the most- and least-used organophosphorus insecticides, respectively.

2.3. OP concentrations in Japanese river water

The runoff of surface water from land to which OPs have been applied has caused river water to become contaminated with OPs (Richards and Baker, 1993). The amounts and types of OPs in freshwater will depend strongly on the local agricultural intensity and crop varieties. OPs concentrations in Japanese river water will be directly related to the use of OPs to control pests (all concentrations shown in Table 2 were taken from the literature). Butamifos, chlorpyrifos, diazinon, dimethoate, fenitrothion, iprobenfos, isoxathion, malathion, and tolclofos-methyl have been detected in Japanese river water. Of these, diazinon and fenitrothion were found most often and chlorpyrifos, dimethoate, and malathion were found least often. The organophosphorus insecticides (chlorpyrifos, diazinon, dimethoate, fenitrothion, isoxathion, and malathion) were more common (in terms of the number of compounds detected and the detection frequencies) than the organophosphorus herbicides (butamifos) and organophosphorus fungicides (iprobenfos and tolclofos-methyl). However, iprobenfos and isoxathion were found at the highest (10,400 ng/L) and lowest (3 ng/L) concentrations, respectively, among all OPs, as shown in Table 2.

The organophosphorus herbicide butamifos was detected in water from the Kurose River at a mean concentration of 9 ng/L and in water from the Shinano River at a mean concentration of 28 ng/L (Tanabe et al., 2001; Derbalah et al., 2003).

The organophosphorus fungicide tolclofos-methyl was detected in water from the Kurose and Maioka rivers at a mean concentrations of 7–9 ng/L (Sakai, 2002; Derbalah et al., 2003), and iprobenfos was detected in water from the Ashida, Koise, Kurose, Shinano, and Yanamune rivers at mean concentrations of 10–1040 ng/L (Iwakuma et al., 1993; Tanabe et al., 2001; Tahara, 2005; Tsuda et al., 2009).

The organophosphorus insecticide malathion was detected in water from the Shinano River at mean concentration of 33 ng/L (Kondoh et al., 2001; Tanabe et al., 2001; Derbalah et al., 2003), and isoxathion was detected in water from the Ishikari and Kurose rivers at mean concentrations of 3–10 ng/L (Kondoh et al., 2001; Derbalah et al., 2003).

Fenitrothion was found to be a common pollutant of river water at mean concentrations of 6–210 ng/L in the Ashida, Kozakura, Kurose, Seta, Shinano, Minaga, Yanamune, and Yodo rivers (Fukushima, 1987; Numabe et al., 1992; Itagaki et al., 2000; Tanabe et al., 2001; Sudo et al., 2002; Derbalah et al., 2003; Tahara, 2005; Tsuda et al., 2009; Kaonga et al., 2017).

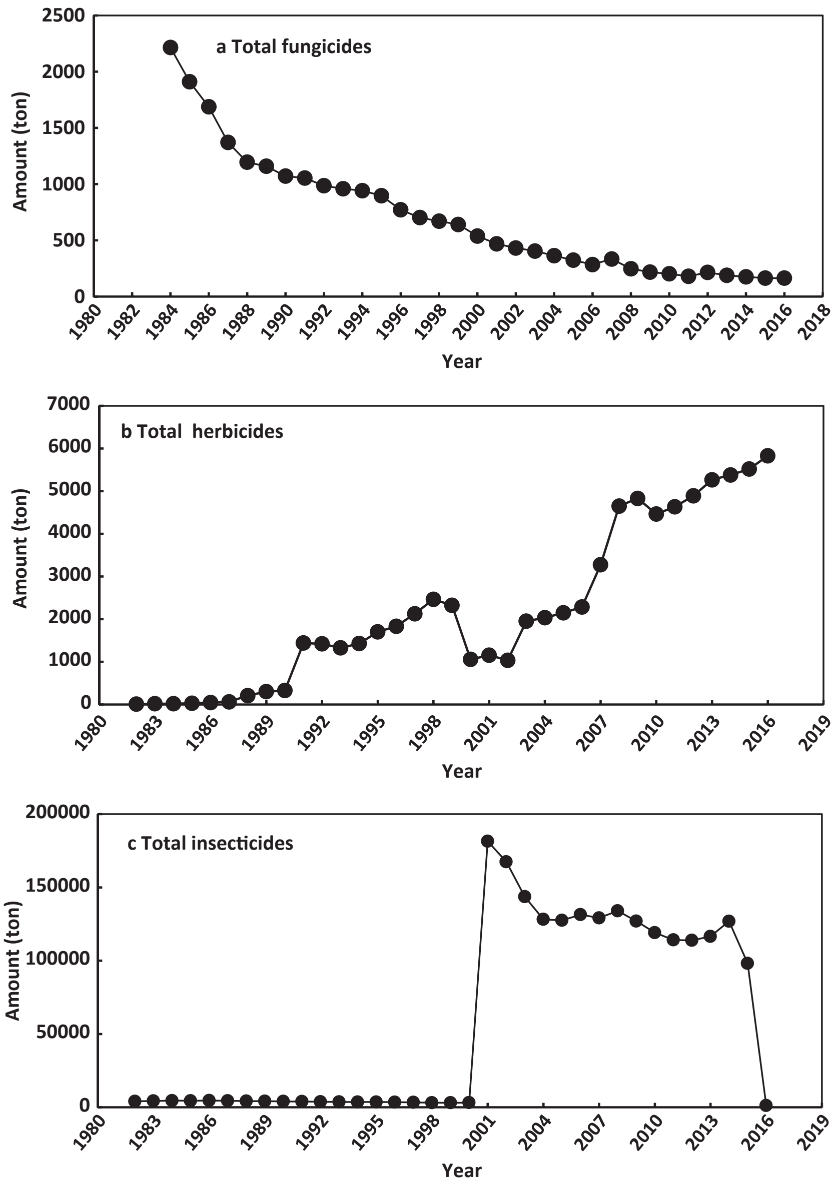

Fig. 6 – Temporal trends in total organophosphate pesticide use ((a) fungicides, (b) herbicides, and (c) insecticides) in Japan (1982–2016).

Diazinon was detected in water from the Ashida, Ishikari, Kurose, Seta, Shinano, Yanamune, and Yodo rivers at mean concentrations of 10–1390 ng/L (Fukushima, 1987; Kondoh et al., 2001; Tanabe et al., 2001; Sudo et al., 2002; Tahara, 2005; Tsuda et al., 2009; Chidya et al., 2018). Dimethoate was found at a concentration of 113 ng/L and chlorpyrifos at a mean concentration of 7 ng/L in water from the Shinano River (Tanabe et al., 2001). OPs were detected in water from the Ashida, Ishikari, Koise, Kozakura, Kurose, Maioka, Minaga, Seta, Shinano, Yanamune, and Yodo rivers. The OP concentrations were highest in water from the Ashida, Kurose, Koise, Shinano, and Yodo Rivers.

The obtained data showed that the OP pesticides were detected with different concentration levels in different rivers in Japan and this may be due to many reasons: (1) different areas have different sources of contamination, (2) different rivers have different instantaneous, daily, annual, and storm event flows, and (3) different areas have different pesticide transport behaviors and properties (Liu et al., 2015). Montuori et al. (2016) found that seasonal agricultural practices and extreme meteorological and hydrological events contribute to variations in OP concentrations in surface water.

The high contamination of Kurose River (located in Hiroshima Prefecture as shown in Fig. 1) water with OP pesticides compared to other rivers may be due the runoff of pesticide residues from a big agricultural area in Hiroshima prefecture, including Higashi-Hiroshima City, that is cultivated with rice and vegetables crops in which high amounts of pesticides were used for controlling pests (Derbalah et al., 2003; Chidya et al., 2018).

Moreover, the obtained pesticide residues data in the present study reflected the high contamination of Shinano River with OP residues (one of the largest rivers in Japan as shown in Fig. 1), and this may be because the Shinano River received runoff from rice fields near the river that reportedly contained much higher concentrations of pesticides (Tanabe et al., 2001; Iwafune et al., 2010).

The high residue levels of fenitrothion and diazinon insecticides in the Yodo River may be due to the highly intensive agricultural activity in the catchment area of this river, where high runoff of pesticide residues from agricultural fields flows to this river (Fukushima, 1987). However, the low contamination of the other rivers with OP residues may be due to the location of the monitoring points, where the ratio between agricultural lands and the total area is low (Phong et al., 2012).

2.4. Risk assessments for OPs

2.4.1. Ecotoxicological risk assessment

The results of the ecotoxicological risk assessment (as RQ_{mean} values) derived using mean measured environmental concentrations are shown in Table 4. The lowest and highest RQs were 0.006 (for tolclofos-methyl) and 258 (for fenitrothion), respectively. Diazinon and fenitrothion pose stronger risks (RQ > 1) than the other OPs for almost all the rivers that were assessed. The highest RQ for diazinon was for the Yodo River (RQ 126) and the next highest for the Kurose River (RQ 31.1). The highest RQ for fenitrothion was for the Shinano River (RQ 257.7) and the next highest for the Ashida River (RQ 26.9). High RQ values were also found for malathion and chlorpyrifos for (RQs 11.7 and 2.5, respectively) for the Shinano River. The butamifos RQs were 0.19–0.92, the dimethoate RQ was 0.081, the iprobenfos RQs were 0.008–0.583, and the tolclofos-methyl RQs were 0.006–0.008, meaning these OPs pose low–moderate risks in most of the rivers. These results indicate that of the nine OPs assessed in river water, diazinon and feniteothion pose elevated ecotoxicological risks.

We concluded that the Ashida, Kurose, Shinano, and Yodo rivers are more contaminated than the other rivers because the OP concentrations and RQ values were higher for these rivers than for the other rivers. These results indicate that the OP concentrations in the Ashida, Kurose, Shinano, and Yodo rivers are unacceptable and may adversely affect algae, aquatic invertebrates, and fish in these rivers.

Table 4 – Ecotoxicological risk assessment results (risk quotients) for the selected organophosphorus pesticides for various rivers in Japan (calculated using mean values).

River	Compound	Year	Mean values		RQ_m *
			MEC (mg/L)	PNEC (mg/L)	
Ashida River	Diazinon	2004	5.6E-05	1.1E-05	5
	Fenitrothion	2004	2.1E-04	7.8E-06	26.9
	Iprobenfos	2004	5.5E-05	1.2E-03	0.046
Ishikari River	Diazinon	2004	1.6E-05	1.1E-05	1.4
	Isoxathion	2001	3.0E-06	5.2E-06	0.6
Koise River	Iprobenfos	1993	7.0E-04	1.2E-03	0.583
Kozakura River	Fenitrothion	1992	2.5E-05	7.8E-06	3.2
Kurose River	Diazinon	2001	1.6E-05	1.1E-05	1.4
		2004	3.8E-05	1.1E-05	3.4
		2016	3.5E-04	1.1E-05	31.1
	Fenitrothion	2001	3.5E-05	7.8E-06	4.5
		2004	8.2E-05	7.8E-06	10.5
		2013	5.4E-05	7.8E-06	6.9
	Iprobenfos	2003	2.1E-05	1.2E-03	0.018
	Isoxathion	2001	1.0E-05	5.2E-06	1.9
	Butamifos	2001	9.0E-06	2.5E-05	0.36
		2004	4.7E-06	2.5E-05	0.188
	Tolclofos-methyl	2001	9.0E-06	1.2E-03	0.008
Maioka River	Tolclofos-methyl	2001	7.0E-06	1.2E-03	0.006
Minaga River	Fenitrothion	2000	8.0E-06	7.8E-06	1
Seta River	Diazinon	2002	2.3E-05	1.1E-05	2.1
	Fenitrothion	2002	6.0E-06	7.8E-06	0.8
Shinano River	Diazinon	1996	3.8E-05	1.1E-05	3.4
	Fenitrothion	1996	2.0E-03	7.8E-06	257.7
	Iprobenfos	1996	1.1E-04	1.2E-03	0.089
	Butamifos	1996	2.3E-05	2.5E-05	0.92
	Chlorpyrifos	1996	7.0E-06	2.8E-06	2.5
	Malathion	1996	1.4E-05	1.2E-06	11.7
	Dimethoate	1996	6.5E-05	8.0E-04	0.081
Yanamune River	Diazinon	2009	1.0E-05	1.1E-05	0.9
	Fenitrothion	2009	4.0E-05	7.8E-06	5.1
	Iprobenfos	2009	1.0E-05	1.2E-03	0.008
Yodo River	Diazinon	1987	1.4E-03	1.1E-05	126
	Fenitrothion	1987	1.4E-04	7.8E-06	18

RQ_m: risk quotient based on mean concentrations; PNEC: predicted no-effect concentration; AF: assessment factor; MEC: measured environmental concentration.

* RQ (risk quotients) classification: low risk 0.01 ≤ RQ < 0.1; medium risk 0.1 ≤ RQ < 1; high risk RQ ≥ 1.

The Shinano River (Fig. 1) is the longest and widest river in Japan and has the third largest basin by area. The Shinano River is in northeastern Honshu, originating in the Japanese Alps and flowing generally northeast through Nagano and Niigata prefectures before reaching the Sea of Japan. The transfer of OPs in river water to the sea means OPs entering rivers will also affect marine organisms, especially fish, and may subsequently affect humans consuming marine organisms.

The Kurose River, in Hiroshima Prefecture (Fig. 1), is approximately 43 km long. The Kurose River flows through urban and agricultural areas on the Kamo Plateau, including Higashi-Hiroshima city, before entering the Seto Inland Sea. The Kurose River has a surface area of approximately 250 km^2. Agricultural runoff and wastewater containing industrial and household pollutants enter the Kurose River. The water flowing from the Kurose River into the Seto Inland Sea will, therefore, transfer OPs that may affect aquatic organisms, especially fish, in the Seto Inland Sea, and these OPs may subsequently affect humans.

The Ashida River (Fig. 1) flows through the eastern part of Hiroshima Prefecture and is the primary drainage system for the Bingo region. The Ashida River water comes from Mihara City and generally flows east toward Sera Town in Hiroshima Prefecture. The Ashida River has dams at Mikawa in Sera Town and Hattabara in Fuchu City, and after the dams passes through Fukuyama before entering the Seto Inland Sea. OPs in the Ashida River may affect aquatic organisms in the Seto Inland Sea and therefore indirectly affect human health.

The Yodo River is the principal river in Osaka Prefecture on Honshu, Japan. The source of the river is Lake Biwa, the country's largest freshwater lake, in Shiga Prefecture to the north. The river has the largest catchment area and population among the rivers that flow in the Seto Inland Sea. The Yodo River showed high concentration and RQ values for diazinon and fenitrothion, and this river flows into the Seto Inland Sea in Osaka bay, which may affect aquatic organisms in the Sea and therefore indirectly affect human health.

Diazinon and fenitrothion pose considerably more ecotoxicological risk than the other OPs in almost all of the rivers that were assessed, which might adversely affect aquatic organisms (algae, aquatic invertebrates, and fish) and human health. Managing the risks posed by diazinon and fenitrothion should, therefore, be prioritized. The RQs indicated that the potential risks posed by butamifos, chlorpyrifos, dimethoate, iprobenfos, isoxathion, malathion, and tolclofos-methyl should not be neglected, even though the concentrations of these OPs are currently below the regulatory limits.

Possible toxicological effects of OP pesticides on aquatic organisms have been reported in previous studies. For example, juvenile *Oncorhynchus kisutch* (coho salmon) exposed to a mixture of OPs showed inhibition of brain acetylcholinesterase (AChE) (improper nervous system function) and decline of liver carboxylesterase (CaE) (impaired detoxifying ability) (Laetz et al., 2014). Previous studies also indicate that the exposure of zebrafish to chlorpyrifos and diazinon resulted in developmental neurotoxicity, abnormalities in developmental endpoints (hatching rate, heartbeat, body length), morphological abnormalities, and inhibition of AChE (Scheil et al., 2009; Selderslaghs et al., 2010; Yen et al., 2011; Sreedevi et al., 2014; Watson et al., 2014; Kristofco et al., 2016). Similarly, Benli and Özku (2010), reported that fenitrothion is highly toxic to Nile tilapia both in terms of behavioral effects and histopathological findings.

A lack of OP risk assessments for humans and the environment may have adversely affected efforts to monitor OP residues, to manage and eliminate OPs, and to decrease the risks posed by OPs. Environmental regulations and policies need to be continually updated because new pollutants continue to be found. A lack of up-to-date research means policies aimed at decreasing pesticide pollution and decreasing the risks posed by pesticides are ineffective. Assessing the risks posed by pesticides to humans and the environment is very important to allow priorities to be identified and policies to be developed to limit the risks posed.

2.4.2. Human risk assessment

The non-carcinogenic human health risks posed by exposure to OPs in river water in Japan are summarized as HQs in Table 5. The HQs were calculated from the mean concentrations of the OPs in the rivers that were assessed. The overall non-carcinogenic risks to children and adults decreased in the order diazinon > dimethoate > fenitrothion > chlorpyrifos > iprobenfos > isoxathion > butamifos > malathion > tolclofos-methyl. The HQs for children ranged from 5.0×10^{-6} to 7.6×10^{-2} while for adults ranged from 2.0×10^{-6} to 3.9×10^{-2}. By definition, the non-carcinogenic risks for the individual pesticides were lower than the total non-carcinogenic risks. Each pesticide, therefore, poses insignificant to no potential health risks to humans at the concentrations found in the rivers that were assessed. The HQs for children were slightly higher than those for adults for all the OPs in all the rivers that were assessed. However, the risks to both children and adults were of the same order of magnitude (10^{-6}–10^{-2}). The diazinon and fenitrothion HQs were higher than the HQs for the other OPs. The highest fenitrothion HQ (1.7×10^{-2}) was found for the Shinano River, and the highest diazinon HQ (4.8×10^{-2}) was for the Yodo River. The highest and lowest HQs for the OPs were for diazinon (4.8×10^{-2}) in the Yodo River and tolclofos-methyl (2×10^{-6}) in the Maioka River, respectively.

The high HQs of diazinion and fenitrothion in the Yodo and Shinano rivers may pose significant human health risk through drinking water because the water from these big rivers are utilized for many purposes, including for drinking water; especially the Yodo River, which is an important source of tap water for 12 million people in the Kinki area (Kawamura and Ebise, 2014).

Exposure to OPs leads to several toxic effects on humans that could be induced by influencing body glucose homeostasis through several mechanisms, including physiological stress, allergies and nausea, adverse physiologic effects, oxidative stress, inhibition of paraoxonase, nitrosative stress, pancreatitis, inhibition of cholinesterase, stimulation of the adrenal gland, and disturbance in the metabolism of tryptophan in the liver (Badrane et al., 2014). Also, exposure to OPs leads to serious health consequences such as neurobehavioral and cognitive abnormalities, teratogenicity, endocrine modulation, immunotoxicity and compromised cognitive development, especially for infants and children, reproductive effects, spontaneous abortions, and fetal death (Epstein, 2014). OP herbicides such as butamifos could show mutagenic effects by

Table 5 – Human health risk assessment results (hazard quotients) for selected organophosphorus pesticides for various rivers in Japan.

River	Compound	Year	Mean MEC (mg/L)	ADI	Hazard quotient (HQ)	
					Children	Adults
Ashida River	Diazinon	2004	5.6E-05		1.2E-02	5.6E-03
	Fenitrothion	2004	2.1E-04		1.8E-03	8.0E-04
	Iprobenfos	2004	5.5E-05		7.0E-05	3.0E-05
Ishikari River	Diazinon	2001	1.6E-05		3.5E-03	1.6E-03
	Isoxathion	2001	3.0E-06	0.003 [a]	4.0E-05	2.0E-05
Koise River	Iprobenfos	1993	7.0E-04		8.7E-04	4.0E-04
Kozakura River	Fenitrothion	1992	2.5E-05		2.2E-04	1.0E-04
Kurose River	Diazinon	2001	1.6E-05		3.5E-03	1.6E-03
		2004	3.8E-05		8.3E-03	3.8E-03
		2016	3.5E-04		7.6E-02	3.5E-02
	Fenitrothion	2001	3.5E-05	0.005 [b]	3.0E-04	1.0E-04
		2004	8.2E-05		7.1E-04	3.0E-04
		2013	5.4E-05		4.7E-04	2.0E-04
	Iprobenfos	2003	2.1E-05		3.0E-05	1.0E-05
	Isoxathion	2001	1.0E-05		1.5E-04	7.0E-05
	Butamifos	2001	9.0E-06		5.0E-05	2.0E-05
		2004	4.7E-06		3.0E-05	1.0E-05
	Tolclofos-methyl	2001	9.0E-06		6.0E-06	3.0E-06
Maioka River	Tolclofos-methyl	2001	7.0E-06	0.064 [a,b]	5.0E-06	2.0E-06
Minaga River	Fenitrothion	2000	8.0E-06		7.0E-05	0.0E+00
Seta River	Diazinon	2002	2.3E-05		5.0E-03	2.3E-03
	Fenitrothion	2002	6.0E-06		5.0E-05	0.0E+00
Shinano River	Diazinon	1996	3.8E-05	0.0002 [b]	8.3E-03	3.8E-03
	Fenitrothion	1996	2.0E-03		1.7E-02	8.1E-03
	Iprobenfos	1996	1.1E-04	0.035 [a]	1.3E-04	6.0E-05
	Butamifos	1996	2.3E-05	0.008 [a]	1.3E-04	6.0E-05
	Chlorpyrifos	1996	7.0E-06	0.001 [b]	3.0E-04	1.4E-04
	Malathion	1996	1.4E-05	0.03 [a,b]	2.0E-05	1.0E-05
	Dimethoate	1996	6.5E-05	0.001 [a,b,c]	2.8E-03	1.3E-03
Yanamune River	Diazinon	2009	1.0E-05		2.2E-03	1.0E-03
	Fenitrothion	2009	4.0E-05		3.5E-04	2.0E-04
	Iprobenfos	2009	1.0E-05		1.0E-05	1.0E-05
Yodo River	Diazinon	1987	1.4E-03		8.4E-02	3.9E-02
	Fenitrothion	1987	1.4E-04		4.8E-04	2.2E-04

HQ_m: hazard quotient based on mean concentrations. ADI: acceptable daily intake. MEC: measured environmental concentration (mean).
[a] PPBD, 2018
[b] USEPA, 2016
[c] JACC, 2010

means of a chlorinated by-product (5-methyl-2-nitrophenol), that could be formed during the chlorination step in the drinking water purification process (Kamoshita et al., 2010). Therefore, the use of many organophosphates has been restricted by the EPA of the United States of America in order to prevent health risks (Epstein, 2014; Yu et al., 2016).

Finally, we can conclude that the method selected for assessing the risks posed by pesticides to human health will largely depend on the data available (including the accuracy and quality of the data) and the desired risk assessment approach. The desired approach will depend on the risks posed by pesticides to those consuming the water and legislation related to drinking water quality.

2.4.3. Challenges and threats

It is very difficult to determine pesticide concentrations in environmental matrices because the pesticide concentrations are generally extremely low, matrix interferences need to be avoided, and the detection methods and quantification procedures are expensive and generally time-consuming. The need to develop, optimize, and validate sensitive analytical methods makes pesticide monitoring expensive. The complex range of pesticides found in environmental media makes it difficult to assess and manage the risks posed by pesticides, to regulate pesticide concentrations in the environment, and to decrease human exposure to pesticides in drinking water. Assessing the risks posed by exposure to combinations of pesticides in water is particularly challenging. Assessing and characterizing the risks posed by pesticides are currently limited because of a lack of information on pesticide degradation and the risks posed by mixtures of pesticides, pesticide by-products, and pesticide degradation products.

3. Conclusions and recommendations

Pesticides such as OPs are important for controlling agricultural pests and decreasing crop losses in the field and during storage. Here, we have shown that large amounts of organophosphorus herbicides have been used in Japan and that OP use continues to increase. However, organophosphorus insecticides and fungicides use in Japan has decreased. Organophosphorus insecticides, which are toxic to humans and other biota, have been the most widely used of the OPs we assessed. OPs, especially organophosphorus insecticides, may compromise environmental quality and pose risks to humans and another biota. It is therefore important to monitor OP use and OP concentrations in environmental media. This is critical because, as mentioned earlier, OPs have been detected in surface water throughout Japan.

The risk assessment results indicated that diazinon and fenitrothion pose strong risks to the Japanese aquatic environment. However, a more comprehensive assessment of the risks posed by these pesticides in river water to both aquatic systems and humans is required. More data on OP concentrations in water are required, and data on OP toxicity, especially to organisms endemic to Japan, and on concentrations of OPs that have chronic effects on organisms, are also required. Data on the concentrations and toxicities of pesticide by-products and degradation products need to be incorporated in risk assessments, and temporal variations in OP concentrations need to be understood better to give more precise and realistic assessments. It is particularly important that research into the responses of aquatic organisms to exposure to OPs in water be performed to allow accurate risk assessments to be performed.

Stringent legislation and policies regulating drinking water quality and purity will offer three major benefits: (1) steps will be taken to control the sources of pesticides to drinking water and decrease pesticide concentrations if legislation regulating the production, use, and application of pesticides is established; (2) the development of more effective pesticide residue remediation techniques will be encouraged, although the techniques will need to be cost-effective and sustainable; and (3) the effect of external factors on pesticide residues in drinking water will need to be assessed. Continual development and modification of pesticide legislation and policies based on modern and renewable pesticide databases, pesticide concentrations in environmental media, and the risks posed by pesticides in the environment will decrease exposure to pesticides and the risks posed to humans and the environment.

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