Table 2 | NDMA concentrations in the samples

Sampling point	Sampling day	NDMA concentration (ng/L)
Arato River		
A1	03/06/2009	2.3 (14)
A1	07/07/2009	1.1
A2	07/07/2009	5.9 (8.0)
A3	03/06/2009	830 (12)
A3	07/07/2009	2,100 (0.9)
A3	16/07/2009	370
A4	03/06/2009	160 (8.9)
A5	03/06/2009	30
A6	14/05/2009	130
A6	07/07/2009	12 (1.5)
Hirose River		
H1	14/05/2009	1.0
H2	14/05/2009	61 (19)
H2	07/07/2009	4.6
H3	14/05/2009	17
H4	14/05/2009	22 (9.8)
H5	14/05/2009	17 (4.9)
H5	07/07/2009	1.9
H6	07/07/2009	1.9
Kamisawa River		
K1	14/05/2009	2.0
K2	03/06/2009	3.7
Kasu River		
Ks1	14/05/2009	5.0
Miya River		
M1	03/06/2009	2.5
M2	03/06/2009	3.5
M3	03/06/2009	1.3
Momonoki River		
Mo1	14/05/2009	1.0
Nira River		
N1	14/05/2009	13
Oh River		
O1	14/05/2009	1.0
Channel		
C1	14/05/2009	2.0
C2	03/06/2009	93 (18)
C3	03/06/2009	1.3
C4	07/07/2009	2.8
C5	07/07/2009	93 (12)
C6	07/07/2009	4.8
C7	16/07/2009	9,300 (10)
C8	16/07/2009	1.4 (12)
C9	16/07/2009	2,600 (5.0)
Sewage effluent		
S1	07/07/2009	95 (8.5)
Industrial discharge		
I1	07/07/2009	78
I2	16/07/2009	11 (3.0)
I3	16/07/2009	33,000 (4.0)

Values in parentheses are relative standard deviation (RSD) (%) ($n = 2$ or 3).

produced from livestock through processes such as heating at this plant.

Next, NDMA load at I3 was estimated to investigate its significance to the Arato and Hirose Rivers. From the NDMA concentration at I3 and its flow rate (about 700–1,000 m^3/day), the NDMA load at I3 was estimated to be about 7.7–11 g/day. In the calculation, the industrial livestock processing plant was assumed to operate only during the day (i.e. 8 h) although information on operating time was not available. Annual mean flow rate of the Arato River upstream of the confluence with the Kamisawa River in 2001–2007 was 1.35 m^3/s (Aisaki 2009). That of the Hirose River near H6 in 2008 was 18 m^3/s (Upper Tone River Office). Note that for the Hirose River, when the values of the measuring instrument were below its lower limit of detection, the values were assumed to be at the lower limit. From these flow rates and NDMA load at I3, the increases in NDMA concentration in the Arato and Hirose Rivers due to NDMA discharge from I3 were estimated to be 66–94 and 5.0–7.1 ng/L, respectively. Based on the fluctuation of NDMA concentration at I3, it was considered that these estimated values were not so different from the NDMA concentrations in the Arato and Hirose Rivers (i.e. A5 and A6, and H6, respectively).

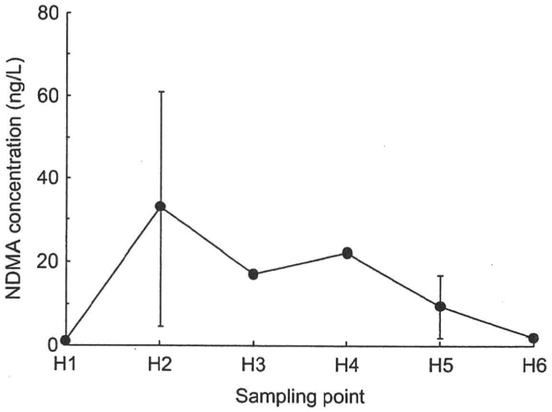

Figure 2 | Profiles of NDMA concentrations in the Hirose River. Mean NDMA concentrations were plotted at the sampling points collected on different days. Error bars show the ranges of NDMA concentration.

Therefore, from the viewpoint of NDMA load, it was confirmed that the industrial discharge at I3 was the main NDMA source in the Arato and Hirose Rivers.

NDMA has been reported in meat and meat products (San Francisco Public Utilities Commission 2007). From the results of the present study, it was not possible to determine why the industrial discharge had such a high concentration of NDMA. However, NDMA may have been formed during livestock processing, and therefore the industrial discharges contained NDMA at high concentrations. Chlorate is present as an impurity in hypochlorite solution, which is widely used as a disinfectant (Asami *et al.* 2009*a*). Therefore, the presence of chlorate in treated water indicates that disinfection using hypochlorite solution was performed in wastewater, although the types of disinfectant existed (e.g. hypochlorous acid/hypochlorite and chloramine produced by the reaction between hypochlorous acid/hypochlorite and ammonia in wastewater) and their levels of consumption could not be determined. Chlorate concentrations in the discharge at I1, I2, and I3 were very low (i.e. <0.05, 0.05, and 1.5 μg/L, respectively). Therefore, it was considered that hypochlorite solution was not dosed or was dosed in very small amounts, and the presence of NDMA in the industrial discharges was not due to disinfection byproducts. These results suggested that the livestock processing plant was the likely source of NDMA in the river water.

With regard to wastewaters containing NDMA at extremely high concentrations, it was reported that the NDMA concentration in stock solutions of metam sodium used for root treatment was 1,100,000 ng/L, and those in wastewater at printed circuit board (PCB) manufacturing facilities using dimethyldithiocarbamate (DTC)-based chemical treatments ranged from 139 to 56,000 ng/L (Sedlak *et al.* 2005). It was also reported that NDMA concentrations in untreated wastewaters from a drum recycling facility and automobile crankcases were above 750,000 and 350,000 ng/L, respectively (Sedlak *et al.* 2005). Moreover, it was reported that NDMA concentration in wastewater mainly from a clothing factory was 10,000 ng/L (Kosaka *et al.* 2009*a*). Thus, the NDMA concentration in the industrial discharge from the industrial livestock processing plant was lower than in some of these wastewaters and untreated wastewaters reported previously. However, so far, it has not been reported that the industrial discharge from livestock processing contained NDMA at extremely high concentration. In addition, in the previous studies described above, at least some wastewaters were influents to municipal wastewater treatment plants, where they were mixed with other influents and subjected to biological treatment. The removal efficiencies of NDMA by biological treatment processes at municipal wastewater treatment plants are highly variable, ranging from 0 to 75% (Sedlak *et al.* 2005). Therefore, the NDMA concentrations in the influents were considered to be reduced by dilution and biological treatment to some degree before discharge into the environment. In the present study, the NDMA

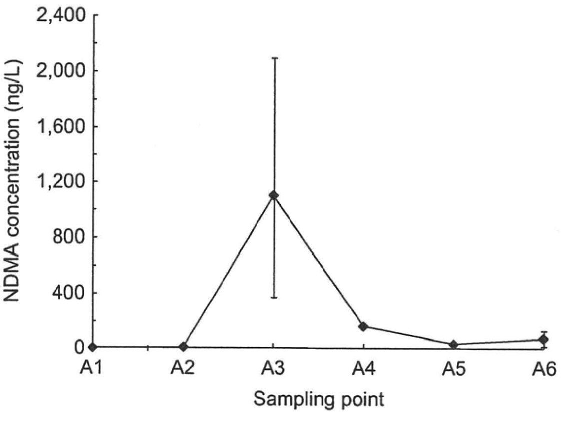

Figure 3 | Profiles of NDMA concentrations in the Arato River. Mean NDMA concentrations were plotted at the sampling points collected on different days. Error bars show the ranges of NDMA concentration.

concentration in the industrial discharge was in the final effluents, which directly impacted the environment. Therefore, NDMA was detected at high levels in some environmental waters (e.g. A3, C7, and C9). NDMA concentrations in the discharges at other similar livestock processing plants were not investigated in the present study, and further investigations are warranted.

NDMA concentrations in some tributaries of the Hirose River other than the Arato River were relatively high, i.e. the NDMA concentrations in the Nira and Kasu Rivers were 13 and 5.0 ng/L, respectively. Therefore, there may be some NDMA sources in the Hirose River in addition to those in common with the Arato River, although the levels of NDMA discharge were lower than that from the discharge at I2.

NDMA formation on chloramination

Figure 4 shows the NDMA concentrations before and after chloramination of the river water at A3, in sewage effluent, and in industrial discharges. Sampling day at A3 was 16 July 2009. As shown in the figure, industrial discharge at I2 was evaluated only by chloramination I.

In the case of I3, NDMA concentrations before chloramination and after chloramination I and II were 33,000, 34,000, and 34,000 ng/L, respectively. Therefore, NDMA was present at high levels in I3, but there were no significant amounts of NDMA precursors by chloramination at I3. Similarly, I1, I2, and A3 did not contain significant levels of NDMA precursors. These results were of interest because DOC was high for I1 and I3 and DON was also high for I1 (Table 1). This was considered to be because industrial discharge from the livestock processing plant did not contain significant amounts of NDMA precursors on chloramination or most of the NDMA precursors were transformed into NDMA during livestock processing. Waste water at PCB manufacturing facilities using DTC-based chemical treatments was reported to contain high levels of both NDMA and NDMA precursors (Sedlak *et al.* 2005). This tendency of the presence of NDMA precursors was different from the observations at the livestock processing plant in the present study.

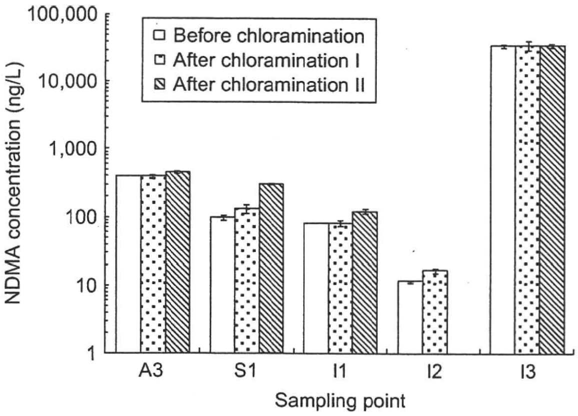

Figure 4 | NDMA concentrations before and after chloramination. Chloramination I conditions: reaction time, 24 h; chloramine concentrations at 24 h, 3.0 ± 0.5 mg/L; pH 7.0 (5 mM phosphate buffer); temperature, 20°C. Chloramination II conditions: reaction time, 10 d; chloramine dose, 2 mM (140 mg/L); pH 7.0 (5 mM phosphate buffer); temperature, 20°C. For I2, only chloramination I was performed. Error bars show standard deviations of repetition analyses.

In the case of S1, NDMA concentrations before chloramination and after chloramination I and II were 95, 130, and 290 ng/L, respectively. S1 contained NDMA precursors. This result was consistent with those of previous studies using municipal wastewater effluents (Mitch & Sedlak 2004; Schreiber & Mitch 2006). The NDMA concentrations after chloramination I and II suggested that S1 had lower levels of NDMA precursors that were transformed rapidly into NDMA than those that were transformed slowly.

CONCLUSIONS

(1) NDMA was detected at high concentrations in the Arato and Hirose Rivers, located in the upper Tone River basin in the Kanto region of Japan. The highest concentrations were 2,100 and 61 ng/L, respectively. The NDMA source in these rivers was industrial discharge from a livestock processing plant located near the Arato River.

(2) The industrial discharges (i.e. I1, I2, and I3) did not contain significant amounts of NDMA precursors. However, S1 did contain NDMA precursors, and the levels of NDMA precursors that were transformed rapidly into NDMA were lower than those that were transformed more slowly.

ACKNOWLEDGEMENTS

We thank Ms. Nobue Yoshida of the National Institute of Public Health for help with sample analysis. This study was financially supported in part by a research grant from the Ministry of Health, Labour, and Welfare, Japan.

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Perchlorate: Origin and Occurrence in Drinking Water

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Abbreviations

CCL	Contaminant Candidate List
CCL 1	first Contaminant Candidate List
CCL 2	second Contaminant Candidate List
CCL 3	third Contaminant Candidate List
DEP	Department of Environmental Protection
DHS	Department of Health Services
DOD	Department of Defense
DPH	Department of Public Health
DWEL	drinking water equivalent level
EPA	Environmental Protection Agency
FAC	free available chlorine
FDA	Food and Drug Administration
FY	fiscal year
IC	ion chromatography
ITRC	Interstate Technology and Regulatory Council
LC	liquid chromatography
MCL	maximum contaminant level
MRL	minimum reporting level
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NASA	National Aeronautics and Space Administration
PWS	public water system
RfD	reference dose
SDWA	Safe Drinking Water Act
UCMR	Unregulated Contaminant Monitoring Regulation
UCMR 1	First Unregulated Contaminant Monitoring Regulation

Introduction

Perchlorate is both a naturally occurring and a man-made chemical existing as an anion in water. Perchlorate compounds are manufactured in the form of their salts and perchloric acid. The most common perchlorate salts are ammonium, sodium, and potassium perchlorates. Perchlorate compounds are used in various products, including rocket/missile propellants, munitions, explosives, fireworks, airbag initiators, and road flares. Perchlorate compounds are also used in manufacturing processes (e.g., electroplating and electropolishing operations). Perchlorate is known to interfere with iodine uptake by the thyroid gland. The United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) of 0.7 $\mu g\,kg^{-1}$ per day of perchlorate, which translates to a drinking water equivalent level (DWEL) of 24.5 $\mu g\,l^{-1}$. The federal maximum contaminant level (MCL) for perchlorate has not yet been established. However, perchlorate was determined by the US EPA to be a contaminant on the Contaminant Candidate Lists (CCLs), a series of lists comprising the first CCL (CCL 1), second CCL (CCL 2), and third CCL (CCL 3). In January 2009, the US EPA also released an interim health advisory level of perchlorate at 15 $\mu g\,l^{-1}$. Several states have established advisory levels of perchlorate in the range of 1–18 $\mu g\,l^{-1}$. The Massachusetts Department of Environmental Protection (MA DEP) set a perchlorate MCL of 2 $\mu g\,l^{-1}$ for drinking water in the state in July 2006, whereas the California Department of Public Health (CA DPH) set its own perchlorate MCL at 6 $\mu g\,l^{-1}$ in October 2007.

In 1997, the California Department of Health Services (CA DHS now CA DPH) found perchlorate in drinking water wells in eastern Sacramento County, California, following the development of an analytical method for perchlorate using ion chromatography (IC) coupled with suppressed conductivity detection, which was able to detect concentrations as low as 4 $\mu g\,l^{-1}$. Since then, the occurrence of perchlorate has been investigated in many states in the United States. Recently, more sensitive and more accurate analytical methods using liquid chromatography (LC) or IC coupled with mass spectrometry (MS) or tandem mass spectrometry (MS/MS) were developed. ^{18}O-enriched perchlorate is typically used as the internal standard for perchlorate analysis by LC/MS(/MS) or IC/MS(/MS). Perchlorate has been detected in water as well as in various media (e.g., soil, food, milk, beverages, and plants). The initial studies on perchlorate detection were mostly conducted in the United States. However, the occurrence of perchlorate has recently been investigated in other countries and its presence in the environment has been reported. Investigation of the source of perchlorate is important for reducing perchlorate contamination and protecting human health. However, identifying the sources of perchlorate contamination definitively is not always possible. The potential sources of both naturally occurring and man-made perchlorate were summarized by the Interstate Technology and Regulatory Council (ITRC) perchlorate team.

Origins of Perchlorate

Anthropogenic perchlorate is considered the main source of perchlorate contamination in the environment. The potential sources are manufacturers of perchlorate and perchlorate-containing products and those using it in operations, alongside other users of perchlorate-containing products. However, perchlorate is present naturally in many groundwaters. Perchlorate is soluble, stable, and mobile in water. Once it is released into the environment, it may move into surface water and groundwater, and therefore, it is detected in drinking water. In this section, the potential sources of the perchlorate contamination are described together with examples of its presence as a contaminant in drinking water, groundwater, and surface water. More detailed information is available from the ITRC perchlorate team and MA DEP.

Naturally Occurring Perchlorate

Naturally occurring perchlorate is considered to be formed mainly during natural atmospheric processes. Although the mechanism of perchlorate formation is uncertain, the results of experiments simulating atmospheric processes suggested that perchlorate is formed from chloride aerosol by lightning and the exposure of chloride to ozone in the atmosphere. Perchlorate concentrations in 22 precipitation samples from Lubbock, Texas, were in the range of <0.01 to $1.6\,\mu g\,l^{-1}$, with a mean concentration of $0.2\,\mu g\,l^{-1}$. The perchlorate concentration in bulk atmospheric deposition through the late Holocene in north-central New Mexico was thought to be $0.093 \pm 0.005\,\mu g\,l^{-1}$ using the evapotranspiration factor. Moreover, it was reported that perchlorate concentrations in precipitation, specifically that from thunderstorms, ranged from <0.04 to $24.4\,\mu g\,l^{-1}$.

However, the occurrence of perchlorate in groundwaters was investigated in 54 counties of West Texas and in 2 counties of eastern New Mexico. Perchlorate was detected at levels of $\geq 0.1\,\mu g\,l^{-1}$ in 56% of the total of 1030 wells examined and in 52 of the 56 counties. Perchlorate concentrations in some groundwaters were high (up to $200\,\mu g\,l^{-1}$) but were mostly $<4\,\mu g\,l^{-1}$. The source of perchlorate in the area was likely to be atmospheric deposition. Perchlorate concentrations in the groundwaters of the Middle Rio Grande Basin in north-central New Mexico were reported to range from 0.04 to $1.8\,\mu g\,l^{-1}$ and varied with radiocarbon age of the dissolved inorganic carbon in the groundwaters. As no anthropogenic source is known in this area, the source of perchlorate is considered to be atmospheric deposition. Moreover, the occurrence of perchlorate in 326 groundwater samples collected from across the United States was investigated. Perchlorate was detected at concentrations $\geq 0.12\,\mu g\,l^{-1}$ in 137 of 326 groundwaters. Perchlorate concentrations in 109 of these 137 groundwaters were $<1\,\mu g\,l^{-1}$, and those in the remaining 28 groundwaters ranged from 1.0 to $10.4\,\mu g\,l^{-1}$. Thus, it is considered that perchlorate is naturally present in many groundwaters.

Perchlorate is also known to be contained in the nitrate deposits of the Atacama Desert in Chile. These nitrate deposits have been imported into the United States for over a century and used as fertilizer and as oxidizer (e.g., in gunpowder, explosives, and fireworks). Thus, historical use of fertilizer made from the Atacama nitrate deposits is considered a possible source of perchlorate contamination in some of the groundwaters in the United States. The origin of perchlorate in these Atacama nitrate deposits was investigated by measuring the oxygen isotope ratios of perchlorate and was considered to be atmospheric perchlorate.

Man-made Perchlorate

Perchlorate manufacture

Perchlorate manufacture is a potential source of perchlorate in the environment. Two cases of large-scale perchlorate contamination by a perchlorate manufacturer have been reported: one in Henderson, Nevada, and the other in the Tone River Basin, Japan. There are several similarities between the two cases. First, perchlorate entering the river extensively contaminated the downstream basin area. Second, the river waters contaminated by perchlorate are used as source waters for the drinking water supply of a large population, 15–20 million for the case in Henderson, Nevada, and around 20 million in the case of the Tone River Basin, Japan. Third, the river waters in both cases are also used for irrigation.

Perchlorate contamination was discovered in Henderson, Nevada, in 1997. The source of the contamination was a perchlorate-manufacturing facility of Kerr-McGee (now Tronox). At the site, perchlorate was detected at $24\,\mu g\,l^{-1}$ in drinking water, $3\,700\,000\,\mu g\,l^{-1}$ in groundwater, and $120\,000\,\mu g\,l^{-1}$ in surface water. Through the contaminated groundwater, perchlorate was introduced into the Las Vegas Wash and contaminated downstream areas, including Lake Mead and the lower Colorado River. Perchlorate contamination of the groundwater in Henderson was also attributable to another perchlorate-manufacturing facility of Pacific Engineering Production Company of Nevada (now American Pacific Corporation). Perchlorate was manufactured at these facilities until 1998 and 1988, respectively. A control strategy was implemented after the discovery of perchlorate contamination. Perchlorate concentrations in surface waters, such as the Las Vegas Wash, Lake Mead, and the lower Colorado River have declined by 85%, 70%, and 60%, respectively, since treatment of perchlorate began in 1999. The load of perchlorate entering the Las Vegas Wash has decreased from approximately 900–1000 pounds per day (400–450 kg per day) before any controls to approximately 100–150 pounds per day (45–70 kg per day), representing a decrease of around 85%.

Perchlorate contamination was discovered in the Tone River Basin, Japan, in 2006. **Figure 1** shows perchlorate concentrations in the river waters in (**a**) the upper Tone River Basin and (**b**) the middle and lower Tone River Basin, from March to June 2006. The main sources of perchlorate were two industrial effluents located upstream of the Tone River Basin. One was industrial effluent from a facility manufacturing perchlorate and chlorate situated on the upper Tone River. The perchlorate concentration reported in the industrial effluent was 1100 $\mu g\,l^{-1}$ and the estimated load of perchlorate from the industrial effluent was 120–130 kg per day. The other was the industrial effluent from a facility conducting electrolysis processes other than for the manufacture of perchlorate and chlorate (details are described in the following text). As shown in **Figure 1**, the river waters in the Tone River Basin were largely contaminated by perchlorate derived mainly from these two sources. The river waters in the Tone River Basin flow toward the Tokyo Metropolitan Area and are used as the source of drinking water in the area. Perchlorate concentrations in some groundwaters in the Tone River Basin were also high, with a maximum concentration of 37 $\mu g\,l^{-1}$.

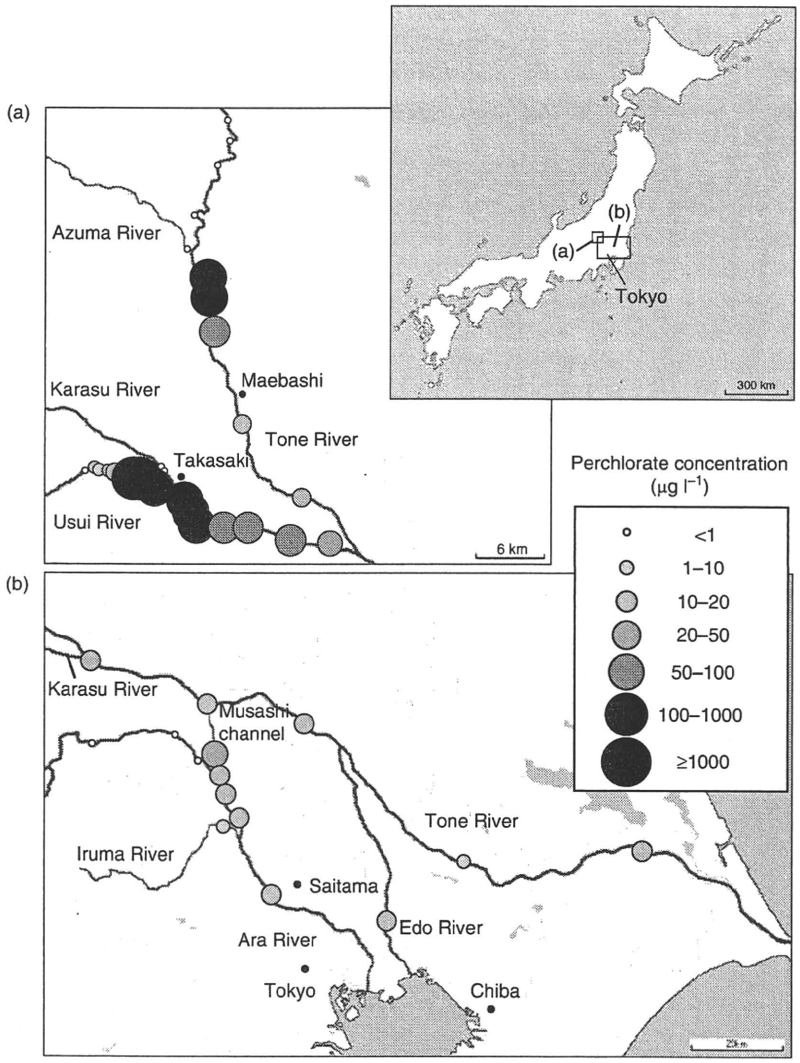


Figure 1 Perchlorate concentrations in the river waters in (a) the upper Tone River Basin and (b) the middle and lower Tone River Basin, Japan, March to June 2006.

Manufacturers of perchlorate-containing products and those using perchlorate in operations

Table 1 shows some of the perchlorate-containing products and the purpose of perchlorate use in manufacturing processes. Manufacturers of perchlorate-containing products and manufacturers using perchlorate in operations are considered to be potential sources of perchlorate in the environment.

In the United States, manufacturing of propellants, explosives, ordnance, rockets, and flares was included as potential source of perchlorate release into the environment as of April 2003 by the US EPA. Among the data on the list for which the suspected source was a manufacturer of perchlorate-containing products, the highest perchlorate concentration was 640 000 $\mu g\,l^{-1}$ observed in monitoring of well waters in Arkansas and California, and both the suspected sources were rocket manufacturers. In Japan, perchlorate was detected at 400 $\mu g\,l^{-1}$ in a river in Okayama prefecture, and a chemical facility manufacturing airbags located upstream was the likely source of contamination. However, perchlorate was present at levels ranging from below the limit of detection to 3.26 $\mu g\,l^{-1}$ in a public water system (PWS) of the Town of Tewksbury, Massachusetts, its source being the Merrimack River. The source of perchlorate in the river was industrial effluent from a perchloric acid user.

Usage of perchlorate-containing products

As shown in **Table 1**, perchlorate compounds are used in various products and their use may result in perchlorate contamination in the environment. Solid propellants and munitions are the main applications of perchlorate compounds in the United States. However, commercial explosives and fireworks are also known to be potential sources of perchlorate.

Solid propellants

Among the perchlorate compounds, ammonium perchlorate is commonly used in solid rocket/missile propellants. Launch failure and the disposal of solid propellants may result in the release of perchlorate into the environment. Manufacturing, testing, research, handling, and disposal of rockets and propellants were included as potential sources of perchlorate release into the environment as of April 2003 by the US EPA. The facilities of propellant users, for example, the Department of Defense (DOD) and the National Aeronautics and Space Administration (NASA), are also listed under known sources of perchlorate release in the United States as of March 2005. High levels of perchlorate, at levels of thousands or tens of thousands of micrograms per liter, were detected at some of these sites.

Munitions

Perchlorate may be contained in munitions, munition components, and training devices, including solid fuel rockets, mines, torpedo warheads, smoke-generating compounds, signal flares, parachute flares, star rounds for pistols (illumination rounds), thermite-type incendiaries, tracer rounds, incendiary bombs, fuses, jet-assisted take-off devices, and training simulators. Perchlorate contamination may occur through their storage, disposal, or use. Perchlorate contamination has been reported at many military facilities in the United States. Sixty-three DOD facilities in 25 states were listed by the US EPA as known perchlorate releasers in the United States as of March 2005. Perchlorate contamination in drinking water, groundwater, or surface water was reported in 54 of these 63 facilities (**Table 2**). The highest perchlorate concentrations detected were 720 $\mu g\,l^{-1}$ in drinking water, 276 000 $\mu g\,l^{-1}$ in groundwater, and 16 000 $\mu g\,l^{-1}$ in surface water.

Commercial explosives

Perchlorate salts, such as sodium, ammonium, and potassium perchlorate, are used in some explosive products. They are used as emulsions, water gels, delay elements in detonators, and in some seismic explosives. Perchlorate contamination may occur through the incomplete detonation of these products.

The sources of perchlorate contamination in three PWSs in the towns of Millbury, Westford, and Boxborough, Massachusetts, are suspected to have resulted from the explosives used at construction sites. In Millbury, perchlorate was detected from two PWSs wells at concentrations of 45.3 and 21.6 $\mu g\,l^{-1}$, respectively, in May 2004. Perchlorate was also detected in surface water runoff systems and monitoring wells at levels ranging from tens to hundreds of micrograms per liter. Explosives

Table 1 Some perchlorate-containing products and manufacturing processes using perchlorate compounds (ITRC perchlorate team and MA DEP)

Use of perchlorate compound

Additive in polyvinyl chloride
Airbag initiators
Analytical testing agents
Ejection seats
Electroplating operations
Electropolishing operations
Engine oil testing
Etching of brass and copper
Explosives
Fireworks
Leather tanning
Oxygen generators
Paints and enamels
Photographic flash powder
Propellant in rocket engines
Road flares
Safety matches
Textile bleaching agent

Table 2 Known perchlorate contamination in drinking water, groundwater, and surface water at DOD facilities as of March 2005

Category	*No. of facilities*	*No. of states*	*Highest perchlorate detection*		
			Concentration ($\mu g\,l^{-1}$)	*Facility/site*	*State*
Drinking water	11	6	720	China Lake	California
Groundwater	44	22	276 000	Naval Surface Warfare Center, Indian Head Division	Maryland
Surface water	16	8	16 000	Holloman Air Force Base	New Mexico

Note: The lists do not show the entire detection of perchlorate in drinking water, groundwater, and surface water at DOD facilities. They represent the extent of perchlorate detection data currently known to the US EPA as reported from various sources. Perchlorate was detected in some categories (drinking water, groundwater, and surface water) at the same facilities. The total number of DOD facilities and states where perchlorate was detected were 54 and 24, respectively. In some cases, only the fact that perchlorate was detected was reported.

containing perchlorate that were used at the construction site are suspected to have been the source of the perchlorate. In Westford, perchlorate was found at 2 $\mu g\,l^{-1}$ from a PWSs well in July 2004. By subsequent investigation, MA DEP concluded that blasting at the highway garage site using explosives containing up to 30% ammonium perchlorate was the likely source of perchlorate. In Boxborough, perchlorate was detected in two of five condominium wells, with a peak concentration of 1300 $\mu g\,l^{-1}$. MA DEP suspected blasting at a construction site of a new wastewater treatment plant to be the source of perchlorate, although information about the types of explosives used was not obtained.

Fireworks

Fireworks are a potential source of perchlorate contamination due to atmospheric deposition and debris. MA DEP reported that fireworks displays were likely sources of perchlorate contamination ($\geq 1\,\mu g\,l^{-1}$) for at least three PWSs. These three PWSs are small, noncommunity wells, and the perchlorate concentrations in the wells were primarily of the order of micrograms per liter. The effects of fireworks displays on perchlorate concentration in a small lake located in Ada, Oklahoma, were also investigated from 2004 to 2006. Perchlorate concentrations preceding fireworks displays in the lake ranged from 0.005 to 0.081 $\mu g\,l^{-1}$, with a mean value of 0.043 $\mu g\,l^{-1}$, and increased within 14 hours after each of the displays. The maximum perchlorate concentration observed after the display in July 2006 was 44.2 $\mu g\,l^{-1}$. Since then, perchlorate concentrations decreased and returned to the background level within 20–80 days after the display. In addition, it was reported that the perchlorate concentration of a river in Japan was affected by a fireworks display, rising to a high concentration of 79 $\mu g\,l^{-1}$ just after the display conducted on a barge on the river. As the perchlorate concentration at the same location dropped to 0.39 $\mu g\,l^{-1}$ 5 days after the display, fireworks displays are considered to have short-term effects on perchlorate concentration in the river.

A field study of the impact of fireworks displays on perchlorate contamination was conducted on the University of Massachusetts campus by MA DEP. Fireworks displays had occurred at the site since 1995, and eight monitoring wells installed at the location allowed sampling to take place from June 2004, before the annual fireworks display, to July 2006. Perchlorate concentration in groundwater ranged from not detected to 62.2 $\mu g\,l^{-1}$ in the 2004 predisplay sample, where the groundwater showed contamination from earlier fireworks displays. It was also indicated that the impact of perchlorate on groundwater from the launch area may be migrating downgradient.

Unintended by-product

Sodium perchlorate is manufactured electrolytically from sodium chlorate, which is manufactured from brine in the electrolysis process. Manufacture of sodium chlorate is a potential source of perchlorate because perchlorate is generated as an unintended by-product in the electrolysis process. Sodium chlorate is used as herbicide, mainly as a defoliant. It was reported that perchlorate content in one chlorate defoliant was 24 $mg\,kg^{-1}$. It was also reported that perchlorate is generated as an unintended by-product in electrolysis processes other than those for the manufacture of perchlorate and chlorate.

Perchlorate contamination in the Tone River Basin, Japan, was discovered in 2006 (**Figure 1**). As mentioned earlier, two industrial effluents were the main sources of perchlorate: one from a facility manufacturing perchlorate and chlorate and the other from a facility conducting electrolysis processes other than those for the manufacture of perchlorate and chlorate. In the latter case, the perchlorate concentration in the industrial effluent was 15 000 $\mu g\,l^{-1}$, and it was concluded that perchlorate was generated as an unintended by-product of the electrolysis processes. The effluent entered the Usui River, one of the tributaries of the Tone River, and the maximum concentration of perchlorate in the Usui River was 2300 $\mu g\,l^{-1}$. The estimated perchlorate load from the industrial effluent was 40–78 kg per day, which was comparable to that from the manufacture of perchlorate and chlorate located near the Tone River.

Perchlorate as an unintended by-product was also reported in a water distribution system. In 2002, perchlorate concentration was determined by the Texas Commission for Environmental Quality to be 32 $\mu g\,l^{-1}$ in an elevated storage tank. A subsequent investigation concluded that the most likely source of perchlorate was the storage tank itself, where perchlorate was generated electrochemically *in situ* from chlorinated drinking water in the corrosion protection system. Laboratory experiments confirmed this suspicion. It was also suggested that perchlorate generation was dependent on the type of metal used for the anode.

Hypochlorite solution, which is used as a disinfectant in water purification processes, is known to contain perchlorate alongside other oxihalides (e.g., chlorite, chlorate, and bromate) as impurities. Hypochlorite solutions used in water systems (PWSs or private water systems) are typically commercial sodium hypochlorite solutions or on-site hypochlorite solutions generated by the electrolysis of brine. It was reported that perchlorate concentrations in 32 commercial hypochlorite solutions and 6 hypochlorite solutions generated on-site that were used in water systems were in the range of 170–33 000 $\mu g\,l^{-1}$ (median concentration, 2300 $\mu g\,l^{-1}$) and 13–660 $\mu g\,l^{-1}$ (median concentration, 32 $\mu g\,l^{-1}$), respectively (**Table 3**). Perchlorate concentrations in the hypochlorite solutions were higher in cases in which the levels of free available chlorines (FACs) in the solutions measured in the laboratory (8.0–16.4%) were lower. Perchlorate concentrations in the commercial hypochlorite solutions are considered to increase in accordance with the decay of FACs in the solutions. Another study showed that perchlorate concentrations in hypochlorite solutions increase during storage. In general, the concentration of perchlorate originating from hypochlorite solution is low in finished drinking water (0.2–0.4 $\mu g\,l^{-1}$). However, in two cases in Japan, the perchlorate concentration in finished drinking water in a PWS was found to be $\geq 1\,\mu g\,l^{-1}$ (6.1 $\mu g\,l^{-1}$ in October 2006 and 1.1 $\mu g\,l^{-1}$ in February 2007). The hypochlorite disinfectant was the suspected source in both cases as perchlorate concentrations in the raw waters were low ($<0.05\,\mu g\,l^{-1}$) and those in the hypochlorite solutions were high (13 000 $\mu g\,l^{-1}$ in February 2007). Such cases highlight the risks of perchlorate contamination in water systems by hypochlorite solutions with low FACs and perchlorate accumulation.

Occurrence of Perchlorate in Drinking Water

Since the discovery of perchlorate in drinking water wells in eastern Sacramento County, California, in 1997 by CA DHS, the occurrence of perchlorate in water systems has been investigated throughout the United States. In the case of Japan, the occurrence of perchlorate in drinking water sources and some tap waters was first reported in 2006, and studies of its occurrence in water systems, including a national survey, were subsequently conducted. Despite a limited number of investigations of the occurrence of perchlorate, perchlorate contamination of water systems in some other countries has been reported. It is difficult to remove perchlorate in the conventional water purification processes and ozone/activated carbon processes because perchlorate is highly soluble in water. Ion exchange and anaerobic biological treatment processes are techniques available for such processing. Perchlorate concentrations in various types of bottled water (e.g., drinking waters of PWSs, spring waters, and well waters) of various countries have also been investigated.

Drinking Water in Water Systems

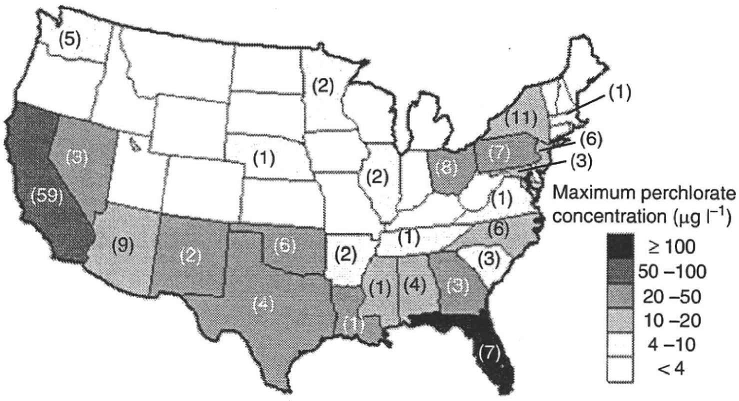
United States

A national survey of perchlorate in PWSs was conducted in 2001–05 under the first Unregulated Contaminant Monitoring Regulation (UCMR 1). The UCMR program collects data on contaminants suspected to be present in drinking water but that do not have health-based

Table 3 Perchlorate concentration in hypochlorite solution used in water systems

Category	*No. of samples detected/no. of samples analyzed*	*Range of FAC measured (%)*	*Perchlorate concentration ($\mu g\,l^{-1}$)*	
			Range	*Median*
Commercial hypochlorite solution	32/32	8.0–16.4	170–33 000	2300
On-site generation	6/6	1.0–7.2	13–660	32

Note: Samples were collected in September–October 2006, except for five commercial hypochlorite solutions that were collected in February–March 2007. The range of labeled FACs in commercial hypochlorite solutions was 12–13.2%, except in four samples for which data could not be obtained.



Puerto Rico: maximum 420 μg l^{-1}(1)
Northern Mariana Islands: maximum 14 μg l^{-1}(1)

Figure 2 Maximum perchlorate concentrations in PWSs by UCMR 1 (final data set). The detection data are available from the website of US EPA. Numbers in parentheses are the number of PWSs in each state or territory in which perchlorate was detected at ≥4 μg l^{-1}. Alaska and Hawaii are not illustrated but perchlorate was not detected in these states.

standards set under the Safe Drinking Water Act (SDWA). The results of perchlorate detection in UCMR 1 are shown in **Figure 2**. Perchlorate was found at a minimum reporting level (MRL) of 4 μg l^{-1} or more in 160 of 3870 PWSs in 26 states and 2 territories, and in 647 of the 34 728 samples tested. The perchlorate concentrations detected were in the range of 4–420 μg l^{-1}, with a mean of 9.9 μg l^{-1}. The maximum perchlorate concentration, 420 μg l^{-1}, was found in a PWS in Puerto Rico. Of the 160 PWSs in which perchlorate was detected, 8 were small systems (supplying a population of ≤10 000) and 152 were large systems (supplying a population of >10 000). The contaminated water type was surface water in 3 of the 8 small systems and groundwater in the remaining 5, whereas for large systems, it was surface water for 88 of 152 and groundwater in the remaining 64. The US EPA occurrence data for UCMR 1 (the final data set) have been released and detailed analyses as of July 2005 are also available.

Statewide investigations of perchlorate in PWSs have also been conducted by several states in the United States (e.g., California, Massachusetts, Texas, and Arizona). In California, the occurrence of perchlorate in drinking water sources has been investigated by CA DHS since 1997. In 1999, perchlorate was added to the list of unregulated chemicals for which monitoring is required by CA DHS. According to the results from July 2003 to July 2008, perchlorate was detected at ≥4 μg l^{-1} in 274 of approximately 10 600 sources. These 274 sources are active and standby sources of 82 PWSs in 12 counties and are mostly groundwater. The highest perchlorate concentrations in source water in each county ranged from 4 to 96 μg l^{-1}.

In Massachusetts, the statewide occurrence of perchlorate in community and nontransient/noncommunity PWSs was reported in 2005 and perchlorate was detected at ≥1 μg l^{-1} in 9 of 591 PWSs investigated. The water type of eight of the nine PWSs was groundwater. The likely sources of perchlorate identified were blasting agents, fireworks, and industrial use of perchloric acid. According to perchlorate monitoring results as of March 2006, perchlorate was detected at ≥1 μg l^{-1} from 10 PWSs. The highest perchlorate concentrations in finished drinking water in each PWS ranged from 1.51 to 1300 μg l^{-1}.

Japan

Perchlorate concentrations in a total of 66 water systems (46 PWSs and 20 private water systems) selected from across Japan were investigated in October 2006 and February 2007. In the survey of October 2006, perchlorate concentrations in tap waters of 3 of 41 water systems (21 PWSs and 20 private water systems) were ≥1 μg l^{-1} (1.2–6.1 μg l^{-1}), which was confirmed by an additional survey conducted for these 3 water systems in March 2006 (1.1–1.7 μg l^{-1}). The sources of perchlorate in two of these three water systems were uncertain, with hypochlorite solution used for disinfection being the suspected source in the remaining water system. In the survey of February 2007, perchlorate concentrations in the tap waters of 4 of 25 PWSs were ≥1 μg l^{-1} (5.5–15 μg l^{-1}). The source waters used for the four PWSs were river waters from the Tone River Basin. Another study reported perchlorate concentrations ranging from 0.06 to 37 μg l^{-1} in 30 tap waters tested in February to June 2006. Perchlorate was found at levels of ≥1 μg l^{-1} in tap waters from the Tone River Basin and perchlorate concentrations were ≥10 μg l^{-1} in 13 tap waters examined. At present, in Japan, the area where drinking water is most widely contaminated by perchlorate is in the Tone River Basin.

Table 4 Perchlorate concentration in finished drinking water of 42 PWSs in the Tone River Basin, Japan, September–October 2006

Category	*Water type*	*No. of samples detected/no. of samples analyzed*[a,b]	*No. of PWSs detected/no. of PWSs investigated*[a,b]	*Range of perchlorate concentration (μg l^{-1})*[c]
Upper basin	Surface water	0/6	0/6	0.12–0.86
	Groundwater	2/5	2/5	0.08–24
Middle basin	Surface water	21/22	15/16	0.22–14
Lower basin	Surface water	11/17	10/15	0.23–1.8

[a] The number of samples is higher than that of PWSs because several samples were collected from some PWSs.

[b] Detected level of perchlorate in finished drinking water is ≥1 μg l^{-1}.

[c] Perchlorate was detected at ≥0.05 μg l^{-1} in all finished drinking waters.

In fact, a study on the occurrence of perchlorate in PWSs has focused on the Tone River Basin. Perchlorate concentrations in 42 PWSs in the Tone River Basin were investigated in September–October 2006 (**Table 4**). The numbers of PWSs in the upper, middle, and lower Tone River Basin found to have perchlorate concentrations ≥1 μg l^{-1} in finished drinking waters were 2, 15, and 10, respectively. Widespread perchlorate contamination of drinking water in the Tone River Basin was demonstrated, although the perchlorate concentrations decrease in downstream areas.

Other Countries

In Korea, perchlorate concentrations in tap waters of four cities (Pusan, Daegu, Milyang, and Yangsan) were investigated in 2006. The source waters for drinking water supply of these four cities are the surface waters of the Nakdong River Basin. Perchlorate was detected from all seven tap waters sampled, in the range of 0.15–35 μg l^{-1}. Perchlorate was also detected in the range of <0.05 to 60 μg l^{-1} in the Nakdong River and its tributaries. Perchlorate concentrations in the Yeongsan River, which is also used as the source of drinking water supply, were in the range of 0.08–2.5 μg l^{-1}, although the perchlorate concentrations in tap waters sourced from the Yeongsan River were not reported.

In China, perchlorate concentrations in PWSs in Beijing were investigated from September 2001 to July 2002. Perchlorate concentrations detected in finished drinking waters ranged from 0.2 to 6.8 μg l^{-1}. Perchlorate contamination was observed in the finished drinking water drawn from raw groundwater. Examination of seasonal variations of perchlorate concentration in finished drinking water revealed the highest concentration in November, the drought season.

In Canada, it was reported that perchlorate concentrations in 12 tap waters of 12 cities in 3 provinces ranged from 0.016 to 0.168±0.004 μg l^{-1}. For five of these tap waters, the effects of filtration using either a household water filter or the reverse osmosis system on perchlorate concentrations in tap waters were investigated, and decrease in the perchlorate concentrations in all tap waters was reported (perchlorate concentrations in tap waters before filtration, 0.035±0.001 to 0.089±0.001 μg l^{-1}; after filtration, 0.005 to 0.012±0.001 μg l^{-1}).

Bottled Water

In the fiscal year (FY) 2004 (i.e., from 1 October 2003 to 30 September, 2004), the US Food and Drug Administration (FDA) investigated perchlorate concentrations in bottled waters (e.g., drinking waters from PWSs and spring waters) collected from across the United States and found that perchlorate concentrations in 50 of 51 bottled waters were <0.5 μg l^{-1} and that in the remaining one bottled water was 0.56 μg l^{-1}. It was also reported that perchlorate concentrations in 21 bottled waters purchased from various local merchants representing various source types (e.g., drinking waters from PWSs, spring waters, and artesian waters) and treatment processes ranged from <0.05 to 0.74 μg l^{-1}. In 2004, the Massachusetts DPH reported that perchlorate concentrations in 50 bottled waters (e.g., drinking waters from PWS, spring waters, and artesian well waters) of 6 countries (i.e., United States, Canada, France, Italy, Norway, and Fiji) for sale in Massachusetts, which were submitted by bottled water companies, were <1 μg l^{-1}. Of the data submitted by the bottled water companies, some were perchlorate concentrations in finished bottled water and others were those in source waters. It was also reported that perchlorate concentrations in 9 of 10 bottled waters from 5 countries (i.e., France, India, Germany, Canada, and Portugal) were low, ranging from below the level of detection to 0.198±0.017 μg l^{-1}, and that in the remaining 1 bottled water from Portugal was 5.098±0.040 μg l^{-1}. Perchlorate concentrations in 5 bottled waters from PWSs in Japan were in the range of <0.05 to 0.92 μg l^{-1} and those in the remaining 59 bottled waters (e.g., natural and purified waters) mostly from Japan were in the range of <0.05 to 0.57 μg l^{-1}. Perchlorate concentrations in the bottled waters for sale in China were also reported. Perchlorate concentrations in seven bottled purified waters were found to be <0.002 μg l^{-1}. Perchlorate concentrations in 21 of 22 bottled natural mineral waters were in the range of <0.002 to 0.332±0.017 μg l^{-1} and that in the remaining 1 was 2.013±0.015 μg l^{-1}. From the reported data, it appears that perchlorate concentrations in bottled waters are generally low (up to sub-microgram per liter), with only some samples tested showing levels of several micrograms per liter.

See also: Perchlorate: Human Toxicity.

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Sensitivity analysis using a diffuse pollution hydrologic model to assess factors affecting pesticide concentrations in river water

Koji Tani, Yoshihiko Matsui, Kentaro Narita, Koichi Ohno and Taku Matsushita

ABSTRACT

We quantitatively evaluated the factors that affect the concentrations of rice-farming pesticides (an herbicide and a fungicide) in river water by a sensitivity analysis using a diffuse pollution hydrologic model. Pesticide degradation and adsorption in paddy soil affected concentrations of the herbicide pretilachlor but did not affect concentrations of the fungicide isoprothiolane. We attributed this difference to the timing of pesticide application in relation to irrigation and drainage of the rice paddy fields. The herbicide was applied more than a month before water drainage of the fields and runoff was gradual over a long period of time, whereas the fungicide was applied shortly before drainage and runoff was rapid. However, the effects of degradability-in-water on the herbicide and fungicide concentrations were similar, with concentrations decreasing only when the rate constant of degradation in water was large. We also evaluated the effects of intermittent irrigation methods (irrigation/artificial drainage or irrigation/percolation) on pesticide concentrations in river water. The runoff of the fungicide, which is applied near or in the period of intermittent irrigation, notably decreased when the method of irrigation/artificial drainage was changed to irrigation/percolation. In a sensitivity analysis evaluating the synergy effect of degradation and adsorbability in soil, the degradation rate constant in soil greatly affected pesticide concentration when the adsorption coefficient was small but did not affect pesticide concentration when the adsorption coefficient was large. The pesticide concentration in the river water substantially decreased when either or both the degradation rate constant in soil and adsorption coefficient was large.

Key words | adsorption, degradation, isoprothiolane, pollutograph, pretilachlor

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INTRODUCTION

Although global attention is now being paid to their health hazards, pesticides are still necessary for agriculture to improve production efficiency and reduce labor requirements. Various kinds of pesticides are applied to rice paddy fields, particularly in countries where rice is a staple food. Rice cropping on paddy fields requires a large amount of fresh natural water, which is discharged to the river by artificial drainage or percolates into the ground. In Japan, about two-thirds of water use is for agricultural purposes, and about 90% of this water is used for rice cropping (Ministry of Land, Infrastructure, Transport and Tourism, Japan 2006). Pesticides applied to paddy fields enter environmental waters more easily than pesticides applied to upland fields because paddy water is discharged directly into rivers and lakes. Therefore, pesticides applied to rice paddy fields have a greater potential to contaminate river

doi: 10.2166/wst.2010.540

water, some of which is the source of drinking water. It is therefore important to understand how the pesticides applied to paddy fields influence the pesticide concentrations in river water.

On dry fields, half-life in soil and soil/water adsorption coefficient are considered to be two key environmental fate properties for pesticides (Chen *et al.* 2002), but runoff of rice-farming pesticides applied directly onto ponded paddy water is influenced by properties such as water solubility, the adsorbability to soil (the soil–water partitioning coefficient normalized for the organic carbon content, K_{OC}), and half-lives for pesticide degradation in soil and water (Iwakuma *et al.* 1993; Sudo *et al.* 2002; Capri & Karpouzas 2007). Some studies have suggested that the magnitude of the pesticide runoff differs depending on the solubility of the pesticides (Ueji & Inao 2001; Ebise & Inoue 2002), whereas other studies have indicated a correlation between sorption behaviors of pesticides and their loss (Fajardo *et al.* 2000). Correlations to K_{OC} and water solubility (WS) could be taken to indicate the same phenomena because pesticides with high K_{OC} are mostly low in WS and vice versa (Lyman *et al.* 1990). Although K_{OC} and WS are essentially different pesticide properties, these two properties are not generally evaluated separately when assessing pesticide concentrations in runoff. Runoff rates are reported to be well correlated with another sorption-related parameter, the octanol–water partition coefficient, log P_{OW}, rather than with the water solubility of herbicides (Nakano *et al.* 2004). Watanabe *et al.* (2007) reported that K_{OC} seems to be a stronger indicator of the aquatic fate of an herbicide compared to WS, suggesting that sorption rather than dissolution is the key phenomenon driving rice-farming pesticide runoff. However, the effects of K_{OC} and WS on pesticide runoff have not been separately and quantitatively analyzed, nor have the effects of half-lives for degradation in soil and water been analyzed.

Irrigation-water management practices strongly influence rice pesticide runoff, and consequently the runoff quantity and pesticide concentration in the runoff water could be decreased by improving management practices (Miao *et al.* 2003; Christen *et al.* 2006; Numabe & Nagahora 2006). For minimizing the risk of high pesticide loads entering surface water bodies, prolongation of paddy closure after pesticide application has been studied as a useful strategy (Karpouzas *et al.* 2006). The fate and transport of three herbicides in rice production using different water management practices have been studied, and results have indicated an advantage of increasing the water holding period and the excess water storage depth in reducing runoff of pesticides from paddy plots over the practice of overflow drainage (Vu *et al.* 2006; Watanabe *et al.* 2007; Phong *et al.* 2008). The practice of intermittent irrigation with a shallow water depth and a high drainage gate to maintain a high excess water storage depth and increase the water holding period saved irrigation water and prevented herbicide runoff, whereas the practice of continuous irrigation and overflow resulted in significant losses of water as well as herbicides (Inao *et al.* 2008).

Rice pesticide concentrations are also of concern downstream, after their discharge from paddy fields, where river water may be taken as a source of drinking water. Pesticide concentrations in river water are considered to be changed through a complex system affected by various factors, including geographic and hydrologic elements, agricultural practices, and the physicochemical and biologic properties of the pesticides (Matsui *et al.* 2002, 2005). It is therefore difficult to evaluate the individual effects of these factors on pesticide concentrations in downstream regions of river systems merely by field observations or experiments; modeling and simulation are useful tools in this regard. In this study, we evaluated the factors that affect the concentrations of pesticides (an herbicide and a fungicide) in river water by a sensitivity analysis using a diffuse pollution hydrologic model.

MATERIALS AND METHODS

Model river basin and pesticide diffuse pollution model

The Kakkonda River, Iwate, Japan, which has a 191-km^2 catchment area consisting mainly of forest and rice paddy fields, was selected as a model river for conducting the sensitivity analysis. Details of the diffuse pollution hydrologic model are described elsewhere (Matsui *et al.* 2006*a*), but briefly in the model the river basin was divided into a grid of 1-km^2 cells. Each cell was subdivided into compartments including a river water compartment and several rice paddy ponding compartments representing the rice paddy fields of each farmer in the river basin. It is assumed that applied pesticides reach the paddy fields (the loss due to the drift of pesticide, the effect of application mode, the effect of spray formulation, and the effect of adjuvants were not accounted). In the compartment consisting of solids and water, an instantaneous equilibrium was assumed between the dissolved and adsorbed fractions at the solid–water interface, and the equilibrium relationship was described by the adsorption coefficient K_{OC}. Pesticide degradations in soil and water were each described by first-order reaction kinetics with a degradation rate constant. A set of differential mass-balance equations was defined to describe the dynamics of pesticide and water in each compartment based on mass conservations for the pesticide and water. This model was first applied to predict the concentrations of paddy-farming pesticides in river water from a large catchment (1,882 km^2, Matsui *et al.* 2006*a*). Although the model was calibrated with hydrologic data only, 68% of the observed concentration data were in the range of model prediction with the Monte Carlo inputs: the Monte Carlo method was applied to account for the uncertainty in the model inputs relating to farming work schedules and pesticide adsorption/degradation rates in the large catchment. The model predicted pesticide concentrations within an order-of magnitude accuracy, and the pesticide rankings according to the predicted concentration roughly agreed with those observed (Matsui *et al.* 2006*b*). By using improved model inputs after collecting precise information on farming work schedules of the farmers within the catchment area and obtaining pesticide adsorption/degadation rates for rice paddy soils in the river basin, the model's capability to reproduce observations of rice farming pesticide concentrations in river water was further verified (Matsui *et al.* 2007).

Farming data and target pesticides

For the sensitivity analysis, the model used precise data of agricultural activity, such as the places where pesticide was applied and the irrigation schedule, so that the effects of each factor on pesticide concentration in river water in a river basin could be clearly evaluated. The farming data of the rice paddy fields in the river basin, including the irrigation and pesticide application dates and the quantity of pesticide applied for each paddy field for all 372 farmers in the catchment area, were obtained by courtesy of the farmers in the catchment area and compiled into a database for input to the model. The target pesticides were the herbicide pretilachlor and the fungicide isoprothiolane, which are popular pesticides in rice cropping in the river basin. The herbicide (67 kg) was applied in the middle or end of May 2004, within 0.5 or 1 month after transplanting the seedlings, and the fungicide (153 kg) was applied around July 2004, about 1.5 months before harvest (see Figure 1). For water management, a water level of a few centimeters was maintained from May to June, after which the water was drained. In August and September, paddy fields were irrigated and drained intermittently to rehydrate and oxygenate the soil, respectively. The characteristics of the pesticides are listed in Table 1.

RESULTS AND DISCUSSION

Effects of pesticide degadation in the soil, adsorption, and application period

Sensitivity analysis was applied to the diffuse pollution hydrologic model, which is capable of predicting the pesticide concentrations in river water (Matsui *et al.* 2006*a*,*b*, 2007). Before using the sensitivity analysis, the model was verified with the data of Nakano *et al.* (2004) who reported that the runoff rates of six herbicides in the Kozakura River, Japan, were well correlated with log P_{OW}, as shown in Figure 2. We conducted model simulations of the same six herbicides in the Kakkonda River with the model input values for the pesticide characteristics (Table 2). The trend in the relationship between the pesticide runoff rate and the log P_{OW} (the logarithm of the octanol–water partition coefficient) obtained by our model simulation for the Kakkonda River was similar to the trend observed in the Kozakura River, although our pesticide runoff rate values were lower. These lower values for the Kakkonda River could be a result of runoff rate dependency on the length of the river in relation to the catchment area as the catchment area of the Kakkonda River (191 km^2) is

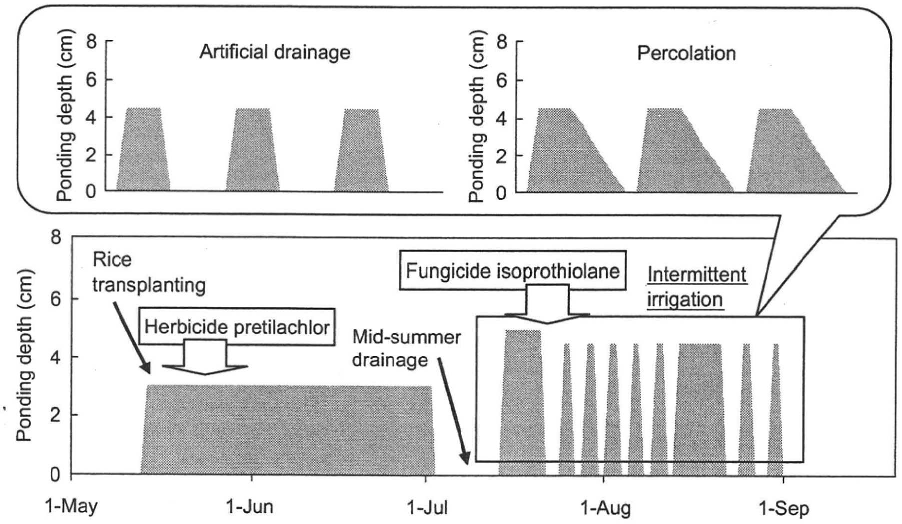

Figure 1 | Irrigation schedule and ponding depth of a rice paddy field with artificial drainage and percolation in the Kakkonda River basin.

much larger than that of the Kozakura River (15.4 km^2). Because the trend was the same for the two rivers, we performed a sensitivity analysis of the model simulation to provide quantitative information on pesticide concentration in river water in relation to pesticide characteristics.

In the sensitivity analysis, model simulations were conducted in which the adsorption coefficient and the degradation rate constant in soil were varied through a range of 0.01 to 100 times their actual values to determine the effects of pesticide degadation and adsorption: the range of the variations in the adsorption coefficient and the degradation rate constant in soil and were determined to cover actual values of pesticides (Tomlin 2003). The sensitivity of the pesticide degradability in soil affecting the pesticide concentration in river water was different for the two pesticides (see Figure 3A). Although an increasing the degradation rate constant in soil reduced the concentration of the herbicide in river water, the effect on the fungicide was not as noticeable. Increasing the degradation rate constant in soil by a factor of 100 (from the default values of $2.3 \times 10^{-2}\,\mathrm{d}^{-1}$ for the fungicide and the herbicide; see the dotted line in Figure 3A and Table 1) decreased the herbicide concentration in the river water by about 30% and the fungicide concentration by 20%. Decreasing the degradation rate constant in soil by a factor of 100 increased the herbicide concentration by about 40%, while the fungicide concentration scarcely changed.

The adsorbability affected the concentration of the herbicide in river water but had little effect on the concentration of the fungicide (Figure 3B). The effects of the pesticide adsorbability were greater than those of the pesticide degradability on the concentrations of both the herbicide and the fungicide. Runoff behavior can be assessed by a time-series analysis. The fungicide was applied

Table 1 | Default values of the model input

	Water solubility (mg/L)	**Adsorption coefficient, K_{OC} (mL/g)**	**Degradation rate constant in soil[*] (d^{-1})**	**Degradation rate constant in water[*] (d^{-1})**
Isoprothiolane	54[†]	1,230[‡]	2.3×10^{-2}[‡]	2.3×10^{-2}[‡]
Pretilachlor	50[†]	1,160[§]	2.3×10^{-2}[†]	4.9×10^{-2}[§]

[*] Calculated from half-life values by assuming first-order kinetics.
[†] Tomlin (2003).
[‡] Matsui *et al.* (2007).
[§] Food Safety Commission of Japan (2008).

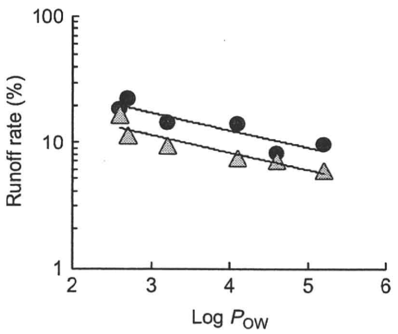

Figure 2 | Effect of log P_{OW} on pesticide runoff rates. Gray triangles indicate the simulation results. Black circles are the observed values from Nakano *et al.* (2004).

in July and ran off rapidly over a short period of time during artificial drainage of the rice paddy fields (Figure 4A). About 65 kg (42%) of the 153 kg of fungicide applied to the rice paddy fields flowed into the river soon after its application. In contrast, the herbicide was applied in May, more than one month before any drainage of the rice paddy fields (Figure 4B). The herbicide ran off slowly, and only 7 kg (10%) of the 67 kg of applied herbicide flowed into the river, indicating that more of the herbicide is degraded by or adsorbed to the paddy soil than the fungicide. This difference in runoff characteristics is a result of the different application periods for the herbicide and fungicide.

To further confirm this result, model simulations were conducted with the assumption that the fungicide isoprothiolane was applied in May prior to drainage, while the herbicide pretilachlor was applied in July at the time of drainage. By interchanging these application periods, the simulation showed that the total runoff of isoprothiolane decreased from 65 kg (42%) to 19 kg (12%), and the total runoff of pretilachlor increased from 7 kg (10%) to 19 kg (28%) (Figure 5). Not only the quantity of pesticide runoff but also the runoff patterns changed. In this model simulation, pretilachlor rapidly flowed into the river because the rice paddy fields were being drained at the time of herbicide application. The runoff pattern of pretilachlor in this model simulation (Figure 5B) and the runoff pattern of the fungicide isoprothiolane in the original model simulation (Figure 4A) were similar. Therefore, the effects of the degradability-in-soil and the adsorbability on the pesticide runoff are primarily dependent on the pesticide application period and corresponding water management of rice paddy fields.

Pesticide degadation in water and water solubility

The effect of pesticide degadation-in-water on pesticide concentration was evaluated by varying their the degradation rate constant in water through a range of 0.01 to 100 times their default values ($2.3 \times 10^{-2}\,\mathrm{d}^{-1}$ for the fungicide and $4.9 \times 10^{-2}\,\mathrm{d}^{-1}$ for the herbicide; see Table 1) in the model simulations. Increasing the degradation rate constant in

Table 2 | Properties of the pesticides in Figure 2

	Log P_{OW}[*]	Water solubility (mg/L)	Adsorption coefficient, K_{OC} (mL/g)[†]	Degradation rate constant in soil[‡] (d^{-1})	Degradation rate constant in water[‡] (d^{-1})
Simetryn	2.6	400[§]	290[‖]	5.5×10^{-3}[¶]	5.5×10^{-3}[¶]
Dymron	2.7	1.2[§]	940[**]	1.4×10^{-2}[§]	1.4×10^{-2}[††]
Mefenacet	3.2	4[§]	890[**]	1.8×10^{-2}[¶]	1.8×10^{-2}[¶]
Pretilachlor	4.1	50[§]	1,160[‡‡]	2.3×10^{-2}[§]	4.9×10^{-2}[‡‡]
Esprocarb	4.6	4.9[§]	2,800[**]	1.4×10^{-2}[§]	1.4×10^{-2}[††]
Pyributicarb	5.2	0.32[§]	3,500[**]	6.3×10^{-2}[§]	6.3×10^{-2}[††]

[*] Nakano *et al.* (2004).
[†] Geometric means of reported values.
[‡] Calculated from half-life values by assuming first-order kinetics.
[§] Tomlin (2003).
[‖] Estimated by the PCKOCWIN model (US Environmental Protection Agency 2007).
[¶] Estimated from the result of the BIOWIN3 model (Aronson *et al.* 2006).
[**] Ministry of the Environment of Japan (2009).
[††] Assumed the same value as the degradation-in-soil coefficient.
[‡‡] Food Safety Commission of Japan (2008).

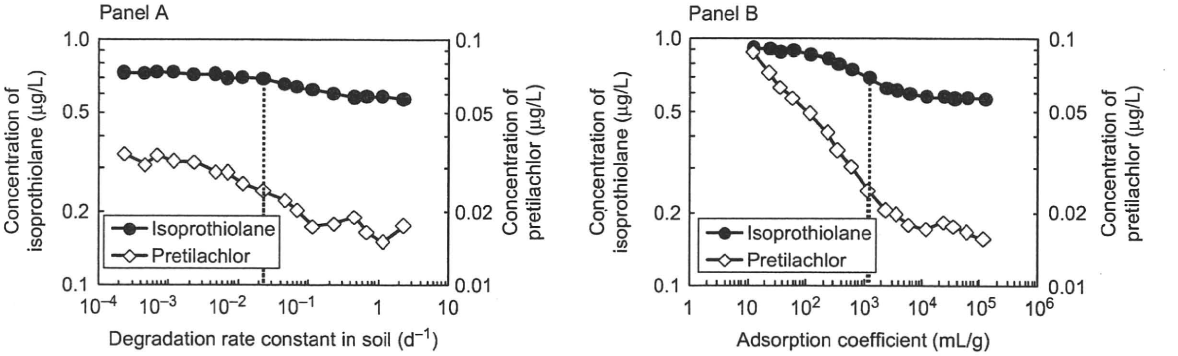

Figure 3 | Effect of pesticide degradability-in-soil (Panel A) and adsorbabilty (Panel B) on the average concentrations of the two pesticides in the river water 2 months after pesticide application on the paddy field. Vertical dotted lines indicate the actual values for the respective pesticides.

water decreased the fungicide concentration only when the degradation rate constant in water was greater than about $10^{-2}\,d^{-1}$ (Figure 6). This trend was also seen for the herbicide, indicating that pesticide degadation in water is similar regardless of whether an herbicide or fungicide is used and irrespective of application periods. When the pesticide degradation rate constant in water was less than approximately $10^{-2}\,d^{-1}$ (indicated by the solid line in Figure 6), the pesticide concentration remained unchanged regardless of pesticide degradation rate constant. This suggests that pesticides applied to rice paddy fields experience minimal degadation in the ponded water of the paddy field, in runoff, or in the river when their degradation rate constant in water is less than approximately $10^{-2}\,d^{-1}$.

The effect of water solubility on pesticide behavior was evaluated by varying the value of water solubility through a range of 10^{-4} to 100 times their default values (54 mg/L for the fungicide and 50 mg/L for the herbicide; see Table 1) in model simulations. Although the effect of water solubility on herbicide concentration was less than that on fungicide concentration, both herbicide and fungicide concentrations showed a similar trend (Figure 7). A decrease in water solubility decreased the fungicide concentration only when water solubility was less than approximately 1 mg/L.

Pesticide concentrations in the river were only minimally affected by water solubility greater than approximately 1 mg/L (solid line in Figure 7), suggesting that above this level pesticides are in the dissolved form and therefore are more likely to run off the fields. In contrast, the pesticide applied on rice paddy fields could remain mostly in the undissolved form in the paddy field when water solubility is less than about 1 mg/L. This would result

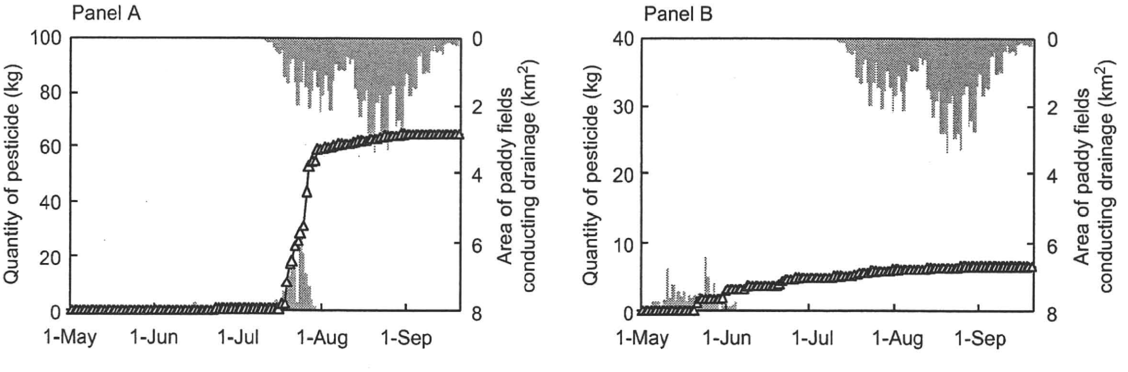

Figure 4 | Time-series runoff behavior of the fungicide isoprothiolane (Panel A) and the herbicide pretilachlor (Panel B) in 2004. Bars along the x-axis indicate the daily quantity of applied pesticide, and bars along the top axis indicate the total area of rice paddy fields conducting drainage in the model catchment. Open triangles indicate the cumulative amount of pesticide runoff into the river.

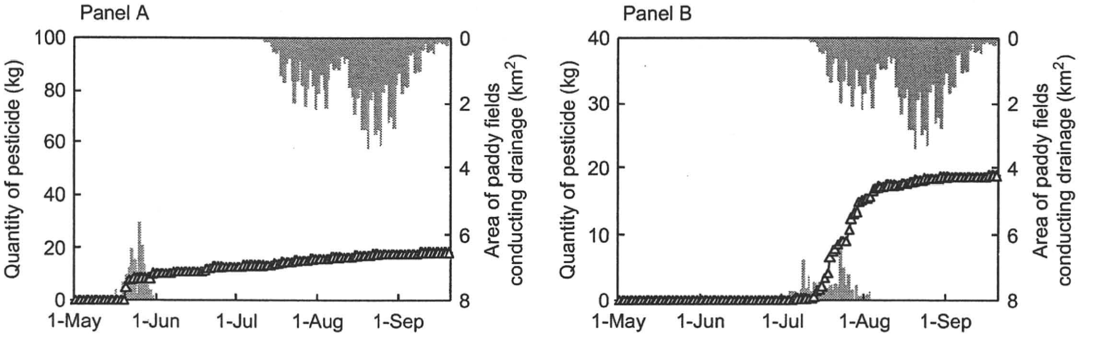

Figure 5 | Fictive time-series runoff behavior of isoprothiolane (Panel A) and pretilachlor (Panel B). Pesticide applications were interchanged; the fungicide isoprothiolane was applied in May prior to drainage, while the herbicide pretilachlor was applied in July at the time of drainage. Bars along the *x*-axis indicate the daily quantity of applied pesticide (in kg), and bars along the top axis indicate the total area of rice paddy fields conducting drainage in the model catchment. Open triangles indicate the cumulative amount of pesticide runoff into the river (in kg).

in greater pesticide degadation because runoff of the undissolved fraction could be delayed.

In an earlier study of pesticide outflow from rice paddy fields, the pesticide runoff rate was strongly correlated with water solubility (Maru 1990). Water solubility affects pesticide runoff, but highly soluble compounds tend to have low adsorbability (low adsorption coefficients in soil) and vice versa (i.e. the soil adsorption coefficient and water solubility are related (Lyman *et al.* 1990)); hence, both water solubility and adsorbability are correlated with pesticide runoff (Watanabe *et al.* 2007). However, the mechanisms by which water solubility and adsorbability affect pesticide runoff are basically different. Pesticides with low water solubility exist in soil in an undissolved form and are less likely to be transported as run off, whereas pesticides with high adsorbability are adsorbed on the soil phase and would not, therefore, be transported with drainage water. Although the correlation between water solubility and concentration has been noted for pesticides (Maru 1990; Nakano *et al.* 2004; Watanabe *et al.* 2007), our sensitivity analyses suggest that the correlation includes a component involving adsorbability and pesticide concentration, in particular for pesticides with water solubility greater than 1 mg/L.

Irrigation/artificial drainage and irrigation/percolation

Some rice paddy fields have well-drained soil. In these cases, during intermittent irrigation periods, farmers may shut off the water intake from irrigation canals and allow the water level to recede by percolation instead of artificial drainage (Figure 1). Percolation would be expected to result

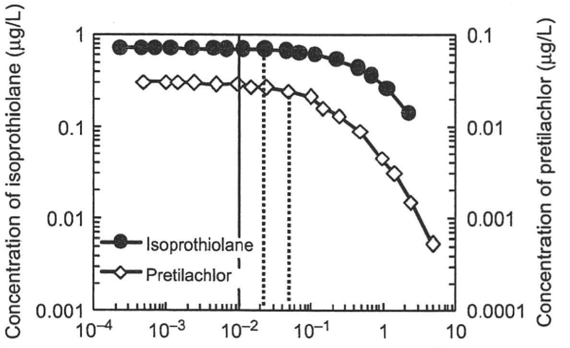

Figure 6 | Effect of pesticide degradability-in-water on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates $10^{-2}\,d^{-1}$.

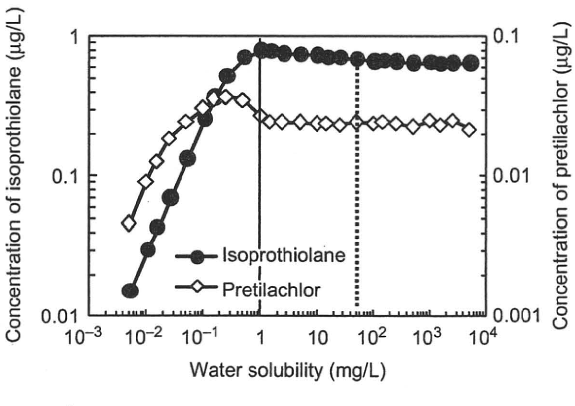

Figure 7 | Effect of pesticide water solubility on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates 1 mg/L.