

Behavior of Pesticides in Drinking Water Purification System and their Occurrence in Water Resource

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Abstract

We investigated the performance of ozonation, chlorination, and granular activated carbon (GAC) adsorption processes. These are to remove the pesticides and their metabolites included in the list of the pesticides approved as complementary items in Japan. All these total to 130 substances. The result showed that many substances were hard to remove by ozonation or chlorination. For GAC adsorption, the results show that it can remove most substances efficiently regardless of the water temperature. Thus we found that the combination of ozonation and GAC adsorption is an effective method of removing pesticides.

Also, we estimated the load amount in the raw water of Osaka Municipal Waterworks Bureau (OMWB) based on the degradability of pesticides and the shipping amount from the Yodo river basin. Consequently, we found that the higher load amount tends to frequent detection of pesticides in raw water.

Keywords: Pesticides; Chlorination; Ozonation; GAC Adsorption; Water Resource, degradability

INTRODUCTION

Generally speaking, water quality accidents have been caused mainly by oils, surface active reagents and chemicals flowing into water sources. And in some cases, those accidents have caused mass deaths of fish which occurs due to pesticides flowing into the river. Therefore, figuring out the occurrence of pesticides in the water source and the behavior in water purification process is a key to monitoring them.

In March of 2013, the Ministry of Health, Labour and Welfare of Japan announced significant changes in the list of the pesticides approved as complementary items (hereinafter called "the List"). These changes increased the number of approved pesticides from 102 to 120. However, there is little information about the new pesticides that were added to the List.

So, we investigated those pesticides regarding to their removability by ozonation, chlorination, and GAC adsorption with performance experiments. Then we conducted degradation experiments and estimated how much they affected raw water.

MATERIALS AND METHODS

Targeted Pesticides and their Analytical Methods

We conducted the experiments and monitoring on 130 substances in total, including 112 of the 120 listed pesticides and their degradation metabolites. As previously reported ^{1) 2)}, we have been monitoring these substances by direct injection analysis method by LC-MS/MS or the analysis method by GC-MS using solid phase extraction. The breakdown is as shown in Table-1. The hatched area in Table-1 identifies the pesticides added to the List in 2013 and those we have been monitoring since or before 2015.

Table-1: Targeted Pesticides

No.	Pesticides	Substances to be analyzed	No.	Pesticides	Substances to be analyzed	No.	Pesticides	Substances to be analyzed
2	2,2-DPA(Dalapon)		40	Chlorpyrifos	Chlorpyrifos			Fenthion(MPP)
3	2,4-D(2,4-PA)				Chlorpyrifos oxon			MPP sulfoxide
4	EPN	EPN	41	Chlorothalonil(TPN)		85	Fenthion(MPP)	MPP sulfone
		EPN oxon	42	Cyanazine				MPP oxon
5	MCPA		43	Cyanophos(CYAP)				MPP oxon sulfoxide
6	Asulam		44	Diuron(DCMU)				MPP oxon sulfone
7	Acephate		45	Dichlobenil(DBN)				
8	Atrazine		46	Dichlorvos(DDVP)		86	Phenthoate(PAP)	
9	Anilofos		48	Disulfoton		87	Fentrazamide	
10	Amitraz			(Ethylthiometon)		88	Phthalide	
11	Alachlor		51	Dithiopyr		89	Butachlor	
12	Isoxathion	Isoxathion	52	Cyhalofop-butyl		90	Butamifos	Butamifos
		Isoxathion oxon	53	Simazine(CAT)				Butamifos oxon
		Isufenphos	54	Dimethametryn		91	Buprofezin	
13	Isufenphos	Isopenphos oxon	55	Dimethoate		92	Fluazinam	
14	Isoprocarb(MIPC)		56	Simetryn		93	Pretilachlor	
15	Isoprothiorane(IPT)		57	Dimepiperate		94	Procymidone	
16	Iprobenfos(IBP)				Diazinon	95	Prothiofos	
18	Indanofan		58	Diazinon	Diazinon oxon	96	Propiconazole	
19	Esprocarb		59	Dymron		97	Propyzamide	
20	Edifenphos		61	Tiadinil		98	Probenazole	
	(Edifenphos, EDDP)		62	Thiuram		99	Bromobutide	
21	Etofenprox		63	Thiodicarb		100	Benomyl	Carbendazim(MBC)
22	Etridiazole		64	Thiophanate-methyl		101	Pencycuron	
		α -Endosulfan	65	Thiobencarb		102	Benzobicyclon	
23	Endosulfan (Benzoepin)	β -Endosulfan	67	Terbucarb(MBPMC)		103	Benzofenap	
		Endsulfate	68	Triclopyr		104	Bentazon	
24	Oxadiclefomefone		69	Trichlorfon(DEP)		105	Pendimethalin	
25	Oxine-copper		70	Tricyclazole		106	Benfuracarb	Carbofuran
26	Oryastrobin		71	Trifluralin		107	Benflurarin	
27	Cadusafos		72	Napropamide			(Bethrodine)	
28	Cafenstrole		74	Piperophos		108	Benfuresate	
29	Cartap	Nereistoxin	75	Pyraclonil		109	Fosthiazate	
30	Carbaryl(NAC)		76	Pyrazoxyfen		110	Malathion(Malathon)	Malathion(Malathon)
31	Carpropamid		77	Pyrazolynate				Malaoxon
32	Carbofuran	Carbofuran		(Pyrazolate)		111	Mecoprop(MCPP)	
-	Carbofuran	Carbosulfan	78	Pyridafenthion		112	Methomyl	
33	Quinoclamrin(ACN)		79	Pyributicarb		113	Metalaxyl	
34	Captan		80	Pyroquilon		114	Methidathion(DMTP)	
35	Cumyluron		81	Fipronil		115	Methyldymron	
36	Glyphosate	Glyphosate	82	Fenitrothion(MEP)	Fenitrothion(MEP)	116	Methominostrobin	
		AMPA			MEP oxon	117	Metribuzin	
37	Glufosinate	Glufosinate	83	Fenobucarb(BPMC)		118	Mefenacet	
38	Clomeprop		84	Ferimzone		119	Mefenacet	
39	Chlornitrofen(CNP)	Chlornitrofen(CNP)				120	Molinate	
		CNP-amino						

The hatched area identifies the pesticides added to the List in 2013

Sample Water

The experiments were conducted using raw water and rapid sand filtrated water from the OMWB's Kunijima Water Purification Plant. Purified water supplied by a ultrapure water purification system was also used. Raw water taken from Yodo river, is treated by the following processes; coagulation-sedimentation, mid-ozonation, rapid sand filtration, post-ozonation, GAC adsorption, and the finished water is distributed to the city after post chlorination process.

EXPERIMENTAL CONDITIONS

Ozonation

An ozone generator (WAT-08 manufactured by Round Science) was used for batch ozonation experiments. The ozone gas was supplied at a rate of 0.25 mg/L per minute for 30 to 60 minutes to

have it contact 1 L of sample water prepared by adding 2 to 100 µg/L of pesticides to rapid sand filtrated water (at temperatures of 20°C to 24°C). The residual ozone in the sample is removed by adding ascorbic acid immediately after the contact time, then samples were analyzed.

Chlorination

Samples were prepared by adding 2 to 200 µg/L of pesticides in purified water, followed by adding chlorine water⁴⁾ at an injection rate of 5 mg/L. Then they were stored the sample at 20°C and at the pH value of 7 under the light-shielding condition. After a prescribed time, residual chlorine is removed by adding ascorbic acid and then samples were analyzed.

GAC Adsorption

This experiment used a glass cylindrical column with a diameter of 5 cm and a length of 90 cm filled with GAC (made from coal) that had been used at the OMWB's Kunijima Water Purification Plant for about five years as well as new GAC to a layer thickness of 20 cm. Samples were prepared by adding pesticides in a concentration of approximately 1.25 to 250 µg/L to rapid sand filtrated water (of 26°C and 8°C). The samples were made to flow through the column filled with GAC at the flow rate of 45 mL/min (i.e., at the space velocity [SV] of 7/h) for 30 or more minutes. Then we collected the samples and then performed analysis.

Degradation in Raw Water

Raw water was used after filtered thorough grass fiber filter paper (with a pore size of 1.0 µm). Samples were prepared by adding prescribed concentration of pesticides to raw water (i.e., 10 or 100 µg/L for pesticides subject to LC-MS/MS or 2 µg/L subject to GC/MS). Samples were stored at 20°C in glass bottles under a light-shielding condition for five days and then samples were analyzed.

Water Solubility

For water solubility, we used EPI Suite⁵⁾ or the actual measurement data described in abstracts on pesticides or evaluation reports of pesticides. We selected to use estimates from EPI Suite for pesticides without available actual measurement data.

Monitoring Locations and Frequencies

OMWB owns three purification plants along the Yodo river: Toyono, Niwakubo, and Kunijima Water Purification Plants. We monitored the raw water taken in at each intake five times annually (from May to September).

Consumption (Shipping Amount) of Pesticides

Since it is difficult to obtain information on the consumption of pesticides, we determined the shipping amount for the five prefectures (Osaka, Kyoto, Shiga, Mie, and Nara) across which the Yodo river system extends by assuming that the shipping amount equals the consumption and referencing the Handbook for Agricultural Chemicals⁶⁾.

Detection Index Values and Their Evaluation

To evaluate the detection of pesticides, we used detection index values based on the total runoff estimation method of pesticides. The relationship between the detection index values and the detected values for the respective pesticides is given by formula (1). Note that the detection index values for finished water should not exceed 1.

$$DI = \sum_i \frac{DV_i}{GV_i} \cdots (1)$$

DI: Detection index value, DV_i: Detected value for pesticide i, GV_i: Target value for pesticide i

RESULTS AND DISCUSSIONS

Results for the Performance Experiments

The indices used in the ozonation experiment are CT values ($\text{mg-O}_3 \cdot \text{min/L}$) obtained by multiplying the residual ozone concentration by the contact time. The results with a CT value of 2.8 are shown in Figure-1. We also included the removal rate with a CT value of 5 in Figure-1. This is based on the approximation, assuming cases where the injection rate of ozone is increased. Among the researched pesticides, there were many substances that are almost not degraded (i.e., resulting in a removal rate less than 80%), regardless of the CT value. Also, the rate at which ozone reacts on pesticides, differed significantly from substance to substance. We found pesticides that degrade in a short time (such as oxaziclomefone). We also found pesticides that are slow to degrade, and deemed to be a good candidate for the increase of the injection rate of ozone (such as pyraclonil). And lastly, we also found pesticides that are almost not degraded (such as pyrazoxyfen).

Figure-1 also shows the results of the chlorination experiment, observed 2 hours and 24 hours later, respectively. When observed after a 2-hour contact time, 56 substances that degraded at a rate of 80% or higher. There were 67 substances did not reach a removal rate of 20%. In addition, after a 24-hour contact time, many residual pesticides were found. Amongst the tested pesticides, there were many pesticides that do not degrade when subjected to chlorination alone.

Furthermore, the results of experiments for GAC adsorption are shown in Figure-2. The results varied, based on the water solubility of the substances tested. Adsorption by the aged GAC removed, at a rate of 80% or higher, 123 substances at a water temperature of 26°C and 102 substances at a water temperature of 8°C. Also, the treatment with new GAC removed almost all substances at a rate near 100%. Hence, the GAC treatment is deemed very effective to remove the tested pesticides. However, the result of experiment with aged GAC (at a water temperature of 26°C) showed a removal rate of approximately 20 to 30% for substances with water solubility of 100,000 mg/L (i.e.; 2,2-DPA (dalapon), acephate, and trichlorfon (DEP)). And for glufosinate, its removal rate was approximately 70% according to its high water solubility of 500,000 mg/L. Thus, substances with very high water solubility are hard to remove with GAC. At the water temperature of 8°C, this tendency was even more remarkable; the removal rate became low with other pesticides, most of which have higher water solubility. This is deemed attributable to the existence of a certain biological treatment in the GAC layer. Also, it is inferred that the removal rate of substances with high water solubility is affected by the physical adsorptive capacity of GAC.

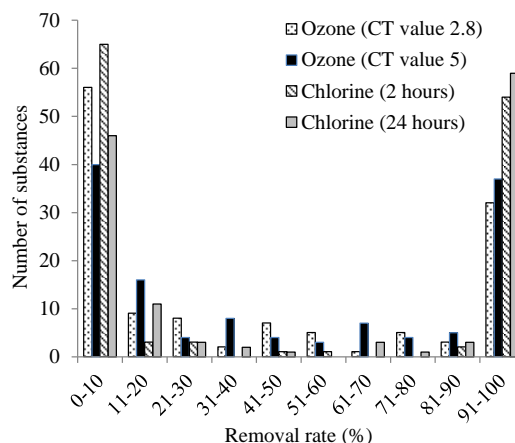


Figure-1: Removal Rate with Ozonation and Chlorination and the Number of Pesticides

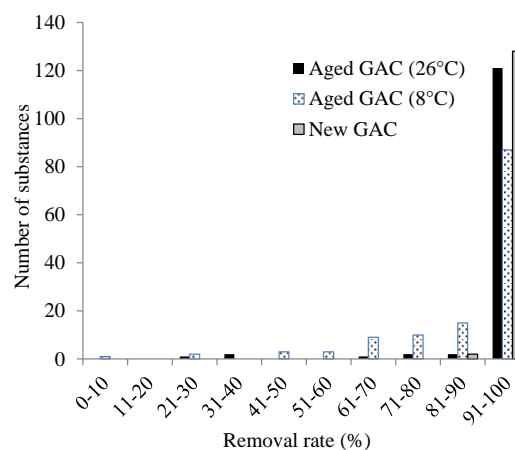


Figure-2: Removal Rate with GAC Adsorption and the Number of Pesticides

Results of the Experiments for Estimation about Degradability

Figure-3 shows the degradability observed 5 days after adding pesticides to raw water. The degradability of 21 substances was 60% or higher while that of 94 substances was 20% or lower. Hence, we found that many of the pesticides monitored by OMWB are slow or hard to degrade in the environmental water (i.e., the Yodo river water).

Given that the arrival time in the stream is about one day, the 21 substances with a degradability of 60% or higher when observed 5 days later are deemed to have less impact on the OMWB's raw water, even when spread upstream.

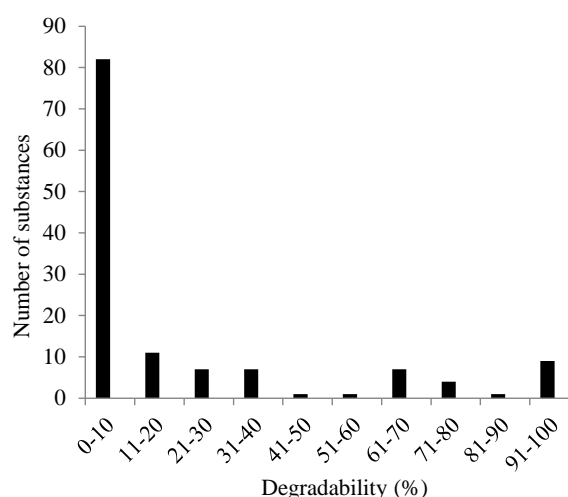


Figure-3: Degradability After 5-Day Period in Raw Water

Relationship Between the Performance and Structure of Ozonation and Chlorination

For both ozonation and chlorination, the degradability of a substance is largely dependent on the molecular structure of the substance⁷⁾. Table-2 shows the primary molecular structure and removal rate for each of the pesticides included in the new List that are hard to degrade (i.e., of which the removal rate is less than 20% when ozonation or chlorination is used). All of them have a very low removal rate because of the stable molecular structure belonging to each pesticide. Note that there is a tendency that if a substance has a highly reactive side chain, its removal rate can be significantly improved.

Table-2: Pesticides Included in the New List That Are Hard to Degrade Through Ozonation or Chlorination and Their Classification in Terms of Molecular Structure

No.	Structural Classification	Pesticides	Ozonation (Removal rate: %)		Chlorination (Removal rate: %)	
			CT2.8	CT5	2h	24h
5	Phenoxy acid	MCPA	46	67	10	14
18	Hetero	Indanofan	2	7	0	16
27	Organic Phosphorus	Cadusafos	6	9	100	100
35	Urea	Cumyluron	9	19	0	3
38	Phenoxy acid	Clomeprop	19	33	7	11
42	Triazine	Cyanazine	0	0	0	14
43	Organic Phosphorus	Cyanophos(CYAP)	6	15	100	100
52	Diphenyl ether	Cyhalofop-butyl	9	19	0	0
61	Anilide	Tiadinil	92	99	4	14
75	Hetero	Pyraclonil	83	96	11	84
76	Pirazole	Pyrazoxyfen	7	13	2	13
77	Pirazole	Pyrazolynate(Pyrazolate)	18	29	20	76
87	Amide	Fentrazamide	5	13	3	10
89	Acid Amide	Butachlor	0	0	0	0
102	Allyl	Benzobicyclon	0	10	99	100
103	Pyrazole	Benzenofenap	6	17	16	63
108	Hetero	Benfuresate	23	41	0	1
109	Organic Phosphorus	Fosthiazate	4	7	100	100
116	Strobilurin	Methominostrobin	16	24	0	15
117	Triazine	Metribuzin	10	20	100	100

Results of Monitoring and Relationship with the Consumption of Pesticides

Figure-4 shows the transition of the detection index values of the OMWB's raw water. The detection index values tended to be higher for the Toyono Purification Plant. This is deemed to be because the Toyono Purification Plant, located upstream of the Yodo river, is geographically closer to the area with a high consumption of pesticides, and thus under a higher influence, than the other two purification plants. These detection index values had lowered year by year since 2004 and were almost not detected during the years from 2010 to 2012. On the other hand, the detection index values have increased since 2013, the year of the transition to the new List. This suggests that the pesticides used across the entire Yodo river watershed may be replaced with new ones.

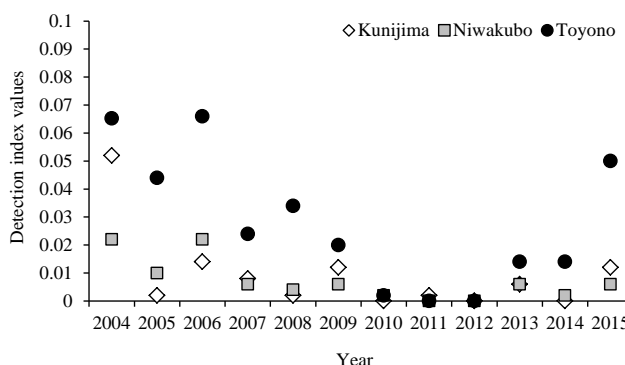


Figure-4: Transition of Detection Index Values (average) in the OMWB's Raw Water.

Table-3 shows detection counts of pesticides that exceeded the quantitation limits during the recent two years after the transition to the new List. The pesticides which had been continuously detected before new List had approved (i.e; pyroquilon, bromobutide, and bentazon), were still detected. And there were pesticides newly added to the List that were detected several times, such as pyraclonil. Particularly in 2015, about the half of the top 10 of pesticides detected were the pesticides included in the new List, implying that the pesticides in use were changing. On the other hand, several pesticides were detected in the OMWB's raw water. All of the frequently detected pesticides shown in Table-3 had degradability less than 10% in raw water after the 5-day period, except for oxaziclomefone, approximately 33%.

Table-3: Pesticide Detection Counts in the OMWB's Raw Water.
(Number of times detected beyond the quantitation limits, where n = 15)

2014			2015		
No.	Pesticide	Count	No.	Pesticide	Count
1	Pyroquilon	9	1	Bromobutide	14
2	Pretilachlor	6		<u>Pyraclonil</u>	12
	<u>Pyraclonil</u>	5	2	Benomyl (resolvent MBC)	12
3	Bromobutide	5		Bentazon	12
	Dimethametryn	5	5	Pyroquilon	11
	Fenobucarb (BPMC)	4	6	<u>Orysastrobins</u>	10
6	Bentazon	4		<u>Oxadiclefomefone</u>	8
	<u>Benfuresate</u>	4	7	<u>Methominostrobins</u>	8
	EPN	3		Mefenacet	6
9	Isofenphos	3	9	Cafenstrole	6
	Dymron	3	-	-	-

* The underlined pesticides were added to the List in 2013 that the OMWB started to monitor in or before 2015.

We estimated the load amount in the downstream area of the Yodo river system. Figure-5 shows the degradability of pesticides obtained as the result of this experiment and made a comparison with the detection counts in the raw water based on the shipping amount in the Yodo river system. It is assumed that the residual rate is given by subtracting the degradability after the 5-day period from 100% and that the estimated load amount is the product of the pesticide shipping amount in the Yodo river system and the residual rate.

The estimated load amount and detection counts had basically the same tendency. We suggest that pesticides of which the shipping amount in the Yodo river system is ranked top and of which the degradability in water is low are likely to affect the OMWB's raw water. Also, there were some substances deemed to have been adsorbed in the soil after sprayed because of their high water solubility, stability in water, and soil adsorption coefficient⁸⁾. A typical example is the fact that glyphosate was not detected at all during the survey period even though ranked at the top.

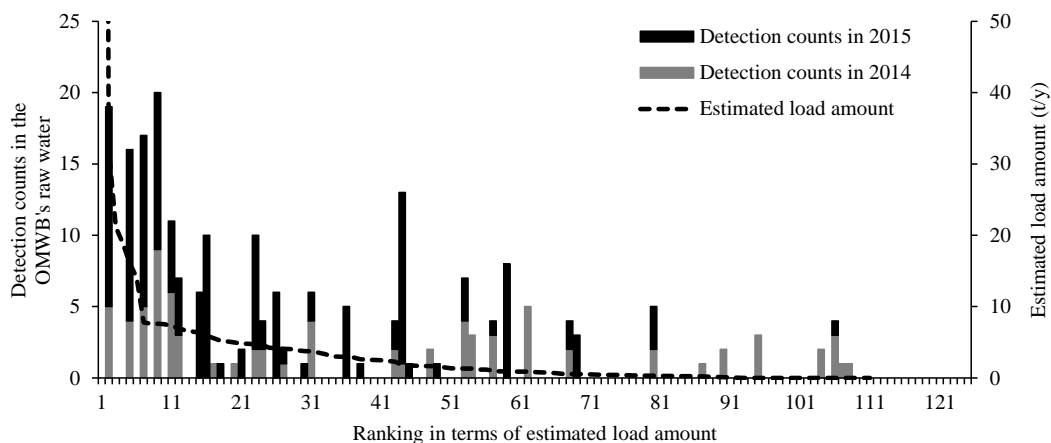


Figure-5: Load Amount in the Downstream Area of the Yodo River System and the Detection Counts in the Raw Water

According to these results, monitoring of pesticides must be performed with much attention paid particularly to pesticides with a high shipping amount and with low degradability in the evaluation experiment.

CONCLUSIONS

Many substances that cannot be degraded by ozonation or chlorination, were discovered among the 130 substances. They included the pesticides and their degradation metabolites monitored by OMWB. However, GAC adsorption was found applicable to many substances.

The risk of pesticides from the water resource can effectively be reduced by the combination of ozonation and GAC adsorption. And the reactivity of pesticides with ozone and chlorine could estimate to some extent, from their chemical structures.

The detection index values of raw water had lowered year by year since 2004, and stayed low during the years from 2010 to 2012. However, they increased since 2013, the year of the transition to the new List. This suggests that the impact of pesticides were not reduced in the Yodo river system. Also, the pesticides used in the areas around the watershed may have been replaced with new ones.

In addition, we estimated the load amount in the downstream area of the Yodo river basin. This was based on the degradability of pesticides obtained as the result of the experiment. Also, the shipping amount in the Yodo river system is concerned. It is revealed that the larger estimated load amount leads to a higher detection count in the OWMB's raw water. According to these results, monitoring of pesticides must be performed with much attention paid particularly to pesticides with a high shipping amount and with low degradability in the raw water. This concept is sufficiently applicable not only to the Yodo river system, but also to other water resources and provides an effective basis for selecting the pesticides that should be monitored with high priority.

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