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Removals of pesticides and pesticide transformation products during drinking water treatment processes and their impact on mutagen formation potential after chlorination

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Abstract

Removal efficiencies of 28 pesticide transformation products (TPs) and 15 parent pesticides during steps in drinking water treatment (coagulation–sedimentation, activated carbon adsorption, and ozonation) were estimated via laboratory-scale batch experiments, and the mechanisms underlying the removal at each step were elucidated via regression analyses. The removal via powdered activated carbon (PAC) treatment was correlated positively with the log K_{ow} at pH 7. The adjusted coefficient of determination (r^2) increased when the energy level of the highest occupied molecular orbital (HOMO) was added as an explanatory variable, the suggestion being that adsorption onto PAC particles was largely governed by hydrophobic interactions. The residual error could be partly explained by π-π electron donor–acceptor interactions between the graphene surface of the PAC particles and the adsorbates. The removal via ozonation correlated positively with the energy level of the HOMO, probably because compounds with relatively high energy level HOMOs could more easily transfer an electron to the lowest unoccupied molecular orbital of ozone. Overall, the TPs tended to be more difficult to remove via PAC adsorption and ozonation than their parent pesticides. However, the TPs that were difficult to remove via PAC adsorption did not induce strong mutagenicity after chlorination, and the TPs that were associated with strong mutagenicity after chlorination could be removed via PAC adsorption. Therefore, PAC adsorption is hypothesized to be an effective method of treating drinking water to reduce the possibility of post-chlorination mutagenicity associated with both TPs and their parent pesticides.

Keywords: Activated carbon adsorption; Coagulation and sedimentation; Disinfection by-product; Ozonation; Removal mechanisms; Toxicity.

1. Introduction

Pesticides probably account for the largest amount of chemical substances intentionally released to the environment. An immense quantity of pesticides is applied to fields throughout the world to increase crop production by controlling pests. Pesticides induce physiological responses in pests. Those reactions may harm both target and nontarget organisms, including humans (Hernández et al. 2013). Pesticide residues in the environment have therefore received considerable attention based on concerns over their adverse effects on humans and other nontarget species. In many countries, selected pesticides are listed in drinking water standards and guidelines and are intensively monitored in natural waters (García de Llasera and Bernal-González 2001, Nakano et al. 2004), including sources of drinking water (Schipper et al. 2008, Mekonen et al. 2016). Additionally, much effort has been made to remove pesticides during drinking water treatment (Broséus et al. 2009, Nam et al. 2014).

Pesticides undergo both biotic and abiotic degradation after being applied to agricultural fields. During degradation, pesticides are rarely mineralized into carbon dioxide, water, and other inorganic materials; in most cases they are just converted into a number of transformation products (TPs) (Sinclair et al. 2006, Escher and Fenner 2011). Because some TPs are more toxic than their parent pesticides (Martínez Vidal et al. 2009, Fenner et al. 2013), the occurrence of pesticide TPs in natural waters, in particular sources of drinking water, has attracted increasing attention. Intense monitoring of pesticide TPs in natural waters in recent years (Kondo et al. 2012, Reemtsma et al. 2013) has revealed that some pesticide TPs are occasionally present at higher concentrations than their parent pesticides (Hladik et al. 2008, Kameya et al. 2012). Removal of pesticide TPs during drinking water treatment has also attracted attention. Removals are estimated by quantifying and comparing the concentrations in raw and finished waters in full-scale drinking water treatment plants (Coupe and Blomquist 2004) or investigated in laboratory-scale experiments (Gustafson et al. 2003, Hladik et al. 2005).

Most research on pesticide TPs has concerned pesticides applied to upland fields. In contrast, information regarding the removal of TPs derived from pesticides used in rice farming is quite limited. Benner et al. (2013) have reviewed removals via drinking water treatment of many types of micropollutants, including pesticides and their TPs, but only 5 of 23 targeted pesticides were relevant to rice farming. In many countries, especially Asian countries, much agricultural land is used for rice farming. Moreover, rice-farming pesticides tend to enter river water via runoff at higher rates than other pesticides used in upland fields because they are dusted directly over the ponding water of paddy fields and are thus easily released with rainfall runoff or discharges during water-ponding depth control (Matsui et al. 2006), even though the rice-farming pesticides do not generally differ from the upland-filed pesticides in terms of physicochemical properties. Actually, most of the pesticides detected in river water are used in rice farming in Japan, although annual pesticide consumption for upland fields is no less than that for rice paddy fields (Matsui et al. 2002). Hence there is a need for research on the removal of TPs derived from pesticides used in both rice-farming and upland-field agriculture.

Chlorine, which is widely used for disinfection in the final step of drinking water treatment, reacts with inorganic and organic compounds in the water and converts them into a wide variety of by-products. The mutagenicity of raw drinking water is dramatically increased after chlorination (Cheh et al. 1980, Vartiainen and Liimatainen 1986), a clear indication that mutagenic by-products are generated during chlorination. The increase of mutagenicity might be partly due to pesticides in the raw water, because some pesticide solutions have evinced mutagenicity after chlorination although they did not before chlorination (Takanashi et al. 2013). The fact that some pesticide TPs have also increased mutagenicity after chlorination (Takanashi et al. 2014) may partly account for the increase of mutagenicity. From the standpoint of drinking water safety, the mutagenicity of finished water must be low, and hence there is a need for a method to remove such pesticides and TPs from water before chlorination.

In this study, we therefore focused on pesticide TPs derived from both upland-field agriculture and rice farming. The objectives of the study were to (1) investigate the removals of 43 compounds (28 TPs and 15 parent pesticides) during steps in drinking water treatment (coagulation–sedimentation, activated carbon adsorption, and ozonation) via laboratory-scale experiments, (2) elucidate the removal mechanisms associated with each process, and (3) discuss whether the processes were effective in reducing mutagenicity derived from TPs and their parent pesticides after chlorination.

2. Materials and methods

2.1 Target compounds and preparation of experimental raw water

Table 1 lists the target compounds used in the present study. The pesticides were selected so as to cover wide range of physicochemical properties such as log K_{OW} from fungicides, herbicides, and insecticides whose TPs were commercially available. The structures of the target compounds are shown in Table S1. The TPs and pesticides were purchased from Wako Pure Chemical Industries (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), Cosmo Bio Co., Ltd. (Tokyo, Japan), or Sigma-Aldrich Co. LLC. (Darmstadt, Germany) and used without further purification. Chemical standards of the compounds except diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol were dissolved in acetone at 20 mg/L each to prepare a mixed stock solution for the batch coagulation experiments. Each chemical standard except diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol was dissolved in acetone at 20 mg/L to prepare each stock solution for the batch adsorption and ozonation experiments. Each chemical standard of diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol was dissolved in Milli-Q water (Milli-Q Advantage, Millipore Co., Bedford, MA, USA) at 5, 5, 50, 50, and 3 mg/L, respectively, which was individually used as each stock solution for all batch experiments.

All experiments were conducted with raw water of a drinking water treatment plant (Moiwa Drinking Water Treatment Plant, Sapporo, Japan) withdrawn from the Toyohira River (Sapporo, Japan) four times (26/10/2012, 15/10/2013, 6/10/2014, and 17/11/2014), and was characterized by a dissolved organic carbon concentration of approximately 1.0 mg-C/L, turbidity of 1–7 NTU, and alkalinity of approximately 20 mg-$CaCO_3$/L. The river waters withdrawn on 26/10/2012 and 15/10/2013 were used for coagulation experiments, that withdrawn on 6/10/2014 was used for ozonation, and that withdrawn on 17/11/2014 was used for powdered activated (PAC) adsorption. We confirmed that none of the target compounds was detected in the river waters. The final concentration of each compound was approximately 10 μg/L. To avoid the effect of unintentional carry-over of acetone on coagulation, the acetone was removed from the solution prior to the coagulation experiments by warming the solution at 58 °C in a water bath. Nitrogen gas was then introduced into the solution for 120 min to purge out the dissolved acetone. Preliminary studies confirmed that this procedure reduced the dissolved acetone concentration from 500 mg/L to 10 μg/L, the same as the concentration of each target compound. The stock solutions of diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol were then added to the solution at concentrations of 10 μg/L each because preliminary studies had shown that these compounds volatilized during purging with nitrogen gas. The resulting solution (referred to as experimental raw water) was then used for the batch coagulation experiments.

Table 1 Target compounds used in the present study.

	Parent pesticides Transformation products	Measurement method	Monitored m/z	Purchased from	Remaining ration after coagulation	Remaining ratio at 10 min of PAC contact time (R_{PAC})	Second order decomposition rate constant with O_3 (k_{ozone})	MFP	
					–	–	k_{ozone}, M^{-1} s^{-1}	net rev. μM^{-1}	after PAC[e]
	Fungicides								
	Chlorothalonil	GC/MS	366	Wako	0.94 ± 0.01	0.23	–	negative [c]	0
	1,3-Dicyanobenzene	GC/MS	128	Aldrich	1.21	0.46	–	10 [c]	5
#	*Pencycuron*	LC/MS^p	329.1415	Wako	0.99 ± 0.01	0.15 ± 0.03	$(4.7 \pm 1.9) \times 10^3$	negative [d]	0
#	Phenylurea	LC/MS^p	137.0709	Wako	0.98 ± 0.01	0.35 ± 0.00	$(4.9 \pm 1.4) \times 10^3$	negative [d]	0
	Thiophanate methyl	LC/MS^p	343.0529	Wako	1.14 ± 0.05	0.18 ± 0.03	$(3.4 \pm 0.2) \times 10^4$	380 [b]	68
	2-Aminobenzimidazole	LC/MS^p	134.0713	Wako	1.00 ± 0.01	0.11 ± 0.03	$(1.7 \pm 0.3) \times 10^4$	260 [b]	30
	Methyl-2-benzimidazole cabamate	LC/MS^p	192.0768	Wako	1.00 ± 0.01	0.07 ± 0.02	$(6.5 \pm 0.9) \times 10^3$	410 [b]	28
	Herbicides								
#	*Cafenstrole*	LC/MS^p	351.1485	Wako	1.06 ± 0.04	0.24 ± 0.01	$(1.0 \pm 0.1) \times 10^3$	negative [d]	0
#	3-(2,4,6-Trimethylphenylsulfonyl)-1,2,4-triazole	LC/MS^p	252.0801	Wako	0.99 ± 0.01	0.45 ± 0.01	$(9.4 \pm 2.7) \times 10^2$	negative [d]	0
#	*Mefenacet*	LC/MS^p	299.0849	Wako	0.99 ± 0.00	0.10 ± 0.03	$(2.9 \pm 1.0) \times 10^3$		
#	2(3H)-Benzothiazolone	LC/MS^p	152.0165	Tokyo Chemical	0.98 ± 0.03	0.12 ± 0.01	–	14 [d]	2
#	2-Aminothiophenol	LC/MS^p	249.0515	Tokyo Chemical	0.97 ± 0.01	0.07 ± 0.01	$(7.5 \pm 5.7) \times 10^5$	120 [d]	9
#	*Tefuryltrione*	LC/MS^p	460.1191	Hayashi	1.02 ± 0.09	0.69 ± 0.03	$(2.7 \pm 0.5) \times 10^3$		
#	2-chloro-4-(methylsulfonyl)-3-[(tetrahydrofuran-2-ylmethoxy)methyl]benzoic acid	LC/MS^p	349.0507	Hayashi	1.05 ± 0.06	0.62 ± 0.02	$(3.5 \pm 2.3) \times 10^3$		
#	*Thiobencarb*	GC/MS	100	Wako	0.97 ± 0.01	0.23	–	81 [a]	19
#	p-Chlorobenzyl alcohol	GC/MS	77	Tokyo Chemical	1.06 ± 0.08	0.57	–	negative [b]	0
	Insecticides								
#	*Diazinon*	LC/MS^p	305.1083	Wako	1.06 ± 0.02	0.29 ± 0.01	$(3.4 \pm 0.6) \times 10^3$	49 [a]	14
#	2-Isopropyl-6-methylpyrimidin-4-ol	LC/MS^p	153.1022	Aldrich	0.98 ± 0.02	0.51 ± 0.02	$(3.9 \pm 0.5) \times 10^3$	21 [b]	11
#	Diazinon oxon	LC/MS^p	289.1312	Wako	1.03 ± 0.01	0.40 ± 0.01	$(1.9 \pm 0.6) \times 10^2$	62 [b]	25
#	Diethyl phosphate	LC/MS^p	155.0468	Cosmo	1.02 ± 0.02	1.00 ± 0.02	$(1.4 \pm 0.1) \times 10^2$	negative [b]	0
	Dichlorvos	LC/MS^p	220.9532	Wako	0.99 ± 0.01	0.47 ± 0.11	$(5.0 \pm 2.5) \times 10^3$	20 [a]	9
	Dimethyl phosphate	LC/MS^p	127.0155	Wako	0.99 ± 0.01	0.97 ± 0.06	$(4.3 \pm 1.2) \times 10^1$	5.2 [b]	5
	Disulfoton	GC/MS	88	Cosmo	0.87	0.23	–	46 [a]	11
	Disulfoton oxon	GC/MS	88	Wako	0.94 ± 0.01	0.63	–	negative [b]	0
	Disulfoton sulfoxide	LC/MS^p	291.0307	Cosmo	0.95 ± 0.03	0.42	–	47 [b]	20
#	*Etofenprox*	GC/MS	163	Wako	0.29 ± 0.01	0.19	$(6.7 \pm 0.6) \times 10^3$	negative [d]	0
#	2-(4-Ethoxyphenyl)-2-methylpropanol	LC/MS^p	212.1645	Tokyo Chemical	1.01 ± 0.01	0.21	$(1.0 \pm 0.3) \times 10^4$	78 [d]	16
#	*Fenitrothion*	GC/MS	125	Wako	0.93 ± 0.00	0.16	$(1.2 \pm 0.0) \times 10^3$	170 [a]	28
#	3-Methyl-4-nitroanisole	GC/MS	150	Aldrich	0.99 ± 0.01	0.06 ± 0.06	$(1.1 \pm 0.9) \times 10^4$	negative [b]	0
#	3-Methyl-4-nitrophenol	LC/MS^n	152.0353	Wako	0.93 ± 0.04	0.14 ± 0.00	$(2.5 \pm 0.3) \times 10^4$	2000 [b]	278
#	Fenitrooxon	LC/MS^p	262.0475	Wako	0.96 ± 0.02	0.12 ± 0.02	$(4.6 \pm 2.6) \times 10^2$	390 [b]	45
#	Methyl paraoxon	LC/MS^p	248.0319	Aldrich	0.97 ± 0.02	0.14 ± 0.01	$(5.4 \pm 0.5) \times 10^2$		
#	trimethyl phosphate	LC/MS^p	141.0311	Wako	0.99 ± 0.01	0.96 ± 0.15	$(7.0 \pm 2.0) \times 10^1$	negative [b]	0
#	*Malathion*	LC/MS^p	331.0433	Wako	1.01 ± 0.01	0.24 ± 0.01	$(2.8 \pm 0.1) \times 10^3$	260 [a]	62
#	Diethyl fumarate	GC/MS	127	Wako	1.08 ± 0.00	0.60	–	17 [b]	10
#	Diethyl maleate	GC/MS	99	Wako	0.97 ± 0.05	0.80	–	13 [b]	10
#	Diethyl L-(-)-malate	LC/MS^p	191.0914	Wako	1.14 ± 0.02	0.43 ± 0.09	$(4.6 \pm 2.3) \times 10^2$		
#	Diethyl L-(+)-tartrate	LC/MS^p	207.0863	Wako	0.99 ± 0.01	0.72 ± 0.02	$(1.9 \pm 0.0) \times 10^2$	24 [b]	17
#	Malaoxon	LC/MS^p	315.0662	Wako	1.02 ± 0.02	0.31 ± 0.03	$(3.4 \pm 1.8) \times 10^2$	negative [b]	0
	Methidathion	GC/MS	145	Wako	1.01 ± 0.02	0.39	–	51 [a]	20
	Methidathion oxon	LC/MS^p	286.9920	Wako	0.95 ± 0.00	0.43	–	negative [c]	0
	Pyriproxyfen	GC/MS	136	Wako	0.95 ± 0.01	0.09	–	negative [d]	0
	4-Phenoxyphenol	GC/MS	186	Wako	1.00 ± 0.01	0.26	–	negative [d]	0

LC/MS^p, LC/MS in positive ion mode; LC/MS^n, LC/MS in negative ion mode.

Aldrich, Sigma-Aldrich Co. LLC., Darmstadt, Germany; Cosmo, Cosmo Bio Co., Ltd., Tokyo, Japan; Tokyo Chemical, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan; Wako, Wako Pure Chemical Industries, Ltd., Osaka, Japan.

\# Pesticides appricable for rice-farming filed and their TPs.

– Not tested.

[a] Takanashi, H., Kishida, M., Abiru, K., Kondo, T., Kameya, T., Matsushita, T., Nakajima, T., Ohki, A. (2013) A screening study on the mutagen formation potential of 44 pesticides, *Journal of Water Supply: Research and Technology–AQUA*, **62**(1), 14-22.

[b] Takanashi, H., Hama, T., Nakajima, T., Ohki, A., Kondo, T., Kameya, T. and Matsushita, T. (2014) A screening study of mutagen formation potential (MFP) of pesticide transformation products in water environments (PTPWs) to investigate the MFP changes from their parent pesticides through transformations, *Journal of Water Environment Technology*, **12**(1), 25-32.

[c] Takanashi, H., Hama, T., Nakajima, T., Ohki, A., Ueda, T., Matsushita, T., Kondo, T. and Kameya, T. (2016) Quantitative structure-activity relationship of pesticide and their transformation products in water environments to mutagen formation potential, *Environmental science*, **29**, 229-237 (in Japanese).

[d] This study

[e] The number of net revertant colonies after chlorination at the concentration which was expected after 1 μM of a compound was treated with 10 mg/L of PAC addition for 10 min, which was calculated from MFP and R_{PAC}.

The batch studies of PAC adsorption and ozonation were conducted individually for each compound. The stock solution of each compound except diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol was added to the river water at approximately 10 μg/L. Dissolved acetone was purged out from the solution by the same procedure described above to obtain the experimental raw water for the batch adsorption and ozonation experiments. The experimental raw water for diazinon, malathion, malaoxon, diethyl L-(+)-tartrate, and 2-aminophenol was prepared individually by simply adding each stock solution to the river water at 10 μg/L.

2.2 Batch coagulation–sedimentation experiments

Batch coagulation experiments were conducted with 1 L of the experimental raw water in glass beakers at 20 °C. The pH of the water was adjusted with aqueous NaOH to maintain a final pH of 7.0 after coagulation–sedimentation. The water was supplemented with polyaluminum chloride (PACl; 250A, Taki Chemical Co., Ltd., Kakogawa, Japan) at the coagulant dose that had been used in the Moiwa drinking water treatment plant on the day the raw water was sampled (1.0 and 1.4 mg-Al/L for the water withdrawn on 15/10/2013 and 26/10/2012, respectively). The water was then stirred rapidly for 1 min (G = 200 s^{-1}, 61 rpm) and slowly for 10 min (G = 20 s^{-1}, 13 rpm). The water was then left at rest for 60 min to allow the aluminum floc particles that had been generated to settle. Samples were taken from the beaker before coagulant dosing and after settling (supernatant) for quantification of the target compounds. The ratio of the concentrations of each compound after and before sedimentation was used as a metric of the degree of removal via coagulation. The experiments were conducted twice.

2.3 Batch PAC adsorption experiments

Batch PAC adsorption experiments were conducted at 20 °C. Five hundred milliliters of each experimental raw water was filtered through a 0.45-μm membrane filter (PTFE; Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and then transferred to a 1-L glass vessel. The pH of the water was adjusted with HCl to ensure that the final pH after adsorption was 7.0. The water was supplemented with 10 mg/L of PAC (median diameter, 18.9 μm; Taiko W, Futamura Chemical Co., Ltd., Nagoya, Japan) and then stirred with impeller blades at 150 rpm. Samples were withdrawn from the vessel at adsorption times of 0, 10, 20, 40, and 60 min and filtered through a 0.45-μm membrane filter (PTFE; Toyo Roshi Kaisha) to remove any PAC particles. The concentrations of the target compounds in the filtrates were measured. The ratio of the concentration of each compound remaining at 10 min of PAC contact time to the concentration before PAC contact (R_{PAC}) was used as a metric of the removal during PAC adsorption (adsorption rate). This metric was chosen because some compounds reached equilibrium at 20 min or later but others did not. Therefore, differences in R_{PAC} did not simply reflect the extent of adsorption rate with PAC after 20 min. The experiments were conducted twice.

2.4 Batch ozonation experiments

Batch ozonation experiments were conducted at 20 °C. Five hundred milliliters of each experimental raw water were filtered through a 0.45-μm membrane filter and then transferred to a 1-L glass vessel. The pH of the water was adjusted to 7.0 with HCl. Ozone gas was continuously introduced into the glass vessel at a constant flow rate of 0.3 mg-O_3/(L·min) via a lab-scale ozone generator (Pretty O_3; Metawater Co. Ltd., Tokyo, Japan) while the water was stirred with a magnetic stirrer. Eighty-milliliter samples of the water were withdrawn from the glass vessel at 0, 0.5, 2, 5, and 15 min. Dissolved O_3 was measured in a 20-milliliter aliquot, and the concentration of the target compound was measured in the remaining 60 mL after the residual ozone had been quenched with 1.2 stoichiometric equivalents of Na_2SO_3. To facilitate comparison of the decomposition of target compounds during ozonation, the second-order decomposition rate constant with ozone (k_{ozone}) was calculated for each compound and used as a metric of removal during ozonation. The experiments were conducted twice.

2.5 Quantification of target compounds with a liquid chromatograph-mass spectrometer

The target compounds identified with the "LC/MS" measurement method in Table 1 were quantified via a hybrid quadrupole-orbitrap mass spectrometer (MS; Q-Exactive, Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled with a liquid chromatograph system (LC; UltiMate 3000, Thermo Fisher Scientific). A five-microliter sample of each solution was assayed with the LC on a 50 mm × 2.1 mm Hypersil Gold column (1.9-μm particle size, Thermo Fisher Scientific). The mobile phase was a binary gradient of 2 mM ammonium formate in Milli-Q water (solvent A) and 100% methanol (solvent B) at a flow rate of 200 μL/min as follows: for 2-(4-ethoxyphenyl)-2-methylpropanol, 2(3H)-benzothiazolone, 2-aminothiophenol, and 2-aminobenzimidazole, 99:1 (v/v) A/B for 2 min, increase linearly to 60% B over a period of 2 min, increase linearly to 75% B over a period of 6 min, increase linearly to 99% B over a period of 5 min, decrease linearly to 1% B over a period of 0.1 min, and then hold at that ratio for 2.9 min. For the other compounds, 99:1 (v/v) A/B for 1.5 min, increase linearly to 60% B over a period of 1 min, increase linearly to 99% B over a period of 5.5 min, hold at that ratio for 1.5 min, decrease linearly to 1% B over a period of 0.5 min, and then hold at that ratio for 2 min. The MS was operated in an electrospray ionization mode with a spray voltage of 3.0 kV. The temperatures of the capillary and electrospray ionization probe heater were 220 and 450 °C, respectively. The flow rates of the sheath gas, auxiliary gas, and sweep gas were 50, 50, and 50 units, respectively. The S-lens ratio frequency level was set to 78. Target compounds were quantified in selected-ion-monitoring mode (resolution = 70,000). Table 1 shows the relevant ion modes and *m*/*z* values.

2.6 Quantification of target compounds with a gas chromatograph-mass spectrometer

The target compounds identified with the "GC/MS" measurement method in Table 1 were quantified via a gas chromatograph-mass spectrometer (GC/MS; GC, 7890A; MS, 5975C; Agilent Technologies, Inc., Palo Alto, CA, USA) coupled to a capillary column (J&W DB5-ms; length, 30 m; internal diameter, 0.25 mm; thickness, 0.25 μm; Agilent Technologies). Before GC/MS analysis, each sample was subjected to solid-phase extraction with a Sep-Pak PS2 cartridge (Nihon Waters K. K., Tokyo, Japan) to increase the concentration in acetone by 100-fold. One microliter of the resulting concentrate was injected into the GC in a splitless mode. The column temperature was controlled as follows: 50 °C for 2 min, increase linearly to 170 °C over a period of 12 min, hold at that temperature for 3 min, increase linearly to 200 °C over a period of 10 min, increase linearly to 300 °C over a period of 10 min, and then hold at that temperature for 10 min. The temperatures of the ion source and injector were 300 and 220 °C, respectively. Helium at 20 mL/min was used as a carrier gas. The measurements were performed in a selected ion-monitoring mode with naphthalene-d_8, phenanthrene-d_{10}, anthracene-d_{10}, 9-bromoanthracene, and chrysene-d_{12} as internal standards. The *m*/*z* values used for the quantification of the interests are shown in Table 1.

2.7 Estimation of partial structures contributing to the extent of removal via PAC adsorption and ozonation

To identify the partial structures contributing to the extent of removal via PAC adsorption and ozonation, regression analyses were performed between metrics of the removal of the target compounds (R_{PAC} and log k_{ozone} for the PAC adsorption and ozonation, respectively) as dependent variables and the numbers of partial structures in the compounds as explanatory variables. First, the number of partial structures was counted via the KAshinhou Tool for Ecotoxicity on Platform for Assessment from Structure (Ministry of the Environment, Government of Japan). Both the dependent and explanatory variables were normalized before the regression analyses. Second, a simple linear regression analysis was performed between the removal metrics and the numbers of partial structures. Descriptors (i.e., partial structures) with $r^2 > 0.1$ were selected. When the variance inflation factor (VIF) indicated multicollinearity between any two of the selected descriptors, one of the descriptors was withdrawn (Details of the selection are described in the Results and discussion section). Finally, a multiple linear regression analysis was performed between the removal metric and the remaining descriptors using a step-down procedure.

The octanol/water partition coefficients (log K_{ow} values) of the target compounds at pH 7 were calculated with Marvin Sketch (ChemAxon, Budapest, Hungary). The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the target compounds were calculated with Winmostar (X-Ability Co. Ltd., Tokyo Japan).

3. Results and discussion

3.1 Coagulation–sedimentation

The concentrations of almost all compounds tested did not change after coagulation–sedimentation (Table 1, Fig. 1). This result was not surprising because coagulation is an effective way to destabilize small suspended and colloidal particulate matter (Crittenden et al. 2012), but soluble micropollutants such as pesticides and their TPs are not directly associated with suspended and colloidal particulate matter. Our results are consistent with previous reports that most micropollutants are difficult to remove by coagulation–sedimentation (Miltner et al. 1989, Hladik et al. 2005, Jiang and Adams 2006, Benner et al. 2013).

Of all the compounds, only etofenprox was removed by coagulation–sedimentation (Table 1). Removal of micropollutants via coagulation–sedimentation has been reported to be governed by adsorption onto natural materials present in the water (Thuy et al. 2008): micropollutants associated with the surfaces of suspended particles and coagulation flocs can be removed during sedimentation, and this mechanism is primarily responsible for micropollutant removal during coagulation–sedimentation (Benner et al. 2013). Hydrophobicity of a compound is therefore a major determinant of the removal efficiency of the compound with coagulation (Thuy et al. 2008). Because etofenprox was the most hydrophobic (log K_{ow} at pH 7 = 6.3) of the compounds tested, it was the compound most likely to adsorb onto natural particulate matter in the water and to then co-settle with the particulate matter during coagulation. Benner et al. (2013) have reported that hydrophobic chemicals with log K_{ow} values of >6 can generally be removed during coagulation, in agreement with our results.

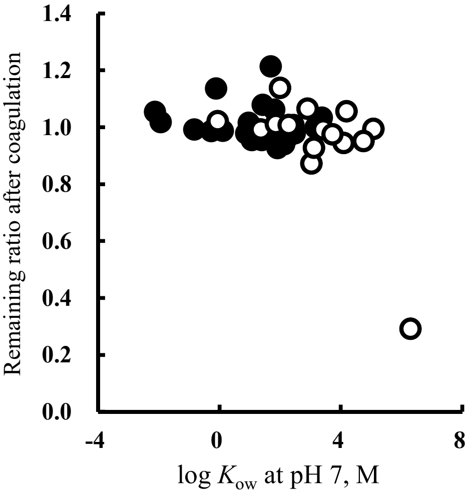

Fig. 1 Relationship between remaining ratio after coagulation and log K_{ow} at pH 7. Black and white circles represent TP and parent pesticide, respectively.

3.2 PAC adsorption

Values of R_{PAC} varied widely among compounds, from 0.06 to 1.00 (Table 1). R_{PAC} was weakly and negatively correlated ($r^2 = 0.40$) to log K_{ow} at pH 7: the lower the log K_{ow}, the higher the R_{PAC} (Fig. 2). Nonpolar compounds have a tendency to adsorb more strongly to nonpolar adsorbents such as activated carbon (Crittenden et al. 2012), in agreement with our results. No substantial difference was observed between the rice-farming and the upland-field pesticides (Fig. S1).

The TPs (black circles, Fig. 2) seemed to be more

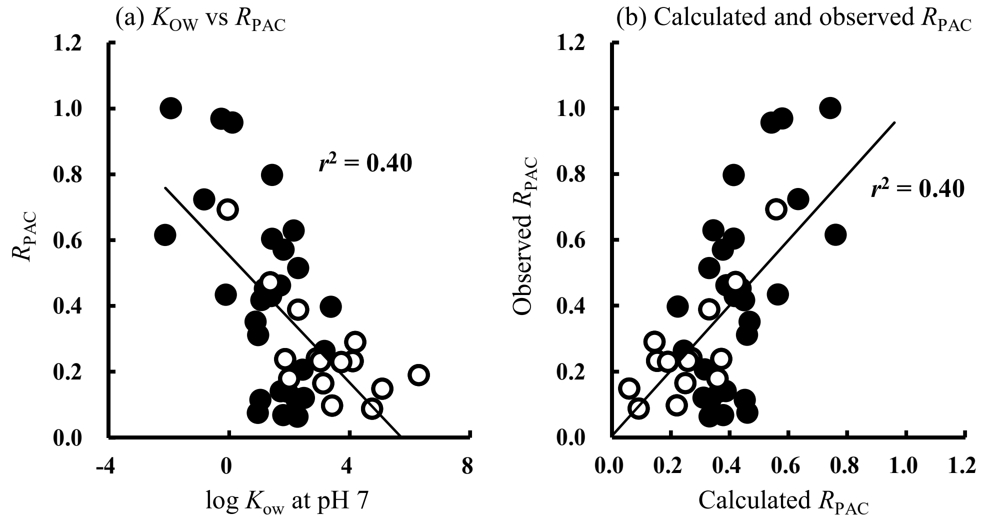

Fig. 2 (a) Relationship between remaining ratio at 10 min of PAC adsorption (R_{PAC}) and log K_{ow} at pH 7. (b) Comparison between the calculated and observed R_{PAC} values. Black and white circles represent TP and parent pesticide, respectively.

difficult to remove via PAC adsorption than their parent pesticides (white circles). The R_{PAC} ratios of five TPs and their parent pesticides were roughly the same (0.8–1.2, Fig. 3), but 18 TPs were more difficult to remove via PAC adsorption than their parent pesticides ($R_{PAC} > 1.2$). Only five TPs were easier to remove via PAC adsorption than their parent pesticides ($R_{PAC} < 0.8$). Gustafson et al. (2003) have also reported the same pattern. A TP is typically more polar than its parent compound (Benner et al. 2013, Fenner et al. 2013). The decrease of adsorptive removal due to transformations in the environment was most likely associated with a decrease of hydrophobicity from the parent pesticides to the TPs.

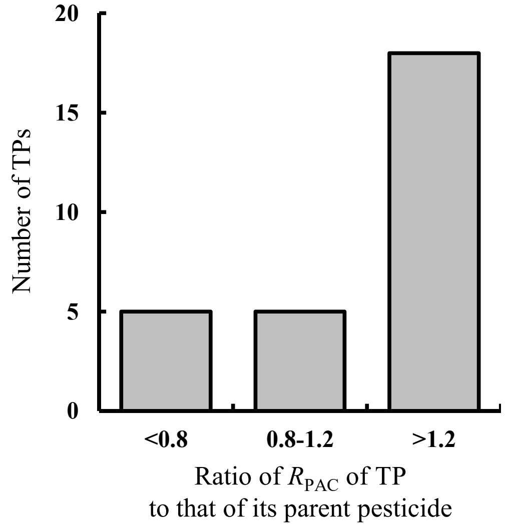

Fig. 3 Comparison of R_{PAC} between TP and its parent pesticide.

The group of TPs that were most difficult to remove via PAC adsorption included diethyl phosphate (R_{PAC} = 1.00), dimethyl phosphate (R_{PAC} = 0.97), and trimethyl phosphate (R_{PAC} = 0.96). These TPs may be generated in the environment from the organophosphorus insecticides diazinon (Ibanez et al. 2006), dichlorvos (Benoit-Marquié et al. 2004), and fenitrothion (Durand et al. 1992), respectively, although their parent pesticides were more efficiently removed via PAC adsorption (Table 1). That these TPs are very hydrophilic (log $K_{ow} < 0.1$ at pH 7) most likely reduced their removability via PAC adsorption. The second group ranked by difficulty of removal included diethyl maleate (R_{PAC} = 0.80), diethyl L-(+)-tartrate (R_{PAC} = 0.72), and tefuryltrione (R_{PAC} = 0.69). Diethyl maleate and diethyl L-(+)-tartrate are reportedly photodegradation products of the organophosphorus insecticide malathion (Bavcon Kralj et al. 2007) and have very low log K_{ow} values at pH 7 (–1.2 and –0.7, respectively). Unlike diethyl maleate and diethyl L-(+)-tartrate, tefuryltrione is a herbicide, not a TP. Tefuryltrione (log K_{ow} = 0.0 at pH 7) was the parent pesticide that was least removable via PAC adsorption

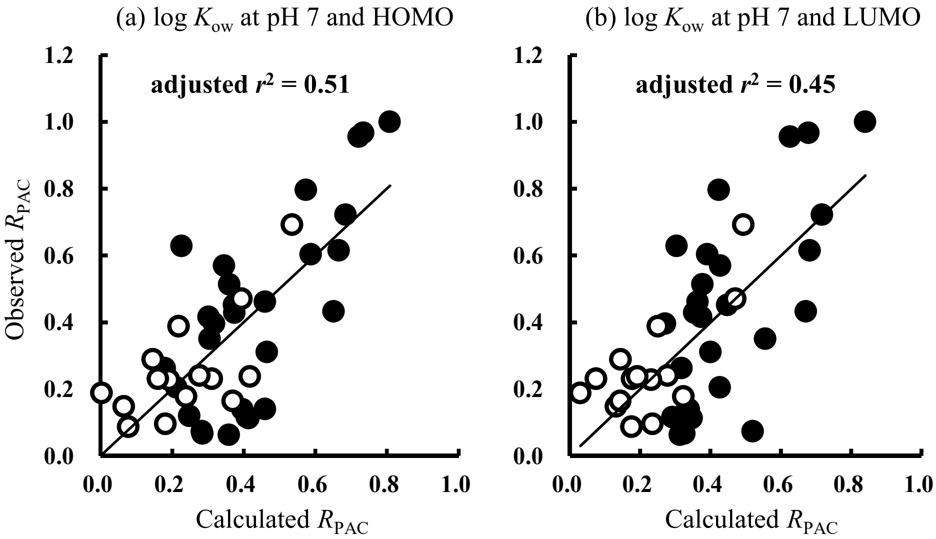

Fig. 4 Comparison between the calculated and observed R_{PAC} values (remaining ratios after 10 min of PAC adsorption). Regression analysis was conducted with explanatory variables (a) log K_{ow} at pH 7 and energy level of HOMO and (b) log K_{ow} at pH 7 and energy level of LUMO. Black and white circles represent TP and parent pesticide, respectively.

in the present study. The recent increase of tefuryltrione use and its low acceptable daily intake suggest that tefuryltrione should be monitored in drinking water and source waters (Kamata et al. 2017).

Lin and Xing (2008) reported that the extent of adsorption of phenolic compounds to carbon nanotubes was in the order of phenol < catechol < pyrogallol, even though their log K_{ow} were in the same order. They concluded that the increase in the extent of adsorption was due to the increased strength of π-π interactions between the phenolic compounds and the graphene surface. A similar tendency has been reported in adsorption of chlorophenols to granular activated carbon by Hamdaoui and Naffrechoux (2007). The graphene surface is highly polarizable, and it accordingly has the potential to act as an adsorbent that attracts π-acceptors and π-donors to the electron-rich graphene surface area near edges and to the relatively electron-poor central regions, respectively (Lin and Xing 2008). One electron is transferred from the HOMO of the graphene surface to the LUMO of the adsorbate molecule in the former case; one electron is transferred from the HOMO of the adsorbate molecule to the LUMO of the graphene surface in the latter case. These electron transfers are presumed to enhance the π-π interactions between the adsorbate and the graphene surface. Greater adsorption of an adsorbate is therefore expected when the transfer of the electron between the adsorbate and the graphene surface is most exergonic. This conclusion suggests that the residual errors in the regression analysis between R_{PAC} and log K_{ow} might be explained by π-π interactions. When the energy level of the LUMO was added to the regression analysis between R_{PAC} and log K_{ow} as an explanatory variable, the r^2 increased from 0.40 to 0.45 (Figs. 2 and 4b). When the energy level of the HOMO was added to the regression analysis, the r^2 increased even further to 0.51. These results are consistent with our hypothesis that the π-π electron donor–acceptor interactions account in part for the extent of adsorptive removal. In addition, the change of the increase of the r^2 value from 0.45 to 0.51 suggests that the graphene surface of the activated carbon used in this study probably acted as an acceptor of electrons from the target compounds rather than as a donor of electrons to them.

To identify the partial structures that contributed to the

Table 2 Results of multiple linear regression analysis of removal via PAC adsorption (R_{PAC}, remaining ratio at 10 min of adsorption).

Descriptor	Standard partial regression coefficient (β)	*t*-value	*p*-value
Aromatic rings	–0.13	–4.64	< 0.01
–OH bonded with heteroatoms	0.10	3.74	< 0.01
$–NO_2$ bonded with aromatic rings	–0.08	–2.98	< 0.01

extent of removal during PAC adsorption, regression analyses were performed on R_{PAC} and the number of partial structures in the target compounds. Among the 134 descriptors of the partial structures, 11 (–NO2 [$ aromatics], aromatic c–NO_2, fatty NO_2, aromatic atom, aromatics, heteroatom–OH, fatty C–OR, fatty C–PO_4, benzene, fused aroma, and P=O) were selected as partial structures that might be related to the adsorbability of the compounds tested. This hypothesis was tested via simple linear regression analysis. However, multicollinearity (VIF > 15) was detected between any two of the descriptors "–NO_2 [$ aromatics]", "aromatics c–NO_2", and "fatty NO_2", as well as between "aromatic atom" and "aromatics". Each of the compounds selected to have "–NO_2 [$ aromatics]", "aromatics c–NO_2", and "fatty NO_2" had the same partial structure: a –NO_2 moiety bonded to an aromatic ring. The developer of the software used in this study had not released the definition of each descriptor at the time of the study. For the further regression analysis, we nevertheless assumed the descriptor "aromatics c–NO_2" to be an indicator of the partial structure "–NO_2 bonded with aromatic rings". The descriptor "aromatic atom" was the number of atoms contained in aromatic rings, whereas the descriptor "aromatics" was the number of aromatic rings; both of these descriptors were metrics of the number of aromatic rings. Accordingly, we selected the descriptor "aromatics" as a representative of the partial structure "aromatic rings" for further regression analysis. After addressing the issues associated with multicollinearity, we selected eight descriptors as partial structures that might be related to the adsorbability of the compounds (VIF < 3). Further multiple linear regression analysis in accord with a step-down procedure suggested that three descriptors (aromatics, heteroatom–OH, and aromatics c–NO_2) were related to adsorbability (Table 2). The adjusted r^2 of the multiple regression was 0.57. The significance probabilities (*p* values) of the descriptors were 0.00, the indication being that the standard partial regression coefficients were appropriate. Among the descriptors, the descriptor "aromatic rings" had the largest absolute value of the standard partial regression coefficient β, but the value of β (–0.13) was not large in magnitude. The negative value of β suggested that the compounds with aromatic rings might have tended to be removed more easily by PAC adsorption. Lin and Xing (2008) have reported that the adsorption affinity of a compound to carbon nanotubes increases with increasing number of aromatic rings of the compound, a conclusion consistent with our results.

3.3 Ozonation

The second-order decomposition rate constant with ozone varied from 43 to 750,000 M^{-1} s^{-1} among the compounds tested (Table 1). The rate constant was positively correlated with the energy level of the HOMO (r^2 = 0.59) (Fig. 5). Oxidation is a major chemical reaction expected in ozonation: an electron is transferred from the HOMO of the compound to the LUMO of ozone (or other oxidants such as the hydroxyl radical). Accordingly, the higher the energy level of the HOMO of a compound is, the more easily the electron is transferred from the compound to an ozone molecule, the result being more rapid oxidation.

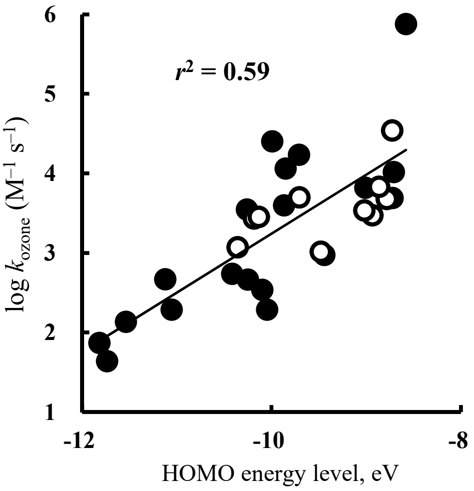

Fig. 5 Relationship between logarithm of second-order decomposition rate constant with ozone (log k_{ozone}) and HOMO energy level. Black and white circles represent TP and parent pesticide, respectively.

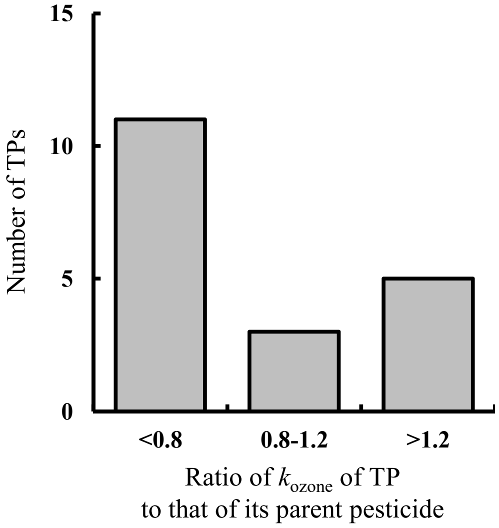

Fig. 6 Comparison of k_{ozone} between TP and its parent pesticide.

Other researchers have reported the same pattern (Hu et al. 2000, Kušić et al. 2009). Most of the TP decomposition rate constants (black circles, Fig. 5) were smaller than those of their parent pesticides (white circles). The decomposition rate constants of 11 of the TPs investigated in this study were less than 80% of the decomposition rate constants of their parent pesticides (Fig. 6); the decomposition rate constants of five of the TPs exceeded the decomposition rate constants of their parent pesticides by more than 20%. These observations suggest that the pesticides became resistant to decomposition by ozone after undergoing transformations in the environment. No substantial difference was observed between the rice-farming and the upland-field pesticides (Fig. S1).

To identify partial structures that contributed to decomposition with ozone, regression analyses were performed on log k_{ozone} versus the numbers of partial structures in the target compounds. Among the 134 descriptors of partial structures, simple linear regression analysis identified 20 descriptors (aromatic c-NH_2, aniline single, amine S (aromatics), aromatic thiol, thiophenol, aromatic c-SH, all SH for classes, fatty P, phosphorus [P], aromatics, aromatic atom, –N [$ aromatic], P=O, fatty N NO, fatty O, aniline, heteroatom–OH, heteroatom–OMe, fatty C–PO_4, and benzene) of partial structures of the compounds tested that might have been related to the extent of decomposition with ozone. Because multicollinearity (VIF > 15) was detected between any two of the descriptors "aromatic c-NH_2", "aniline single", and "amine S (aromatics)", we selected the descriptor "aromatic c–NH_2" as representative of compounds having a –NH_2 moiety bonded to an aromatic ring. The descriptors "aromatic thiol", "thiophenol", "aromatic c–SH", and "all SH for classes" had large VIF values (>15); from among these, the descriptor "aromatic c–SH" was selected as representative of compounds having a –SH moiety bonded to an aromatic ring. The descriptor "fatty P" was selected, but the descriptor "phosphorus [P]" was withdrawn; and the descriptor "aromatics" was selected, but the descriptor "aromatic atom" was withdrawn. After the selection based on multicollinearity, 11 descriptors were selected (VIF < 7). One of the descriptors was either "–NH_2 bonded with aromatic rings" or "–SH bonded with aromatic rings" because in this study compounds having –NH_2 groups bonded with aromatic rings had –SH groups bonded with aromatic rings, and we could not distinguish the effect of these two groups on the extent

Table 3 Results of multiple linear regression analysis of decomposition with ozone (log k_{ozone}, second-order decomposition rate constant with O_3).

Descriptor	Standard partial regression coefficient (β)	*t*-value	*p*-value
P=O bond	−0.57	−4.58	< 0.01
$-NH_2$ bonded with aromatic rings *or* –SH bonded with aromatic rings	0.48	3.86	< 0.01

of decomposition with ozone. Further multiple linear regression analysis with the step-down procedure suggested that three descriptors (P=O, aromatic c–NH_2, and aromatic c–SH) were related to the extent of decomposition with ozone (Table 3). The adjusted r^2 of the multiple regression was 0.58. The very small *p* values (0.00) associated with both descriptors indicated that the standard partial regression coefficients were significantly different from zero.

The descriptor "P=O bond" had a large negative standard partial regression coefficient (β = −0.57), the suggestion being that compounds with P=O bonds tended to be more difficult to decompose with ozone. The phosphoryl group, which includes a P=O bond, acts as an electron acceptor because of the electronegativity of the P atom (Baumgartner 2014). In general, compounds that have electron-donor substituents degrade rapidly in oxidation processes, whereas those having electron-acceptor groups degrade slowly (von Gunten 2003, Kušić et al. 2009). Accordingly, compounds with P=O bonds likely tended to react more difficult to decompose with ozone. The descriptor either "–NH_2 bonded with aromatic" or "–SH bonded with aromatic rings" had a large positive standard partial regression coefficient (β = 0.48), the suggestion being that compounds with either thiol or amino groups tended to be more easily decomposed with ozone. Because both –NH_2 (Kušić et al. 2009) and –SH (Bocci 2006) are electron-donor groups, compounds with these functional groups were expected to react rapidly with ozone. Actually, von Gunten (2003) has reported that compounds containing amino groups are effectively oxidized by ozone, and those with thiol groups also react rapidly with ozone. Our results are consistent with these observations, but the present study did not reveal whether the thiol or amino group enhanced the extent of decomposition with ozone.

3.4 Mutagenicity formation potential of compounds difficult to remove by coagulation–sedimentation and PAC adsorption

If a compound is removed from the aqueous phase by entrapment in flocs during coagulation or by adsorption onto PAC particles, it will not contact chlorine, which is applied to the water in the final disinfection process. The mutagenicity of the compound potentially caused by chlorination can therefore be decreased simply by coagulation or adsorption onto PAC. In contrast, during the ozonation process, a compound is oxidized and then transformed into other by-products that are still present in the aqueous phase, and the resulting by-products accordingly contact chlorine. Whether the mutagenicity associated with the compound increases or decreases after subsequent chlorination therefore depends on the compounds generated during ozonation and is not simply explained by the disappearance of the compound. Actually, Matsushita et al. (2016) have reported that a pre-ozonation process increased the mutagenicity of a solution containing the X-ray contrast medium iopamidol after chlorination, even though iopamidol itself completely disappeared during the pre-ozonation step. We therefore investigated the effectiveness of coagulation–sedimentation and PAC adsorption in reducing potential mutagenicity after subsequent chlorination by using mutagenicity formation potential (MFP) (Takanashi et al. 2013, Takanashi et al. 2014, Takanashi et al. 2016) as an index of toxicity induced after chlorination. The investigation did not address the effectiveness of ozonation.

As mentioned in section 3.1, the only compound removed in the coagulation process was etofenprox. Several compounds were difficult to remove even via PAC adsorption (section 3.2). Diethyl phosphate, dimethyl phosphate, and trimethyl phosphate were among the compounds most difficult to remove; diethyl maleate, diethyl L-(+)-tartrate, and tefuryltrione were in the group next most difficult to remove. However, diethyl phosphate and trimethyl phosphate did not induce mutagenicity after chlorination, and the MFPs of dimethyl phosphate (5.2 net revertant colonies [net rev.] μM^{-1}), diethyl maleate (13 net rev. μM^{-1}) and diethyl L-(+)-tartrate (24 net rev. μM^{-1}) were relatively small among the compounds tested in the present study (Table 1). The implication is that possible health effects related to the induction of gene mutation would be small, even though these compounds are found in tap water. In contrast, the MFP of tefuryltrione has not yet been reported, but chlorination completely transforms tefuryltrione into 2-chloro-4-(methylsulfonyl)-3-[(tetrahydrofuran-2-ylmethoxy)methyl]benzoic acid (CMTBA) (Kamata et al. 2017), and CMTBA is reportedly very stable during chlorination (Kamata et al. 2017). Because CMTBA does not induce mutagenicity (Food Safety Commission Government of Japan 2009), the MFP of tefuryltrione is expected to be negative.

Among the compounds tested in the present study, seven had very high MFPs that exceeded 100 net rev. μM^{-1}. These compounds included 3-methyl-4-nitrophenol, which may be produced in the environment, is a major TP of the organophosphorus insecticide fenitrothion (Misra et al. 1993, Matsushita et al. 2006), and had the largest MFP of 2000 net rev. μM^{-1}. However, each of the seven compounds was effectively removed via PAC adsorption ($R_{PAC} < 0.24$). Overall, PAC adsorption appeared to be an effective treatment for the reduction of potential mutagenicity caused by chlorination, not only for the parent pesticides but also for their TPs.

4. Conclusions

1. Coagulation–sedimentation was ineffective in removing all compounds (28 TPs and 14 parent pesticides) tested in the present study, with the exception of the most hydrophobic pesticide, etofenprox.
2. Removal via PAC adsorption correlated positively with log K_{ow} values at pH 7, the indication being that relatively polar compounds were more difficult to remove via PAC adsorption. Removal correlated positively with the energy level of the HOMO, the suggestion being that the graphene surface of PAC particles likely acts as an acceptor of electrons from the target compounds, and electron transfer may enhance the strength of the π-π interactions between the adsorbates and the graphene surface. Multiple linear regression analysis between the extent of removal and the partial structures of the target compounds suggested that the compounds with aromatic rings tended to be more easily removed via PAC adsorption.
3. Removal via ozonation correlated positively with the energy level of the HOMO, probably because compounds with a relatively high energy level HOMO could more easily transfer an electron to the LUMO of ozone or other oxidants such as hydroxyl radicals. Multiple linear regression analyses suggested that compounds with P=O bond and $-NH_2$ or –SH groups tended to be easily decomposed by ozone.
4. The parent pesticides tested in this study tended to

become more difficult to remove via both PAC adsorption and ozonation after transformation into their TPs in the environment.

5. The compounds that were difficult to remove via PAC adsorption did not induce strong mutagenicity after chlorination, and the compounds that induced strong mutagenicity after chlorination could be removed by PAC adsorption. PAC adsorption is therefore likely to be an effective way to reduce the potential mutagenicity caused by chlorination, not only for the parent pesticides but also for their TPs.

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Supplementary information

Removals of pesticides and pesticide transformation products during drinking water treatment processes and their impact on mutagen formation potential after chlorination

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Table S1 Structures of target compounds used in the present study.

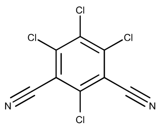
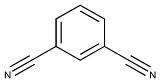
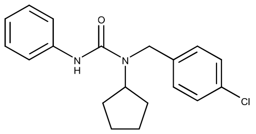
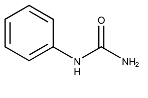
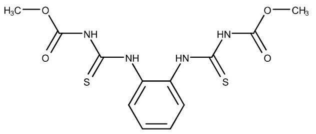
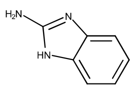
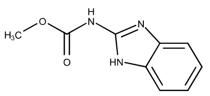
Parent pesticides Transformation products	Structure	log K_{OW}	HOMO energy level, eV	LUMO energy level, EV
Fungicides				
Chlorothalonil		4.10	-10.35	-1.75
1,3-Dicyanobenzene		1.69	-10.41	-0.96
Pencycuron		5.08	-8.78	0.01
Phenylurea		0.88	-8.72	0.45
Thiophanate methyl		2.00	-8.72	-1.10
2-Aminobenzimidazole		1.04	-9.71	-1.89
Methyl-2-benzimidazole carbamate		1.80	-9.01	-1.30

Table S1 (continued)

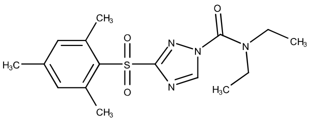
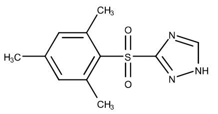
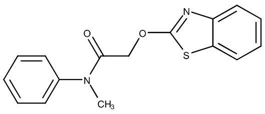
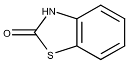
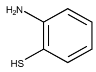
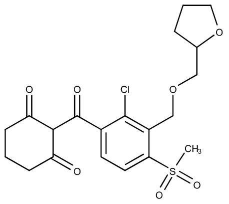
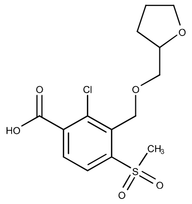
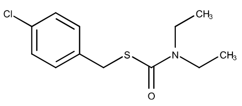
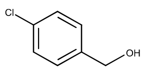
Herbicides				
Cafenstrole		2.91	-9.48	-0.63
3-(2,4,6-Trimethylphenylsulfonyl)-1,2,4-triazole		1.19	-9.44	-0.51
Mefenacet		3.42	-8.93	-0.58
2(3H)-Benzothiazolone		2.48	-9.03	-0.44
2-Aminothiophenol		0.96	-8.58	0.11
Tefuryltrione		-0.05	-10.18	-1.33
2-Chloro-4-(methylsulfonyl)-3-[(tetrahydrofuran -2-ylmethoxy)methyl]benzoic acid		-2.12	-10.26	-1.36
Thiobencarb		3.73	-9.17	-0.28
4-Chlorobenzyl alcohol		1.81	-9.51	-0.06

Table S1 (continued)

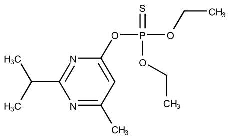
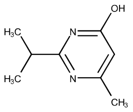
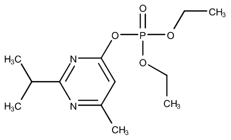
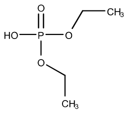
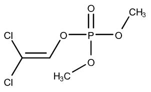
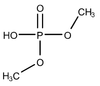
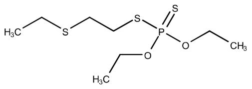
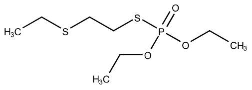
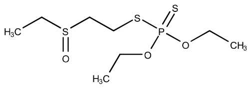
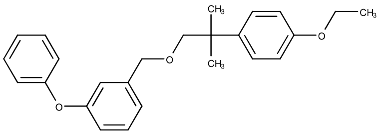
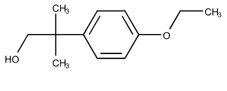
Insecticides				
Diazinon		4.19	-9.02	-0.82
2-Isopropyl-6-methylpyrimidin-4-ol		2.29	-9.87	-0.13
Diazinon oxon		3.38	-10.05	-0.20
Diethyl phosphate		-1.93	-11.54	0.75
Dichlorvos		1.37	-9.71	-0.03
Dimethyl phosphate		-0.26	-11.74	0.66
Disulfoton		3.03	-8.58	-1.71
Disulfoton oxon		2.14	-8.68	-1.18
Disulfoton sulfoxide		1.07	-8.79	-1.53
Etofenprox		6.30	-8.86	0.15
2-(4-Ethoxyphenyl)-2-methylpropanol		2.44	-8.71	0.63

Table S1 (continued)

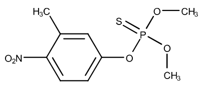
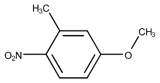
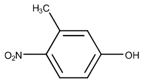
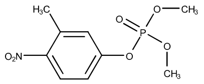
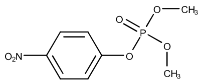
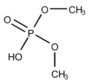
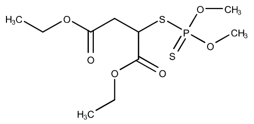
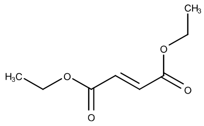
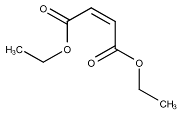
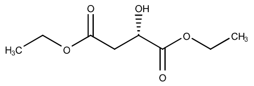
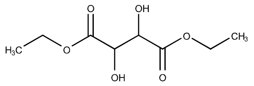
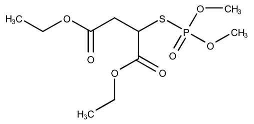
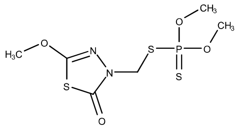
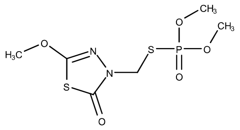
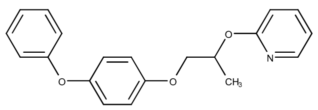
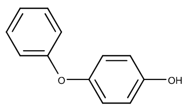
Fenitrothion		3.12	-10.36	-2.02
3-Methyl-4-nitroanisole		2.27	-9.85	-0.93
3-Methyl-4-nitrophenol		1.92	-9.99	-1.01
Fenitrooxon		2.23	-10.25	-1.23
Methyl paraoxon		1.71	-10.41	-1.29
Trimethyl phosphate		0.11	-11.82	0.44

Table S1 (continued)

Malathion		1.86	-10.13	-2.83
Diethyl fumarate		1.43	-11.34	-0.92
Diethyl maleate		1.43	-11.23	-0.52
Diethyl L-(-)-malate		-0.11	-11.12	0.74
Diethyl L-(+)-tartrate		-0.82	-11.05	0.50
Malaoxon		0.97	-10.10	-1.32
Methidathion		2.29	-8.69	-1.65
Methidathion oxon		1.40	-9.55	-1.39
Pyriproxyfen		4.75	-8.72	0.18
4-Phenoxyphenol		3.17	-8.80	0.13

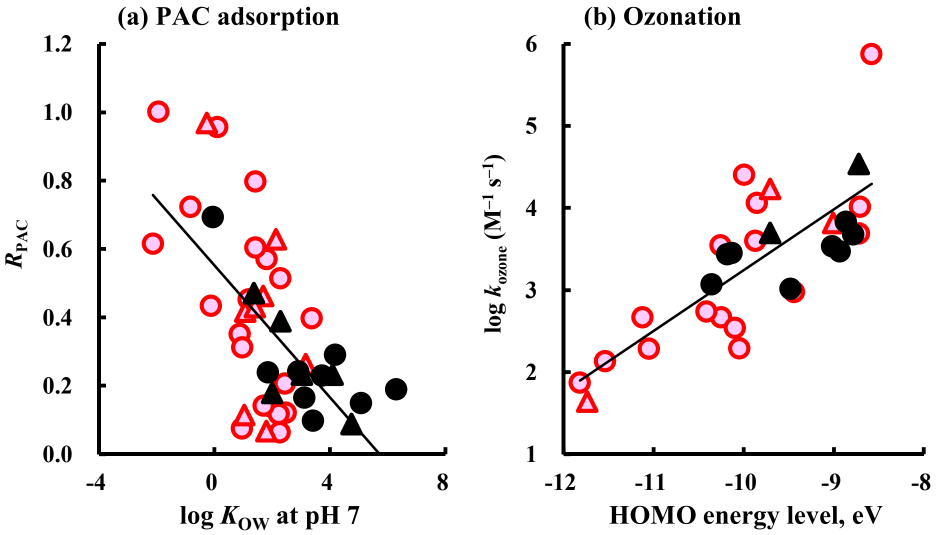


Fig. S1 Comparison between rice-farming and upland-filed pesticides and their TPs. (a) PAC adsorption. (b) ozonation. ○, TPs of rice-farming pesticides; △, TPs of upland-field pesticides; ●, rice-farming pesticides; ▲, upland-field pesticides.