Effects of chlorine on organophosphorus pesticides adsorbed on activated carbon: Desorption and oxon formation

Koichi Ohno[a],*, Takehiro Minami[a], Yoshihiko Matsui[a], Yasumoto Magara[b]

[a]Department of Socio-Environmental Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[b]Creative Research Initiative "Sousei", Hokkaido University, N21W10, Sapporo 001-0021, Japan

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ABSTRACT

We investigated effects of chlorination on four organophosphorus pesticides (diazinon, isoxathion, malathion, and tolclofos-methyl) adsorbed on powdered activated carbon (PAC). Following adsorption of each pesticide on 10 mg/L of PAC in water, chlorine was added. After 30 min of chlorination, the corresponding oxons were detected in the water, but the parent compounds were not detected. Molar ratios of the oxon concentration in solution after 30 min of chlorine addition to the initial pesticide concentration before the adsorption process were 4.1% and 7.9% for diazinon, 3.9% and 5.8% for isoxathion, 1.2% and 1.7% for malathion, and 1.4% and 1.4% for tolchlofos-methyl, in the case of 2 and 5 mg/L of chlorine addition. The results suggested that the oxons were desorbed from the PAC by chlorination. The concentrations of the desorbed oxons gradually decreased with time, apparently owing to their readsorption by the PAC. Results from additional experiments suggest the following sequence of events: (i) adsorbed pesticides are oxidized by chlorine on the surface of the PAC and transformed into corresponding oxons; (ii) the oxons are released from the PAC; (iii) the released oxons are gradually readsorbed by the PAC, decreasing their concentrations in the water phase.

1. Introduction

Organophosphorus pesticides are widely used throughout the world and are frequently detected in surface and ground waters (Gomezgomez et al., 1995; Tanabe et al., 2001; Sankararamakrishnan et al., 2005; Gilliom et al., 2006). These pesticides are mostly dissolved in water and cannot be easily removed by solid/liquid separation processes such as coagulation and sand filtration. An effective and simple method for removing pesticides is the addition of powdered activated carbon (PAC) at the inlet of a water purification process train.

To prevent the growth of algae in a sedimentation basin with plate or tube settlers and in a rapid sand filter, chlorine is sometimes also added at the inlet. This process, known as pre-chlorination, is also used to oxidize iron, manganese, ammonia, and other compounds. Intermediate chlorination, which is the addition of chlorine between sedimentation and filtration processes, is used as an alternative to pre-chlorination.

Thus, it is likely that chlorine will come into contact with PAC in both pre-chlorination and intermediate chlorination, although the contact time and degree will differ. This contact between chlorine and PAC is undesirable, because chlorine reacts with the surface of the PAC and decreases its capacity to adsorb targeted pollutants (Sontheimer et al., 1988). Furthermore, Gillogly et al. (1998) showed that a taste- and

odor-causing compound, 2-methylisoborneol, that was initially adsorbed on PAC could be released back into the water following the addition of chlorine. Huang and Yeh (1999) showed that chlorination of natural organic matter adsorbed on PAC caused the appearance of chlorination byproducts such as trihalomethanes and adsorbable organic halogens in the aqueous phase. Also, Voudrias et al. (1985) found that the addition of chlorine to water containing phenols adsorbed on granular activated carbon caused the formation of a variety of chlorinated derivatives in the aqueous phase. These reactions might also occur with organophosphorus pesticides that are adsorbed on PAC.

Organophosphorus pesticides containing phosphorus–sulfur double bonds (P$=$S) are oxidized to their corresponding oxons, with phosphorus–oxygen double bonds (P$=$O), by chlorination (Magara et al., 1994; Wu and Laird, 2003). These oxons are relatively persistent by chlorination although some of the oxons degrade further (Magara et al., 1994; Arai et al., 2005; Kamoshita et al., 2007). *In vitro* assays, such as analysis of acetylcholinesterase (AChE) inhibition, show that these oxons are more potent AChE inhibitors than their parent compounds (Monnet-Tschudi et al., 2000; Tahara et al., 2005). A survey of source water and finished water collected from 12 community water systems found that organophosphorus insecticides detected in source water were not detected in the finished potable water (Coupe and Blomquist, 2004). Although this could be due to complete removal by the water treatment processes, Duirk and Collette (2006) suggest that the parent pesticides were transformed into the more potent AChE inhibitors, oxon forms, which were not measured in the survey. Therefore, it is important to understand the behavior of not only organophosphorus pesticides, but also their corresponding oxons.

In the present study, we investigated the effects of chlorination of organophosphorus compounds adsorbed to PAC. We also investigated the mechanisms of the desorption and the readsorption of the pesticides and their oxons from PAC.

2. Materials and methods

2.1. *Reagents and materials*

Four organophosphorus pesticides (diazinon, isoxathion, malathion, and tolclofos-methyl) were used as adsorbates in this study. Diazinon, diazinon oxon, isoxathion, isoxathion oxon, malathion, and tolclofos-methyl were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Malaoxon came from Dr. Ehrenstorfer-Schäfers (Augsburg, Germany), and tolclofos-methyl oxon came from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan). The physico-chemical and toxicological properties of these compounds are listed in Table 1. Acceptable daily intake values for the oxons are not available because they are unintended chemicals and oxidative transformed substances of the parent pesticides. All

Table 1 – Physico-chemical and toxicological properties of the organophosphorus pesticides and their corresponding oxons

Compound	CAS #[a]	Molecular weight	Logarithm of octanol–water partition coefficient ($\log K_{ow}$)		Water solubility at 25 °C (mg/L)		ADI[b] (mg/kg bw per day)
			Tomlin (2006)[c]	USEPA (2007)[c]	Tomlin (2006)[c]	USEPA (2007)[c]	
Diazinon	333-41-5	304.35	3.30[d]	3.81[d]	60[d,e]	40[d]	0.002[f,g]
Diazinon oxon	962-58-3	288.29		2.07[d]		245[h]	
Isoxathion	18 854-01-8	313.31	3.88[d]	3.73[d]	1.9[d]	1.9[d]	0.003[g]
Isoxathion oxon	32 306-29-9	297.25		2.13[i]		192[h]	
Malathion	121-75-5	330.35	2.75[d]	2.36[d]	145[d]	143[d,e]	0.3[f], 0.02[g]
Malaoxon	1634-78-2	314.29		0.52[i]		7500[d,j]	
Tolclofos-methyl	57 018-04-9	301.13	4.56[d]	4.56[d]	1.1[d]	1.1[d]	0.064[g]
Tolclofos-methyl oxon	97 483-08-4	285.07		3.00[i]		41[h]	

[a] Chemical Abstracts Service number.
[b] Acceptable daily intake.
[c] See references.
[d] Experimental value.
[e] At 20 °C.
[f] Joint meeting on Pesticide Residues (JMPR) (2002).
[g] Japanese Ministry of Health, Labour and Welfare (2004).
[h] Estimated by WSKOW v.1.41.
[i] Estimated by KOWWIN v.1.67.
[j] At 22 °C.

other reagents were purchased from Wako Pure Chemical Industries, Ltd.

To suppress fluctuations in the pH, we prepared raw water for experiments by adding 20 mg/L of sodium hydrogen carbonate to ultra-pure water (18.2 MΩ cm resistivity) obtained by reverse osmosis using an Osmoclear system (Organo Corp., Tokyo, Japan) followed by a Puric MX-II water purification system (Organo Corp.). Stock solutions of individual pesticides were prepared at 1 g/L in acetonitrile, and the standard working solutions were obtained by dilution with 0.15% acetic acid in water. Individual pesticide solutions for adsorption and chlorination experiments were prepared by the direct addition of each pesticide reagent to the raw water without assistance of organic solvent, followed by sonication for about 0.5 h by use of an ultrasonic bath, Model 8210 (Branson Ultrasonics Corp., Danbury, CT, USA). Next, the solution was filtered through a 0.45-μm hydrophilic polytetrafluoroethylene (PTFE) membrane filter (Advantec, Tokyo, Japan) to remove any undissolved residue. These pesticide solutions were prepared for every experiment. For adsorption and chlorination experiments, the solution was diluted with the raw water. The targeted pesticide concentration for experiments was basically around 100 μg/L, but the concentration was not constant because the dissolution of pesticide reagents fluctuates without the help of organic solvent. Therefore, we measured the initial pesticide concentration for every experiment prior to PAC and chlorine addition.

Thermally activated, wood-based PAC (Taikou-W; Futamura Chemical Industries Co., Ltd., Nagoya, Japan) was used as an adsorbent. The BET surface area and median particle diameter of the PAC were 862 m²/g and 7.6 μm. The PAC was dried in an oven at 105 °C for 20 min and stored in a desiccator before use.

2.2. Experimental procedures

2.2.1. Chlorination of PAC following adsorption of organophosphorus pesticide

PAC (10 mg) was added to 1 L of pesticide solution in a beaker. The solution was then stirred with a mixer at 300 rpm for 1 h. Next, the pre-determined amount of sodium hypochlorite was added to the solution, and the solution was stirred again. The pH of the solution was maintained at 7.4 ± 0.1, although it rose to ∼8.0 for a few minutes following the addition of the chlorine. Water samples were collected before (initial concentration) and after the adsorption process and every 30 min for 2 h after the addition of chlorine.

2.2.2. Extraction of pesticides and their oxons adsorbed on PAC

Compounds adsorbed on PAC were extracted as follows. First, 500 mL of the PAC solution was filtered through a 0.45-μm hydrophilic PTFE membrane filter to capture the PAC on the filter. The filter and the attached PAC were placed in a beaker, covered with 20 mL acetonitrile, and sonicated for 10 min in the ultrasonic bath. After the sonication, the suspension and the filter were transferred to a test tube with a ground stopper, mixed with 30 mL of acetonitrile, and shaken for 10 min. The suspension was then filtered through a 0.2-μm hydrophobic PTFE membrane filter (Advantec), and the concentrations of the parent pesticide and its oxon were measured in the filtrate.

2.3. Analytical methods

Residual chlorine was analyzed by the DPD colorimetric method (Standard Method 4500-Cl G (APHA, 2005)) using DPD total chlorine reagent packs (Hach Company, Loveland, CO, USA). Pesticides and their corresponding oxons were analyzed using a liquid chromatography (LC)—tandem mass spectroscopy (MS–MS) system. LC was carried out with an Agilent 1100 high-performance LC system (Agilent Technologies, Inc., Palo Alto, CA, USA) with a Mightysil RP-18 column (150 mm × 2.0 mm internal diameter; Kanto Chemical Co., Inc., Tokyo, Japan). The mobile phases were 0.15% acetic acid in water (eluent A) and 0.15% acetic acid in acetonitrile (eluent B). The gradient elution programs were as follows. For the analysis of diazinon, malathion, and their oxons, the initial composition was 40% B. This was followed by a linear gradient to 90% B over 7 min and maintenance at 90% B for 5 min. For the analysis of isoxathion, tolclofos-methyl, and their oxons, the initial composition was 50% B. This was followed by a linear gradient to 95% B over 2 min and maintenance at 95% B for 5 min. The flow rate was 0.2 mL/min, the injection volume was 5 μL, and the column temperature was maintained at 40 °C. Mass analysis was performed with an API 3000 MS–MS system (Applied Biosystems, Foster City, CA, USA). The operating parameters of the electrospray-ionization-positive mode were optimized by evaluating the sensitivity and fragmentation of each compound. For each compound, the precursor and product ions were chosen for quantitation (Table 2).

3. Results and discussion

3.1. Effect of chlorine on PAC following adsorption of an organophosphorus pesticide

Before chlorination, 10 mg/L of PAC was added to each pesticide solution. After 1 h of adsorption, 0.5–1.1% of the diazinon remained in the water, and the concentrations of the other pesticides (isoxathion, malathion, and tolclofos-methyl) were below the detection limits (0.03 μg/L). Following

Table 2 – Precursor and product ions in LC-MS-MS analysis		
Compound	Precursor ion (m/z)	Product ion (m/z)
Diazinon	305.2	169.2
Diazinon oxon	289.2	153.2
Isoxathion	314.0	105.3
Isoxathion oxon	298.3	242.1
Malathion	331.1	127.1
Malaoxon	315.1	127.1
Tolclofos-methyl	301.1	125.1
Tolclofos-methyl oxon	285.0	109.0

adsorption, chlorine was added to the PAC solution. After 30 min of chlorination, the parent pesticides were not detected in the water, but their corresponding oxons were detected (Fig. 1). When 2 mg/L of chlorine was added, molar ratios of oxon concentration in water after 30 min of chlorine addition to the parent pesticide concentration before PAC and chlorine addition were 4.1% for diazinon, 3.9% for isoxathion, 1.2% for malathion, and 1.4% for tolclofos-methyl, and when 5 mg/L of chlorine was added, the ratios were 7.9%, 5.8%, 1.7%, and 1.4%, respectively. The ratios were therefore higher at 5 mg/L than at 2 mg/L chlorine for each pesticide except for tolclofos-methyl, the ratio was the same in this case. Subsequent samples ($t > 30$ min) showed that the concentrations of the released oxons decreased with time. This result implies that the peak concentration of oxon in water was reached after less than 30 min of chlorination.

3.2. Mechanism of decrease in the level of released oxon with chlorination time

As mentioned above, the concentration of the released oxon decreased with chlorination time. There are two possible explanation for this finding: that the oxons were further degraded, and that the oxons were readsorbed on the PAC. To determine which of these explanations is correct, we divided the solution into two parts, one with and the other without PAC, after 30 min of chlorination. To prepare the solution without PAC, the suspension was filtered through a 0.45-μm hydrophilic PTFE membrane filter. The oxon and residual chlorine concentrations were measured over time (Fig. 2). The oxon concentrations decreased with time in the solutions with PAC, but not in the solutions without PAC (but with residual chlorine). This was true of all four pesticides, although the trend was weaker for malathion and tolclofos-methyl. Therefore, the progressive decrease in oxon levels in water appeared to be due to the readsorption of the oxons by PAC rather than to further degradation. Kamoshita et al. (2007) added about 1.0 mg/L of chlorine to a number of single oxon solutions, of which concentration was 5.7–12 μg/L. The residual ratios of the four oxons by 24-h contact with chlorine were 76% for diazinon oxon, 61% for isoxathion oxon, 99% malaoxon, and 104% for tolxlofos methyl oxon. Diazinon oxon and isoxathion oxon appeared to relatively degrade, but they degrade only a little, less than 10%, by 4-h contact with chlorine. These results supported our results.
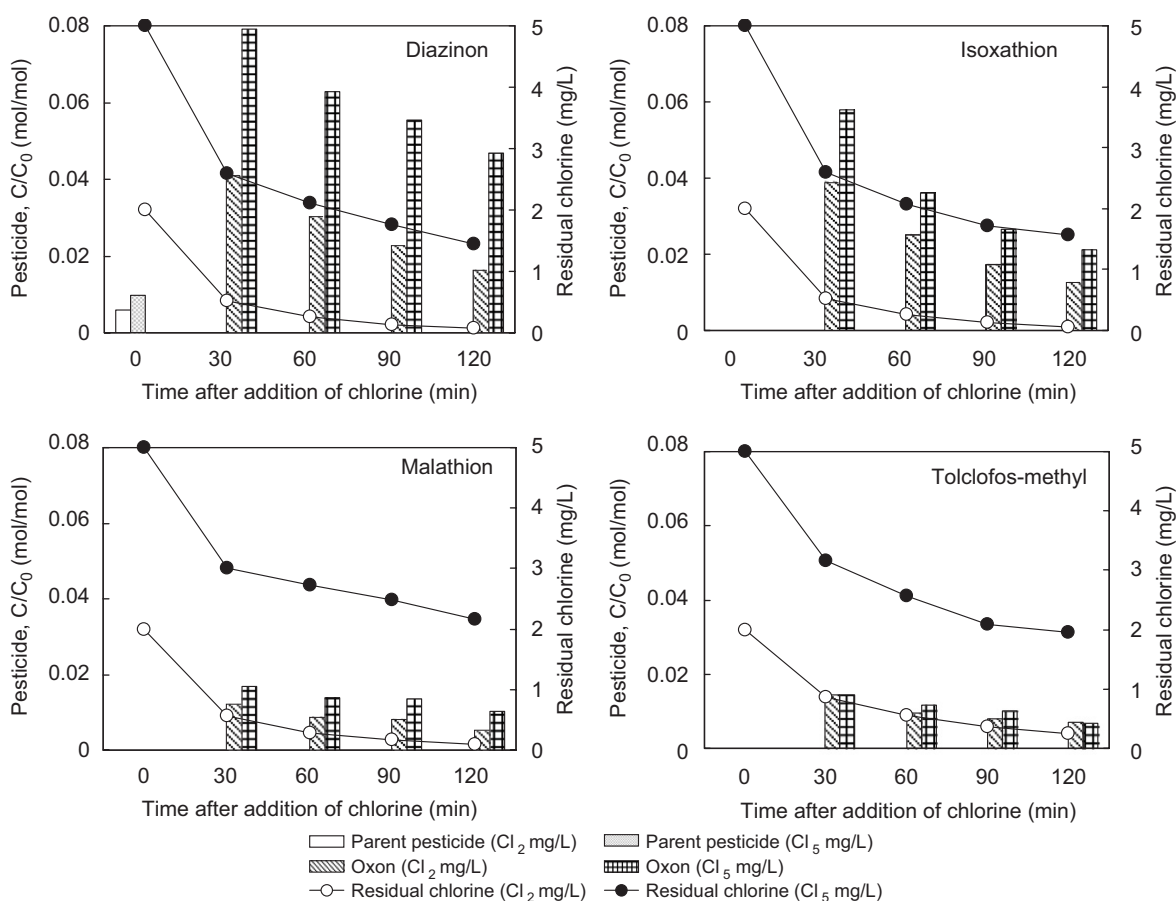

Fig. 1 – Aqueous pesticide and chlorine concentrations following chlorination of suspensions containing PAC with pre-adsorbed parent pesticide. Initial pesticide concentrations (C_0) in the solutions were 0.44 μM (135 μg/L) for diazinon, 0.38 μM (118 μg/L) for isoxathion, 0.65 μM (216 μg/L) for malathion, and 1.27 μM (383 μg/L) for tolclofos-methyl. C, measured concentration.
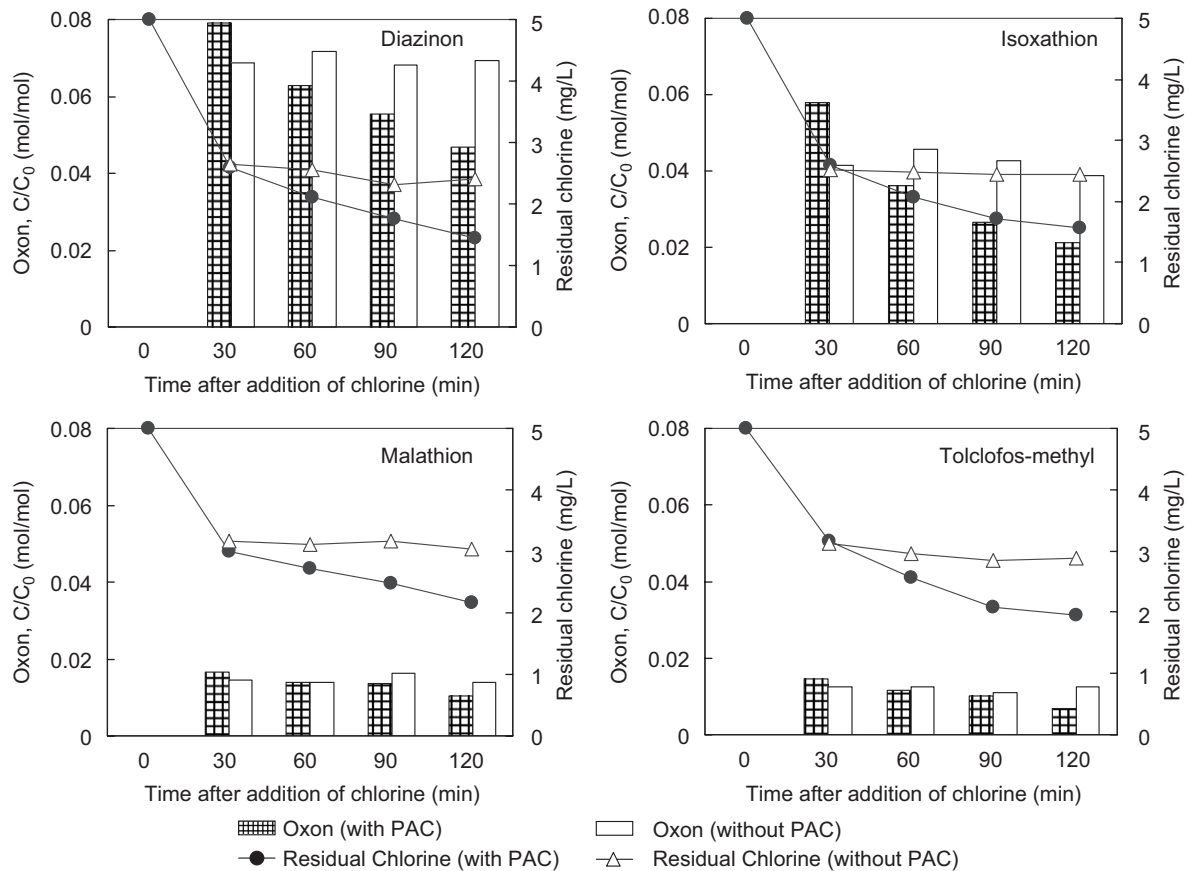
Fig. 2 – Effects of PAC on the decrease in the concentration of released oxons with chlorination time. To produce solutions without PAC, PAC was removed by filtration following 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentrations of the parent pesticide solution were the same as in Fig. 1.

As shown in Fig. 2, the residual chlorine decreased with time in the solutions with PAC but not in the solutions without PAC. This is due to progressive oxidation of the PAC by chlorine. This oxidation causes a decrease in the number of adsorption sites, which may reduce the rate of oxon readsorption. To examine this effect, we performed the chlorination experiment using isoxathion, and after 30 min, we divided the solution into two parts, one of which was treated with sodium thiosulfate to quench the residual chlorine (Fig. 3). Owing to the action of PAC as a catalyst (Sontheimer et al., 1988), the oxon could be further degraded when both PAC and chlorine are present, but we found that the oxon concentration in water decreased faster when chlorine was absent. These results indicate that the dominant factor in the decrease in the released oxon concentration is not the further degradation of the oxon, but rather its readsorption to the PAC. The results also show that the residual chlorine continues to oxidize the surface of the PAC, decreasing the adsorptive capacity.

We considered that the desorption of oxons was due to the decrease of the adsorptive capacity of PAC by chlorination. The observed data also suggested that readsorption rate of oxons was slower than adsorption rate of the parent pesticides (Figs. 1–3), for almost all the parent pesticides were adsorbed on PAC for 1 h as mentioned in the result of the first
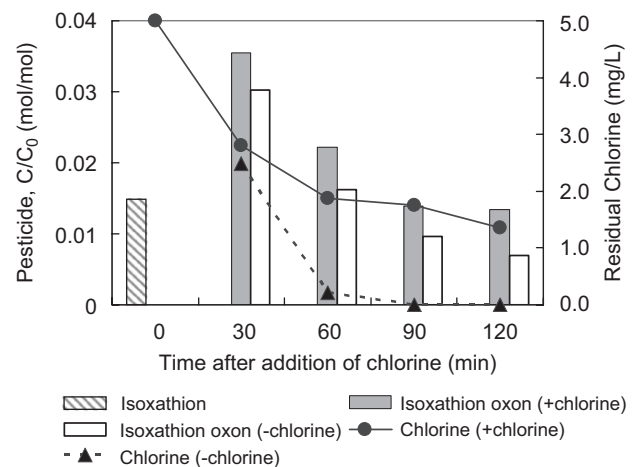

Fig. 3 – Effect of chlorine on isoxathion oxon concentrations released during 30 min of chlorination. For the condition without chlorine, chlorine was quenched after 30 min of chlorination. The initial chlorine dose was 5 mg/L, and the initial concentration of isoxathion in the solution was 2.8 μM (880 μg/L).

experiment. This slower adsorption rate of oxons can be also explained by the decrease of the adsorptive capacity. There are, however, other possible explanations for the slower

adsorption rate and for the dominant desorption of the oxons: the oxons may have slower adsorption rates. The lower adsorption capacity is consistent with the physico-chemical data (Table 1): the oxons have lower octanol–water partition coefficient (K_{ow}) than the parent pesticides. Therefore, the slower readsorption rate of the oxons was considered to be due to the combination of the decrease of adsorption capacity and the lower adsorption capacity of the oxons.

3.3. Mechanism of the desorption of oxon forms from PAC

Our results showed that chlorination of the PAC caused the desorption of previously adsorbed organophosphorus pesticides. The desorbed substances, however, were not the parent pesticides but the oxon forms (Fig. 1). One possible explanation for these results is that chlorine oxidizes the sites where the parent pesticide was adsorbed, causing the pesticide to be released back into the water, where it is oxidized to the corresponding oxon. A second possibility is that the adsorbed parent pesticide is first oxidized to the corresponding oxon on the PAC and then released from its adsorption site. To examine these two possibilities, we performed the chlorination experiment using isoxathion solution, and measured the levels of isoxathion and its oxon after 30 min (Fig. 4). After the chlorination, ~80% of the isoxathion was degraded to the isoxathion oxon. Following the chlorination of isoxathion-adsorbed PAC, the parent isoxathion was not detected (Fig. 1). If the first explanation were correct, the parent isoxathion should have been detected. Therefore, it appears that the second explanation is correct.

To investigate the reaction of isoxathion on the PAC surface during chlorination, we extracted the compounds adsorbed on the PAC after 30 min of contact with chlorine. We found that 53% of the compound adsorbed on the PAC was isoxathion oxon and 47% was isoxathion (Fig. 5). Thus, approximately half of the isoxathion adsorbed on the PAC remained untransformed, and the remaining half was transformed to the oxon form. These findings support the
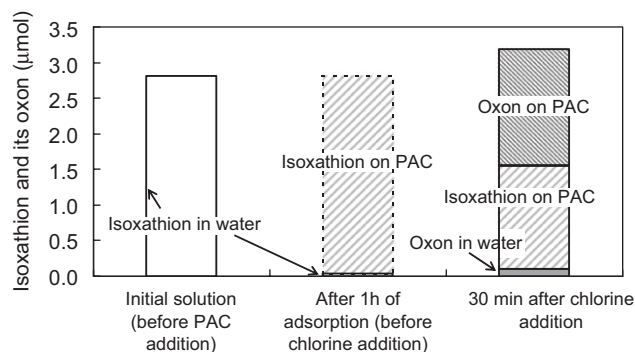
Fig. 5 – Change in the state of isoxathion and its oxon during the adsorption and chlorination experiment. The initial chlorine dose was 5 mg/L. The amount of isoxathion adsorbed on PAC after 1 h of adsorption was an estimate, whereas the amounts of isoxathion for the other samples were experimentally measured.

idea that organophosphorus pesticides are oxidized to their oxon forms on the PAC and then released. Furthermore, if the isoxathion was released from the PAC and then transformed to the oxon form in the water phase, both the isoxathion and the oxon should have been detected in the water phase, because not all of the isoxathion in the water phase was transformed to the oxon form after 30 min of chlorination (Fig. 4). In the experiment in which isoxathion was adsorbed by PAC and chlorinated, however, isoxathion was not detected in the water phase. Thus, it is unlikely that isoxathion adsorbed on the PAC surface was released and then transformed to the oxon form in the water phase.

4. Conclusions

We investigated the effects of chlorination of organophosphorus compounds adsorbed to PAC. The oxons rather than the parent pesticides were detected in the water phase after chlorination. In addition, the concentrations of the desorbed oxons decreased with chlorination time. This result can be explained by the readsorption of oxons in the water phase by PAC. Results from additional experiments suggest that the parent pesticides adsorbed to PAC are first oxidized to the corresponding oxon, then released from the adsorption sites. In the case of isoxathion, after 30 min of chlorination, approximately half of the parent compound adsorbed to the PAC surface was converted into the corresponding oxon.

In this study, we focused on the clarification of mechanism of desorption and oxon formation of organophosphorus pesticides that were pre-adsorbed on PAC by contact with chlorine. To elucidate the mechanism more clearly, we conducted the chlorination experiments with the pesticide solutions at much higher concentrations than environmentally relevant concentrations. The reactivity of chlorine and the pesticides that are adsorbed on PAC at lower concentrations remained unrevealed. As a result of this study, however, we may provide the following recommendations for water purification facilities that have a possibility for contact
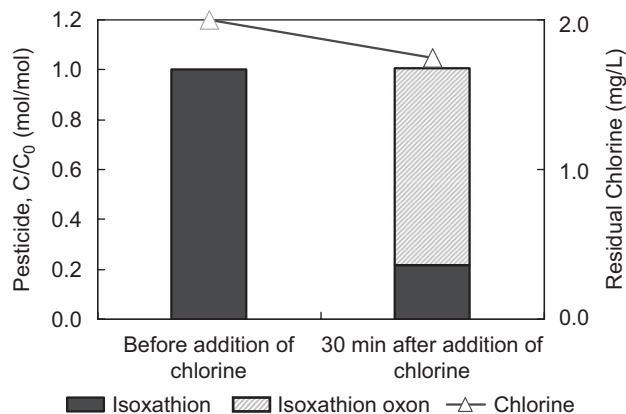

Fig. 4 – Concentrations of isoxathion and its oxon after direct chlorination in aqueous solution. The initial concentration of isoxathion in the solution was 0.20 µM (62 µg/L), and the chlorine dose was 2.0 mg/L.

between PAC and chorine: oxon concentrations in addition to those of the parent pesticides should be monitored in finished water, and longer contact time between PAC and the desorbed oxons for readsorption should be taken.

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