Impact of prechlorination on organophosphorus pesticides during drinking water treatment: Removal and transformation to toxic oxon byproducts

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ABSTRACT

Prechlorination is commonly used to minimize operational problems associated with biological growth as well as taste and odor control during drinking water treatment. However, prechlorination can also oxidise micropollutants into intermediate byproducts. This could impose profound effects on the safety of the finished water if the transformed byproducts are more toxic and less removable. This study investigated the effect of prechlorination on decomposition and subsequent removal of the four organophosphorus pesticides (OPPs): chlorpyrifos, diazinon, malathion and tolclofos-methyl using a simulated conventional water treatment process of powdered activated carbon assisted coagulation-sedimentation-filtration (PAC-CSF) and postchlorination. It was found that, following prechlorination, not only did the percentage of OPPs oxidation vary significantly, but also the concentration of transformed oxons, which are more toxic than their parent compounds, increased as the major identified oxidation byproducts in water. Removal of these oxons proved to be more difficult by the PAC-CSF than their parent OPPs, because they are more water soluble and more hydrophilic. Both the OPP oxidation and oxon formation increased with chlorine dose during prechlorination. Meanwhile, the continuing chlorination of OPPs by residual free chlorine during PAC-CSF further complicated the pesticide removal processes, generally resulting in a gradually increased formation of oxons. Moreover, in the final treatment stage of postchlorination, the more chlorine-reactive pesticides, malathion and diazinon, were completely oxidised and the formation of corresponding oxons was increased with the prechlorine dose. In contrast, a certain amount of the less chlorine-reactive pesticide tolclofos-methyl still remained in solution after postchlorination, accompanied by an increased formation of tolclofos-methyl oxon with prechlorine dose. Since the oxons are resistant to further oxidation and less adsorbable during the PAC-CSF process, the gross removal of these pesticides and their oxons decreased with increase of the prechlorine dose. This led to an accumulation of the more toxic oxons in the finished water, especially at higher chlorine doses during prechlorination. The significance of this work is the demonstration that, under circumstances where prechlorination is used and source water contains traces of OPPs, alternative practices should be prioritized to avoid the potential risks involved in consumption of the treated water.

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1. Introduction

Organophosphorus pesticides (OPPs) have been widely used in agriculture for decades to maintain and increase crop yields around the world (Baldwin, 2012). Because of their chemical stability and the amounts applied, these toxic chemicals have caused various degrees of contamination in aquatic environments and have been frequently detected in natural waters (Schwarzenbach et al., 2006; Mitra et al., 2011; Rathore and Nollet, 2012). The concentration of an OPP in surface water varies from regions around the world. The maximum concentrations of malathion and diazinon up to 2000 and 775 ng/L respectively in some of the European waters and, up to 101.6 and 75.9 μg/L in some of the developing countries were

reported (Konstantinou et al., 2006; Fadaei et al., 2012). Toxicological and epidemiological studies have shown that traces of pesticide residues (at μg/L or even ng/L level) in drinking water can potentially cause adverse human health effects, such as cytotoxicity, mutagenicity, genetic malformations, neurodevelopmental disorders and damage to the immune system, as well as endocrine-disrupting effects for mammals (Sultatos, 1994; Larson et al., 1997). Therefore, the fate of these OPPs in source waters during drinking water treatment is an important research topic.

Conventional coagulation-sedimentation-filtration (CSF) process is likely not effective in removing of the OPPs from water, due to their small molecular size and relatively high water solubility (Stackelberg et al., 2004; Jiang and Adams, 2006; Huerta-Fontela et al., 2008). However, chlorination, a process commonly used for disinfection during water treatment, has been reported to be effective in oxidising the OPPs which characteristically contain the phosphorothioate subgroup (P=S) (Acero et al., 2008; Ohno et al., 2008; Duirk et al., 2009). Reaction of chlorine with OPPs such as chlorpyrifos and diazinon followed the second order kinetics with respect to the concentrations of chlorine and OPP in solution. Hypochlorous acid (HOCl) was reported to be the primary oxidant; the two OPPs were almost oxidised completely after 1 h reaction time at a moderate chlorine dose (2.5 mg/L) (Acero et al., 2008; Duirk et al., 2009). A survey of source water and treated drinking water collected from 12 community water systems showed that molecules of OPPs containing the P=S bond (such as malathion, diazinon and chlorpyrifos) in source water were no longer detected in the finished drinking water (Coupe and Blomquist, 2004). However, in fact, these chemicals were not mineralized during chlorination. Instead, they were merely transformed into a more toxic molecular form of oxons via substitution of the sulfur atom of the P=S bond in the parent molecules with an oxygen atom forming a phosphorus-oxygen double bond (P=O) in the transformation products (Cole et al., 2005; Tahara et al., 2005; Duirk et al., 2009). The oxon transformation products of chlorpyrifos and malathion were reported to be at least a 100 times more toxic than their respective parental forms and diazoxon was 10 times more toxic than its parent pesticide (Sparling and Fellers, 2007). Therefore, chlorination alone does not eliminate or reduce the toxicity of these substances during water treatment. From the view point of drinking water safety, it is important to examine not only the oxidation of OPPs, but equally importantly also their transformation byproducts (i.e., formation and toxicity) and the gross removal of these toxic substances during water treatment processes.

Prechlorination has been used to minimize operational problems associated with biological slime formation on filters, pipes, and tanks, to enhance taste and odor removal, for oxidation and removal of hydrogen sulfide or reduction of iron and manganese (Edzwald, 2011). During this process, OPPs in raw water may react with free chlorine to form oxidation byproducts, while the remaining residual chlorine may exert continuing effects in the subsequent treatment processes. This would affect the removal of OPPs and their transformation products during the treatment processes.

The key objective of this study was to examine the oxidation and removal behavior of OPPs through a laboratory-simulated water treatment system including prechlorination, powdered activated carbon assisted coagulation sedimentation and filtration (PAC-CSF) treatment and postchlorination disinfection. The identification of the major oxidation or transformation byproducts of the four OPPs (chlorpyrifos, diazinon, malathion and tolclofos-methyl) following chlorination at typical chlorine doses was first established. Then standard jar tests were employed to simulate and evaluate the fate and removal efficiency of OPPs and their oxidation byproducts in the different stages of the designated water treatment system.

2. Materials and methods

2.1. Materials and reagents

Chlorpyrifos (99.7% purity), chlorpyrifos oxon (99.5% purity), diazinon (98.5% purity), malathion (99.7% purity), malaoxon (99.1% purity), and tolclofos-methyl (97.9% purity) were purchased from Sigma-Aldrich Corporation (Bellefonte, PA, USA). Diazoxon (98% purity) and tolclofos-methyl oxon (99% purity) were purchased from AccuStandard Inc. (New Haven, CT, USA). The molecular weight (MW), water solubility, octanol-water partition coefficient (logKow) of these pesticides and their oxons are given in Table 1. Methanol (HPLC grade) was purchased from Merck Chemicals (Darmstadt, Germany). Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, analytical grade), sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$, analytical grade), and sodium hypochlorite (NaClO, 5% of free active chlorine) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ultrapure water (18.2 MΩ cm) was produced by an Elga Purelab Ultra Analytic system (Bucks, UK). Powdered activated carbon (PAC) was obtained from the Yuqing Water Treatment Material Corporation (Henan, China). The PAC was dried in an oven at 150 °C for 1 h and stored in a desiccator before use. The BET (Brunauer-Emmett-Teller) surface area and the total pore volume of the PAC were determined as 803 m^2/g and 0.542 cm^3/g, respectively.

GF/C (diameter 47 mm, pore size 1.2 μm) and GF/D (diameter 47 mm, pore size 2.7 μm) glass microfiber filters were purchased from Whatman Co. (Maidstone, Kent, UK). The polypropylene syringe filter (pore size 0.2 μm, GHP Acrodisc) was obtained from the Pall Gelman Laboratory (Ann Arbor, MI, USA). All the glassware was cleaned following the procedures specified in USEPA Method 506 (US EPA, 1995).

Stock solutions of 10 g/L for the individual pesticides were prepared in pure methanol. The stock solution of $Al_2(SO_4)_3$ was prepared at 25 g/L using ultrapure water. The commercial sodium hypochlorite solution was directly used as stock solution. All of the stock solutions were stored in amber glass bottles at 4 °C.

2.2. Sampling

The raw water sample was taken from Heihe Reservoir to the south of Xi'an, China. It was then filtered through a 2.7 μm GF/D glass microfiber filter, and stored in amber glass bottles in a refrigerator at 4 °C. Major quality parameters of the raw water are summarized in Table 2.

2.3. Experimental procedures

2.3.1. Identification of the oxidation byproducts

To identify the chlorination byproducts, experiments at this stage were carried out in ultrapure water solutions (50 mL) of the four OPPs (chlorpyrifos, diazinon, malathion and tolclofos-methyl) at a high concentration of 10 μM for each of them. A high dose of sodium hypochlorite (130 μM or 10 mg/L) was used for the purpose of oxidation byproduct analysis. Solution pH was adjusted to 7.3 (the same as the raw water sample) at 2 mM phosphate buffer concentration. After 30 min contact time, 20 μL sodium thiosulphate solution (100 g/L) was added into the solution to quench the remaining free chlorine. For gas chromatography-mass spectrometry (GC-MS) analysis, the chlorinated samples were extracted using a liquid-liquid microextraction (LLME) protocol: (i) 30 mL chlorinated water sample was first transferred to a glass vial (40 mL, with a Teflon-lined screw cap); (ii) 13.5 g sodium sulfate was then added and dissolved in the water sample by hand-shaking; (iii) 2 mL methyl tert-butyl ether (MTBE) was also mixed

Table 1
Properties, multiple reaction monitoring (MRM) conditions and sensitivity of the detection method for each of the OPPs and their oxons.

Name	Properties			Retention time (min)	MRM conditions			Sensitivity	
	Molecular weight	logKow (USEPA, 2007)	Water solubility (mg/L) (USEPA, 2007)		Cone voltage (V)	Transition	Collision energy (eV)	LOD (µg/L)	LOQ (µg/L)
Chlorpyrifos	350.59	4.96	1.1	10.23	33	349.91 > 197.86^Q 349.91 > 152.89^C	15 14	0.018	0.055
Chlorpyrifos oxon	334.52	2.89	26	8.77	34	333.84 > 277.87^Q 333.84 > 197.74^C	20 27	0.020	0.068
Diazinon	304.35	3.81	40	9.19	30	304.91 > 168.93^Q 304.91 > 152.85^C	20 20	0.007	0.023
Diazoxon	288.29	2.07	245	7.80	30	288.93 > 152.93^Q 288.93 > 152.85^C	15 15	0.008	0.025
Malathion	330.36	2.36	145	8.24	27	330.86 > 126.75^Q 330.86 > 98.74^C	11 18	0.003	0.01
Malaoxon	314.29	0.52	7500	6.98	33	314.86 > 126.75^Q 314.86 > 98.74^C	15 17	0.004	0.013
Tolclofos-methyl	301.13	4.56	1.1	9.15	30	300.98 > 124.78^Q 300.98 > 174.86^C	17 24	0.027	0.090
Tolclofos-methyl oxon	285.06	3.00	41	7.93	22	284.98 > 108.78^Q 284.98 > 174.86^C	16 21	0.026	0.087

Note: ^{Q} Quantitation ion. ^{C} Confirmation ion.

Table 2
Raw surface water quality.

Parameter	Value	Parameter	Value
Temperature	24.2 °C	Na^+	6.3 mg/L
pH	7.3	K^+	2.2 mg/L
Conductivity	267 µS/cm	Ca^{2+}	48 mg/L
Turbidity	4.15 NTU	Mg^{2+}	4.6 mg/L
DOC	4.37 mg/L	SO_4^{2-}	30.2 mg/L
UV_{254}	0.127 1/cm	Cl^-	18.6 mg/L
Alkalinity ($CaCO_3$)	77.1 mg/L	F^-	0.7 mg/L

into the solution by hand-shaking (for 3 min); (iv) phase separation was completed within 5 min, and then 1 mL of the upper layer MTBE was transferred to a new glass vial for GC-MS analysis.

2.3.2. Prechlorination

Prechlorination experiments were conducted in 1000 mL amber glass bottles with stoppers. The raw water samples were spiked with chlorpyrifos, diazinon, malathion and tolclofos-methyl stock standard solutions, to the three concentrations: 1, 10 and 50 µg/L for the four individual OPPs. In the prechlorination experiments, a predetermined amount of chlorine was added and immediately mixed into the above OPPs-spiked raw water by hand-shaking. At a preset reaction time, a 5 mL sample was taken from each of the bottles and measured for chlorine residual immediately without delay. At the same time, another 5 mL sample was withdrawn and sodium thiosulphate was added into it to quench the remaining chlorine for determination of the OPPs and their oxidation byproducts. The chlorinated water solutions were then immediately transferred to a 1 L beaker, which was then covered by aluminum foil for the following jar test experiments.

2.3.3. Jar test procedures

Bench-scale jar test experiments were performed using a jar test apparatus (JJ-4C, Suzhou Well Scientific Ltd, China) where the stirring intensity (rpm) and time were preset. To simulate the PAC assisted CSF (or PAC-CSF) process, the following procedures were employed: a dose of PAC (10 mg/L, around the dose commonly used in drinking water treatment plants (Westerhoff et al., 2005)) and a dose of $Al_2(SO_4)_3$ (from 15 to 165 µM) were added into the beaker containing prechlorinated water, followed immediately by 250-

rpm rapid mixing for 1 min, then 30-rpm slow mixing for 15 min, and a quiescent settling for 30 min.

At the end of sedimentation, the supernatant was sampled and filtered using a 1.2 µm GF/C filter. A 50 mL sample was taken for the measurement of dissolved organic carbon (DOC), UV_{254} and the concentration of OPPs and their oxidation byproducts. Another 250 mL sample was transferred to an amber glass flask with stopper and then 1 mg/L chlorine was added for postchlorination. After a 30 min reaction time of postchlorination, 50 µL sodium thiosulphate solution (100 g/L) was added to quench the residual chlorine. The water samples were then used for further analyses for the concentrations of the OPPs and their oxidation byproducts. All the experiments were conducted in triplicate at 25 ± 1 °C, with the average values and standard deviations being reported.

2.4. Analytical methods

The concentration of chlorine was measured using the standard method 4500-Cl (DPD colorimetric method) (APHA, AWWA, WEF, 2012). The turbidity and pH of water samples were measured using a turbidity meter (2100P, Hach, USA) and a portable pH meter (Sension1, Hach, USA), respectively. The concentration of the TOC and DOC were determined using a TOC analyzer (Elementar Vario TOC Select, Germany). The UV absorbance at 254 nm was determined by using a UV–Vis spectrometer (DR 5000, Hach, USA) with 1 cm quartz cuvettes.

A 7890 A gas chromatograph coupled with a 7000 A triple quadrupole mass spectrometer (GC-QqQ-MS/MS) (Agilent Technologies, Palo Alto, CA, USA) was used for identifying the structure of the oxidation byproducts. A 7693 Series autosampler was used for sample injection and MassHunter Workstation Software rev. B.04.00 (Agilent Technologies) was used for data acquisition. A 1.0 µL volume of the prepared samples was injected into the GC in splitless mode and an Agilent J&W HP-5MS column (30 m × 0.25 mm I.D. ×0.25 mm film thickness, 5% phenyl methyl siloxane) was used for chromatographic separation. The chromatographic conditions were as follows: the oven temperature started from 80 °C for 3 min, then increased at 10 °C/min to 260 °C and was maintained there for 2 min. The injector temperature was 210 °C. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. The mass spectrometer was operated in electron

ionization (EI) mode at 70 eV in the full-scan mode, and mass spectra of the analytes in the ratio range of mass: charge (m/z) between 80 and 500 were recorded.

The concentrations of the OPPs and their chlorination byproducts were measured using an ACQUITY™ ultra-performance liquid chromatography (UPLC) system (Waters Corporation, Milford, MA, USA) equipped with an ACQUITY™ UPLC BEH C_8 column (2.1 × 100 mm, 1.7 μm particle size, Waters). Before injection 30% methanol (v/v) was spiked into the standard solutions or surface water samples to avoid the loss of analytes due to adsorption in the detection system (Li et al., 2015). The mobile phase was composed of UPW and MeOH and the flow rate was 0.2 mL/min. The separation process started with 10% MeOH for 3.0 min, the MeOH concentration was then increased to 100% within 9.0 min and retained for 2 min. Finally it was dropped back to 10% for 3 min for equilibrium before the next injection. The column temperature was maintained at 35 °C; the full loop injection volume of the auto-sampler was 10 μL. Detection was carried out using a TQD triple quadrupole mass spectrometer with electrospray ionization (ESI) in positive MRM mode (Waters Corporation, Milford, MA, USA). The desolvation temperature was set at 350 °C and the source temperature at 110 °C. The capillary voltage was set at 3.5 kV. The desolvation gas and cone gas were nitrogen (99.99%) with flow rates of 500 L/h and 30 L/h, respectively. The collision gas was argon (99.99%) with a flow rate of 0.12 mL/min. Masslynx 4.1 software was used for data acquisition and processing (Waters Corporation, USA). The OPPs and their oxidation byproducts was fragmented using collision induced dissociation (CID) with the settings, limits of detection (LODs) and limits of quantification (LOQs) are shown in Table 1.

3. Results and discussion

3.1. Identification of the chlorination byproducts

The characteristic peaks of the oxidation byproducts of the chlorinated pesticides solutions were identified based on GC-QqQ-MS/MS by comparing the total ion chromatograms (TICs) of the OPPs solutions before and after chlorination. The mass spectra of the four OPPs and their oxidation byproducts are presented in Fig. 1. The possible structure of these oxidation byproducts was analyzed through comparison of mass spectra between the measured and the standard mass spectra of the National Institute of Standards and Technology (NIST) Mass Spectral Database (Yuan et al., 2009). From the NIST database, the oxidation byproducts of malathion, diazinon, chlorpyrifos and tolclofos-methyl were identified as malaoxon, diazoxon, chlorpyrifos oxon and tolclofos-methyl oxon, respectively. These oxidation byproducts were thus further confirmed, in the present study, by the chromatograms of commercial standards of malaoxon, diazoxon, chlorpyrifos oxon and tolclofos-methyl oxon measured by GC-QqQ-MS/MS. Apart from these oxon analogues, no other major oxidation byproducts were identified, as reported previously (Zhang and Pehkonen, 1999; Acero et al., 2008; Ohno et al., 2008; Duirk et al., 2009). It was proposed that, when chlorine (mostly HOCl) reacts with the phosphorothioate subgroups of the OPPs, the subgroup of P=S could be oxidised to or transformed into the corresponding oxon P=O, which reportedly resists further chlorine oxidation (Acero et al., 2008; Duirk et al., 2009).

3.2. Optimization of coagulant dose and comparative removal of the OPPs and the oxons by CSF and PAC-CSF

As practised during water treatment, coagulant ($Al_2(SO_4)_3$) dosage was optimized based mainly on the removal of natural organic material (NOM) of the raw natural water by measuring DOC and UV_{254}. The removal efficiencies of DOC and UV_{254} versus $Al_2(SO_4)_3$ dosage are shown in Fig. 2. For the CSF process, with the increase of the coagulant dosage from 15 to 120 μM, the removal efficiencies of NOM in terms of DOC and UV_{254} gradually increased from around 20%–74.6% and 77.3%, respectively, and then plateaued off with further increase of the coagulant up to 165 μM. A similar trend was observed for the PAC-CSF process in the removal of DOC and UV_{254}, but with only a marginally increased removal (0%–3.5%) than the CSF with addition of 10 mg/L PAC. The addition of PAC in the coagulation system did not promote NOM removal significantly, likely due to its molecular sizes being comparatively larger to the pore sizes of PAC (Humbert et al., 2008), since it can be seen below that the same amount of PAC addion increased OPP adsorption significantly. A coagulant dose of 120 μM as $Al_2(SO_4)_3$ which would produce a sweep coagulation for turbidity and NOM removal (Duan and Gregory, 2003) was selected, as the optimal coagulant dosage for the following experiments.

The removal efficiencies of OPPs and their oxons were also assessed at the optimum $Al_2(SO_4)_3$ dosage of 120 μM with and without concurrent addition of 10 mg/L PAC. The results are illustrated in Fig. 3. In the absence of PAC, the removal efficiencies for these pesticides and their oxons were small, from 2% to 18%. This indicates that coagulation by inorganic coagulant $Al_2(SO_4)_3$ alone was not sufficient in removing these pesticides. This observation is consistent with the previous studies, in which the removal efficiencies for most of the organic micropollutants through conventional CSF treatment were often limited except for those with high hydrophobicity (Snoeyink and Chen, 1985; Huerta-Fontela et al., 2008; Alexander et al., 2012). Also, a further increase in coagulant dose up to 165 μM above the optimum produced no further increase in the removal efficiency (data not shown). It has also been reported that organic micropollutants could be better removed by coagulation if they are very hydrophobic or associated with NOM polyelectrolytes or mineral particles in water (Snoeyink and Chen, 1985; Alexander et al., 2012). In comparison, removal efficiency of these pesticides was found to be greatly increased with the addition of 10 mg/L PAC together with $Al_2(SO_4)_3$ (Fig. 3). For example, the removal efficiency of malathion was increased from 5% to 38% with addition of PAC to the coagulation system. It appears that the OPPs with their smaller molecular size relative to the NOM could readily diffuse into small PAC pores to reach many more adsorption sites, resulting in a higher removal efficiency than the NOM polyelectrolytes (Li et al., 2003). Nevertheless, the present study showed that the oxidation transformation products of these pesticides, oxon analogues, have evidently lower removal efficiencies by PAC adsorption compared with their parent molecules (Fig. 3), though they have a relatively similar molecular size (Table 1). Generally, molecules with relatively larger size, and low solubility would exhibit a better adsorption capacity on activated carbon; but those with high polarity and short carbon chains would possess a weak adsorbability due to the reduced hydrophobic interactions between the adsorbates and surface of PAC (Dąbrowski et al., 2005; Lee et al., 2006; Huerta-Fontela et al., 2008). With comparatively greater polarity and smaller hydrophobicity (with lower log$K$ow) and higher water solubility (Table 1), the oxons would show a lower adsorption on PAC than the OPPs. Therefore, prechlorination of the OPPs could produce more toxic and less removable (via coagulation or PAC adsorption) byproducts. This would potentially create more problems rather than provide a solution for OPPs removal in view of treated water quality. Below, the effects of prechlorination on removal of the OPPs are investigated together with the removal of their oxons, at each of the treatment stages, particularly the PAC-CSF process since it produced physical removal for both of these two toxic chemicals.
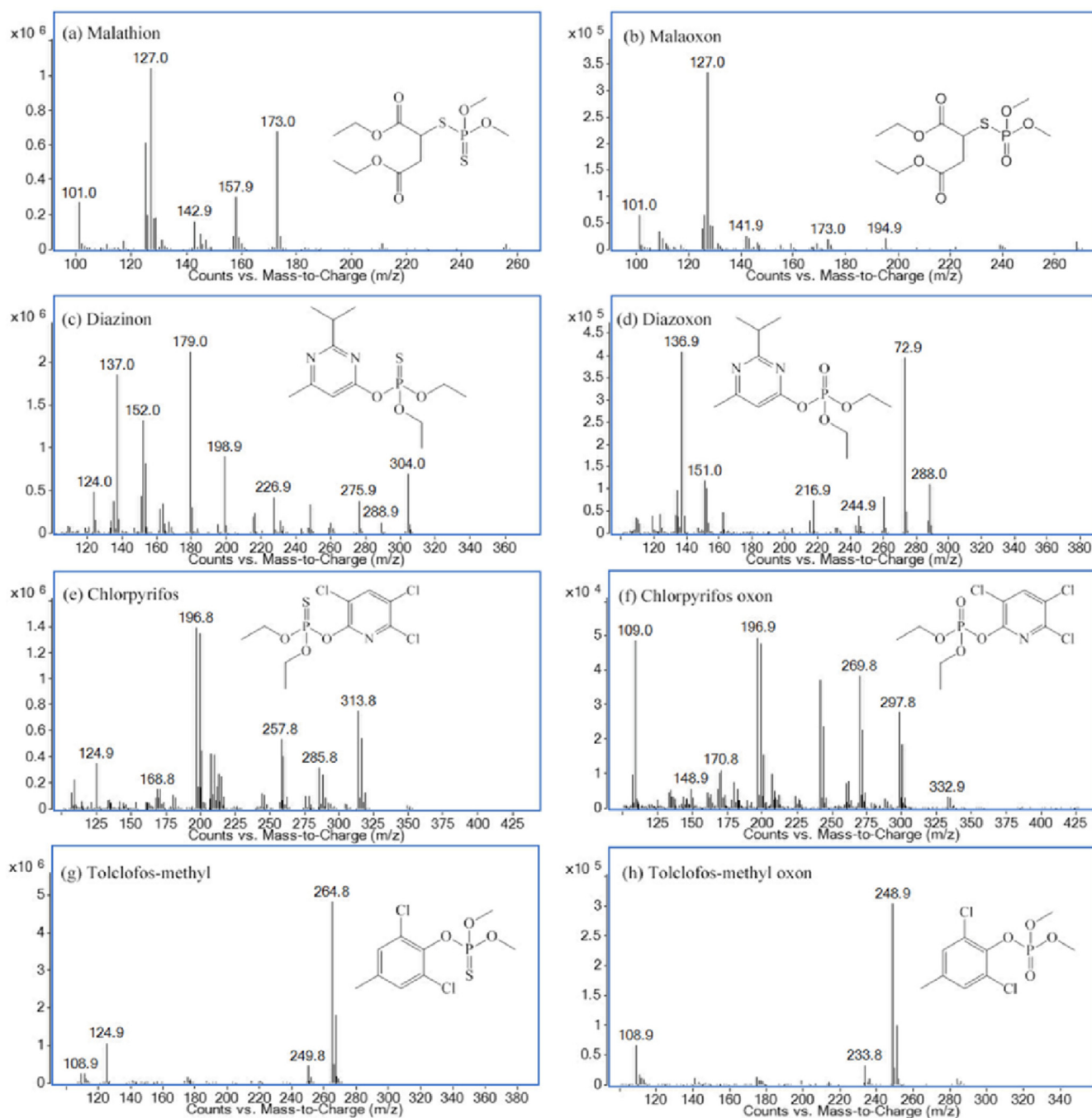
Fig. 1. The full scan mass spectra of the four OPPs and their corresponding oxons in EI mode, and their possible molecular structures according to the NIST Mass Spectral Database. (a) malathion; (b) malaoxon; (c) diazinon; (d) diazoxon; (e) chlorpyrifos; (f) chlorpyrifos oxon; (g) tolclofos-methyl; (h) tolclofos-methyl oxon.

3.3. Effects of prechlorination on transformation and removal of OPPs by PAC-CSF treatment and postchlorination

3.3.1. Effect of prechlorine dose

In water treatment, prechlorine dose varies according to raw water quality and treatment purposes. The effects of prechlorine dose in the range of 0–3 mg/L on the transformation of the four OPPs and removal of the OPPs and their transformation products (i.e. oxons) were investigated at the three treatment stages of prechlorination, PAC-CSF and postchlorination. The results are shown in Fig. 4. During prechlorination, it was found that the concentration of these OPPs in solution decreased with the increase

of prechlorine dose, while the concentrations of their oxons were increased correspondingly. At a low prechlorine dose ($\leq$0.75 mg/L), where there was no residual chlorine left in solution at the end of prechlorination (Fig. 4(a)), only a small percent of the OPPs was oxidised (e.g., for chlorine dose 0.75 mg/L, 24%, 31%, 12%, and 12% for malathion, diazinon, chlorpyrifos, and tolclofos methyl, respectively). As the prechlorine dose was further increased (>0.75 mg/L), the concentration of the four pesticides decreased greatly with a concomitant increase in the formation of the corresponding oxons in solution. For example, at a prechlorine dose of 3 mg/L, 80%, 88%, 43%, 31% of malathion, diazinon, chlorpyrifos, and tolclofos methyl was oxidised respectively. By comparison of the
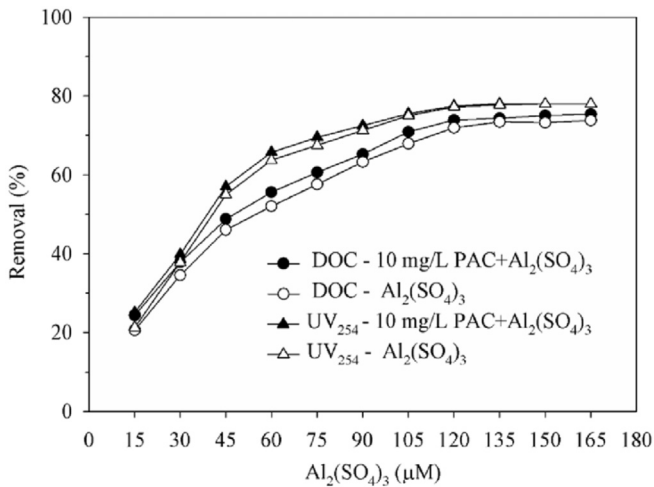
Fig. 2. Removal of DOC and UV_{254} at different $Al_2(SO_4)_3$ dosages with or without concurrent addition of 10 mg/L PAC.
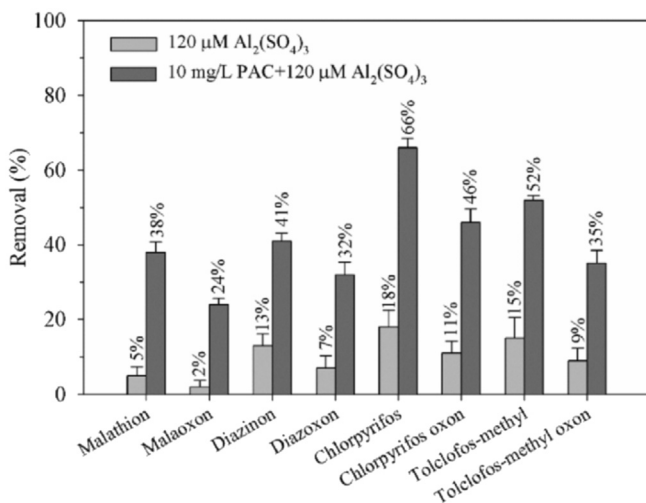

Fig. 3. The removal efficiencies of OPPs (initial concentration: 10 μg/L) and their oxons (initial concentration: 10 μg/L) at the optimal coagulant dosage in the absence and presence of 10 mg/L PAC.

oxidation efficiencies of the four OPPs, malathion and diazinon were found to be more chlorine-reactive than the two others. Previous studies showed that reaction rate coefficients of OPPs varied with the different OPP species, which were correlated with the proposed molecular descriptors within each subgroup of the OPP class (Duirk et al., 2009). Interestingly, the present study revealed that the transformation ratio of these OPPs from the parent molecules to their oxons ($[\Delta C_{oxon}]/[\Delta C_{opp}]$) also varied according to the different individual species. The average transformation ratios in the prechlorination process were: 90.4%, 78.7%, 93.8%, 97.2% for malathion, diazinon, chlorpyrifos and tolclofosmethyl, respectively (Table 3). Also, unlike the percentage of the oxidised OPPs, the transformation ratio only slightly declined with the increase of prechlorine dose. The differences in the transformation ratios between these OPPs were most likely caused by the difference in the formation of certain small reaction fragments other than the oxon, which were too small to be detected readily, under the conditions. Previously, it was reported that, although chlorpyrifos undergoes hydrolysis reactions, the rate of the reaction

is slow at the neutral pH condition (Duirk and Collette, 2006). In the present study, no hydrolysis reaction was detected when the four OPPs were dosed alone into the raw water sample (pH 7.3) after 12 h without the presence of chlorine (no data provided). It has been reported that, hypochlorous acid (HOCl, pK_a 7.5) could only oxidise OPPs into the corresponding oxons, while hypochlorite ion (OCl^-) could act as a nucleophile to promote OPP hydrolysis to form other fragmental species, especially at high pH values >9 (Duirk et al., 2009). Probably, the presence of small amounts of OCl^- ions in solution at the pH range (7.4–7.8, after prechlorination in the chlorine dose range) may have catalyzed the hydrolytic reactions, while the intensity of such catalytic effects varied with the individual OPP species. From the results, it appeared that diazinon had a stronger catalyzed hydrolysis reaction than the other three under the reaction conditions at the pH values. Consequently, the gross removal efficiency of diazinon and its oxon (diazoxon) was much more noticeable as compared to the other three in the prechlorination stage, especially at high chlorine dose during the prechlorination (Table 4). From the point of view of safe water supply, it is important to assess the total removal of each OPP together with its corresponding oxon from water, rather than only the parent OPP molecules. The gross removal efficiency (R_{Gross}, %) was calculated using Equation (1).

$$R_{Gross}(\%) = \frac{([OPP]_{start} + [Oxon]_{start}) - ([OPP]_{end} + [Oxon]_{end})}{[OPP]_{initial}} \times 100\%$$

(1)

Here $[OPP]_{start}$ and $[Oxon]_{start}$ are molar concentrations of OPP and the corresponding oxon at the start of each reaction stage, $[OPP]_{end}$ and $[Oxon]_{end}$ are molar concentrations of OPP and corresponding oxon at the end of each reaction stage, and $[OPP]_{initial}$ is the initial molar concentration of OPP added to the raw water. Total gross removal efficiency for a specific OPP is the sum of R_{Gross} at each reaction stage during the treatment processes.

Following prechlorination, during the PAC-CSF treatment, several reactions may be involved simultaneously: (i) coagulation and PAC adsorption of the parent OPPs and the corresponding oxons; (ii) oxidation of the OPPs and continuing formation of the oxons in solution; (iii) reaction of the OPPs adsorbed on the PAC surface with chlorine in solution (Ohno et al., 2008). From the experimental results (Fig. 4, the final pH at this stage is 6.5), the concentrations of the four OPPs declined as the prechlorine dose was increased at this treatment stage. In comparison, the concentration of oxons either slightly decreased or increased depending on the prechlorine dose and the individual OPP species. Interestingly, at a low prechlorine dose (0–0.75 mg/L), where there was no free residual chlorine in solution, removal efficiencies of the parent pesticides during the PAC-CSF were found to be decreased with the increase in prechlorine dose (Fig. 4). For example, the removal efficiencies of malathion by the PAC-CSF process (calculated as the difference between the two treatment stages of prechlorination and PAC-CSF) were at 38%, 32%, 27%, and 21% for prechlorine doses 0, 0.25, 0.5, and 0.75 mg/L, respectively (Fig. 4(a)). At the low prechlorine doses (i.e. 0–0.75 mg/L), the pesticides were apparently removed by coagulation and PAC adsorption rather than oxidation, since there was no free chlorine present in solution during the PAC-CSF treatment (Fig. 4(a)). The reasons for the reduced OPP removal efficiency may lie in the following two aspects. First, a reduced concentration of OPPs after prechlorination would lead to a lower rate of diffusion adsorption on PAC of the pesticide molecules (Humbert et al., 2008). Second, an amount of small organic byproducts or fragments might be produced in solution during
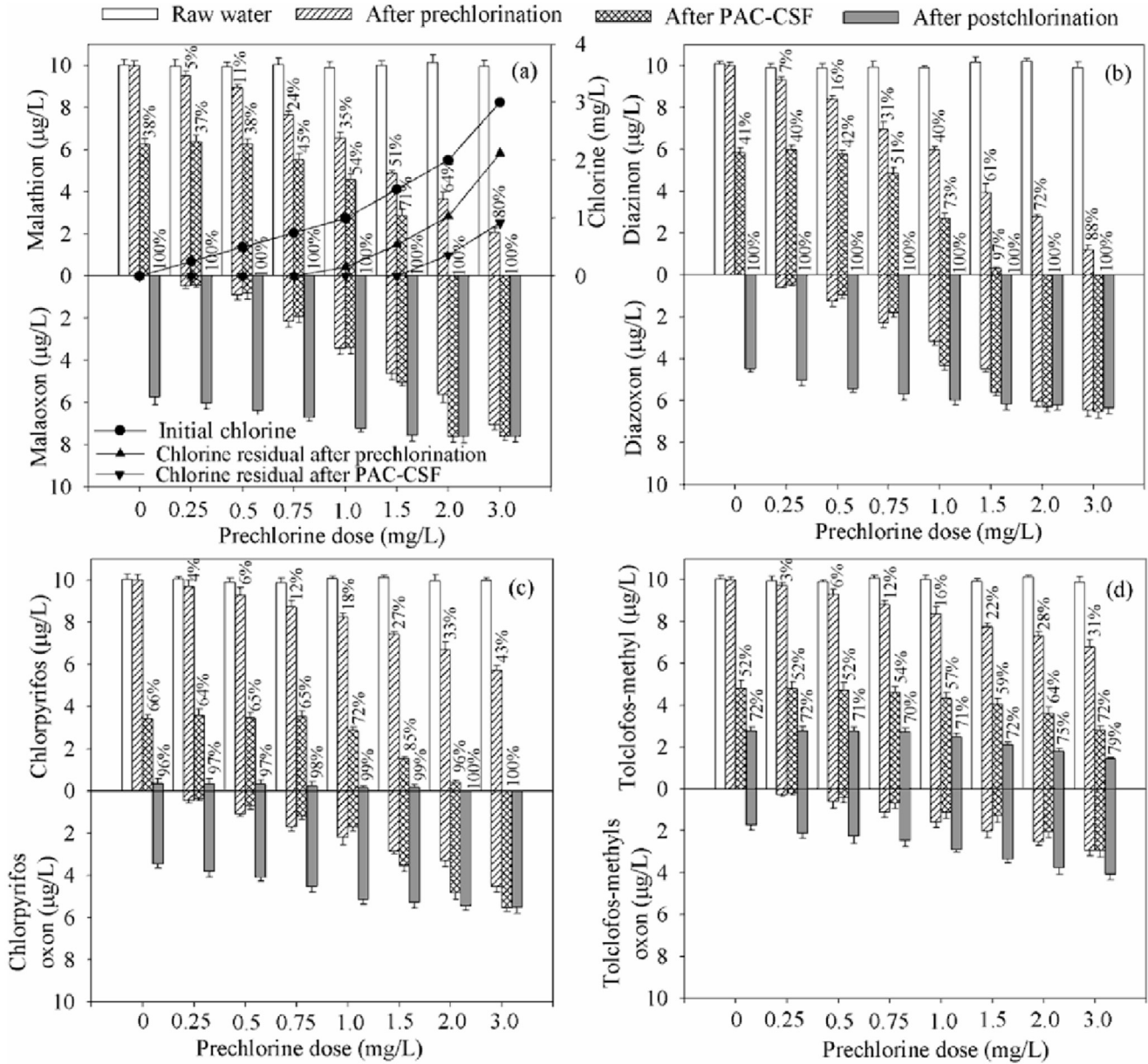
Fig. 4. The effect of initial prechlorine dose on the removal efficiency of the OPPs (initial concentration: 10 μg/L) and the formation of corresponding oxons during the simulated water treatment process. (a) malathion; (b) diazinon; (c) chlorpyrifos; (d) tolclofos-methyl.

Table 3
Molar transformation ratio of the four OPPs to their corresponding oxons during prechlorination and postchlorination.

Chlorine dose (mg/L)	Prechlorination				Chlorine dose (mg/L)	Postchlorination			
	Malathion	Diazinon	Chlorpyrifos	Tolclofos-methyl		Malathion	Diazinon	Chlorpyrifos	Tolclofos-methyl
0	–	–	–	–	1	89.6	80.1	92.7	96.6
0.25	94.2	81.8	102.2	103.6	1	92.8	80.5	94.9	95.8
0.5	90.2	84.6	94.7	98.4	1	93.2	81.3	88.6	97.6
0.75	89.6	77.1	93.1	98.1	1	90.9	83.5	93.6	97.4
1	92.1	80.2	92.5	96.8	1	87.7	73.6	94.6	95.3
1.5	90.7	72.0	96.9	93.3	1	92.9	79.6	90.6	106
2	86.8	81.2	94.6	96.0	1.36	–	–	95.8	97.2
3	89.4	73.9	95.9	94.5	1.91	–	–	–	93.1
Average values	90.4	78.7	94.6	97.2		91.5	79.7	93	97.5

Table 4
Gross removal efficiencies (R_{Gross}, %) for each OPP plus its corresponding oxon after prechlorination (Pre-Cl), PAC-CSF and postchlorination (Post-Cl).

Cl dose (mg/L)	R_{Gross} (%)															
	Malathion and oxon				Diazinon and oxon				Chlorpyrifos and oxon				Tolclofos-methyls and oxon			
	Pre-Cl	PAC-CSF	Post-Cl	Total	Pre-Cl	PAC-CSF	Post-Cl	Total	Pre-Cl	PAC-CSF	Post-Cl	Total	Pre-Cl	PAC-CSF	Post-Cl	Total
0	0.0	37.5	5.0	42.5	0.0	41.1	13.7	54.8	0.0	65.8	1.1	66.9	0.0	51.8	3.2	55.0
0.25	−0.2	32.0	7.4	39.2	0.4	35.3	14.1	49.8	1.3	61.6	1.3	64.2	−0.1	49.9	0.9	50.7
0.5	1.0	27.7	7.1	35.8	2.3	29.5	13.2	45.0	1.1	62.3	−2.4	61.0	0.1	48.2	1.1	49.4
0.75	2.5	23.3	7.4	33.2	6.9	25.8	10.1	42.8	1.4	57.7	0.6	59.7	1.5	46.0	0.5	48.0
1	−0.7	19.9	7.6	26.8	7.6	21.1	10.7	39.4	2.6	58.0	−3.9	56.7	0.5	44.7	2.0	47.2
1.5	4.7	16.2	3.3	24.2	15.7	24.9	−1.7	38.9	−0.7	51.1	1.7	52.1	1.7	45.0	−0.3	46.4
2	8.4	16.1	0.4	24.9	13.6	23.1	1.1	37.8	1.5	48.1	−2.2	47.4	3.1	41.0	2.1	46.2
3	8.5	15.1	0.2	23.8	23.0	11.0	0.2	34.2	−2.8	47.5	−0.4	44.3	1.7	40.4	1.9	44.0

prechlorination of NOM (Kim and Yu, 2005), which would compete for adsorption sites on the PAC with OPPs (Humbert et al., 2008; Hyung and Kim, 2008). Compared with the parent molecules, an even smaller removal efficiency for the corresponding oxons was seen and the concentration of the oxons at the low prechlorine dose was reduced only slightly after the PAC-CSF treatment process because of the limited removal capability by coagulation and PAC adsorption for the oxons as mentioned before (see Section 3.2 and Fig. 3).

As the prechlorine dose was increased to give an extra amount of free residual chlorine in solution after prechlorination (i.e.≥1 mg/L) (Fig. 4(a)), the continuing chlorination would occur during the PAC-CSF to create a complex effect on the OPPs oxidation and the oxon formation. With the increase of free residual chlorine in solution the concentrations of malathion, diazinon, chlorpyrifos and tolclofos-methyl dropped more sharply than at the low pre-chlorine doses, and concentrations of the oxons might increase or decrease depending presumably on the rate of their formation and coagulative removal and PAC adsorption during that time (Fig. 4(a–d)). For the more chlorine-reactive OPPs, such as malathion and diazinon, the parent pesticide molecules became undetectable in solution at prechlorine doses ≥2 mg/L (Fig. 4(a), (b)). For the less chlorine-reactive tolclofos-methyl, its concentration was still relatively high under the same condition (Fig. 4(d)). At a high prechlorine dose, the residual free chlorine would produce a continuing oxidation process for the OPPs remaining in solution during PAC-CSF after the prechlorination. This appeared to lead to a significant reduction of their concentration in solution and also a further formation of the oxons. As aforementioned, the overall removal and reaction processes of OPPs at this stage could involve several processes. Reaction of chlorine with PAC could reduce the PAC adsorption capacity for organic trace pollutants (Huang et al., 2007). Besides, pesticides adsorbed on PAC could also be oxidised to the corresponding oxons by free chlorine, and then possibly released from the adsorption sites back into solution, which could then undergo a readsorption process (Ohno et al., 2008). On the one hand, for the more chlorine-reactive and less adsorbable pesticides, such as malathion and diazinon, at the high chlorine doses the continuing chlorination at this stage becomes the predominant reaction mechanism. For these two pesticides, the parent molecules were effectively oxidised with a large amount of subsequent corresponding oxon formation; simultaneously concentrations of the oxons kept increasing with prechlorine dose until the parent molecules were depleted completely in solution (Fig. 4(a), (b)). On the other hand, for less chlorine-reactive and more adsorbable OPPs, such as tolclofos-methyl, coagulation and PAC adsorption becomes relatively more important for its removal. For this type of OPP, the amount of parent molecule removal was evidently greater than the amount of the corresponding oxon formation because of the relatively more effective adsorptive removal of the parent

molecule during PAC-CSF treatment (Fig. 4 (c) and (d)). Furthermore, due to the differences in the degree of oxidation and in the removal capacity by the coagulation and PAC adsorption between the different target OPP molecules, the gross removal efficiency (R_{Gross}) of a parent molecule together with its corresponding oxon for the more chlorine-reactive and less adsorbable pesticides (malathion and diazinon) was considerably smaller than that for the less chlorine-reactive and more adsorbable pesticides (tolclofos-methyls) during this treatment stage (See Table 4). Understandably, the higher the prechlorine dose the more the less coagulable and less adsorbable oxons formed in solution. As a result, R_{Gross} by the PAC-CSF decreased for all the pesticides as the prechlorine dose increased (Table 4).

In postchlorination, the final treatment stage, the chlorine oxidation of the OPPs seemed to be more effective in terms of oxidation of these pesticides and formation of their oxons (pH after postchlorination is at around 6.8) (Fig. 4). This may be because the contaminants competing with OPPs for free chlorine, such as NOM, in source water have been largely removed. For the more chlorine-reactive pesticides, malathion and diazinon, all of the parent molecules remaining in solution after the PAC-CSF were oxidised and could not be detected after 30 min postchlorination, regardless of the prechlorine dose. Meanwhile, the concentration of the corresponding oxons (malaoxon and diazoxon) increased according to the transformation ratio (Fig. 4, Table 3). Note that the transformation ratios are almost the same for both the prechlorination and postchlorinaiton. In comparison, the less chlorine-reactive tolclofos-methyl was not completely oxidised even after the postchlorination and the total concentration of oxons kept increasing as the prechlorine dose increased. The reasons for the continuing increase of oxons with prechlorine dose was that, at higher prechlorine doses more parent molecules were converted to the less adsorbable oxons, which reduced the gross removal efficiency of the parent pesticides and oxons during PAC-CSF treatment. Then postchlorination was able to oxidise the remaining parent OPPs and converted them into oxons. These, together with those previously formed, led to the overall increase of oxons in the final solutions. Since the oxons are much more toxic, this phenomenon is of importance for water treatment, particular for safe drinking water quality control.

Finally, there was a trend of decrease in the gross removal of the OPPs together with the corresponding oxons during postchlorination with the increase of prechlorine dose. As discussed above, the gross removal efficiencies are dependent on reactivity to chlorination and the adsorbability of the OPPs. The removal efficiency for the four pesticides is in the order: chlorpyrifos > tolclofos-methyl > diazinon > malathion. The most chlorine-reactive and least adsorbable malathion was the least removable of the pesticides. Based on the above observations, when preoxidation is applied in water treatment, attention must be

paid so that, not only is the degradation or removal of the OPPs ensured but the toxicity and concentration of the decomposed or converted products can be examined. Thus, treated water quality safety can be assessed accordingly. If the source water contains OPPs, the prechlorination and its continuing reactions in the subsequent processes could affect the corresponding transformation and the formation of the more toxic oxons. This could consequently affect the removal of these OPPs and their oxons from finished water, raising public health concerns.

3.3.2. Effect of initial pesticide concentration

The influence of the initial concentration of the four OPPs was investigated at a prechlorine dose of 0.9 mg/L (at which there was only a trace of negligible chlorine residual left in solution after the prechlorination). The results are shown in Fig. 5. It can be seen that the percentage of oxidation for the four OPPs decreased with the increase of OPP initial concentration during prechlorination. For example, a 27% reduction of tolclofos-methyl in solution was observed at 1 μg/L after prechlorination, while the value declined to 16% and 12% as the OPP concentration increased to 10 μg/L and 50 μg/L, respectively. Previously a greater removal efficiency of the pesticide antipyrine was reported at a lower initial concentration at a constant chlorine dosage (Cai et al., 2013). Since the transformation ratio is constant, a larger fraction of the OPPs were consequently oxidised to oxons at lower initial OPPs concentrations following pre-chlorination.

During the PAC-CSF treatment process, since there is no free residual chlorine, treatment mechanisms during the PAC-CSF treatment involved only coagulation and PAC adsorption. It was found that the reduction or removal percentage of the four OPPs at the small initial concentration of 1 μg/L was found clearly to be lower than those at 10 μg/L and 50 μg/L (Fig. 5). For example, the reduction in concentration of malathion during the PAC-CSF treatment was 8, 13 and 12% at the initial doses of 1, 10 and 50 μg/L, respectively. The observed phenomenon is in line with the previous study that, unless the initial concentration is very low, the percentage of micropollutant removal efficiency by adsorption would not change greatly with the initial micropollutant concentration at a given PAC dose (Knappe et al., 1998). From Fig. 5, by comparison of the reductions in OPP concentration during the PAC-CSF between the OPPs and their oxons, the removal of the oxons by PAC-CSF was not as effective as for their parent molecules. This is because the oxons are more hydrophilic and more water soluble as discussed before (see Section 3.2, Fig. 3).

During postchlorination, similarly to the trends in prechlorination, the total percentage concentration reduction of OPPs was decreased with the increase of initial concentration (Fig. 5). For example, at initial concentrations of 1 μg/L, malathion, diazinon and chlorpyrifos were almost not detected in solutions, indicating a complete oxidation or transformation of the OPPs to the corresponding oxons under the conditions (Fig. 5 (a)), while a small amount of these OPPs were detected in solution at a high initial concentration of 50 μg/L (Fig. 5 (c)). From the results of oxons detected in solutions after the postchlorination at the initial OPP concentrations of 1 μg/L, 10 μg/L and 50 μg/L, it can be calculated that a higher percentage of the corresponding oxons for each parent pesticide was observed at a lower initial concentration. This is largely due to a higher percent of OPPs being oxidised to the less adsorbable oxons at a lower concentration, resulting in a reduced physicochemical adsorptive removal during PAC-CSF, as aforementioned.

4. Conclusions

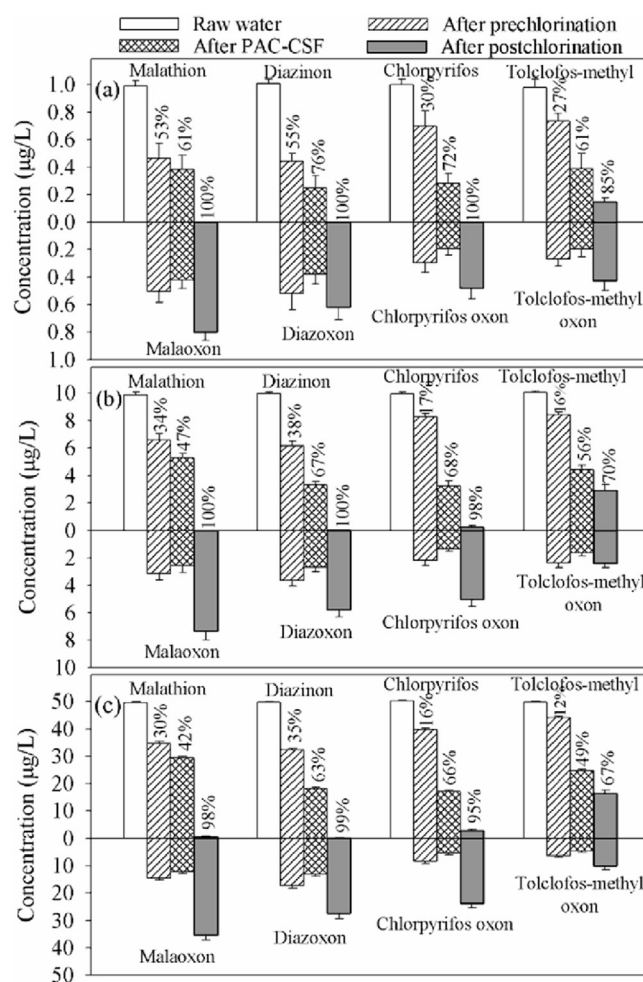This study investigated the effect of prechlorination on the

Fig. 5. The effect of initial OPPs concentration on the removal efficiency of the OPPs and the formation of corresponding oxons with the addition of 0.9 mg/L prechlorine. (a) 1 μg/L; (b) 10 μg/L; (c) 50 μg/L.

transformation and removal of four important OPPs in a simulated conventional drinking water treatment process, including prechlorination, PAC-CSF and postchlorination. During prechlorination, the oxidation efficiency of OPPs was increased with the increase of prechlorine dose. However, most of the chlorinated OPPs were transformed to the more toxic corresponding oxons. The oxons were less removable by the PAC-CSF because they are more hydrophilic and more water soluble than their parent OPP molecules. The transformation ratios of the OPPs to their oxons varied significantly with the individual species of the OPPs, but were only slightly affected by prechlorine dose. The ratios are found at 90.4%, 78.7%, 93.8%, 97.2% for malathion, diazinon, chlorpyrifos and tolclofos-methyl, respectively. The remaining fractions of the pesticides were probably hydrolyzed due to the OCl⁻ catalytic effect during the reaction time. The gross removal efficiencies of the pesticides together with the corresponding oxons from water were found to be dependent on their chlorine-reactivity and physicochemical absorbability during PAC-CSF treatment. Of the four pesticides, malathion and diazinon are more chlorine-reactive and less adsorbable by the PAC-CSF, while chlorpyrifos and tolclofos-methyl were less chlorine-reactive but more adsorbable. The gross removal efficiencies of malathion and diazinon together with their oxons were evidently lower than those for chlorpyrifos and tolclofos-methyl. A high percentage of these pesticides could end

up in their more toxic oxon forms in the treated drinking water, especially for the more chlorine-reactive and less adsorbable pesticides at higher prechlorine dose, creating potential problems for safe drinking water supply.

Acknowledgements

References

Acero, J.L., Benitez, F.J., Real, F.J., González, M., 2008. Chlorination of organophosphorus pesticides in natural waters. J. Hazard. Mater. 153 (1), 320–328.

Alexander, J.T., Hai, F.I., Al-aboud, T.M., 2012. Chemical coagulation-based processes for trace organic contaminant removal: current state and future potential. J. Environ. Manag. 111, 195–207.

American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), 2012. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.

Baldwin, C.J., 2012. Sustainability in the Food Industry. Wiley-Blackwell.

Cai, M., Zhang, L., Qi, F., Feng, L., 2013. Influencing factors and degradation products of antipyrine chlorination in water with free chlorine. J. Environ. Sci. 25 (1), 77–84.

Cole, T.B., Walter, B.J., Shih, D.M., Tward, A.D., Lusis, A.J., Timchalk, C., Richter, R.J., Costa, L.G., Furlong, C.E., 2005. Toxicity of chlorpyrifos and chlorpyrifos oxon in a transgenic mouse model of the human paraoxonase (PON1) Q192R polymorphism. Pharmacogenet. Genom. 15 (8), 589–598.

Coupe, R.H., Blomquist, J.D., 2004. Water-soluble pesticides in finished water of community water supplies. J. Am. Water Works Assoc. 96 (10), 56–68.

Dąbrowski, A., Podkościelny, P., Hubicki, Z., Barczak, M., 2005. Adsorption of phenolic compounds by activated carbon-a critical review. Chemosphere 58 (8), 1049–1070.

Duan, J., Gregory, J., 2003. Coagulation by hydrolysing metal salts. Adv. Colloid Interface Sci. 100, 475–502.

Duirk, S.E., Collette, T.W., 2006. Degradation of chlorpyrifos in aqueous chlorine solutions: pathways, kinetics, and modeling. Environ. Sci. Technol. 40 (2), 546–551.

Duirk, S.E., Desetto, L.M., Davis, G.M., 2009. Transformation of organophosphorus pesticides in the presence of aqueous chlorine: kinetics, pathways, and structure- activity relationships. Environ. Sci. Technol. 43 (7), 2335–2340.

Edzwald, J.K., 2011. Water Quality & Treatment: a Handbook on Drinking Water. McGraw-Hill, New York.

Fadaei, A., Dehghani, M.H., Nasseri, S., Mahvi, A.H., Rastkari, N., Shayeghi, M., 2012. Organophosphorous pesticides in surface water of Iran. Bull. Environ. Contam. Toxicol. 88 (6), 867–869.

Huang, W.J., Cheng, B.L., Cheng, Y.L., 2007. Adsorption of microcystin-LR by three types of activated carbon. J. Hazard. Mater. 141 (1), 115–122.

Huerta-Fontela, M., Galceran, M.T., Ventura, F., 2008. Stimulatory drugs of abuse in surface waters and their removal in a conventional drinking water treatment plant. Environ. Sci. Technol. 42 (18), 6809–6816.

Humbert, H., Gallard, H., Suty, H., Croué, J.P., 2008. Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC). Water Res. 42 (6), 1635–1643.

Hyung, H., Kim, J.H., 2008. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. Environ. Sci. Technol. 42 (12), 4416–4421.

Jiang, H., Adams, C., 2006. Treatability of chloro-s-triazines by conventional drinking water treatment technologies. Water Res. 40 (8), 1657–1667.

Kim, H.C., Yu, M.J., 2005. Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Res. 39 (19), 4779–4789.

Knappe, D.R., Matsui, Y., Snoeyink, V.L., Roche, P., Prados, M.J., Bourbigot, M.M., 1998. Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters. Environ. Sci. Technol. 32 (11), 1694–1698.

Konstantinou, I.K., Hela, D.G., Albanis, T.A., 2006. The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environ. Pollut. 141 (3), 555–570.

Larson, S.J., Capel, P.D., Majewski, M., 1997. Pesticides in Surface Waters: Distribution, Trends, and Governing Factors. CRC Press.

Lee, J.W., Choi, S.P., Thiruvenkatachari, R., Shim, W.G., Moon, H., 2006. Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes. Dyes Pigments 69 (3), 196–203.

Li, Q., Snoeyink, V.L., Mariãas, B.J., Campos, C., 2003. Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. Water Res. 37 (4), 773–784.

Li, W., Liu, Y., Duan, J., Saint, C.P., Mulcahy, D., 2015. The role of methanol addition to water samples in reducing analyte adsorption and matrix effects in liquid chromatography–tandem mass spectrometry. J. Chromatogr. A 1389, 76–84.

Mitra, A., Chatterjee, C., Mandal, F.B., 2011. Synthetic chemical pesticides and their effects on birds. Res. J. Environ. Toxicol. 5 (2), 81–96.

Ohno, K., Minami, T., Matsui, Y., Magara, Y., 2008. Effects of chlorine on organophosphorus pesticides adsorbed on activated carbon: desorption and oxon formation. Water Res. 42 (6), 1753–1759.

Rathore, H.S., Nollet, L.M., 2012. Pesticides: Evaluation of Environmental Pollution. CRC Press.

Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., Von Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313 (5790), 1072–1077.

Snoeyink, V., Chen, A., 1985. Removal of organic micropollutants by coagulation and adsorption. Sci. Total Environ. 47, 155–167.

Sparling, D., Fellers, G., 2007. Comparative toxicity of chlorpyrifos, diazinon, malathion and their oxon derivatives to larval Rana boylii. Environ. Pollut. 147 (3), 535–539.

Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., Reissman, D.B., 2004. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci. Total Environ. 329 (1), 99–113.

Sultatos, L.G., 1994. Mammalian toxicology of organophosphorus pesticides. J. Toxicol. Environ. Health 43, 271–289.

Tahara, M., Kubota, R., Nakazawa, H., Tokunaga, H., Nishimura, T., 2005. Use of cholinesterase activity as an indicator for the effects of combinations of organophosphorus pesticides in water from environmental sources. Water Res. 39 (20), 5112–5118.

United States Environmental Protection Agency (US EPA), 2007. Estimation Program Interface (EPI) Suite (EPI Suite™) Version 3.20. Office of Pollution Prevention and Toxics. USEPA, Washington, DC 20460. Available at: http://www.epa.gov/opptintr/exposure/pubs/episuite.htm.

US EPA Method 506, 1995. Determination of Phthalate and Adipate Esters in Drinking Water by Liquid-liquid Extraction or Liquid-solid Extraction and Gas Chromatography with Photoionization Detection revision 1.1. http://www.caslab.com/EPA-Method-506.

Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environ. Sci. Technol. 39 (17), 6649–6663.

Yuan, F., Hu, C., Hu, X., Qu, J., Yang, M., 2009. Degradation of selected pharmaceuticals in aqueous solution with UV and UV/H$_2$O$_2$. Water Res. 43 (6), 1766–1774.

Zhang, Q., Pehkonen, S.O., 1999. Oxidation of diazinon by aqueous chlorine: kinetics, mechanisms, and product studies. J. Agric. Food Chem. 47 (4), 1760–1766.