



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

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reported (Konstantinou et al., 2006; Fadaei et al., 2012). Toxicological and epidemiological studies have shown that traces of pesticide residues (at $\mu\text{g/L}$ 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 ($\text{P}=\text{S}$) (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 $\text{P}=\text{S}$ 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 $\text{P}=\text{S}$ bond in the parent molecules with an oxygen atom forming a phosphorus-oxygen double bond ($\text{P}=\text{O}$) 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 ($\log K_{ow}$) of these pesticides and their oxons are given in Table 1. Methanol (HPLC grade) was purchased from Merck Chemicals (Darmstadt, Germany). Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, analytical grade), sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, analytical grade), and sodium hypochlorite (NaClO , 5% of free active chlorine) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) 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 $150 \text{ }^\circ\text{C}$ 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 $803 \text{ m}^2/\text{g}$ and $0.542 \text{ cm}^3/\text{g}$, respectively.

GF/C (diameter 47 mm, pore size $1.2 \mu\text{m}$) and GF/D (diameter 47 mm, pore size $2.7 \mu\text{m}$) glass microfiber filters were purchased from Whatman Co. (Maidstone, Kent, UK). The polypropylene syringe filter (pore size $0.2 \mu\text{m}$, 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 $\text{Al}_2(\text{SO}_4)_3$ 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 $4 \text{ }^\circ\text{C}$.

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 $2.7 \mu\text{m}$ GF/D glass microfiber filter, and stored in amber glass bottles in a refrigerator at $4 \text{ }^\circ\text{C}$. 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 $10 \mu\text{M}$ for each of them. A high dose of sodium hypochlorite ($130 \mu\text{M}$ 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, $20 \mu\text{L}$ 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

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