

III. Appendices

E. Water Appendix

4. Water Exposure Assessment: Effects of Drinking Water Treatment on Organophosphate Pesticides

Summary

The weight of evidence from open literature and studies conducted by a registrant, an ORD/EPA laboratory investigation, and a USGS-EPA drinking water reservoir monitoring program show that parent organophosphorus (OP) insecticides in raw drinking water are removed or transformed during drinking water treatment. The most probable degradation pathway is chemical oxidation through chlorination, and in some cases, chemical water softening techniques may contribute to chemical degradation. In the USGS-EPA drinking water monitoring program, oxidation degradation products of organophosphorus pesticides, such as sulfones, sulfoxides, and oxons, have been detected in finished water samples from actual water treatment plants. Additionally, the drinking water reservoir monitoring data suggest that malathion degradation during the water treatment process may have led to malaoxon formation in some finished water samples. Studies have shown that oxons, which may be relatively stable in chlorinated drinking water for periods of 24 - 48 hours, are formed in chlorinated water under laboratory conditions. These data suggest that oxidative degradation products such as oxons, sulfones, and sulfoxides have a likelihood of occurrence in finished drinking water when organophosphorus pesticides are present in raw water.

a. Introduction

This section provides a critical review of the available data which was used to assess water treatment effects on removal and transformation of organophosphorus pesticides and certain degradation products. The review was conducted as an extension of the OPP water treatment literature review presented to a Federal Insecticide, Fungicide, and Rodenticide Act Scientific Advisory Panel (FIFRA SAP) (<http://www.epa.gov/scipoly/2000/september/sept-00-sap-dw-0907.pdf>). Documents in this report included information on the chemistry of chlorination and softening in different water treatment processes and their effects on organophosphorus pesticide degradation, registrant-sponsored water treatment data, and ORD/EPA water treatment data. In addition, water treatment effects are discussed in the USGS-OPP pilot reservoir monitoring section.

The effects of water treatment were evaluated with primary focus on disinfection by chlorination and softening. Chlorine treatment is widely used in the United States, and has been associated with the transformation of certain organophosphorus pesticides to products with toxicity and health concerns. Softening was also considered because organophosphorus pesticides have the potential to hydrolyze under alkaline conditions.

b. Drinking Water Disinfection

Disinfection of raw or untreated water for potable uses is a process that is used to eliminate disease-causing or pathogenic microorganisms. The pathogens are generally bacteria such as *Salmonella*, viruses such as *Poliovirus*, and protozoa such as *Cryptosporidium* and *Giardia*. These microorganisms can be destroyed by physical treatment (heat or boiling), ultraviolet (UV) radiation, and chemical treatment. UV radiation kills by photodegradation of nucleic acids in microorganisms while chemical treatment (chlorine or other oxidants) destroys the pathogens by oxidizing the cell walls. Other chemicals such as ozone, potassium permanganate, copper and silver ions, quaternary ammonium compounds, strong acids and bases can also inactivate microorganisms. In this report, however, the emphasis will be on disinfection by treatment with chlorine and chlorine compounds.

i. Treatment by Chlorine and Chlorine Compounds

Currently in the United States, chlorine and some of its compounds are commonly used for drinking water disinfection. By far, chlorine gas is the most widely used disinfectant in the water treatment utilities and can be also used for oxidizing iron, manganese, hydrogen sulfide, and for controlling tastes, odors, algae, and slime. In place of chlorine gas, other compounds such as sodium hypochlorite (NaClO), chlorine dioxide (ClO₂), and chloramines are also applied in other community water systems.

Chlorine: (Cl₂) is a dense gas typically shipped in pressurized tanks to water treatment facilities. It dissolves in water and undergoes hydrolysis or disproportionation as shown in equation. (1):



The hydrolysis rate is so rapid that the reaction is complete in less than a second. The product HOCl (hypochlorous acid) also hydrolyzes in water to form OCl⁻ (hypochlorite) according to eq.(2), with an acid dissociation constant (pKa) of 7.5. The pKa value suggests that at pH of 7.5, 50% of HOCl exists as HOCl and 50% as OCl⁻. At pH conditions commonly encountered in finished or treated waters (~ pH 6 - 9), molecular Cl₂ is not practically important. At pH > 3 and with chlorine dosage of 100 mg/L, very little or negligible Cl₂ is present. Consequently, the dependence of HOCl dissociation on pH and distribution between of HOCl and OCl⁻ are needed in understanding the efficiency of disinfection by chlorine treatment along with the chlorine effects on pesticides and other organic compounds. HOCl and OCl⁻ have considerably different capabilities of inactivating and destroying microorganisms. HOCl has a greater bactericidal efficiency than OCl⁻. The protonated species HOCl has been reported to be more reactive and has a higher oxidation efficiency than the unprotonated species OCl⁻. Thus, it is important to measure pH as a water quality parameter in water disinfection studies.

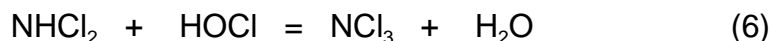
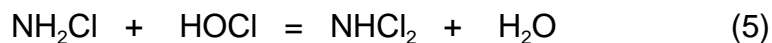
Hypochlorite: Sodium hypochlorite (NaClO) and occasionally calcium hypochlorite [Ca(ClO)₂] are used instead of chlorine gas for water disinfection. Both salts dissolve to form the hypochlorite ion which eventually hydrolyzes in water according to eq. (3):



With the formation of a strong base (OH⁻), the alkalinity of the water can be affected. One mole of NaClO or 0.5 mole of Ca(ClO)₂ will result in an increase of one equivalent of alkalinity. This becomes significant during superchlorination with hypochlorite in which a higher dose is used to achieve disinfection as well as remove iron and manganese and simultaneously control taste and odor.

Chlorine Dioxide: ClO₂, like chlorine, is a dense gas with chlorinous odor. However, unlike chlorine, it remains in a molecular form as ClO₂ in water and does not undergo hydrolysis. Once dissolved in water, it can be transformed under alkaline conditions to chlorite (ClO₂⁻¹) and chlorate (ClO₃⁻¹), both of which are undesirable in drinking water. It does not react with ammonia and does not form trihalomethanes, haloacetic acids, and other halogenated disinfection by-products typically associated with chlorine treatment. Disinfection/oxidation products identified from ClO₂ treatment include aldehydes and carboxylic acids, with low levels of some chlorinated compounds.

Chloramines: Dissolved ammonia present or intentionally added to water can react with hypochlorous acid or hypochlorite to form chloramines. The stepwise reactions can be represented as follows:



The products from reactions (4), (5), and (6) are respectively monochloramine, dichloramine, and trichloramine or nitrogen trichloride. These chloramines have relatively lower biocidal and oxidation efficiency. Collectively, the three chloramine species contribute to the combined chlorine residual. The relative amount of each chloramine depends on pH and molar or dose ratio of Cl:N. The free chlorine residual is associated with the concentration of HOCl or OCl⁻ or both. The total chlorine residual is taken as the sum of the free and combined chlorine residuals which can be analytically determined using procedures in Standard Methods of Analysis.

ii. Reactions of Chlorine with Organic Compounds and Pesticides

Chlorine gas and other chlorine compounds can react with chemicals dissolved in water to form different disinfection products. In the water treatment facilities, the reactions can be generally categorized as oxidation, substitution/addition, and dechlorination.

Oxidation: All the disinfectants used in the United States have the capacity to oxidize certain chemicals in raw or untreated water with varying efficiencies. These chemicals are reduced metal ions, aldehydes, ketones, alcohols, and other organic compounds that include pesticides. Aldehydes and ketones can be converted to carboxylic acids. Thiocarbamates can be transformed to sulfoxides, and eventually to sulfones.. The P=S bond of organophosphate pesticides (OPs) can be oxidized to P=O bond leading to the formation of oxon. Based on the available data, several OPs are transformed to their corresponding oxons (Magara et al (1994); Tierney, et al., 2000). For instance, diazinon is oxidized to diazoxon which is relatively stable in chlorinated water for about 48 hours.

Substitution/Addition Reactions: HOCl or OCl⁻¹ can also react with organic compounds by displacing chemical species and incorporating chlorine atoms. This reaction is responsible for the formation of trihalomethanes and haloacetic acids that are currently regulated under the Disinfection By-Products rule (DBP). Other by-products include chlorinated phenols, aromatic hydrocarbons, and alkenes. Pesticides may also undergo substitution/addition reaction with chlorine to form chlorinated products. Magara et al (1994) presented chlorine treatment effects data that show the transformation of thiobencarb to chlorobenzyl chloride, chlorobenzyl alcohol, chlorobenzyl aldehyde, and chlorobenzoic acid. Some of these treatment transformation products have been detected in a Japanese water purification facility.

Dechlorination: Occasionally, the level of chlorine residual may be high at the end of the treatment train. Thus, it is necessary to reduce the chlorine residual before the finished water is transported through the distribution system. This can be accomplished by dosing with compounds that can react with chlorine or increase the rate of decomposition of chlorine residual.

Compounds typically used for dechlorination include sulfur dioxide and reduced sulfur compounds such as sodium sulfite, bisulfite, and thiosulfate. In some instances, activated carbon can be used for dechlorination. Reactions of sulfur compounds such as sulfur dioxide generate acidic products (hydrochloric and sulfuric acids) that can decrease the alkalinity of the finished water.

c. Water Softening

Raw waters which are hard or those with high levels of calcium and magnesium are typically treated to reduce the concentrations of these two metal cations. This process, known as softening, can be achieved by the use of ion-exchange resins or precipitating agents. When lime and soda ash are added to water, the pH and carbonate alkalinity are increased which favor the precipitation of calcium as calcium carbonate and magnesium as magnesium hydroxide. Under this condition, the pH can increase to about 10 - 11 which can lead to base-catalyzed hydrolysis of pesticides such as organophosphate insecticides. OPs are generally hydrolyzed in the environment by nucleophilic substitution reactions. At pH 7 at 20⁰ C, the hydrolysis half-lives of certain OPs (Larson and Weber, 1994) are

Phosmet ----- 7.1 hours
Malathion ----- 10.5 days
Chlorpyrifos ----- 78 days
Parathion ----- 130 days

At softening pH of 10 -11 likely to be encountered in water treatment plants, hydrolysis rates would be expected to proceed much faster especially for phosmet and malathion.

d. Additional Water Treatment Data on Organophosphate Pesticide Removal and Transformation

ORD Laboratory Study. U.S. EPA. 2001. Laboratory Study on Chlorination and Softening Effects on Pesticide Residues in Drinking Water. Work Assignment (1-22) between EFED and ORD.

A laboratory study was conducted to determine the effects of chlorination and softening on certain pesticides by EPA's AWBERC in Cincinnati, OH. Chlorpyrifos-methyl was one of the pesticides used in the chlorination experiment. Malathion and phorate were used in the softening experiment.

i. Chlorination Jar Test

Well water was taken from a treatment plant in Ohio and then subsequently used in the jar experiments for evaluating the effects of chlorination of several pesticides, including chlorpyrifos-methyl. The test water was spiked with about 20 - 100 ug/L of pesticides from the prepared stock solutions. The chlorination was done under Uniform Formation Conditions (U.C.): pH 8.0 ± 0.2 ; temperature of $20.0 \pm .0^{\circ}\text{C}$; dark incubation time of 24 ± 1 hr.; chlorine residual of 1.0 ± 0.4 mg/L as free chlorine after 24 hr. The samples were dosed with hypochlorite-buffer solution. After the test, the samples was quenched prior to analysis. Chlorpyrifos-methyl, along with the other pesticides, was analyzed according to Method 525.2 (GC/MS). The method detection limit (MDL) for chlorpyrifos-methyl was 0.025 ug/L.

ii. Softening Jar Test

Well water used in the chlorination test was also used in the water softening experiment. The raw water was spiked with < 20 to 300 ug/L of pesticides that include 2 OPs, malathion and phorate. Hardness was reduced by treating the raw water with 150 and 300 mg/L of lime which corresponded to conventional and magnesium softening conditions at about 20°C . Water was exposed to lime 2 hr. before water samples were analyzed using Method 525.2 (GC/MS). The MDLs for malathion and phorate were 0.015 and 0.050 ug/L, respectively.

iii. Results

The well water used in both tests was analyzed for basic water quality parameters. The results of two analyses are summarized in Table III.E.4.1. The water is slightly alkaline and has high hardness.

Table III.E.4.1. Water Quality Parameters Used in the USEPA ORD Laboratory Studies

Parameter	Sample I	Sample II
Hardness (mg/L as CaCO ₃)	315	293
pH	7.44	7.78
Temperature (C ^o)	23.6	23.6
Alkalinity (mg/L as CaCO ₃)	220	230
Turbidity (NTU*)	2.7	1.4
TOC** (mg/L)	1.39	1.36

*NTU=Nephelometric Turbidity Unit

**TOC=Total Organic Carbon

Table III.E.4.2 shows the results of the chlorination and softening jar tests for the 3 OPs. The concentrations represent the mean value of three replicates. About 90% of chlorpyrifos-methyl was removed by chlorine treatment. The reduction in pesticide concentration is most probably due to oxidation of the insecticide to oxons and other products. During softening, relatively higher removal efficiencies were observed in the 300 mg/L treatment than those in the 150 mg/L treatment. More than 99 % of malathion was removed. Lower removal (20%) of phorate was observed. It is believed that alkaline hydrolysis was responsible for the significant concentration reduction of malathion.

Table III.E.4.1. Effects of Chlorination and Softening on OP Pesticides in the USEPA ORD Laboratory Studies

Chlorination	Mean Concentration (ug/L)			% Removal
	Control		Treated	
	t=0	t=24		
Chlorpyrifos-methyl	45	43	<5	> 89*

Softening	Mean Concentration (µg / L)				% Removal	
	Control		150 mg/L	300 mg/L	150 mg/L	300 mg/L
	t=0	t=24				
Malathion	320	320	75	<2	73*	>99*
Phorate	74	75	73	62	2	17*

*Significantly lower than controls at 95%

e. Registrant Sponsored Water Treatment Data

Tierney, D.P., B.R. Christensen, and V.C. Culpepper. 2001. Chlorine Degradation of Six Organophosphorus Insecticides and Four Oxons in Drinking Water Matrix. Submitted by Syngenta Crop Protection, Inc. Greensboro, NC. Performed by Syngenta Crop Protection, En-fate, LLC., and EASI Laboratory.

i. Review Comments

Syngenta Crop Protection provided data which indicate that organophosphorus pesticides (acephate, azinphos-methyl, chlorpyrifos, diazinon, malathion, and methamidophos) are transformed in chlorinated drinking water. Chemical oxidation of the organophosphorus compounds led to the formation of oxons for azinphos-methyl, chlorpyrifos, diazinon, and malathion. The oxons were more stable than their parent organophosphorus pesticides.

Degradation of oxons was attributed to non-chlorine degradation processes and/or hydrolysis. The reviewer notes that chloramines were formed during the experiment. Because chloramines have lower oxidizing potential than hypochlorous acid, the extent of degradation and formation of oxidative degradation products (oxons) may be different under conditions of equivalent or higher free chlorine concentrations.

Preliminary review of this recently submitted data reveals that the following data are needed on experimental method and conditions for a complete Agency review:

Water quality data were not provided in the report. There are no data to assess the impact of sodium thiosulfate on water chemistry. There was differential treatment of control and treatment samples with sodium thiosulfate. Incomplete storage stability data were presented in the report.

ii. Study Objective

The study was designed to assess the impact of chlorine on the degradation of six organophosphorus pesticides (acephate, azinphos-methyl, chlorpyrifos, diazinon, malathion, and methamidophos) and certain transformation products (azinphos-methyl oxon, chlorpyrifos oxon, diazinon oxon, and malathion oxon).

Study 1: Organophosphorus Pesticides and Certain Degradation Products (azinphos-methyl, chlorpyrifos, diazinon, malathion, azinphos-methyl oxon, chlorpyrifos oxon, diazinon oxon, and malathion oxon)

Twenty liter samples of treated drinking water from the Jefferson Parish Louisiana Water Treatment Plant were amended with sodium hypochlorite to yield total residual chlorine concentrations of 1.9 mg/L and 4.1 mg/L. Each bulk water sample was fortified with a working standard mixture of organophosphorus pesticides or organophosphorus degradation products to yield pesticide concentrations of 0.500 ug/L (500 ng/L).

Treatment controls were prepared using a 10 liter sample of finished drinking water from the Jefferson Parish Louisiana Water Treatment Plant. The water sample was amended with sodium hypochlorite to yield a total chlorine residual of 2 mg/L. The total chlorine in the water sample was removed through quenching with 3 grams sodium thiosulfate. A chlorine analysis of the water sample confirmed removal of residual chlorine.

Pesticide fortified water and treatment controls were partitioned into separate 1 liter borosilicate glass jars. The experimental design consisted of 5 sampling times (0, 15 minutes, 30 minutes, 60 minutes, and 24 hours) and 3 chlorine concentrations (treatment control (no chlorine), 2.0 mg/L, and 4 mg/L) and 3 replicates. Treatment controls had 3 replicate for the 0 and 24 hours sampling interval. At each sampling time, the chlorine residual in each 1 liter sample was removed through quenching with ~300 mg of sodium thiosulfate. Residual chlorine removal was verified in a single sample fortified with 4.0 mg/L chlorine.

At each sampling time, replicates samples were refrigerated at 4°C prior to extraction. Samples were extracted using C-18 solid phase extraction disks and analyzed using gas chromatography/mass spectrometry. The limit of detection (LOD) and limit of quantitation (LOQ) were 0.01 ug/L and 0.05 ug/L, respectively. The registrant stated that all concentrations less than the LOQ were considered as non-detections. Quality assurance and control measures were implemented. Each analysis group of 20 samples consisted of experimental samples, method blank, matrix blank, matrix spike at 0.500 ug/L and duplicate matrix spike.

Diazinon, chlorpyrifos, and azinphos methyl were stable in nonchlorinated control water. Malathion, diazinon oxon, chlorpyrifos oxon, malathion oxon, and azinphos methyl oxon had statistically significant ($p=0.05$) degradation in the control water. After 24 hours, the percent remaining was 97% for diazinon, 96% for chlorpyrifos, 76% for malathion, 90% for azinphos-methyl, 90% for diazinon oxon, 85% for chlorpyrifos oxon, 55% for malathion oxon, and 62% for azinphos methyl oxon. The registrant stated the observed degradation may be due to non-chlorine degradation processes and/or hydrolysis.

There was partial degradation of parent organophosphorus insecticides in the 2 mg/L of total chlorine treatment. After 24 hours, the percent parent remaining was 47% for diazinon, 53% for chlorpyrifos, 53% for malathion, and 51% for azinphos methyl. Oxon formation was observed from parent organophosphorus insecticide degradation. Oxon formation, expressed as percent of parent concentration, was 30% for diazinon oxon, 20% for chlorpyrifos oxon, 15% for malathion oxon, and 10% for azinphos methyl oxon. Oxon degradation (21 to 40% of the peak concentration) was observed in the 2 mg/L total chlorine treatment after 24 hours.

Complete degradation of parent organophosphorus compounds occurred in the 4 mg/L total chlorine treatment. The degradation was complete within 30 minutes. Oxidative degradation of parent compounds led to the formation of oxons. Peak oxon concentrations were 60% of diazinon, 74% of chlorpyrifos, 64% of malathion, and 31% of azinphos methyl. Oxon degradation appeared to be partially dependent on oxidation from chlorine. Diazinon oxon and chlorpyrifos oxon had significant degradation in the 4 mg/L chlorination treatment. Malathion oxon and azinphos methyl degradation was not significantly different than the treatment control.

Study 2: Acephate and Methamidophos

Chlorine degradation studies for acephate and methamidophos were conducted using similar procedures as described above. The experimental methods were similar to the previously described study (Study 1) except for the experimental design, pesticide fortification process and analytical methods. Because acephate degrades to form methamidophos, chlorine degradation studies were conducted for the individual compounds rather than a mixture of the two. The pesticide fortification method was different because an acetone co-solvent was used in the working standard solution. The acetone co-solvent was allowed to evaporate prior to reconstitution in deionized water. The reconstituted solution was used to fortify bulk water samples. At each sampling time, replicates samples were refrigerated at 4°C prior to extraction.

At each sampling time, the replicate samples were refrigerated at 4°C prior to extraction. Samples were extracted using AC-2 graphitized solid phase extraction tubes and analyzed using gas chromatography/flame photometric detection. The LOD and LOQ were 0.01 ug/L and 0.05 ug/L, respectively. The registrant stated all concentrations less than the LOQ were considered as non-detections.

Methamidophos and acephate degraded in control water by 14% and 7%, respectively, during a 24 hour incubation period. In the 2 mg/L chlorine treatment, both compounds degraded by ~40% during a 24 incubation period. Acephate and methamidophos were completely degraded within 15 minutes and 24 hours, respectively. Methamidophos was not identified as an oxidative degradation product of acephate.