

III. Appendices

E. Water Appendix

4. Effects of Drinking Water Treatment on Organophosphate Pesticides

The weight of evidence from open literature and studies conducted by a registrant, an ORD/EPA laboratory investigation, and the USGS-EPA drinking water reservoir monitoring program (Appendix III.E.3) 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 pilot reservoir monitoring program, oxidation degradation products of OP 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. Laboratory studies have shown that oxons, which may be relatively stable in chlorinated drinking water for periods of at least 24 - 48 hours, are formed in chlorinated water. 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 that was used to assess water treatment effects on removal and transformation of organophosphorus pesticides and certain degradation products. This 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, or chemical treatment. UV radiation kills by photodegradation of nucleic acids in microorganisms while chemical treatment (chlorine or other oxidants) destroys 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 its related compounds are commonly used for drinking water disinfection. By far, chlorine gas is the most widely used disinfectant in water treatment utilities and also can be used for oxidizing iron, manganese and hydrogen sulfide, and for controlling tastes, odors, algae, and slime. Other compounds, such as sodium hypochlorite (NaClO), chlorine dioxide (ClO₂), and chloramines may be used in place of chlorine gas 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 order to understand 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.

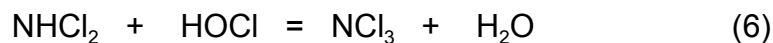
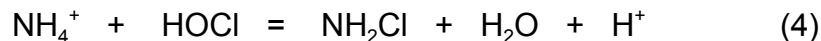
Hypochlorite: Sodium hypochlorite (NaClO) and occasionally calcium hypochlorite [$\text{Ca}(\text{ClO})_2$] are used instead of chlorine gas for water disinfection. Both salts dissolve to form the hypochlorite ion which eventually hydrolyzes in water according to eq. (3):



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 $\text{Ca}(\text{ClO})_2$ 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: ClO_2 , like chlorine, is a dense gas with chlorinous odor. However, unlike chlorine, it remains in a molecular form as ClO_2 in water and does not undergo hydrolysis. Once dissolved in water, it can be transformed under alkaline conditions to chlorite (ClO_2^-) and chlorate (ClO_3^-), 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 ClO_2 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^{-1} 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, leading 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 20^o C, the hydrolysis half-lives of certain OPs (Larson and Weber, 1994) are follows:

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. EPA/ORD Studies on OP Pesticide Removal and Transformation by Water Treatment

EPA/ORD's AWBERC laboratory in Cincinnati, OH, conducted a laboratory study to determine the effects of chlorination and softening on certain pesticides [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.] 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 performed under Uniform Formation Conditions (UFC): pH 8.0 ± 0.2; temperature of 20.0 ± .0^oC; 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 were quenched with sodium sulfite prior to analysis. Chlorpyrifos-methyl, along with the other pesticides, was analyzed according to Method 525.2 (GC/MS), which has a method detection limit (MDL) of 0.025 for chlorpyrifos-methyl.

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 50 and 300 mg/L of lime which corresponded to conventional magnesium softening conditions at about 20°C. Water was exposed to lime for 3 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. The softening experiment was conducted with 3 replicates for each pesticide.

iii. Summary of Results

The well water used in both tests was analyzed for basic water quality parameters and the results are summarized in Table III.E.4.1. The water was slightly alkaline and had high hardness.

Table III.E.4.1. Raw Water Quality Characteristics 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°)	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 OP's. The concentrations represent the mean value of four replicates for chlorination studies and three replicates for softening studies. 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, while phorate removal was lower (20%). 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

Syngenta Crop Protection submitted a study to OPP in 2001 that evaluated the effect of chlorination on six OP pesticides and four of their oxon transformation products [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.]. The results of the study are difficult to interpret because the study does not contain water quality data, appropriate treatment controls, and a complete description of sample storage data.

The data indicate that the six OP 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, and degradation of oxons was attributed to non-chlorine degradation processes and/or hydrolysis. Chloramines were formed during the experiment. Because chloramines have a 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.

i. Study Design

The study was designed to assess the impact of total residual 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: OP Pesticides and Oxon Transformation Products (azinphos-methyl, chlorpyrifos, diazinon, malathion, azinphos-methyl oxon, chlorpyrifos oxon, diazinon oxon, and malathion oxon)

Twenty liter samples of dechlorinated treated drinking water (total residual chlorine concentration=0.02 mg/L as Cl_2) from the Jefferson Parish Louisiana Water Treatment Plant were treated with sodium hypochlorite to yield total residual chlorine (Cl_2) concentrations of 1.9 mg/L and 4.1 mg/L. The free chlorine concentration for the 1.9 mg/L and 4.1 mg/L chlorine treatments was < LOD and ~2 mg/L, respectively. 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 by quenching with 300 mg/L of 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. Three replicates were used for each 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). 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, while malathion, diazinon oxon, chlorpyrifos oxon, malathion oxon, and azinphos methyl oxon had degraded significantly ($p=0.05$) 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 that observed degradation may be due to non-chlorine degradation processes and/or hydrolysis. The pre-treated test water was 7.24.

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.

Degradation of parent to oxons was observed and expressed as percent of parent concentration as follows: 1) 30% for diazinon oxon, 2) 20% for chlorpyrifos oxon, 3) 15% for malathion oxon, and 4) 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 where degradation was complete within 30 minutes. Oxidative degradation of parent compounds led to the formation of oxons with peak oxon concentrations were 60% for diazinon, 74% for chlorpyrifos, 64% for malathion, and 31% for 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 design were similar to the previously described study

(Study 1). Modification in the experimental design are associated with the 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, 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.

ii. Uncertainties in Study

Water quality data, which are essential for understanding the water chemistry, were not provided in the report. Important water quality parameters include pH, hardness, alkalinity, total organic carbon content, and concentrations of free chlorine, residual chlorine, NH_4^+ , Na^+ , Ca^{+2} , Mg^{+2} , SO_4^{-2} , Cl^- , NO_2^- , Br^- and F^- . The Agency needs these data to confirm the registrant's claim that ammonium concentrations in tap water led to the formation of chloramines. The only available water quality data for test waters was pH (7.24). The registrant also submitted partial water quality data which was unitless for alkalinity, hardness, total solids, and fluoride for raw and treated water at the Jefferson Parish water treatment plant. The lack of units prevents use of the water quality data.

There are no data or adequate treatment control to assess the impact of sodium thiosulfate on water chemistry. The treatment control water was treated with 2 mg/L chlorine and then quenched with 300 mg/L sodium thiosulfate. The study did not include a similar sodium thiosulfate treatment regime in the chlorine treatments and a control water sample without sodium thiosulfate. The Agency recommends that treatment control water be treated in the same manner as the water used in chlorine treatments. The addition of sodium thiosulfate in the treatment

control confounds interpretation of the data when compared to the chlorine treatments. Additionally, the lack of treatment control (without sodium thiosulfate) limits the ability to assess the impact of sodium thiosulfate on water chemistry.

Storage stability data used to compute average recovery were incomplete. The registrant claim that average percent recoveries ranged from 80 to 165% for extract storage times greater than 40 days. The registrant submitted additional data on matrix spike recoveries to substantiate the stability of analytes in extracts. Sample extracts were stored for two months prior to chemical analysis. Registrant calculated average matrix spike recoveries ranged from 59 to 83% for the C-18 method and 52 to 108% for the GC/PFD method. The relative percent difference (RPD) for duplicate matrix spikes ranged from 1 to 12% for the C-18 method and 8% to 48% for the GC/PFD method. Based on performance standards, matrix spike recoveries for the C-18 and GC/PFD methods should range from 70 to 120%. These data indicated that analytical recoveries in matrix spikes for most analytes (exceptions chlorpyrifos oxon and methamidophos) could be explained by analytical method performance. Low mean recoveries for chlorpyrifos oxon and methamidophos, however, could not be explained by the method performance alone. The Agency believes the low recoveries of chlorpyrifos oxon and methamidophos suggest that degradation or some other factor contributed to low recoveries in matrix spike samples.