III. Appendices

E. Water Appendix

3. Analysis of the USGS-EPA Pilot Reservoir Monitoring Program

a. Introduction

A pilot reservoir monitoring project initiated by the USEPA's Office of Pesticide Programs (EFED/OPP) and Office of Ground Water and Drinking Water (OGWDW), and USGS National Water Quality Assessment (USGS/NAWQA) assessed pesticide concentrations in raw and finished drinking water (Blomquist et al. 2001). Reservoirs were sampled because they are important sources of drinking water and because they store runoff water and pesticide loadings within their watersheds. Twelve water-supply reservoirs (Figure III.E.3-1) and Community Water Systems (CWSs) were selected based on general vulnerability for pesticide contamination. Selection criteria included small watersheds with high pesticide use and high runoff potential, representation across pesticide use areas, integration with ongoing monitoring efforts, and feasibility of monitoring.

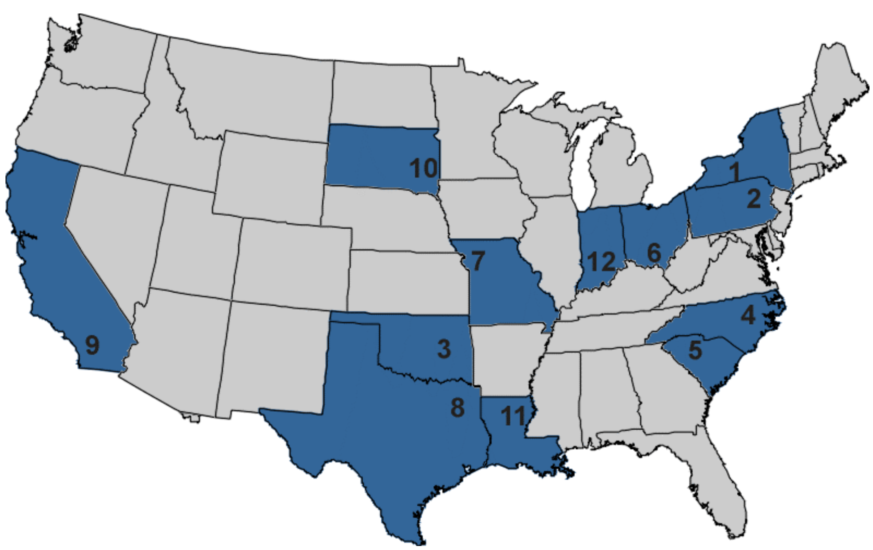

Figure III.E.3-1: Location of Reservoirs in Pilot Monitoring Program

Samples from raw and treated (finished) drinking water and the reservoir outflow provide an integrated water concentration for the reservoir watershed. For each site visit, three samples were collected: 1) raw water from the intake spigot of the public water system, 2) finished water from the compliance tap at the entry point to the distribution center, and 3) ambient reservoir water sample at the reservoir outlet. Samples were taken bi-weekly during the period of intensive pesticide use, such as the post-pesticide application season, and quarterly beyond the four- month post-application period. Two sites were sampled at weekly intervals for six months after the application season to improve the estimate of peak concentrations for short-lived compounds. Raw and finished drinking water samples were taken at most sampling times and analyzed using the USGS analytical schedules 2001, 9060, and 9002. Finished water samples were not quenched to eliminate chemical oxidation from residual chlorine. Out of 186 pesticides and degradation products analyzed, 46 were organophosphorus (OP) pesticides and their degradation products (Table III.E.3.1).

Table III.E.3.1. Organophosphorus pesticides and degradation products included in the reservoir study, USGS Analytical Schedules (2001 and 9002).

PESTICIDE	IUPAC NAME	DEGRADATES
Azinphos-methyl	S-(3,4-dihydro-4-oxobenzo[d]-[1,2,3]-triazin-3-ylmethyl) O,O-dimethyl phosphorodithioate	Azinphos-methyl-oxon
Chlorpyrifos	O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate	Chlorpyrifos, oxygen analog
Diazinon	O,O-diethyl-O-2-isopropyl -6-methylpyrimidin-4-yl phosphorothioate	
Disulfoton	O,O-diethyl S-2-ethylthioethyl phosphoro-dithioate	Disulfoton sulfone, Disulfoton sulfoxide
Ethoprop	O-ethyl S,S-dipropyl phosphorodithioate	O-ethyl-O-methyl-S-propylphosphorodithioate, Ethoprop metabolite 76960
Fonofos	O-ethyl S-phenyl (RS)-ethylphosphonodithioate	Fonofos, oxygen analog
Malathion	diethyl (dimethoxy-thiophosphorylthio) succinate	Malaoxon
Parathion	O,O-diethyl O-4-nitrophenyl phosphorothioate	Paraoxon-ethyl
Parathion-methyl	O,O-dimethyl O-4-nitrophenyl phosphorothioate	Paraoxon-methyl
Phorate	O,O-diethyl S-ethylthiomethyl phosphoro-dithioate	Phorate oxygen analog
Phosmet	O,O-dimethyl S-phthalimidomethyl phosphorodithioate	Phosmet oxon
Methidathion (Supracide)	S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate	
Profenofos	O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate	
Sulprofos (Bolstar)	O-ethyl O-4-(methylthio)phenyl S-propyl phosphorodithioate	
Terbufos	S-tert-butylthiomethyl O,O-diethyl phosphorodithioate	Terbufos-O-analogue sulfon
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate	

PESTICIDE	IUPAC NAME	DEGRADATES
Ethion	O,O,O,O-tetraethyl S,S-methylene bis(phosphorodithioate)	Ethion monoxon
Fenamiphos	ethyl 4-methylthio-m-tolyl isopropylphosphoramidate	Fenamiphos sulfone, Fenamiphos sulfoxide
Tebupirimphos (phostebupirim)		Tebupirimphos oxygen analog
Dicrotophos	3-dimethoxyphosphinoyloxy-N,N-dimethylisocr otonamide	
fenthion	O,O-dimethyl O-4-methylthio-m-tolyl phosphorothioate	Fenthion sulfone, Fenthion sulfoxide
Isofenphos	O-ethyl O-2-isopropoxycarbonylphenyl isopropylphosphoramidothioate	
Temephos	O,O,O,O-tetramethyl O,O-thiodi-p-phenylene diphosphorothioate	
Tribufos	S,S,S-tributyl phosphorotrithioate	
Propetamphos	(E)-O-2-isopropoxycarbonyl-1-methylvinyl O-methyl ethylphosphoramidothioate	
Dichlorvos	2,2-dichlorovinyl dimethyl phosphate	
Sulfotep	O,O,O,O-tetraethyl dithiopyrophosphate	

Ancillary data were also collected for each site to obtain information on watershed properties, water treatment information, and reservoir characteristics. The major cropping patterns in each reservoir watershed are shown in Table III.E.3.2.

Table III.E.3.2: List of Major Crops in Watersheds of Selected Reservoirs in the Reservoir Monitoring Study

State	Cropping Pattern
MO	Not available
TX	Cotton
OH	Corn / soybeans
OK	Not available
CA	Urban / Suburban
IN	Corn / soybeans
SD	Not available
SC	Peach orchards
NC	Tobacco, peanuts
NY	Corn / soybeans
PA	Corn / soybeans

b. Uncertainties and Limitations in Interpreting of Monitoring Data

Some of the uncertainties and limitations associated with interpretation of the reservoir monitoring data are as follows:

- The samples are not truly paired because sampling did not account for the travel time of the pesticide and its transformation products through the water treatment plant. This may limit stoichometric linkage of pesticide degradation and formation of degradation products during water treatment. However, comparisons of pesticide concentrations in raw and finished drinking water are possible because temporal variability of pesticide concentrations is expected to be lower in drinking water derived from reservoirs. Additionally, water samples were taken on the same time scale (hours) as the water treatment cycles for the water utilities.

- OP pesticides had low recoveries in matrix-spiked finished water samples (Personal Communication with Joel Blomquist, UGSG, April 28, 2000), which may be associated with their low stability in finished water. Oxidative transformation products of OP pesticides, such as fenamiphos sulfone and sulfoxide and tebupiriamphos oxygen analog, had higher matrix spike recoveries in treated water than the parent compound. Available data indicate OP compounds are not stable in chlorinated drinking water (Magera, 1994, Tierney, et al. 2001, US EPA,2000). Because OP pesticides generally have lower concentrations in finished water samples, the detection of any OP pesticide in finished water can be viewed as a reliable detection.

- Ancillary data on weather, pesticide use, and watershed vulnerability need to be considered when interpreting occurrence data. Sampling was extended through 2000 because of extreme drought conditions in the northeastern United States and California during the 1999 sampling season. A lower than average rainfall may have impacted pesticide runoff and resulted in fewer detections of pesticides.

c. Methods of Data Analysis

Scientists in the Office of Pesticide Programs (OPP) of EPA analyzed the reservoir monitoring data for the organophosphorus compounds detected in raw and treated waters. In this analysis, reservoir ("outfall") samples were not considered. Summary statistics were generated only for those OP compounds in the cumulative OP assessment (Attachment III.E.1).

Data from the USGS/EPA Reservoir Monitoring Study (Joel Blomquist, 6/11/01, Written Communication) were reformatted in an EXCEL spreadsheet to accommodate formatting requirements for Statistical Analysis Systems (SAS is a Trademark of SAS Institude. Inc., Cary NC.). Sampling dates in the original data set were modified to facilitate translation of date variables. After the modification, EXCEL data sets for USGS schedules 2001, 9060, and 9002 were merged into a common data set using a SAS program. Working with USGS, EPA scientists conducted quality assurance and quality control (QA/QC) programs on the data set to eliminate replicated data or modified data. Each data analysis process is described below.

i. Summary Statistics

The Statistical Analysis Systems (SAS) procedures FREQ and SUMMARY calculated detection frequencies and mean detectable concentrations. Concentration distributions (percentiles) were estimated for OP compounds with 10 or more detections in a reservoir during 1999 and 2000. Only diazinon and malaoxon met the criteria for percentile calculations. Percentiles were computed by two different methods for evaluating non-detects. In Method 1, the detection limit was used as a concentration measurement, while in Method 2, non-detects were set equal to zero. This difference does not apply to the computation of mean detected and maximum detected concentrations. Percentiles were computed by linear interpolation using ©SAS proc univariate (percentile Definition 1). Ranked non-time weighted percentile concentrations were reported for all OP pesticides detected in raw or finished water samples (Blomquist et al., 2001). Annual time weighted mean (TWM) concentrations were calculated for the OP pesticides using the limit of detection (LOD) or zero for non-detections to provide bounding estimates of the TWM.

ii. Considering the Impact of Water Treatment

An analysis of water treatment effects was conducted by further modifying the merged data set to calculate the impact of water treatment on pesticide removal or transformation. In this analysis, all samples with nondetects in both raw and finished water samples were removed, while samples with at least one detection were retained in the database. For those samples with one detection, the non-detection was modified to one-half the limit of detection (LOD). This data manipulation was required to allow calculation of water treatment reduction percentages.

Minimum, median and maximum water treatment reduction percentages were determined for paired raw and finished water samples for each pesticide. Water treatment reduction percentages were estimated using the equation [(raw-finished/raw) *100]. These percentages, though, can only be estimated when pesticides are detected in both raw and finished water samples. In this reservoir monitoring study, most organophosphorus insecticides were detected only in raw water samples or in finished water samples. In order to allow estimation of water treatment reduction factors, non-detections in raw or finished water samples were assumed to be equal to one-half the LOD. Negative values are calculated for samples where finished water concentrations were higher than raw water concentrations. This situation can can occur when detection limits or frequencies are low.

d. Study Methods and Design

i. Chemical Analytical Methods

The reservoir study used three analytical methods: 2001, 9002, and 9060. Method 2001 used a C-18 solid phase extraction and gas chromatography/ mass spectrometry (GC/MS) (Zaugg et al., 1995). This method has been approved and validated for use in the National Water Quality Assessment (NAWQA) program. Methods 9002 and 9060 were under development and validation during the course of the study, but are now currently approved by USGS. Method 9002 (now referred to as method 2002) used a C-18 solid phase extraction and GC/MS (Sandstrom et al., 2001). Method 9060 (now referred 2060) used solid phase extraction and high performance liquid chromatography/mass spectrometry (HPLC/MS) (Furlong et al., 2001). These methods were used to expand information on occurrence of pesticides and degradation products. Because methods 9002 and 9060 were under development and validated during the monitoring study, the data for these methods are considered as provisional by the USGS.

ii. Quality Assurance and Quality Control Assessment

As requested by OPP, USGS assessed quality assurance and quality control (QA/QC) data for OP pesticides and their degradation products (written communication from Blomquist, J. 5/17/02). The QA/QC assessment was conducted for method 2001 and the provisional method 9002 because these methods were used for chemical analysis of the OP pesticides. The QA/QC assessment is based on laboratory fortified samples in reagent grade water samples and fortified matrix raw and finished drinking water samples. All pesticides were fortified in matrix samples at a concentration of 0.1 ug/L. The percent recoveries were calculated by adjusting for actual sample volume and ambient concentration of analyte in non-fortified samples.

The average analyte-matrix contact time was variable for the fortified matrix samples. In general, matrix samples for method 2001 were fortified in the field, shipped to the National Water Quality Laboratory (NWQL), and then extracted within 1-7 days. The matrix samples for method 9002 were fortified at the NWQL. Recoveries from raw and finished waters were analyzed separately because of expected differences in matrix effects. Statistical analyses of analytical recoveries were conducted using a parametric Cochran t-test or a non-parametric Kruskal-Walis test.

Mean analytical recovery of OP pesticides in fortified raw water matrix samples ranged from 70% to 175% for 11 compounds for method 2001 and from 30% to 115% for 31 compounds for provisional method 9002 (Table III.E.3.3). Azinphos-methyl and disulfoton sulfone had the highest mean analytical recoveries in raw water matrix samples. Dichlorvos had the lowest mean analytical recovery in raw water matrix samples. Mean analyte recoveries in finished water matrix samples ranged from 4% to 55% for method 2001 and 3% to 135% for provisional method 9002. Disulfoton and phorate oxon had the lowest mean analytical recovery in finished water matrix samples, while tebupirimphos oxygen analog had the highest mean analytical recovery in finished water samples.

Statistical analysis indicates median analytical recoveries in finished water matrix were significantly lower than recoveries in raw matrix samples for method 2001. A similar observation was found for 19 organphosphorus pesticides in method 9002. Diclorvos and tebupiramphos, however, had significantly higher (P=0.05) median recoveries in finished water when compared to raw water matrix samples. Chlorpyrifos oxygen analog, fenamiphos sulfone, fenamiphos sulfoxide, phosmet oxon, and terbufos-O-analogue sulfone had similar median recoveries between raw water matrix samples and finished water matrix samples.

Table III.E.3.3: Mean recoveries of fortified laboratoy set and matrix samples for OP pesticides from USGS methods 2001 and 9002 (decimal percentage).

Chemical	Lab Set 1999	Lab Set 2000	Raw Matrix	Finished Matrix
Azinphos methyl§	0.81±0.39 (108)	0.86±0.34 (422)	1.75±0.53 (33)	0.38±0.64 (30)
Azinphos-methyl-oxon§	0.48±0.20 (163)		0.85±0.29 (32)	0.55±0.32(28)
Chlorpyrifos§	0.90±0.14 (108)	0.90±0.10 (422)	1.00±0.28 (34)	0.21±0.35 (31)
Chlorpyrifos, oxygen analog	0.40±0.20 (163)		0.44±0.34 (32)	0.59±0.37 (28)
Diazinon§	0.91±0.15 (108)	0.93±0.11(422)	1.09±0.26 (34)	0.26±0.43 (31)
Diclorvos§	0.43±0.16 (163)		0.30±0.22 (34)	0.46±0.24 (28)
Dicrotophos	0.27±0.08 (163)		0.34±0.11 (30)	0.30±0.14 (28)
Dimethoate§	0.39±0.11 (163)		0.57±0.13 (30)	0.05±0.15 (28)
Disulfoton§	0.83±0.18 (108)	0.76±0.14 (422)	0.70±0.30 (34)	0.04±0.16 (31)
Disulfoton sulfone§	0.78±0.14 (163)		1.06±0.24 (32)	0.15±0.33 (28)
Disulfontone sulfoxide§	1.12±0.35 (163)		1.15±0.44 (30)	0.18±0.47 (28)
Ethoprop§	0.94±0.17 (108)	0.86±0.13 (422)	1.07±0.26 (34)	0.55±0.41 (31)
Ethoprop metabolite 76960§	0.80±0.33 (28)		0.95±0.23 (32)	0.80±0.33 (28)
Fenamiphos§	0.62±0.11 (163)		1.09±0.21 (30)	0.04±0.20 (28)

Chemical	Lab Set 1999	Lab Set 2000	Raw Matrix	Finished Matrix
Fenamiphos sulfone	0.63±0.17 (163)		1.12±0.27(30)	1.13±0.46 (28)
Fenamiphos sulfoxide	0.30±0.21 (163)		0.37±0.24 (30)	0.27±0.27 (28)
Malaoxon	1.03±0.41 (28)		1.04±0.29 (32)	1.03±0.41 (28)
Malathion§	0.95±0.19 (108)	0.92±0.14 (422)	1.16±0.36 (34)	0.19±0.33 (31)
Methiadathion§	0.19±0.36 (28)		1.15±0.31 (30)	0.19±0.36 (28)
Paraoxon-methyl§	0.86±0.35(28)		0.79±0.26 (32)	0.86±0.35 (28)
Parathion-methyl§	0.82±0.20 (108)	0.95±0.14 (422)	1.29±0.40 (34)	0.31±0.52 (31)
Phorate§	0.79±0.14 (108)	0.81±0.14 (422)	0.77±0.27 (34)	0.04±0.16 (31)
Phorate Oxygen-Analog§	0.03±0.15 (28)		0.97±0.26 (32)	0.03±0.15 (28)
Phosmet	0.07±0.15 (28)		0.40±0.30(30)	0.07±0.15 (28)
Phosmet Oxon	0.49±0.43 (28)		0.37±0.30 (30)	0.49±0.43 (28)
Tebupiriamphos§	0.19±0.33 (28)		0.98±0.10 (30)	0.19±0.33 (28)
Tebupiramphos oxygen analog§	Not Available		1.01±0.22 (32)	1.35±0.48 (28)
Terbufos§	0.80±0.15 (108)	0.81±0.11 (422)	0.88±0.22 (34)	0.05±0.18 (31)
Terbufos-O-analogue sulfone	1.07± 0.69 (28)		1.12±0.65 (30)	1.07±0.69 (28)
Tribuphos§	Not Available		0.85±0.12 (30)	0.59±0.27 (28)

( )- Number of samples used for mean and standard deviation
§- Indicates significant difference (P<0.05) in median recoveries from raw water and finished water samples

Azinphos-methyl had significantly (P=0.05) higher analytical recoveries in raw water matrix samples than laboratory set samples (Table III.E.3.3). Disulfoton had significantly (P=0.05) lower mean recoveries in raw water matrix samples compared to laboratory set samples. Raw water matrix-enhanced recovery also was found for chlorpyrifos, diazinon, ethoprop, malathion, parathion-methyl, and terbufos. Matrix enhanced recoveries have been found through quality control analysis for National Water Quality Assessment Program (Martin, 1999).

Azinphos-methyl oxon and dicrotophos had significantly higher (P<0.05) mean recoveries in raw water matrix sample compared to the laboratory set recoveries, chlorpyrifos oxygen analog had significantly higher (P=0.05) mean recoveries in finished water compared to laboratory recoveries. There were no significant (P<0.05) differences in recoveries of chlorpyrifos oxygen analog and disulfotone sulfoxide from raw matrix samples and laboratory set samples.

In summary, the OP pesticides and their degradation products in the cumulative OP assessment generally had similar or enhanced recovery in the matrix samples compared to the laboratory set samples. However, parent OP pesticides had lower recoveries in finished water matrix samples compared to laboratory set samples. OP degradation products generally had similar or higher recoveries in finished water matrix samples.

iii. Water Treatment Trains and Basic Water Quality Data

Although the water quality parameters, including pH, hardness, and total organic carbon, varied among the 12 reservoirs (Table III.E.3.4), the physical construct of the treatment train processes was similar.

Source Water ⇨Screens⇨Prechlorination (Preoxidation) ⇨Rapid Mixer⇨Flocculation⇨Filtration⇨Post Disinfection⇨Clearwell

Table III.E.3.4: Average Water Quality Parameters for Raw Water at Candidate Reservoirs

Water Systems	Average Flow Through Time (hours)	Water Quality Properties			
		pH	Alkalinity (mg/L as $CaCO_3$)	Hardness (mg/L as $CaCO_3$)	TOC* (mg/L)
MO	26	7.9 to 9.2	63-120	90 - 145	4.7
TX	10	7.7	100	108	4-8
OH	23	7.7	95	126	5.2
OK	NA	7.9-8.8	137	150	5.8
CA	3.25	7.5	91	250	6-8
IN	8.75	8.2	128	200	4
SD	12-13	9.2	32	NA	NA
SC	4	6.9	17	15	3.8
NC	NA	7	12	NA	NA
LA	NA	NA	NA	NA	NA
NY	0.29	7.8-9.0	40-100	140	4.4
PA	7-9	7.2	7.2	172	2-3

NA-Not available
* TOC= Total Organic Carbon

The average water flow-through time at each treatment plant was less than 24 hours. The most common treatment practices included prechlorination and post disinfection, coagulation, and pH adjustment processes. Chlorine and chlorine dioxide were the most common disinfectants used in the prechlorination process (Table III.E.3.5), while chlorine and chloramines were the most common disinfectants used in the post disinfection process. The most common coagulants used in the treatment trains were aluminum salts and polymers. The data also shows that pH was adjusted by adding lime and sodium hydroxide. Several of the treatment plants used activated carbon in the treatment train. Powdered activated carbon was used as part of the pre-disinfection process in the PA, NY, SC, IN water utilities, while granular activated carbon was used prior to the post disinfection process at the MO, OK, and OH water utilities.

Table III.E.3.5: Treatment trains for utilities in the reservoir monitoring program

State	Treatment Train
MO	(1) Prechlorination with Chlorine Dioxide → (2) Flash Mixer +polymer coagulant →(3) Flocculation/Sedimentation + Lime → (4)Flash Mixer + Sodium silica fluoride → (5) Flocculation/ Sedimentation + Chlorine →(6) Dual Media Filtration + sand with GAC cap → (7) Chlorine added → (8) Clearwell → (9) Distribution
TX	(1) Prechlorination with Chlorine + KMnO4 → (2) Flocculation + Iron salts (ferric sulfate)/pH adjustment (caustic soda) → (3) Filtration- dual media sand/ anthracite → (4) Post-Disinfection with chloramines → (5) Corrosion control- pH adjustment/ fluorisilic acid
OH	1) Prechlorination with Chlorine Dioxide (ClO2) + KMnO4 → (2) Rapid Mix + Aluminum → (3) Flocculation + pH adjustment/ polymers → (4) Settling → (5) Filtration (Rapid sand with GAC) → (6) Post-Disinfection (phosphate/ fluoride/chlorine and caustic soda) → (7) Clearwell → (8) Distribution
OK	(1) Aeration →(2) Prechlorination with ozone →(3) Flocculating/ Clarifier + polymer/ Lime →(4) Solids contact/ clarifier + carbon dioxide→ (5) Post-Disinfection with ozone→ (6) Polyphosphate polymer + chlorine → (7) Mixed media filters- multimedia→ (8) Carbon filter-GAC→ (9) Post-Disinfection with chorine → (10) Clearwell → (11) Distribution
CA	(1) Prechlorination with chlorine (optional)/ aluminum salts → (2) Rapid Mix/ Cationic polymer → →(3) Accelerator + chlorine (optional)/ non-ionic polymer → (4) Pre-chlorination + NaOH→ (5) Dual media filters →(6) Post-chlorination→ (7) Clearwell→ (8) Holding pond
IN	(1) Prechlorination with chlorine + carbon and KMnO4 → (2) Splitter and Rapid Mix + chlorine, aluminum sulfate, polylmer, carbon, ammonia, lime, and KMnO4 → (3) Mixing and settling basin + chlorine, polymer, and carbon added →(4) Filter plant →(5) Fluoride added →(6) Finished water reservoir + chlorine→ (7) Distribution
SD	(1) GAC polymers →(2) Lime, aluminum sulfate, polymers added→(3) Chlorine dioxide, carbon dioxide, and fluoride added → (4) Ammonium polyphosphate →(5) Chlorine added
SC	(1) Prechlorination with chlorine + liquid alum, lime, carbon, and polymer→ (2) Hydraulic flocculators + aluminum salts, polymers →(3) Dual media High Rate Filters →(4) Post-Disinfection with chlorine + fluoride, lime, and phosphate→ (5) Clearwells→ (6) Distribution pumps
NC	(1) Prechlorination + aluminum salts and pre-caustic →(2) Flash Mixer + polymer Flocculator → (3) Sedimentation basin + chlorine→ (4) Dual media filter →(5) Post-disinfection with chlorine + post caustic, fluoride, chlorine, and phosphate →(6) Clearwell →(7) Distribution system
NY	(1) Prechlorination with chlorine + KMnO4/ PAC → (2) Flocculation + aluminum salts/ polymers → (3) Filtration - rapid sand and mixed media → (4) Post-Disinfection with chlorine + fluoride + ortho phosphate → (5) Clearwell →(6) Storage →(7) Distribution

State	Treatment Train
PA	(1) Prechlorination with chlorine dioxide + PAC + KMnO4 + lime →(2) Flocculation/ clarification + aluminum sulfate → (3)Filtration with sand/ anthracite + hydrofluorisilicic acid → (3) Ammonium sulfate + chloramines →(4) Corrosion control + phosphate →(5) clearwell →(6) Reservoir →(7) Distribution

e. Summary of Organophosphorus Detections

The pilot reservoir monitoring study provided two years of raw (525 samples) and finished (249 samples) water occurrence data for 18 active OP parent compounds and 13 transformation products considered in the cumulative OP assessment. This pilot program included OP pesticides that have not been analyzed in most other monitoring studies, such as tribufos, phostebupirim, profenofos and dichlorvos, and some rarely analyzed transformation products.

Of the thirteen OPs detected in either raw or finished drinking water samples, diazinon was, by far, the most frequently detected compound. Although it was found in 35% of 323 raw water samples (Table III.E.3.6), it was not found in 227 finished water samples, suggesting that this pesticide was reduced or transformed by water treatment processes. Unfortunately, the likely transformation product, diazoxon, was not analyzed in the USGS schedules to substantiate that it was found in treated water.

Other OPs and their oxygen analogs also followed a similar pattern of detection, but the number of detections was not sufficient to formulate any definite conclusions. For instance, malathion was detected in 6 of 323 raw water samples (2%), while malaoxon was detected in 11 of 220 finished water samples (5%). It is important to note that three finished and raw water samples (LA water utility on August 26, 1999; September 8,1999 and June 7,2000) showed the presence of only malathion in raw water and malaoxon in finished water. In this situation, malathion may have transformed into malaoxon during the treatment process. Chlorpyrifos was detected in 5% of raw water samples, but neither chlorpyrifos nor its oxygen analog were detected in finished water. Azinphos-methyl and its oxon were both found in raw and finished water. In this study, though, the difference between the number of detections for each was not enough to allow statistical quantification of treatment effects, especially since azinphos methyl and its oxon were only found in the MO water utility.

Some non-persistent parent OP pesticides, such as fenamiphos and disulfoton, were not detected in raw and treated water. However, their longer-lived sulfoxide and sulfone transformation products were detected in raw and finished water samples. The low detection frequencies (<1% or 2 samples) in raw and finished water samples limited a clear quantitative assessment of treatment transformation.

Table III.E.3.6: Summary statistics for organophosphorus pesticides and their degradation products

Chemical	LOD [1]	Raw					Finished				
		No. samples	No. detects	% Detected	Max. ug/L	Mean ug/L	No. samples	No. detects	% Detected	Max. ug/L	Mean ug/L
Azinphos-methyl-oxon	0.031	316	1	0.3%	0.263	0.263	219	4	1.8%	0.026	0.018
Azinphos-methyl	0.001	321	8	2.5%	0.144	0.077	225	5	2.2%	0.114	0.059
Chlorpyrifos	0.004	323	17	5.3%	0.034	0.006	227	.		.	.
Chlorpyrifos, oxygen analog	0.016	316	.		.	.	220	.		.	.
Diazinon	0.002	323	114	35%	0.101	0.023	227	.		.	.
Diclorvos	0.005	316	.		.	.	220	.		.	.
Dicrotophos	0.016	316	.		.	.	220	.		.	.
Dimethoate	0.005	316	4	1.3%	0.022	0.012	220	.		.	.
Disulfoton	0.017	323	.		.	.	227	.		.	.
Disulfoton sulfone	0.005	316	1	0.3%	0.013	0.013	220	.		.	.
Disulfotone sulfoxide	0.016	316	1	0.3%	0.006	0.006	220	.		.	.
Ethoprop	0.003	323	.		.	.	227	.		.	.
Ethoprop metasbolite 76960	0.005	316	.		.	.	220	.		.	.
Fenamiphos	0.016	316	.		.	.	220	.		.	.
Fenamiphos sulfone	0.008	316	1	0.3%	0.005	0.005	220	2	0.9%	0.016	0.012
Fenamiphos sulfoxide	0.031	316	2	0.6%	0.033	0.021	220	1	0.5%	0.022	0.022
Malaoxon	0.016	316	.		.	.	220	11	5.0%	0.556	0.106
Malathion	0.005	323	6	1.9%	0.106	0.032	227	.		.	.
Methidathion	0.008	316	1	0.3%	0.01	0.01	220	.		.	.
Paraoxon-methyl	0.031	316	.		.	.	220	.		.	.
Parathion-methyl	0.006	323	1	0.3%	0.061	0.061	227	.		.	.
Phorate	0.002	323	.		.	.	227	1	0.4%	0.001	0.001
Phorate oxygen analog	0.031	316	.		.	.	220	.		.	.
Phosmet	0.008	316	.		.	.	220	.		.	.
Phosmet oxon	0.016	316	.		.	.	220	.		.	.
Profenofos	0.008	316	.		.	.	220	.		.	.
Tebupiriamphos (Phostebupirim)	0.016	316	.		.	.	220	.		.	.
Terbufos-O-analog sulfon	0.016	316	.		.	.	220	2	0.9%	0.015	0.012
Terbufos	0.013	323	.		.	.	227	.		.	.
Tribufos (DEF, s,s,s-Tr)	0.016	316	.		.	.	220	.		.	.
tebupiramphos oxygen analog	0.008	316	3	0.9%	0.007	0.005	220	.		.	.

(1) LOD = Limit of Detection. The value reported is the most common limit of detection. For some chemicals, the LOD varied during method development.

Diazinon was detected in 10 of 12 reservoirs, and chlorpyrifos was detected in 6 reservoirs, reflecting their widespread use (Table III.E.3.7). The maximum concentration of diazinon was 0.045 ug/L in the raw water of the CA treatment plant. Percentile concentrations of diazinion for the combined 1999 and 2000 sampling season are shown in (Table III.E.3.8). The distribution of diazinon concentrations in raw intake water suggest that the detected concentrations of diazinon were roughly representative of percentile concentrations greater than the 50^{th} percentile. The estimated concentration percentiles were relatively insensitive to the values assumed (either the detection limit or zero) for non-detected samples.

Table III.E.3.7: Summary statistics for water type, year, and water utility (ug/L)

Chemical	State	Year	Water Type	Nondetects		Conc.Estimated [1]		Conc. Measured	
				Samples	LOD Range	Samples	Range	Samples	Range
Azinphos-methyl	MO	2000	Raw	18	0.001-0.05	1	0.034	.	.
	SC	2000	Finished	6	0.001-0.075	5	0.019-0.114	.	.
	SC	2000	Raw	15	0.001-0.1	7	0.029-0.144	.	.
Azinphos-methyl-oxon	MO	2000	Finished	8	0.031	2	0.008-0.01	.	.
	NY	2000	Finished	8	0.31-0.06	2	0.026	.	.
	OK	1999	Raw	20		.	.	1	0.263
Chlorpyrifos	LA	1999	Raw	8		.	.	3	0.005-0.008
	MO	2000	Raw	18	0.004-0.005	.	.	1	0.034
	OH	2000	Raw	8	0.004	2	0.002-0.004	.	.
	OK	1999	Raw	20	0.004	1	0.002	.	.
	OK	2000	Raw	19	0.004-0.005	.	.	1	0.004
	PA	2000	Raw	6	0.004-0.006	2	0.003	3	0.004-0.012
	SC	2000	Raw	20	0.004-0.005	4	0.002	.	.
Diazinon	CA	1999	Raw	1	0.002	.	.	7	0.004-0.045
	IN	1999	Raw	28	0.002-0.01	5	0.003-0.004	4	0.004-0.006
	IN	2000	Raw	1	0.002	1	0.005	9	0.006-0.01
	LA	2000	Raw	10	0.002-0.006	.	.	1	0.01
	MO	1999	Raw	7	0.002-0.01	.	.	14	0.005-0.022
	NC	1999	Raw	5	0.002	2	0.003-0.004	3	0.004-0.012
	OH	1999	Raw	10	0.002	1	0.003	.	.
	OH	2000	Raw	1	0.002	.	.	9	0.008-0.015
	OK	1999	Raw	1	0.002	.	.	20	0.017-0.101
	OK	2000	Raw	.	.	.	.	20	0.012-0.095
	PA	1999	Raw	11	0.002	.	.	1	0.006
	PA	2000	Raw	5	0.002	1	0.002	5	0.005-0.015
	SC	1999	Raw	20	0.002	1	0.002	.	.
	SC	2000	Raw	20	0.002-0.005	4	0.001-0.003	.	.
	TX	1999	Raw	16	0.002-0.006	5	0.003-0.004	1	0.004
Dimethoate	LA	1999	Raw	8	0.005	.	.	1	0.007
	PA	2000	Raw	8	0.005	1	0.006	2	0.012-0.022
Disulfoton sulfone	NY	2000	Raw	9	0.005	.	.	1	0.013
Disulfotone sulfoxide	NY	2000	Raw	9	0.016	1	0.006	.	.
Fenamiphos sulfone	NC	1999	Finished	8	0.008	1	0.007	1	0.016
	NC	1999	Raw	9	0.008	1	0.005	.	.
Fenamiphos sulfoxide	IN	2000	Finished	10	0.031	1	0.022	.	.
	IN	2000	Raw	10	0.031	.	.	1	0.033
	MO	2000	Raw	17	0.031	1	0.008	.	.
Malaoxon	LA	1999	Finished	7	0.016	.	.	3	0.052-0.204
	LA	2000	Finished	3	0.016	3	0.008-0.01	5	0.019-0.556
Malathion	LA	1999	Raw	8	0.005	.	.	3	0.023-0.106
	LA	2000	Raw	9	0.005-0.027	.	.	2	0.008-0.011
	MO	2000	Raw	18	0.005-0.027	.	.	1	0.007
Methidathion	MO	1999	Raw	19	0.008	.	.	1	0.01
Parathion-methyl	LA	1999	Raw	10	0.006	.	.	1	0.061
Phorate	MO	2000	Finished	13	0.002-0.011	1	0.001	.	.
Terbufos-O-analogue sulfon	PA	2000	Finished	9	0.016	2	0.009-0.015	.	.
tebupiramphos (Phostebupirim)	MO	1999	Raw	18	0.008	2	0.003-0.007	.	.
	PA	1999	Raw	12	0.008	1	0.006	.	.

(1) Estimated concentrations are qualified estimate of concentration. This is defined as: Compounds with low or high recoveries (for example, USGS analytical schedule 9002-outside the range of 60 to 120% recovery) or concentrations lower than the laboratory reporting limit.

Table III.E.3.8: Concentration percentiles for diazinon in raw water samples

State	No.	Detected	mean (ug/L)	percentile method	Percentiles (ug/L) 50th	75th	80th	90th	95th	max detected (ug/L)
California	8	7	0.017		[not computed for <10 detections]					0.045
Indiana	48	19	0.0059	1	0.002	0.005	0.0060	0.0082	0.0096	0.010
			.	2	0.000	0.005	0.0054	0.0072	0.0090	.
Louisiana	22	1	0.010		[not computed <10 detections]					0.010
Missouri	40	14	0.0099	1	0.002	0.0060	0.0080	0.011	0.013	0.022
			.	2	0.000	0.0060	0.0070	0.011	0.013	.
N. Carolina	10	5	0.0068		[not computed <10 detections]					0.012
New York	22	0	.							.
Ohio	21	10	0.0102	1	0.002	0.0088	0.011	0.013	0.013	0.015
			.	2	0.000	0.0088	0.011	0.013	0.013	.
Oklahoma	41	40	0.0505	1	0.051	0.066	0.072	0.080	0.087	0.10
			.	2	0.051	0.066	0.072	0.080	0.087	.
Penn..	23	7	0.0076							0.015
S.Carolina	45	5	0.0018		[not computed <10 detections]					0.0030
S.Dakota	21	0	.							.
Texas	22	6	0.0035							0.0040

Of the parent OP compounds, diazinon and chlorpyrifos were the only ones detected in more than three reservoirs while azinphos-methyl had the highest detected concentration (0.114 ug/L in South Carolina raw water). It also had a high detection frequency (32-46%) in raw and finished water samples in the SC reservoir. Azinphos-methyl oxon was not detected in raw or finished water from the SC reservoir. The precision of azinphos-methyl and azinphos methyl-oxon concentrations, though, is low because the detections were estimated at concentrations near the reported detection limit. Analytical detection limits varied among the OP pesticides and their transformation products (Attachment III.E.2). In general, the lowest detection limit was the most commonly reported detection limit.

Malaoxon had the highest concentration of all 31 OP analytes, with maximum finished-water concentrations in Louisiana of 0.556 ug/L in 2000, and 0.204 ug/L in 1999. Malathion concentrations in raw water ranged from 0.023 to 0.106 ug/L in 1999 and 0.008 to 0.011 ug/L in 2000. The percentile concentration of malaoxon in finished water at the LA treatment plant are shown in Table III.E.3.9.

Table III.E.3.9: Concentration percentiles for malaoxon in finished water samples in Louisiana.

Chemical	No. analyzed	No. detects	mean conc.	50th %-ile	75th %-ile	80th %-ile	90th %-ile	95th %-ile	range of detected conc.
Malaoxon (finished water)	21	11	0.11	below LOD	0.052	0.059	0.12	0.20	0.008 - 0.56
Malathion (raw water)	22	5	0.038	[not computed with fewer than 10 detections]					0.008 - 0.11

Table III.E.3.10 summarizes percentile concentrations for the OP pesticides in raw and finished water. Malaoxon and diazinon were the only compounds with sufficient magnitude and range of detections to allow estimation of median, 90th percentile, and maximum concentrations. In most cases, maximum and 90th percentile concentrations were above the LOD while the 50th percentile concentration was normally below the LOD.

Table III.E.3.10: Concentration percentiles for OP compounds in raw and finished water samples in (ug/L).

Chemical	State	Water Type	Max[3]	90th percentile[3]	Median[3]
Azinphos-methyl	SC	Raw	0.144	0.054	
	SC	Finished	0.114	0.038	
Azinphos-methyl-oxon	NY	Raw	0.026	0.013	
	OK	Raw	0.263		
Chlorpyrifos	LA	Raw	0.008	0.005	
	OH	Raw	0.004		
	OK	Raw	0.004		
	PA	Raw	0.015	0.007	
	SC	Raw	0.002		
Diazinon	OH	Raw	0.015	0.013	
	OK	Raw	0.101	0.08	0.051
	PA	Raw	0.012	0.004	
	SC	Raw	0.003	0.001	
	TX	Raw	0.004	0.004	
	CA	Raw	0.045	0.045	0.015
	IN	Raw	0.01	0.008	
	LA	Raw	0.01		
	MO	Raw	0.022	0.011	
	NC	Raw	0.012	0.011	0.001
Dimethioate	LA	Raw	0.007		
	PA	Raw	0.022	0.006	
Disulfoton sulfone	NY	Raw	0.013		
Disulfoton sulfoxide	NY	Raw	0.006		
Fenamiphos sulfone	NC	Raw	0.005	0.002	
	NC	Finished	0.016	0.011	
Fenamiphos sulfoxide	IN	Raw	0.033		
	MO	Raw	0.008		
Malaoxon	LA	Finished	0.556	0.128	0.008
Malathion	LA	Raw	0.106	0.023	
	MO	Raw	0.007		
Methidathion	MO	Raw	0.01		
Parathion-methyl	LA	Raw	0.061		
Phorate	MO	Finished	0.001		
Tebupiramphos	MO	Raw	0.007		
	PA	Raw	0.006		
Terbufos-O-analogue sulfone	PA	Finished	0.015		

Percentile concentrations are taken from Blomquist et al., 2000.

Time-weighted mean concentrations (TWM) for OP pesticides and their degradation products were low in raw and finished waters (Table III.E.11). Diazinon had the highest TWM (0.059 ug/L) in raw water while malaoxon had the highest TWM (0.043 ug/L) in finished water. In general, the bounding estimates of TWM was dependent on the treatment of non-detections in the calculation of TWM. The use of zero for non-detections led to TWM concentrations below the LOD.

Table III.E.3.11: Time weighted annual means (TWM) for OP compounds in raw and finished water samples in (ug/L).

OP	State	Year	Range LOD	Raw TWM (DL)	Raw TWM(0)	Finished TWM(DL)	Finished TWM(0)
azinphos-methyl	SC	1999	0.001-0.10	0.001	0.000	0.001	0.000
		2000		**0.051**	**0.017**	**0.029**	**0.009**
azinphos-methyl-oxon	MO	1999	0.031-0.31	0.031	0.000	0.024	0.000
		2000		0.031	0.000	0.024	0.000
	NY	1999		0.031	0.000	0.031	0.000
		2000		0.031	0.000	0.031	0.007
	OK	1999		**0.035**	0.005	0.013	0.000
		2000		**0.032**	0.000	0.021	0.000
chlorpyrifos	LA	1999	0.004-0.006	**0.006**	0.004	0.004	0.000
		2000		**0.005**	0.000	0.004	0.000
	OH	1999		0.004	0.000	0.004	0.000
		2000		0.004	0.001	0.002	0.000
	OK	1999		0.004	0.000	0.002	0.000
		2000		0.004	0.000	0.003	0.000
	PA	1999		0.004	0.000	0.004	0.000
		2000		**0.005**	0.002	0.004	0.000
	SC	1999		0.004	0.000	0.003	0.000
		2000		0.004	0.000	0.003	0.000
diazinon	OH	1999	0.002 -0.01	0.002	0.000	0.002	0.000
		2000		**0.009**	**0.008**	0.002	0.000
	OK	1999		**0.055**	**0.055**	0.001	0.000
		2000		**0.059**	**0.059**	0.002	0.000
	PA	1999		0.002	0.001	0.002	0.000
		2000		**0.004**	**0.003**	**0.003**	0.000
	SC	1999		0.002	0.000	0.002	0.000
		2000		0.003	0.000	0.002	0.000
	TX	1999		0.002	0.001	0.001	0.000
	CA	1999		**0.030**	**0.030**	0.002	0.000
	IN	1999		**0.003**	0.001	0.002	0.000
		2000		**0.006**	**0.006**	**0.003**	0.000
	LA	1999		0.002	0.000	0.002	0.000
		2000		**0.004**	0.000	0.002	0.000
	MO	1999		**0.005**	**0.003**	0.002	0.000
		2000		0.002	0.000	0.002	0.000
	NC	1999		**0.003**	0.002	0.002	0.000
dimethioate	LA	1999	0.005	0.004	0.000	0.005	0.000
		2000		0.005	0.000	0.005	0.000
	PA	1999		0.005	0.000	0.005	0.000
		2000		**0.006**	0.000	0.005	0.000
disulfoton sulfone	NY	1999	0.005	**0.016**	0.000	**0.016**	0.000
		2000		**0.016**	0.000	**0.016**	0.000
disulfoton sulfoxide	NY	1999		0.005	0.000	0.005	0.000
		2000		0.005	0.000	0.005	0.000
fenamiphos sulfone	NC	1999	0.008	0.008	0.000	0.008	0.000
fenamiphos sulfoxide	IN	1999	0.031	0.031	0.000	0.024	0.000
		2000		0.031	0.001	0.031	0.001
	MO	1999		0.031	0.000	0.024	0.000
		2000		0.025	0.000	0.020	0.000
malaoxon	LA	1999	0.016	0.013	0.000	**0.032**	**0.020**
		2000		0.016	0.000	**0.043**	**0.034**
malathion	LA	1999	0.005-0.027	**0.016**	**0.012**	0.005	0.000
		2000		**0.010**	0.001	**0.009**	0.000
	MO	1999		0.005	0.000	0.004	0.000
		2000		**0.009**	0.001	0.008	0.000
methidathion	MO	1999	0.008	0.008	0.000	0.006	0.000
		2000		0.007	0.000	0.005	0.000
parathion-methyl	LA	1999	0.006	0.008	0.002	0.006	0.000

OP	State	Year	Range LOD	Raw TWM (DL)	Raw TWM(0)	Finished TWM(DL)	Finished TWM(0)
		2000		0.006	0.000	0.006	0.000
phorate	MO	1999	0.002-0.011	0.002	0.000	0.002	0.000
		2000		0.003	0.000	0.003	0.000
tebupiramphos	MO	1999	0.008	0.008	0.000	0.006	0.000
		2000		0.007	0.000	0.005	0.000
	PA	1999		0.007	0.002	0.008	0.000
		2000		0.008	0.000	0.008	0.000
terbufos-O-analogue sulfone	PA	1999	0.008	**0.016**	0.000	**0.016**	0.000
		2000		**0.016**	0.000	**0.016**	0.001

*Shaded gray areas indicate TWM concentrations greater than the lowest LOD.

i. Water Treatment Effects

The concentration of most parent OP insecticides (diazinon, chlorpyrifos, malathion, dimethiate, methyl parathion) fell below the LOD during water treatment. Furthermore, the oxidative degradation products (azinphos methyl-oxon, fenamiphos sulfoxide, malaoxon, and terbufos-O-analogue sulfone) were detected more frequently in finished water than in raw water. Several degradation products (malaoxon, and terbufos-O-analogue sulfone) were not detected in raw water samples.

In analyzing the effects of water treatment on pesticide concentrations, water treatment reduction percentages were used to quantify the water treatment removal. These percentages, though, can be estimated only when pesticides are detected in both raw and finished water samples (Table III.E.3.12). In this reservoir monitoring study, most OP insecticides were detected only in raw water samples or in finished water samples. In order estimate of water treatment reduction factors, non-detections in raw or finished water samples were assumed to be equal to one-half the LOD. Negative values can occur when detection limits or frequencies are low.

Table III.E.3.12: Water treatment reduction percentages and maximum concentrations in raw and finished water for selected OP pesticides

Pesticide	USGS Schedule	Max Raw Conc ug/L	Max Finish Conc ug/L	Min Percent Reduction	Max Percent Reduction
Azinphos-methyl	2001	0.144	0.114	19	41
Azinphos-methyl-oxon	9002	0.263	0.026	0*(-67)	94
Chlorpyrifos	2001	0.012	0.002	0	83
Diazinon	2001	0.101	0.0025	0*(-150)	99
Dimethoate	9002	0.022	0.0025	58	88
Disulfoton sulfone	9002	0.013	0.0025	----	80

Pesticide	USGS Schedule	Max Raw Conc ug/L	Max Finish Conc ug/L	Min Percent Reduction	Max Percent Reduction
Disulfoton sulfoxide	9002	0.006	0.008	---	0*(-33)
Fenamiphos sulfone	9002	0.005	0.016	0*(-300)	0*(-40)
Fenamiphos sulfoxide	9002	0.033	0.022	---	33
Malaoxon	9002	0.008	0.556	0*(-6850)	0
Malathion	2001	0.106	0.0025	64	97
Parathion-methyl	2001	0.061	0.003	---	95
Phorate	2001	0.001	0.001	---	0
Tebupiriamphos	9002	0.007	0.004	33	42
Terbufos-O-analogue sulfone	9002	0.008	0.015	0*(-87.5)	0*(-12.5)

Equation for pesticide reduction calculation= (raw-finished/raw)*100
0* indicates a negative percent reduction was observed. A negative percent reduction indicates the finished water concentration is greater than the raw water concentration.
–Indicates a single pair of raw and finished water was available.

Table III.E.3.9 shows a wide variability in the water treatment removal efficiencies among organophospate compounds. Phosphorothioate and phosphorodithiate compounds (chlorpyrifos, diazinon, parathion-methyl, dimethoate) have high maximum water treatment removal percentages (80-99%), while phorate and azinphos-methyl have lower water treatment reduction percentages. These findings are consistent with those reported in the open literature for chlorination effects on organophosphorus insecticide degradation (Magera, 1994, Tierney, et al. 2001, US EPA,2000).

The reservoir monitoring study shows, that in general, the oxidative degradation products have lower water treatment reduction percentages than their parent compounds. A negative water treatment reduction percentage may indicate that the parent compound is transformed during treatment. For some degradation products, such as malaoxon and terbufos-O-analogue sulfone, chemical transformation is a possible explanation for their occurrence in finished water samples only. For other degradation products, such as azinphos-methyl-oxon, fenaminphos sulfoxide, and fenaminphos sulfone, which were found in both raw and finished water, degradate formation may occur during transport in the watershed or water treatment.

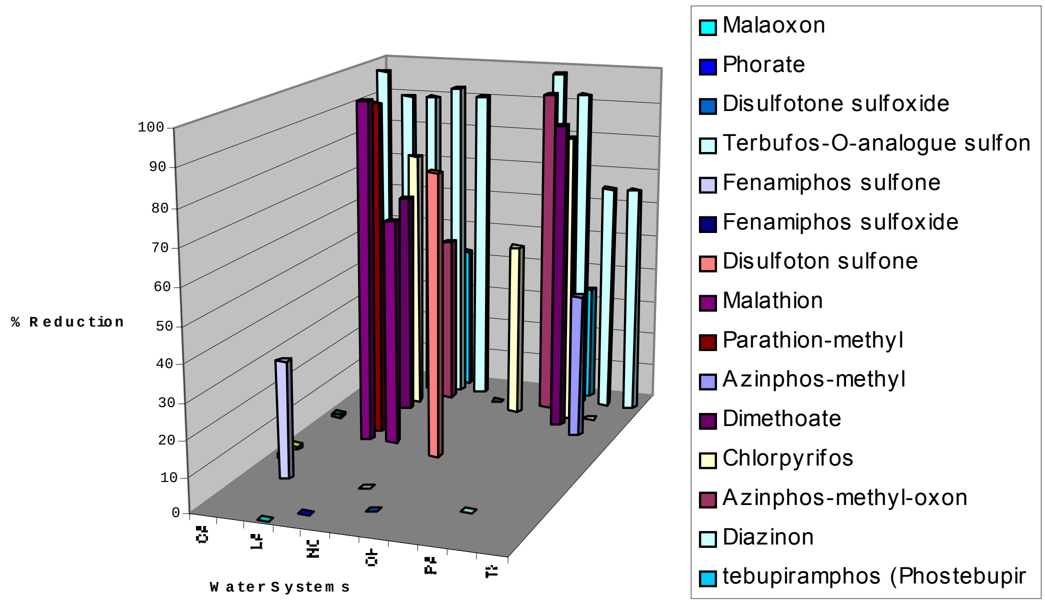

Figure III.E.3.2: Maximum Water Treatment Reduction Percentages Among Reservoirs

Figure III.E.3.2 shows the maximum water treatment reduction efficiencies among the 12 reservoirs that were analyzed in this study. Because individual treatment processes were not evaluated in this study and detections were sporadic, it is difficult to assess the impact of specific water treatment processes on pesticide removal and transformation. Diazinon, which was detected most frequently in the raw water at 10 reservoirs, showed maximum water treatment reduction percentages, ranging from 66-99% among the different water treatment systems. Similar ranges of maximum water treatment reduction percentages were reported for other organophosphorus pesticides. A possible explanation for high water treatment removal efficiency is chemical oxidation to such products as oxons through prechlorination and post-disinfection, which are commonly used processes. Because the diazinon degradation product, diazoxon, was not measured in this study, it is difficult to evaluate any linkage between diazinon degradation and diazoxon formation in finished water samples. However, there were three samples in which malathion was found in raw water and malaoxon was found in finished water at the LA water treatment plant (Figure III.E.3.3). This observation may be explained by chemical oxidation as a result of chlorination.

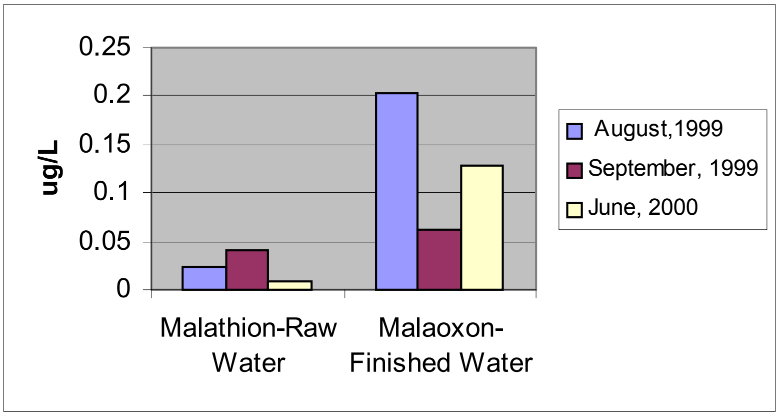

Figure III.E.3.3: Malathion and malaoxon formation in raw and finish water samples at the Louisiana water treatment plant

Another potential degradation pathway of organophosphorus pesticides is base catalyzed hydrolysis through treatment by liming and caustic soda. At this time, though, it is difficult to assess the impact of hydrolysis on OP degradation pathways because information on pH and contact time after pH adjustment were not available for the reservoir monitoring study. In addition, hydrolysis degradation products were not included on the USGS analytical schedules.

ii. Co-occurrence

Co-occurrence of organophosphorus pesticides was found in raw drinking water but not in finished drinking water (Table III.E.13). Twelve percent of the raw samples with OP detections (16 samples from 137 samples) had more than one OP detection. These data suggest that water treatment processes may reduce the occurrence of parent OP pesticides in finished drinking water.

Table III.E.3.13: Co-occurrence frequency of OP pesticides in raw and finish water samples at reservoir water treatment plants

Number of OPs detected per sample	Number of samples (% of samples) with given number of OPs detected			
	Raw water		Finished	
	Samples	%	Samples	%
0	177	56%	194	88.99%
1 or more	137	44%	24	11%
1	121	39%	24	11%
2	12	3.8%	.	
3	4	1.3%	.	
Total	314	100%	218	100

Table III.E.3.14 shows the profile of individual co-occuring OP pesticides and degradation products in raw water samples. These co-occurring pesticides include azinphos-methyl oxon, azinphos-methyl, chlorpyrifos, diazinon, dimethoate, fenamiphos sulfone, fenamiphos sulfoxide, methidathion, and tebupiriamphos, with diazinon co-occuring the most frequently. These results also show that the PA and MO reservoirs had the highest co-occurrences (3 pesticides per sample) among the various reservoirs.

Table III.E.3.14: Co-occurrence profile of organophosphorus insecticides and some transformation products

Sample (State, date)	Azi/oxon	Azinphos	Chlorpyr	Diazinon	Dimeth	Fena/Sn	Fen/Sx	Methidat	Tebupira
IN 7-11-2000				0.010			0.033		
MO 5-17-1999				0.013					E0.007
MO 5-24-1999				0.022					E0.003
MO 7-19-2000		E0.034	0.034				E0.008		
MO 7-6-1999				0.011				0.010	
NC 5-25-1999				0.012		E0.005			
OH 7-6-2000			E0.002	0.009					
OK 6-29-1999	0.263			0.073					
OK 7-6-1999			E0.002	0.066					
OK 8-2-2000			0.004	0.048					
PA 6-29-2000			0.012	0.015	0.022				
PA 7-11-2000			0.008	0.011	0.012				
PA 8-2-2000			0.004	0.005	E0.006				
SC 6-28-2000		E0.042		E0.001					
SC 8-23-2000		E0.144		E0.003					
SC 9-11-2000			E0.002	E0.002					

Explanation: E=estimated concentration. Azi/oxon=Azinphos-methyl oxon; Azinphos=Azinphos-methyl; Chlorpyr(ifos); Dimeth(oate);Fena/Sn=Fenamiphos sulfone; Fen/Sx=Fenamiphos sulfoxide; Methidat(hion);Tebupira(mphos)

iii. Conclusion

The reservoir monitoring program provided significant information on the occurrence of a wide range of OPs and their transformation products in raw and treated drinking water. The magnitude of detectable concentrations and frequency of detection of most OP compounds and degradation products were generally low in raw and finished waters. Widely used compounds such as chlorpyrifos,diazinon, azinphos methyl, and malathion were detected in raw drinking waters, while degradation products of OP compounds were predominantly found in finished drinking water. The maximum concentration for OP pesticides in water was <0.5 ug/L. The magnitude of time weighted mean (TWM) concentrations were generally similar to the limit of detection (LOD) and highly dependent on the treatment of non-detections.

The reservoir monitoring data suggest that parent OP pesticides are removed or transformed during treatment, possibly by chemical oxidation. Oxidative degradation products of OP pesticides, such as sulfones, sulfoxides, and oxons, were detected in certain finished water samples from actual water treatment plants. At this time, the impact of the individual treatment processes is difficult to assess because of variability among the treatment plants in terms of water quality factors, sequence of treatment operations, and dosage of applied treatment chemicals.

Attachment III.E.1: 31 OP chemicals analyzed in the USGS Reservoir Monitoring Study and Used in Analyses.

	Chemical
1	Azinphos-methyl
2	Azinphos-methyl-oxon
3	Chlorpyrifos
4	Chlorpyrofos, oxygen analo
5	Diazinon
6	Diclorvos
7	Dicrotophos
8	Dimethoate
9	Disulfoton
10	Disulfoton sulfone
11	Disulfotone sulfoxide
12	Ethoprop
13	Ethoprop metasbolite 76960
14	Fenamiphos
15	Fenamiphos sulfone
16	Fenamiphos sulfoxide
17	Malaoxon
18	Malathion
19	Methidathion (Supracide)
20	Paraoxon-methyl
21	Parathion-methyl
22	Phorate
23	Phorate oxygen analog
24	Phosmet (Imidan)
25	Phosmet oxon
26	Profenofos
27	Tebupiriamphos (Phostebupirim)
28	Terbufos
29	Terbufos-O-analogue sulfon
30	Tribuphos (DEF, s,s,s-Tr
31	tebupiramphos (Phostebupirim) oxygen analog

Attachment III.E.2: Summary of Reported Detection Limits for Raw, Finished, and Outfall Samples

Limits of detection for nondetects

Chemical	*Detection Limit (ug/L)*	*Samples reported <DL*	*Chemical*	*Detection Limit (ug/L)*	*Samples reported <DL*
Azinphos-methyl	0.0010	555	Ethoprop metasbolite 76960	0.0050	603
	0.0100	13	Fenamiphos	0.0160	603
	0.0150	1	Fenamiphos sulfone	0.0080	600
	0.0200	4	Fenamiphos sulfoxide	0.0310	600
	0.0300	2	Malaoxon	0.0160	587
	0.0400	1		0.0320	1
	0.0500	20		0.0380	1
	0.0600	2		0.0410	1
	0.0700	1		0.0420	1
	0.0750	1		0.0470	1
	0.0800	2	Malathion	0.0050	592
	0.0900	1		0.0070	1
	0.1000	2		0.0090	1
Azinphos-methyl-oxon	0.0310	587		0.0100	3
	0.0600	1		0.0270	18
	0.0630	7		0.0600	1
	0.0800	1	Methidathion (Supracide)	0.0080	600
Chlorpyrifos	0.0040	575		0.0510	1
	0.0050	19		0.1100	1
	0.0060	5	Paraoxon-methyl	0.0310	603
	0.0100	2		0.0060	621
Chlorpyrofos, oxygen analo	0.0160	603	Phorate	0.0020	603
Diazinon	0.0020	469		0.0110	18
	0.0050	17	Phorate oxygen analog	0.0310	602
	0.0060	3		0.0420	1
	0.0070	1	Phosmet (Imidan)	0.0080	603
	0.0100	2	Phosmet oxon	0.0160	601
Diclorvos	0.0050	603		0.0300	2
Dicrotophos	0.0160	603	Profenofos	0.0080	602
Dimethoate	0.0050	599		0.2700	1
Disulfoton	0.0170	604	27. Tebupiriamphos (Phostebupi	0.0160	603
	0.0210	18	Terbufos	0.0130	604
Disulfoton sulfone	0.0050	602		0.0170	18
Disulfotone sulfoxide	0.0160	602	Terbufos-O-analogue sulfon	0.0160	601
Ethoprop	0.0030	604	Tribuphos (DEF, s,s,s-Tr	0.0160	603
	0.0050	18	31. tebupiramphos (Phostebupir	0.0080	599

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