III. Appendices

E. Water Appendix

3. Water Exposure Assessment: Preliminary Analysis of the USGS-EPA Pilot Reservoir Monitoring Program

a. Introduction

A pilot reservoir monitoring project was initiated by the USEPA Office of Pesticide Programs, Environmental Fate and Effects Division (EFED/OPP), USEPA Office of Ground Water and Drinking Water (OGWDW/OPP), and USGS National Water Quality Assessment (USGS/NAWQA) to assess pesticide concentrations in raw and finished drinking water. Reservoirs were selected for sampling because they are important sources of drinking water and because they store runoff water and pesticide loadings within their watersheds.

In this study, twelve water-supply reservoirs and Community Water Systems (CWSs) were selected based on vulnerability for pesticide contamination. Small watersheds with high pesticide use and high runoff potential were given the highest priority in the selection process. Other factors considered were representation across pesticide use areas, integration with ongoing monitoring efforts, and feasibility. Locations of the selected reservoirs are shown below.
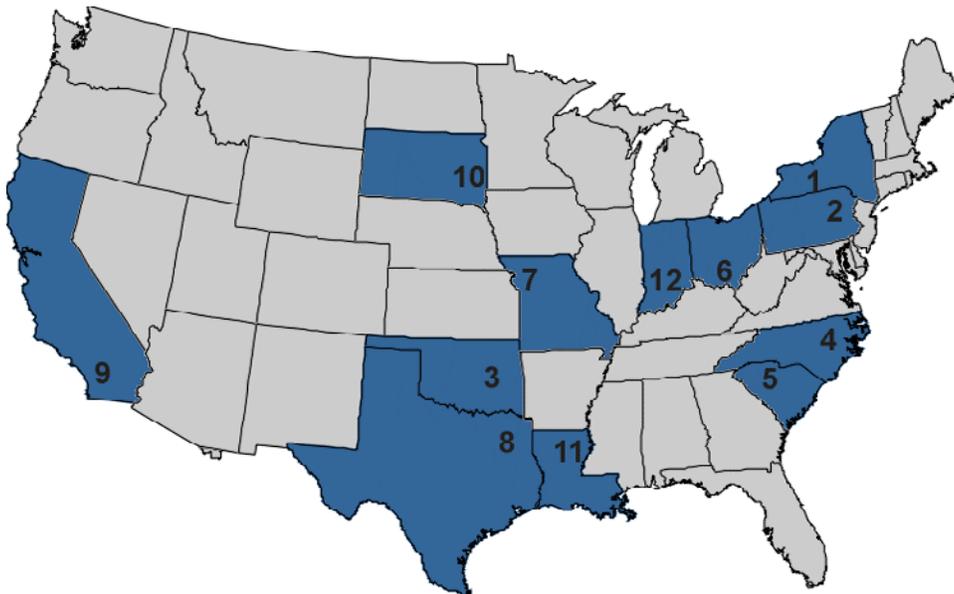

Figure III.E.3.1: Location of Reservoirs in Pilot Monitoring Program

A sampling strategy was designed to measure pesticide concentrations in raw and finished drinking water as well as in reservoir outflow samples to provide an integrated water concentration for the reservoir watershed. For each site visit, the following three water samples were collected: 1) raw water from the intake spigot of the public water system, 2) finished-water at the compliance tap at the entry point to the distribution center, and 3) ambient reservoir water sample at the reservoir outlet. Sampling was designed to coincide with the period of intensive pesticide use, such as the post-pesticide application season. Each site was sampled quarterly for one year with biweekly sampling collection during a four- month post-application period. In addition, 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 each water sample was 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. List of organophosphorus pesticides and their 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	Chlorpyifos, 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

PESTICIDE	IUPAC NAME	DEGRADATES
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	
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		Tebupirimphos oxygen analog
Dicrotophos	3-dimethoxyphosphinoyloxy-N,N-dimethylisocrotonamide	
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. Assessment Process

Scientists in the Office of Pesticide Programs (OPP) of EPA conducted a preliminary data analysis on the reservoir monitoring data for organophosphorus compounds in raw and treated waters. In this analysis, reservoir ("outfall") samples were not considered. Summary statistics were only generated on the organophosphorus compounds in the cumulative OP assessment **(Attachment III.E.1)**. In the near future, OPP plans to conduct a more detailed data analysis, involving calculation of annual time weighted means and estimation of annual percentile concentrations and a comprehensive QA/QC review.

c. Uncertainties and Limitations in Interpretation of Monitoring Data

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

① The samples may not be considered truly paired because the sampling approach did not account for the travel time of the pesticide and its transformation products through the water treatment plant. This lack of exact pairing may limit stoichometric linkage of pesticide degradation and formation of degradation products during water treatment. However, the sampling scheme implemented in the monitoring study allows for comparison of pesticide concentrations in raw and finished drinking water 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.

② Organophosphorus pesticides had low recoveries in matrix-spiked finished water samples (Personal Communication with Joel Blomquist, April 28, 2000), which may be associated with low stability of the organophosphorus pesticides in finished water. Oxidative transformation products of organophosphate pesticides, such as fenamiphos sulfone, fenamiphos sulfoxide, tebupiriamphos oxygen analog, had higher matrix spike recoveries in treated water than the parent compound. Available data indicate organophosphorus compounds are not stable in chlorinated drinking water (Magera, 1994, Tierney, et al. 2001, US EPA,2000). Because organophosphorus pesticides generally have lower concentrations in finished water samples, the detection of any organophosphorus pesticide in finished water can be viewed as a reliable detection.

③ 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. The lower than average rainfall may have impacted pesticide runoff and resulted in lower detections of pesticides.

d. Methods of Data Analysis

Data from USGS/EPA Reservoir Monitoring Data (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 Inst. Inc., Cary NC.). Sampling dates in the original data set were modified to facilitate translation of date variables. After the modification step, 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.

e. Summary Statistics

Summary statistics were determined using Statistical Analysis Systems (SAS) procedures FREQ and SUMMARY to calculate detection frequencies and mean detectable concentrations. Organophosphorus compounds with 10 or more detections in a reservoir during 1999 and 2000 were used to estimate concentration distributions (percentile concentrations).   In this monitoring study, diazinon and malaoxon were the only compounds meeting the criteria for percentile calculations. These 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).

f. Water Treatment Reduction Percentages

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 a pesticide is transformed during treatment or when detection limits or frequencies are low.

g. 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.3.3), 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.3.3: 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.3.4), 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. Powder 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.3.4: 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
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

h. Summary of Organophosphorus Detections

i. Summary Statistics

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 which have not been analyzed in most other monitoring studies, such as tribufos, phostebupirim, profenofos and dichlorvos, and included some toxicologically significant, but 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.3.5), 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 only detected in 6 of 323 raw water samples (1.9%), while malaoxon was only 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 degraded to form malaoxon during the treatment process. Chlorpyrifos was detected in 5.3% 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.

The data illustrate that some non-persistent parent organophosphorus 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 (<0.9% or 2 samples) in raw and finished water samples limited a clear quantitative assessment of treatment transformation.

Table III.E.3.5: 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	.		.	.
Tribuphos (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.3.6). 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.3.7). 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 50th 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.3.6: 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 (Phostebupir	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.3.7: Concentration percentiles for diazinon in raw water samples

State	No.	Detected	mean (ug/L)	percentile method	Percentiles (ug/L)					max detected (ug/L)
					50th	75th	80th	90th	95th	
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		[not computed <10 detections]					0.015
S.Carolina	45	5	0.0018							0.0030
S.Dakota	21	0	.							.
Texas	22	6	0.0035							0.0040

Although diazinon and chlorpyrifos were the only parent compounds detected in more than three reservoirs, azinphos-methyl was detected at the highest 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 2000) in the South Carolina reservoir. Azinphos-methyl oxon, however, was not detected in raw or finished water from the South Carolina 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. As observed in Attachment III.E.2, analytical detection limits were variable among the organophosphorus pesticides and their transformation products**.**   In general, the lowest detection limit was the most commonly reported detection limit.

Of the 31 OP analytes detected, malaoxon had the highest concentration, of all 31 OP analytes. Malaoxon was exclusively detected in finished water samples with a maximum concentration 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.3.8. The distribution of malaoxon concentrations suggest that the 50th percentile concentration is less than the detection limit of 0.016 ug/L.

Table III.E.3.8: 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

i. Water Treatment Effects

The data presented in the summary statistics section indicate that the concentration of most parent organophosphorus insecticides (diazinon, chlorpyrifos, malathion, dimethiate, methyl parathion) was reduced 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 only be estimated when pesticides are detected in both raw and finished water samples **(Table III.E.3.9)**. 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 can occur when a pesticide is transformed during treatment or when detection limits or frequencies are low.

Table III.E.3.9: Water treatment reduction percentages and maximum pesticide concentrations in raw and finished water for selected organophosphorus 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
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 that there is 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 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.
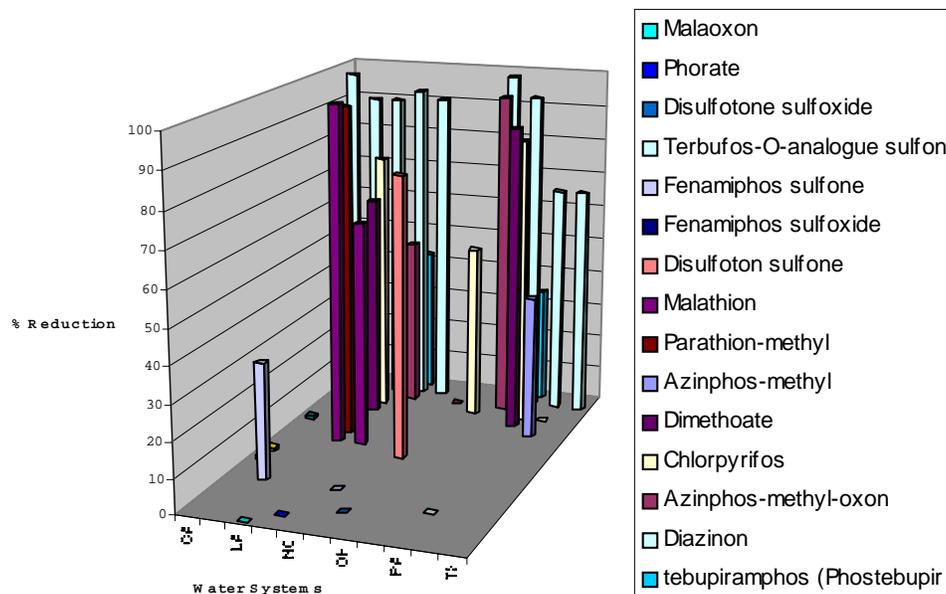
Figure III.E.3.2: Maximum Water Treatment Reduction Percentages Among Reservoirs

Figure III.E.3.2 shows the maximum water treatment reduction efficiencies among the 12 reservoirs which 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.
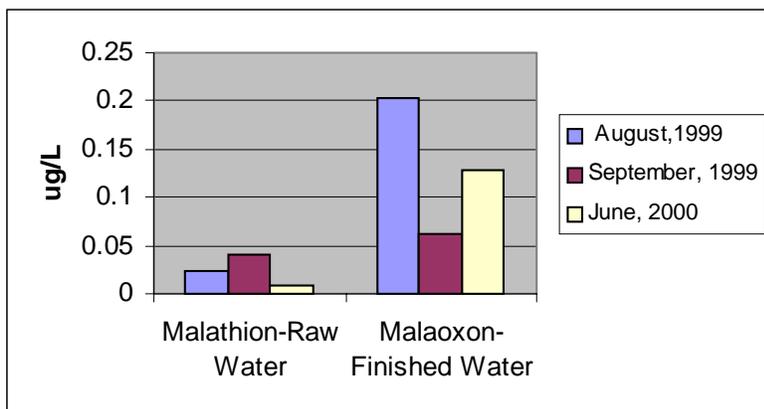
Figure III.E.3.3: Malathion and malaoxon formation in raw and finish water samples at the Louisiana water treatment plant

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 are not available for the reservoir monitoring study. In addition, hydrolysis degradation products were not analytes on the USGS analytical schedules.

j. Co-occurrence

This section summarizes information on the frequency of detection of multiple OPs in water samples, and identifies combinations of OPs that were detected in the same samples. As observed from Table III.E.10, co-occurrence of organophosphorus pesticides was observed in raw drinking water but not in finished drinking water. 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.3.10: 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.3.11 shows the profile of individual co-occuring organophosporus 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.3.11: 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)									

k. Conclusion

The pilot reservoir monitoring program provided significant field information on the occurrence of a wide range of OPs and their transformation products in raw and treated drinking water. The reservoir monitoring data suggest that parent organophosphorus pesticides are removed or transformed during treatment. Oxidative degradation products of organophosphorus pesticides, such as sulfones, sulfoxides, and oxons, were detected in finished water samples from actual water treatment plants. Chemical oxidation through prechlorination and post disinfection treatment processes may provide a plausible explanation for the high removal efficiencies of the organophosphorus pesticides. The impact of the individual treatment processes, however, 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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