Office of Pesticide Programs
Science Policy

The Incorporation of Water Treatment Effects on Pesticide Removal and Transformations in Food Quality Protection Act (FQPA) Drinking Water Assessments

October 25, 2001

Office of Pesticide Programs
United States Environmental Protection Agency
Washington, D.C. 20460

Table of Contents

Executive Summary

The Food Quality Protection Act of 1996 (FQPA) requires that all tolerances for pesticide chemical residues in or on food consider anticipated dietary exposure and all other exposures for which there is reliable information. Drinking water is considered a potential pathway of dietary exposure to pesticides. Because drinking water for a large percentage of the population is derived from public water systems which normally treat raw water prior to consumption, the impact of water treatment on pesticide removal and transformation should be considered in drinking water exposure for risk assessments completed under FQPA. Treated drinking water for the purpose of FQPA exposure assessment will be defined as ambient ground or surface water which is either chemically or physically altered using technology prior to human consumption. Therefore, the objectives of this science policy paper are to: 1) present a preliminary literature review on the impact of different treatment processes on pesticide removal and transformation in treated drinking water derived from ground and surface water sources; and 2) describe how the Office of Pesticide Programs (OPP) will consider the impacts of drinking water treatment in drinking water exposure assessments under FQPA.

Literature Review

A wide variety of factors are taken into account to assess the impact of drinking water treatment on the levels of different pesticides in drinking water. It is important to note that a sizeable proportion of the nation, approximately 23 million people, obtain their drinking water from private wells and other sources that undergo no treatment. For those drinking water sources that are treated, available survey information establishes that there are many distinct types of water treatment processes (and many more combinations of processes) in use throughout the United States. Nearly all public water supply systems use some form of disinfection, and a series of conventional treatment processes (coagulation-flocculation, sedimentation, and filtration). The processes that appear to have the most impact on pesticide removal – granular activated carbon (GAC) and powdered activated carbon (PAC) – are commonly found or used in larger water supply systems but, because of high costs, are rarely used by the smallest systems. Other methods, such as "softening", reverse osmosis, and air stripping are also less frequently used to remediate water quality concerns. In sum, there is enormous spatial and temporal variability in the types of treatment applied to drinking water.

EPA's preliminary review of the literature indicates that conventional treatment (such as coagulation/flocculation, sedimentation, and filtration) has little or no effect on the removal of mobile (hydrophilic or lipophobic) pesticides. Disinfection and softening can facilitate alteration in the chemical structure of the pesticide, or transformation. The type of disinfectant used and the length of contact time between the water and disinfectant are factors which affect the impact on pesticide transformation. There is little information on the chemical identity of transformation products formed as the result of disinfection. However, disinfection can produce toxic by-products of some pesticides (*eg*.,oxons from organophospates). The impact of softening on pesticide transformation is dependent on the potential for alkaline-catalyzed hydrolysis of the pesticide.

The Federal Insecticide, Fungicide, and Rodenticide Act Science Advisory Panel (SAP) evaluated the literature review and concurred with the conclusions (www.epa.gov/scipoly/sap/2000/index.htm#september). The SAP stated that immobile (hydrophobic/lipophilic) pesticides may be removed by conventional water treatment processes.

Proposed Policy

OPP is announcing and seeking public comment on a policy to provide a systematic approach for considering drinking water treatment effects on pesticide removal and transformation in FQPA risk assessments. Because most surface source drinking water receives some form of water treatment prior to human consumption, the proposed treatment policy is generally applicable to surface source drinking water. A similar assumption cannot be made for drinking water systems using ground water because of the importance of private wells in rural areas. Private wells are not generally linked to water treatment systems prior to human consumption. This policy is based on scientific conclusions reached as a result of OPP's literature review and on our assessment of the availability of information for specific pesticides on water treatment effects:

- The Environmental Fate and Effects Division (EFED) will provide available information on the potential and measured effects from drinking water treatment (e.g., flocculation, coagulation, sedimentation, filtration, chlorination, softening, GAC/PAC treatment) to the OPP's Health Effects Division (HED) Metabolism Assessment Review Committee (MARC). The MARC will evaluate this information and determine which, if any, transformation and degradation products might be of toxicological concern. This information will also be considered in FQPA Safety Factor decisions.

- OPP will not generally conclude that treatment mitigates exposure for a specific pesticide without supporting evidence. Therefore, if sufficient pesticide-specific information is not available on effects of a water treatment processes, or if sufficient information is not available on the extent to which specific processes are employed within the pesticide use area, FQPA drinking water assessments will be conducted using pesticide concentrations in raw or ambient waters to represent pesticide concentrations in finished drinking water. This policy is based on the fact that conventional water treatment processes

(coagulation/flocculation, sedimentation, and filtration) are not expected to remove mobile pesticides during treatment.

● If sufficient pesticide-specific information is available on effects of a water treatment process, as well as information on the extent to which such process is employed within the pesticide use area, EFED will attempt to describe quantitatively the potential effects of drinking water treatment for that pesticide in the drinking water assessment. This description will include effects of degradation and formation of transformation products.

● Monitoring data on finished drinking water may also represent in aggregate the effects of treatment in the study area. However, because of the inherent variability associated with water treatment processes, with source water quality, and the limited availability of monitoring data on pesticides in finished drinking water, extrapolating such results to areas outside of the area monitored would be considered on a case-by-case basis. It is anticipated that quantitation of drinking water treatment effects will be limited to pesticides with extensive monitoring data on finished water (e.g. atrazine) or pesticides with monitoring data on finished water from limited use areas (e.g., molinate). Extrapolating treatment effects across compounds with similar structures will be considered on a case-by-case basis.

1.0 Introduction

The Food Quality Protection Act of 1996 (FQPA) amended the Federal Food, Drug, and Cosmetic Act to require that all tolerances (maximum legal residues) for pesticide residues in or on food be "safe." The term "safe" means that EPA has determined there is "a reasonable certainty of no harm" from aggregate exposure to the pesticide residue, including anticipated dietary exposure and all other exposures for which there is reliable information. Drinking water is considered a pathway of potential dietary exposure to pesticides. OPP uses a variety of data, methods, and approaches to assess drinking water exposure for risk assessments completed under FQPA.

Generally, available monitoring data on pesticides in drinking water are limited to concentrations measured in raw or untreated water. OPP recognizes, however, that a large percentage of the population drinks water that has undergone some form of treatment, and where appropriate data permit, OPP intends to consider the impact of drinking water treatment on potential human exposure. The objectives of this paper are to: 1) present a preliminary and general assessment of the impact of different treatment processes on pesticide removal and transformation in treated drinking water derived from ground and surface water sources; and 2) describe how OPP will consider the impacts of drinking water treatment in characterizing its drinking water exposure assessments under FQPA.

2.0 Science Policy and Procedure for Incorporating Water Treatment into FQPA Drinking Water Assessments

2.1 Policy Development Process.

OPP originally developed a background document on this topic in February, 2000, and solicited comment from a variety of internal and external peer reviewers. All external peer review comments addressed technical issues. With the exception of one reviewer, written comments indicated no disagreement with the technical conclusions regarding removal efficiencies of various treatment technologies discussed in the document. The technical peer review comments were addressed in a revised version of the literature review.

The background document was submitted to the FIFRA Scientific Advisory Panel (SAP), a federal advisory committee comprised of external, independent expert scientists, for technical review. A SAP meeting was held on September 29, 2000 to address drinking water treatment effects on pesticide residues in water. The report of the SAP committee on this topic was issued on February 12, 2001. The SAP members generally concurred with the technical conclusions of the document (www.epa.gov/scipoly/sap/2000/index.htm#september). The primary conclusion of the SAP report was that conventional treatment (coagulation/ flocculation, sedimentation and filtration), in general, is not effective in removing residues of mobile (hydrophilic/lipophobic) pesticides from raw surface or ground water. A summary of the SAP comments are as follows:

- Hydrophobic or lipophilic pesticides may be removed through conventional water treatment processes such as coagulation/flocculation, sedimentation, and filtration.
- Predicting the impact of a water treatment process on pesticide removal and transformation is hampered by variability of water treatment processes employed among public water systems and the variability in source water quality.
- Bench scale or "jar" tests can be used to assess the impacts of water treatment processes (e.g., coagulation, flocculation and sedimentation, and adsorption on powdered activated carbon (PAC). Because jar tests are expected to yield higher removal efficiencies than actual water treatment plants, pilot and full scale water treatment plant studies are needed to validate water treatment effects.
- Pesticides that exhibit alkaline hydrolysis may be degraded through high pH water softening processes.
- The impact of disinfection on pesticide transformation should be considered in the drinking water assessments. An evaluation of probable disinfection by-products should be evaluated in this assessment process.
- The Agency should assume that finished water pesticide concentrations are the same as the raw water pesticide concentrations until adequate research is conducted on water treatment effects on pesticide removal and transformation. Exceptions to this approach may occur when chlorination or hydrolysis causes chemical transformation of the pesticide. It is important to consider the health effects of the transformation products.
- Monitoring finished drinking water levels for pesticides found in raw water should be among EPA's highest priorities to assess water treatment effects on pesticide removal

and transformation.

2.2 Policy for Considering Water Treatment in FQPA Drinking Water Assessments

The proposed policy provides a systematic approach for considering drinking water treatment effects on pesticide removal and transformation in FQPA risk assessments. Because most surface source drinking water receives some form of water treatment prior to human consumption, the proposed treatment policy is generally applicable to surface source drinking water. A similar assumption cannot be made for drinking water systems using ground water because of the importance of private wells in rural areas. Private wells are not generally linked to water treatment systems prior to human consumption. This policy is based on scientific conclusions reached as a result of OPP's literature review and on our assessment of the availability of information for specific pesticides on water treatment effects:

- OPP's Environmental Fate and Effects Division (EFED) will provide available information on the potential and measured effects from drinking water treatment (e.g., flocculation, coagulation, sedimentation, filtration, chlorination, softening, GAC/PAC treatment) to the Health Effects Division (HED) Metabolism Assessment Review Committee (MARC). The MARC will evaluate this information and determine which, if any, transformation and degradation products might be of toxicological concern. This information will also be considered in FQPA Safety Factor decisions.

- OPP will not generally conclude that treatment mitigates exposure for a specific pesticide without supporting evidence. Therefore, if sufficient pesticide-specific information is not available on effects of a water treatment processes, or if sufficient information is not available on the extent to which specific processes are employed within the pesticide use area, FQPA drinking water assessments will be conducted using pesticide concentrations in raw or ambient waters to represent pesticide concentrations in finished drinking water. This policy is based on the fact that conventional water treatment processes (coagulation/flocculation, sedimentation, and filtration) are not expected to remove mobile pesticides during treatment.

- If sufficient pesticide-specific information is available on effects of a water treatment process, as well as information on the extent to which such process is employed within the pesticide use area, EFED will attempt to describe quantitatively the potential effects of drinking water treatment for that pesticide in the drinking water assessment. This description will include effects of degradation and formation of transformation products.

- Monitoring data on finished drinking water may also represent in aggregate the effects of treatment in the study area. However, because of the inherent variability associated with water treatment processes, with source water quality, and the limited availability of monitoring data on pesticides in finished drinking water, extrapolating such results to areas outside of the area monitored would be considered on a case-by-case basis. It is anticipated that quantitation of drinking water treatment effects will be limited to

pesticides with extensive monitoring data on finished water (e.g. atrazine) or pesticides with monitoring data on finished water from focused or limited use areas (e.g., molinate). Extrapolating treatment effects across compounds with similar structures will be considered on a case-by-case basis.

2.3 Evaluation of the Water Treatment Data

OPP will evaluate water treatment data submitted to the Agency in support of pesticide registration and reregistration activities. Water treatment data can be derived from studies providing information on the removal/transformation efficiency of the pesticide and identification of transformation by-products. Because there are no standard guideline water treatment studies, water treatment data can be derived from a simple laboratory study (commonly referred to as "jar test") and actual water treatment plant monitoring studies. (Please see Section 3.6 for more details on water treatment assessment techniques.)

The proposed policy states that supporting water treatment data will be considered in drinking water assessments when sufficient and representative pesticide-specific water treatment data are available. Because of the complexity of water treatment technology associated with local water quality conditions across pesticide use areas, as well as the presence of unique or regionally dependent water treatment processes or sequences, it's difficult to establish standard criteria for defining the sufficiency and representative nature of pesticide specific water treatment data. Therefore, OPP will consider the quality of water treatment data on a case-by-case basis.

Criteria for evaluation of water treatment data are expected to be variable because of the various types of water treatment data as well as the variability of treatment across a pesticide use area. Based on recommendations from the FIFRA SAP, general evaluation criteria of water treatment data are as follows:

1.) Laboratory scale treatment studies such as jar tests will be used only to confirm when treatment has no effect on pesticide removal and transformation. This assessment approach was recommended by the SAP because jar tests are known to exaggerate the removal efficiency when compared to actual treatment plants.

2.) When jar tests show pesticide specific removal or transformation, pilot plant or actual water treatment plant monitoring studies are needed to establish realistic removal or transformation efficiencies. These studies should represent the treatment systems and processes found in the pesticide use area. Submission of water treatment and water quality data in the pesticide use are needed to ensure the representative nature (bracketing conditions in the pesticide use area) of the water treatment data. Monitoring data should provide temporally-paired raw water and finished water samples. Also, paired samples may be required for individual treatment processes if interactive effects are expected from sequential treatment processes.

OPP is willing to work with the scientific community (including pesticide registrants) to

design scientifically defensible and cost-effective protocols for a particular pesticide that could generate reliable information on which to base quantitative estimates of treatment effects. Currently, EFED is working with the Office of Research and Development (ORD) to develop water treatment protocols. How OPP will qualitatively and/or quantitatively factor drinking water treatment data into its estimates or characterization of pesticide concentrations in drinking water will be detailed in a future policy paper.

3.0 LITERATURE REVIEW OF THE IMPACTS OF WATER TREATMENT ON PESTICIDE REMOVAL AND TRANSFORMATIONS IN DRINKING WATER

3.1 Overview

3.1(a) Summary of the Impact of Water Treatment on Pesticide Removal and Transformation

OPP concludes from the literature review that, in general, the conventional   water treatment at most Community Water Systems (CWSs), specifically coagulation-flocculation, sedimentation, and conventional filtration, does not remove and transform pesticides in finished drinking water. Disinfection and water softening, which also routinely occur at CWSs can, however, lead to pesticide transformation and, in some cases, pesticide removal or degradation. This finding is important because disinfection and covential coagulation/filtration are commonly used treatment processes at CWSs in the United States. Chemical disinfection has been shown to form pesticide degradation products, which may or may not correspond to degradation products currently considered in OPP risk assessments. Particularly for those pesticide degradation by-products which are not observed in standard metabolism and other studies required by OPP, there may be limited information on the nature and toxicological importance of the pesticide. The type of disinfectant used and the length of contact time with the disinfectant are important factors in assessing water treatment effects.

Powdered activated carbon (PAC) filtration, granulated activated carbon (GAC) filtration, and reverse osmosis (RO) have been demonstrated to be highly effective processes at removing organic chemicals, including certain pesticides (primarily acetanilide herbicides), but specific data on removal of most pesticides are not available. Also, air stripping is only effective for volatile pesticides or those with a high Henry's Law Constant. Among these organic removal treatment processes, PAC is the more common method because it can be used in concert with conventional water treatment systems with no significant additional capital investment. Available data suggest that about 46% of large CWSs (serving > 100,000 people) use PAC at some time during the year, and that most of these systems are surface water-based systems (SAIC, 1999). Air stripping is an effective water treatment for volatile pesticides (Henry's Law Constants > 1 X 10^{-3} atm m^3/mole), but this method is used at very few CWSs (less than 1% of CWSs).

A preliminary correlation analysis of the environmental fate properties of pesticides considered in this paper with removal efficiencies does not indicate any trends or relationships, making it difficult to predict removal efficiency for specific compounds without additional data. However, Speth and Miltner, 1998 reported that, in general, compounds with Freundlich coefficients on activated carbon greater than 200 ug/g (L/ug)$^{1/n}$ would be amenable to removal by carbon sorption.

3.2 Background

The Food Quality Protection Act (FQPA) of 1996 requires that all non-occupational routes of pesticide exposure be considered in aggregate and cumulative dietary human health exposure assessments for pesticide tolerance reassessment. Because drinking water is a route of potential dietary exposure, it is factored into FQPA dietary exposure assessments. FQPA drinking water exposure assessments are based on screening models (*e.g.* First Index Reservoir Scenario Tier (FIRST), GENeric Estimated Environmental Concentration (GENEEC), and Pesticide Root Zone Model (PRZM)/ EXposure Analysis Modeling System (EXAMS), pesticide occurrence data in ambient waters [*e.g.*, NAtional Water Quality Assessment (NAWQA)], and appropriate pesticide occurrence data in drinking water such as compliance monitoring data. Generally, neither the models nor modeling data support the estimation of pesticide concentrations in "treated" drinking water.   Treated drinking water for the purpose of FQPA exposure assessment will be defined as ambient ground or surface water which is either chemically or physically altered using technology prior to human consumption.   As a potential refinement to FQPA drinking water exposure assessments, water treatment effects (including both pesticide removal as well as transformation) need to be considered and appropriately factored into the aggregate human health risk assessment process under FQPA.

Assessment of the impacts of drinking water treatment processes on the level of pesticide concentrations in ambient water and the resulting levels in treated water requires an understanding of the removal efficiency for various pesticides and treatment processes, as well as an understanding of the spatial and temporal distribution of treatment systems within potential pesticide use areas. Assessment of treatment processes is further complicated because each water treatment system is uniquely designed to accommodate local water quality conditions (nature and levels of organic, inorganic, and biological contaminants), the number of persons served, and economic resources.

3.3 Technical Approach in Assessing Water Treatment Data

OPP reviewed Agency documents, including research articles by scientists of EPA/ Office of Research and Development (ORD) and EPA publications, basic textbooks on water treatment, and publications in the open literature to compile information on the removal and potential transformation of pesticides detected in raw waters. Information obtained through personal communication was also considered. This information was then summarized in tabular form to highlight the removal efficiencies associated with different treatment processes and different methods used to estimate these efficiencies. These methods include bench scale studies (jar tests), pilot plant studies, and full-scale treatment operations that used distilled water, surface water, and groundwater, as raw water. The pesticide removal efficiencies were derived from studies and investigations in which the levels of pesticides, before and after treatment, were quantitatively analyzed. The majority of these treatment operations were not designed specifically to remove the pesticides.

When available, data on the chemical transformation of pesticides in certain treatment operations were presented. Pesticide transformation products would not be typically expected from treatment processes involving phase separations such as flocculation and sedimentation. However, chemical transformation of pesticides is expected from chemical or biochemical reactions resulting from addition of acidic or basic compounds, biochemically mediated transformations, and treatment chemicals that alter the redox potential of the systems under consideration.

3.4 Regulatory History

Drinking water from community water systems (CWSs) and non-community water systems (NCWSs) is regulated under in the Safe Drinking Water Act (SDWA). Based on this law, maximum contaminant levels (MCLs) have been established by EPA for 83 contaminants, including 24 pesticides, some of which are no longer approved for use. The MCL for each contaminant is based on a consideration of the best available technology (BAT) as well as occurrence and human exposure, health effects and toxicity, analytical methods, and economics. The MCL is established to be as close to the maximum contaminant level goal (MCLG) as feasible. The MCL for each contaminant is based on consideration of the best available technology (BAT), as well as health effects and toxicity, occurrence and human exposure, analytical methods, and economics. There are 14 currently registered pesticides with MCLs.

The SDWA requires disinfection of all public water supplies and establishes criteria of filtration requirements for public water supplies derived from surface water. Additionally, the Surface Water Treatment Rule of 1989 (SWTR) requires all public water systems using surface water or groundwater under the influence of surface water to disinfect drinking water. Systems may be required to filter their water if certain water quality criteria (*e.g.*, turbidity, removal of *Giardia* cysts and viruses, compliance with total trihalomethane MCL) and site-specific objectives (watershed control program) are not met. In 1991, the criteria of SWTR were amended to include removal of *Cryptosporidium*. These regulations serve to establish the baseline treatment processes for public water systems.

The 1996 amendments to the SDWA were designed to focus on small system treatment technologies (US EPA,1998). The amendments were designed to: 1) identify technologies that small systems can use to comply with the Surface Water Treatment Rule (SWTR) and National Primary Drinking Water Regulations (NPDWR); 2) identify best available technologies (BATs) for larger systems; and 3) evaluate emerging technologies as potential compliance or variance technologies for both existing and future regulations. Small treatment systems, as defined in the 1996 amendment of SDWA, serve populations of 10,000 or fewer people.

Granular activated carbon (GAC) under the SDWA is the best available technology (BAT) for removing synthetic organic chemicals (SOC); virtually all pesticides are SOCs. Other recommended BATs are aeration technologies for removal of dibromochloropropane and chlorination or ozonation for removal of glyphosate.

The Disinfectants/Disinfection By-Products Rule (D/DBP) was finalized in 1998. The rule deals with the halogenated compounds generated during disinfection or chlorination of raw waters with dissolved organic matter (humic acids, fulvic acids, etc.). Maximum residual disinfectant limits (MRDLs) have been set and allowable levels of disinfection by-products such as trihalomethanes, haloacetic acids, haloketones, haloacetonitriles, etc.) were established.` In a similar fashion, the European Union (EU) has issued the drinking water directive of 1998 that sets a maximum concentration of 0.0001 mg/L for individual pesticides or degradation products and 0.0005 mg/L for total pesticide residues in drinking water after treatment (Acero et al, 2000, http://europa.eu.int/water/water-drink/98_83en.pdf).

3.4(a) Pesticides Currently Regulated Under the SDWA

Under the current SDWA, allowable levels of some pesticides should not exceed their MCLs. These MCLs are established to be protective of human health and must be "feasible." Feasibility is determined by BAT removal efficiency, levels of contaminants in raw water, water quality parameters, and the contaminant concentrations that can be accurately quantified analytically. The MCLs of the 14 currently registered pesticides are:

Pesticide	MCL (µg/L)
Atrazine	3
Alachlor	2
Aldicarb	3
Carbofuran	40
2,4-D	70
Diquat	20
Endothall	100
Glyphosate	700
Lindane	0.2
Methoxychlor	40
Oxamyl	200
Pentachlorophenol	1
Picloram	500
Simazine	4

3.5 Water System Statistics

Under the SDWA, a public water system (PWS) is any system which provides water for human consumption through water pipes or has at least 15 service connections or regularly serves an average of at least 25 people individuals daily for 60 days in the year. A PWS is either a community water system (CWS) or non-community water system (NCWS). Non-transient non-community water systems are defined as water systems that serve less than 25 of the same people for at least six month period. An example of non-transient community water system is a well serving a school or hospital. Transient non-community water systems are water systems that do not regularly serve at least 25 of the same people over a six month period. An example of a non-

transient non-community water system is a well serving a campground or roadside rest area.

Approximately 23 million people in the United States obtain their drinking water from sources other than public water systems. The remaining 252 million people in the United States obtain their drinking water from Community Water Systems (CWSs), with 84 million people relying on solely groundwater-based systems and about 168 million people relying on surface water in part or in whole (Personal Communication with Chuck Job USEPA/OW, 2000). In general, CWSs are regulated under the Safe Drinking Water Act (SDWA) and are required to meet certain standards. This means that these systems generally use some form of water treatment, particularly of surface water, prior to distribution into homes and businesses.

Typically, the sophistication of the water treatment technology is dependent on the population served, type of source water, and physico-chemical properties of the source water (USEPA, 1997). These factors are discussed in the following sections.

3.5(a) Population Served (Size of Water Treatment Facilities)

The size of Community Water Systems (CWSs) is expected to be dependent on the water demand or population served. Based on the 1995 CWS survey (USEPA, 1997), 85% of CWSs are small systems serving 3,300 or fewer people. Medium (serving 3,301 to 50,000 people) and large (serving > 50,000 people) CWSs account for only 13% and 2% of CWS systems, respectively. Although these medium and large systems represent only 15% of number of CWS, they are responsible for serving approximately 90% population.

3.5(b) Types of Water Treatment Associated with Different Source Waters

The percentage of CWSs using no water treatment technologies has decreased between 1976 to 1995 (EPA 815-R-001a). CWSs using no water treatment typically are small CWSs (serving < 500 people) using surface water or small to medium size CWSs using ground water (US EPA, 1999). Although there are larger CWSs (serving 501 to 100,000 people) using groundwater with no water treatment, they represent a relatively small percentage (0.9 to 16% of systems) of the CWS systems. With the exception of the small CWSs (serving < 500 people) using surface water, all CWSs withdrawing from surface water are using some type of water treatment. This trend can be attributed to EPA's promulgation of the Surface Water Treatment Rule of 1989.

The 1995 Community Water System Survey identified approximately 38 different water processes for water systems using mixed source waters. Water treatment is mainly established for the following purposes: disinfection, sediment removal, organic removal, and corrosion control. Disinfection is the most common treatment process for CWSs using only groundwater (Table 3.1). The predominant treatment processes for CWSs using surface water are disinfection/oxidation, flocculation/coagulation, and conventional (sand or gravel) filtration (Table 3.2). Water systems using a mixture of ground and surface waters generally use similar treatment technologies as are used for the predominant source water type (USEPA, 1997).

Control of turbidity is the main difference in treatment strategies for CWS using surface water or surface water/ground water.

Table 3.1. Percent of Ground Water Systems with Treatment[1]

Treatment Category	Population Category (Number of People Served)							
	Less than 100	101-500	501- 1,000	1,001- 3,000	3,301- 10,000	10,001- 50,000	50,001 - 100,000	More than 100,000
Disinfection	52.8	77.9	84.0	79.7	86.8	96.5	86.3	96.4
Aeration	1.5	6.3	17.1	19.9	29.7	33.0	49.1	44.1
Oxidation	3.2	6.6	9.4	4.2	10.9	9.3	18.6	5.4
Ion Exchange	0.7	1.6	3.8	1.9	4.6	3.3	1.2	0
Reverse Osmosis	0	1.2	0	0.9	1.2	0.7	1.2	0
GAC	0	0.5	0	0.4	0	6.7	7.5	9.0
PAC	0	0	0	0	0.2	0.3	0	1.8
Filtration	11.8	8.0	15.9	14.9	29.5	29.6	50.3	51.4
Coagulation/ Flocculation	1.5	5.4	4.2	3.4	8.1	15.1	24.2	25.2
Lime/Soda Ash Softening	2.1	3.7	4.1	5.2	7.0	12.2	17.4	32.4
Recarbonation	0	0.5	0	1.1	3.0	6.1	7.5	10.8

1- Data taken from SAIC, 1999.

Table 3.2. Percent of Surface Water Systems with Treatment[1]

Treatment Category	Population Category (Number of People Served)							
	Less than 100	101-500	501- 1,000	1,001- 3,000	3,301- 10,000	10,001- 50,000	50,001 - 100,000	More than 100,000
Disinfection	92.8	94.1	100	100	96.0	98.0	100	100
Aeration	0	0	1.4	5.5	8.5	3.5	10.3	14.3
Oxidation	0	2.0	7.2	5.8	7.7	10.5	5.7	4.6
Ion Exchange	0	0	0	0	0	0	0	0
Reverse Osmosis	0	0	0	0	0	0	0	0
GAC	3.9	4.3	1.4	2.3	4.7	10.2	14.9	11.2
PAC	0	2.0	3.0	4.6	18.6	24.6	34.2	45.9
Filtration	78.5	71.2	79.3	81.7	86.5	96.3	88.0	93.4
Coagulation/ Flocculation	27.5	52.6	70.2	78.5	95.4	94.5	93.7	99.5

Table 3.2. Percent of Surface Water Systems with Treatment[1]

Treatment Category	Population Category (Number of People Served)							
	Less than 100	101-500	501- 1,000	1,001- 3,000	3,301- 10,000	10,001- 50,000	50,001 – 100,000	More than 100,000
Lime/Soda Ash Softening	3.9	8.1	20.5	17.5	10.8	6.9	5.7	5.1
Recarbonation	0	0	0	0	0	0	1.1	5.1

1-Data are taken from SAIC, 1999.

Water treatment in PWSs consists of a sequence of individual treatment processes. Conventional treatment, defined as a sequence of processes typically used in water treatment, may include the following treatment processes: clarification (sedimentation), filtration, softening, recarbonation, and chlorination (Miltner, et al. 1989). The selection of treatment processes to be used at a given PWS, however, is dependent on several factors including, seasonal changes/requirements, water quality, watershed properties, population served, and economics. Therefore, water treatment processes at each PWS consist of a unique set of processes which cannot be generalized or exactly replicated. Disinfection/oxidation processes, for example, can vary with regard to the selection of disinfectant, location of disinfection process in water treatment process, and may depend on the microorganisms present in the source water, turbidity of source water, and the nature and presence of organic and inorganic contaminants. Modification of any variable in the disinfection process can drastically alter the efficiency of the process, as well as the production of byproducts in finished water. The chemical and physical engineering of sequential water treatment processes needs to be considered in assessing pesticide removal and transformation.

3.6 Water Treatment Assessment Techniques

Basic water treatment assessment approaches fall into three categories: relational (regression modeling), experimental (prototype studies), and actual field monitoring. The relational or correlative approach relies on regressing pesticide removal for a specific process to environmental fate properties of pesticides. The pesticides whose removal rates have been reported in the literature do not have sufficiently variable properties to develop regression equations that apply to a wide range of chemicals. Therefore, OPP's preliminary analysis could not establish any clear relationship or trend between the ability of a specific water treatment process to reduce the concentration of a pesticide in water and the environmental fate and characteristics of the pesticide. (Please see Section 3.9).

Prototype studies are the standard approach to assess and optimize water treatment processes (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). The most common approach is the bench scale laboratory study commonly referred to a " jar" study. A jar study is a static mixed reactor system (mixed water in a jar). Although there is no standard test protocol for jar studies, a standard protocol has been proposed by Lytle, 1995. The test study is recommended to assess the impact of primary water treatment processes including coagulation, flocculation, and sedimentation (J.M.M. Consulting Engineers, 1985). Jar tests are also recommended to assess

turbidity removal; appropriate dose of coagulants; impact of polymeric aids; impact of mixing time; and control measures for iron and manganese precipitation (J.M.M. Consulting Engineers, 1985). Advantages of jar studies are the relative ease and costs associated with the method. Disadvantages of jar tests as a method for determining impacts of conventional drinking water treatment on the levels of pesticides in finished water are that they typically do not permit evaluation of how characteristics of the raw source water (*e.g.*, turbidity or pesticide concentration) by which vary both temporally and spatially--may affect the ability of the water treatment process to reduce pesticide concentrations (Carrol, 1985 and Lytle, 1995). Another disadvantage of jar studies is that they do not evaluate the combination of treatment processes operating at a plant scale.

More refined prototype studies are pilot scale and plant scale studies. These types of studies are recommended to assess filtration processes (J.M.M. Consulting Engineers, 1985). Filtration variables evaluated using pilot scale studies are: filter media size, bed depth, filter media type, filtration rates, filter washing conditions. Other specialized studies can be conducted to assess specific treatment issues including volatile organic carbon (VOC) removal using packed towers, air loading rates in air stripping, disinfectant dose and type, or evaluation of adsorption from GAC. The actual scale of the special studies should be commensurate with simulation of full scale water treatment processes (J.M.M. Consulting Engineers, 1985).

Actual monitoring at water treatment plants is conducted for regulatory and research purposes. The general approach of the monitoring studies is to analyze raw source water at the water system intake and finished drinking water. The major advantage of this approach is that the whole water treatment process is evaluated rather than an individual process. A disadvantage of water plant monitoring is the difficulty in conducting precise temporally-paired raw and finished water sampling. This type of sampling is required to estimate removal or transformation efficiencies. Also, an assessment on the impact of individual treatment processes within the water plant requires paired sampling before and after each treatment.

3.7 Water Treatment Processes and Removal Efficiencies

3.7(a) Conventional Treatment

A typical system for surface water treatment generally consists of pre-settling, coagulation/flocculation (sediment removal), granular filtration (sediment removal), corrosion control (pH adjustment or addition of corrosion inhibitors), and disinfection (J.M.M. Consulting Engineers, 1985; Faust and Aly, 1999; USEPA, 1989). It is important to note there are many variations on this common sequence, regarding points of addition of a wide variety of chemicals (e.g., chlorine, ammonia, ozone, coagulants, filter aids, PAC, etc.). The pre-settling process is a preliminary removal of materials (including non-colloidal sediment) from the raw water. The water is then treated with alum and polymers to encourage flocculation of the colloidal materials (including suspended sediment) and then allowed to settle. Next, the water is passed through a granular filter comprised of sand and possibly anthracite. After filtering, the water is conditioned to prevent corrosion and then disinfected using either chlorine or chloramines.

A modification to the typical treatment process is the use of granular activated carbon (GAC) or powder activated carbon (PAC) for the control of odors and taste in the finished water. This modification is applied through the filtration process either through the formation of a filtration bed using GAC or through the addition of PAC prior to coagulation/flocculation and filtration.

3.7(a)1 Coagulation/Flocculation

Coagulation and flocculation is a two-step process to remove inorganic and organic colloidal materials from water (J.M.M. Consulting Engineers, 1985). Colloidal materials are particles that are so small (less than 10 µm) that they stay suspended in the water. They often have charged surfaces that cause them to repel each other. The coagulation process neutralizes the colloid's surface charge, which is then followed by mixing, and eventually causes flocculation (the joining of individual particles) of the colloids into aggregates called "flocs". The flocs are then large enough to settle from the water column. This process is needed to remove turbidity (inorganic colloids) and color (organic colloids). Removal of organic colloids such as humic and fulvic acids is critical because they are known precursors to the formation of disinfection by-products (e.g., trihalomethanes) when chlorine is added.

Commonly used coagulants are inorganic salts [alum ($Al_2(SO_4)_3$) , aluminum chloride ($AlCl_3$), ferric sulfate ($Fe_2(SO_4)_3$) , ferric chloride ($FeCl_3$)]. Certain organic polymers are also used. Inorganic salts are effective coagulants because Al^{+3} and Fe^{+3} hydrolyze to form positively charged hydrolysis species for neutralization of the surface charge for colloid destabilization. Additionally, these ions hydrolyze to form amorphous hydroxides, $Al(OH)_3$ and $Fe(OH)_3$, which cause physical aggregation through colloid entrapment. The time required for coagulation/flocculation to occur is a critical factor. Typically, coagulation and sweep floc formation is rapid (0.5 to 30 seconds). Water is typically held in a flocculation basin for 15 to 45 minutes (USEPA,1989). The optimum pH range for coagulation is about 6.5 (J.M.M. Consulting Engineers, 1985 and USEPA,1989). Higher pH, above pH 8, will result in dissolution of the $Al(OH)_3$ flocs. Recommended alum dose rates range from 5 to 150 mg/L (USEPA, 1989). Natural and synthetic polymers are also used to form different charges (cationic and anionic) for neutralization of various surface charges. Cationic polymers (positive charge) are generally used as primary coagulants. Typical polymer dosages range from 1.5 to 10 mg/L (USEPA, 1989). Nonionic and anionic polymers are used to strengthen flocs. They can be added at alum at polymer ratios ranging from 100:1 to 50:1 (USEPA,1989). Jar tests are recommended to evaluate coagulant doses.

Organic compounds potentially removed through coagulation/flocculation are hydrophobic, low molecular weight acidic functional groups (e.g., carbonyl and carboxyl functional groups), or high molecular weight compounds (USEPA, 1989). Coagulation processes have been developed to take advantage of adsorption on surfaces of $Al(OH)_3$ and $Fe(OH)_3$ flocs (USEPA, 1989). EPA recommendations include:

Acidification - Add acid prior to coagulant addition to encourage cationic species

formation and sorption on colloid surfaces;

Flocculation - Addition of anionic polymer after the coagulant addition; and,

Adsorption Process - Addition of powdered activated carbon to, or with, the addition of coagulant for organic removal.

Miltner *et al.*, (1989) provide information on the possible removal of pesticides with conventional treatment. In this study, three triazine pesticides (atrazine, simazine, and metribuzin), two acetanilides (alachlor and metolachlor), linuron, and carbofuran were spiked into Ohio River water in jar tests. The initial concentrations of the pesticides (C_o) as shown in Table 3.3, range from 34.3 to 93.4 µg/L. After alum coagulation [$Al_2(SO_4)_3$@$4H_2O$: 15-30 mg/L], the initial turbidity of the raw water (6 - 42 NTU, Nephelometric Turbidity Units) dropped to less than 1 NTU in the settled water. Table 3.3 summarizes the data obtained on the possible removal of the eight pesticides during alum coagulation. No removal of the triazine pesticides, linuron, and carbofuran was observed. The removal of alachlor and metolachlor was low and ranged from 4 to 11 % percent.

Table 3.3. Removal of Pesticides by Coagulation.

Pesticide	Coagulant (dose, mg/L)*	Initial Concentration (µg/L)	% Removal
Atrazine	Alum (20)	65.7 (SW)*	0
Simazine	Alum (20)	61.8 (SW)	0
Metribuzin	Alum (30)	45.8 (SW)	0
Alachlor	Alum (15)	43.6 (SW)	4
Metolachlor	Alum (30)	34.3 (SW)	11
Linuron	Alum (30)	51.8 (SW)	0
Carbofuran	Alum (30)	93.2 (SW)	0

From Miltner et al., 1989
* SW =surface water

3.7(a)2 Softening

Water softening is used to lower the water hardness, which is represented by the summation of calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in water. Hardness reduces the effectiveness of soaps and detergents and hard water often leaves films and deposits on surfaces in contact with it. The recommended hardness of drinking water can range from 50 to 150 mg/L (J.M.M. Consulting Engineers, 1985). Water softening can be achieved through precipitation of Ca^{+2} and Mg^{+2} or ion exchange. Precipitation of $CaCO_3$ and $Mg(OH)_2$ requires adjusting the pH to between 9.3 and 10.5. Alteration of pH may be accomplished using either lime or caustic soda (NaOH). After precipitation, the water pH is lowered using recarbonation

(dissolving CO_2 in water). Ion exchange using cation exchange resins is another technique used in water softening.

The process of softening or softening-clarification was evaluated for its ability to remove pesticides from water. Data collected from the full-scale treatment plants indicated that atrazine, cyanazine, metribuzin, alachlor and metolachlor at initial concentrations in parts per billion level (μg/L) were not removed during the softening-clarification process. In contrast, parent carbofuran was reported as 100% removed. During softening when the pH of the solution reached between 10 to 11, alkaline hydrolysis of carbofuran could have taken place, especially if there was sufficient detention or contact time. However, no analysis of degradation products was reported. Based on environmental fate data from EPA/OPP (USEPA, 1999) and Nanogen Index (1975), carbofuran hydrolyzes under alkaline conditions to form carbofuran-7-phenol and 3-hydroxycarbofuran.

Table 3.4. Removal of Pesticides Associated with Softening-Clarification at Full-Scale Treatment Plants.

Pesticide	Initial Concentration (μg/L)	% Removal
Atrazine	7.24	0
Cyanazine	2.00	0
Metribuzin	0.53 - 1.34	0
Simazine	0.34	0
Alachlor	3.62	0
Metolachlor	4.64	0
Carbofuran	0.13 - 0.79	100

From Miltner et al. (1989)

3.7(a)3 Sedimentation

Sedimentation is effective in removing materials and particulates with densities greater than water (1 g/cm^3) (J.M.M. Consulting Engineers, 1985), which settle out under the influence of gravity. Sedimentation in the water treatment process occurs following flocculation and generally precedes filtration. Additionally, sedimentation may occur in retention basins before water enters the water treatment plant. No data were available or reviewed to assess the effectiveness of sedimentation on pesticide removal and transformation.

3.7(a)4 Filtration

Filtration is considered an integral step in the water treatment process for particulate removal, including microorganism (*Giardia lamblia*), algae, colloidal humic compounds, viruses, asbestos fibers, and suspended clays (J.M.M. Consulting Engineers, 1985). Conventional filtration has been defined as "a series of processes including coagulation, flocculation, sedimentation, and filtration resulting in particulate removal" (40 CFR 141.2).   For this paper,

filtration will be defined as a process of particulate removal through interaction with filter media either through straining or non-straining mechanisms (J.M.M. Consulting Engineers, 1985). Filters can be made using screens (*e.g.*, polyethylene, stainless steel, cloth), diatomaceous earth, and granular materials (*e.g.*, sand, anthracite coal, magnetite, garnet sand, and ground coconut shells). These filters can effectively remove particulate materials with diameters of up to 10 mm. Coagulation-flocculation generally precedes sedimentation, which precedes filtration. This sequence of treatment is common in conventional water treatment processes. Water flow through filters can be controlled by gravity (granular filters) or under pressure (diatomaceous earth filters). Factors impacting filter efficiency are related to the particulate size, granular size distribution, filtration rate, surface properties of the filter, and head pressures (J.M.M. Consulting Engineers, 1985, USEPA, 1989)**.** No data were reviewed to assess the effectiveness of filtering (except granular activated carbon) on pesticide removal and transformation. Other filter configurations may include filter adsorbers (capping a sand filter with GAC) or post-filter adsorbers (separate GAC beds after sand filtration).

3.7(b) Disinfection/Chemical Oxidation

Disinfection is the process for inactivation or destruction of pathogens (including bacteria, amoebic cysts, algae, spores, and viruses) in water (J.M.M. Consulting Engineers, 1985). Disinfection also has the the potential to remove some pesticides through oxidation. Inactivation or destruction of pathogens occurs through chemical oxidation of cell walls or other mechanisms. Chemical disinfectants listed in sequential order from highest to lowest oxidation potential are ozone (O_3), chlorine dioxide(ClO_2) , chlorine (Cl_2), and chloroamines (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). Other advanced oxidation processes (AOP) are ozone (O_3)-hydrogen peroxide (H_2O_2), Ultraviolet (UV)-O_3, O_3 at high pH (pH > 8), or potassium permanganate ($KMnO_4$) (USEPA, 1989). Physical disinfection process utilizes ultraviolet radiation (UV), which encourages photodegradation of nucleic acids in microorganisms (USEPA, 1989). This process is conducted at wavelengths ranging 250 to 270 nm (USEPA, 1989).

Primary disinfection occurs prior to or during the water treatment process. Chlorine, O_3, and ClO_2 are used as the primary disinfectants. The target dose rate for chlorination is to achieve a maximum free chlorine concentration (hypochlorous acid + hypochlorite) of 1 mg/L (USEPA, 1989). Secondary disinfection is used to establish residual concentrations of disinfectants in drinking water. Monochloramine and chlorine are used as secondary disinfectants. Although the order of oxidation potential generally describes the effectiveness of the disinfectant (a high oxidation potential is highly effective), the kinetics of oxidation can alter the relative effectiveness of disinfectants. The effectiveness of chemical disinfection also is dependent on water quality (including turbidity, quantity and types of organics, pH, and temperature), contact time, and application time in the water treatment process (J.M.M. Consulting Engineers, 1985 and USEPA 1989).

Water quality is an important factor in controlling disinfectant effectiveness as well as formation of byproducts. The pH of the water is critical in controlling the distribution of the active chlorine species (hypochlorous acid) and hydroxy radicals from ozone (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). The water turbidity is critical in determining the

disinfectant dose as well as the amounts and kinds of disinfection by-products. Water high in turbidity requires a higher disinfectant concentration because of disinfectant demand exerted by the particulates. Bench-scale studies (e.g., jar tests) are recommended to determine the disinfectant dosage.

A major consideration regarding chemical disinfection is the formation of disinfection by-products. Maximum concentrations of disinfection byproducts are expected when there are high concentrations of organic compounds or when there is long contact time with the disinfectant (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). Water treatment processes that remove natural or synthetic organics prior to disinfection are expected to minimize disinfectant by-product concentrations in drinking water due to removal of precursor materials. Halogenated disinfection by-products are expected from chlorine and chlorine dioxide (USEPA, 1989). Chloroamines are not expected to form comparable quantities of disinfection by-products when compared to chlorine. Ozone is recommended as an alternative disinfectant to reduce the concentrations of disinfectant by-products (AWWA Water Quality and Treatment Handbook).

In laboratory studies conducted by Miltner $et\ al.$ (1987), different oxidants were tested for their ability to remove alachlor in water. The oxidants were O_3, Cl_2, ClO_2, H_2O_2, and $KMnO_4$. Table 3.5 shows the chemical oxidation results using different doses of the oxidants, alachlor concentration, and contact time. Only ozone was found to remove alachlor, with removal efficiencies ranging from 75 to 97% for distilled water, groundwater and surface water. The remaining oxidants such as ClO_2, H_2O_2, and $KMnO_4$ were largely ineffective in removing alachlor in distilled water samples. In surface water samples, low removal efficiencies were exhibited by Cl_2 and ClO_2.

Table 3.5. Removal of Alachlor by Chemical Oxidation

Oxidant	Oxidant dose (mg/L)	Alachlor Concentration (μg/L)	Contact Time (Hr)	% Removal
Ozone	6.9	139 (DW)*	0.22	95
	2.6-9.3	145 (GW)**	0.22	79 - 96
	2.3-13.7	0.39 - 5.0 (SW)***	0.22	75 - 97
Chlorine	4.0-6.0	31 - 61 (SW)	2.5 - 5.83	0 - 5
ClO_2	3.0	61 (SW)	2.5	9
	10.0	58 (DW)	22.3	0
H_2O_2	10.0	58 (DW)	22.3	0
$KMnO_4$	10.0	58 (DW)	22.3	0

* From Miltner et al., 1987
*DW=distilled water   **GW=Groundwater   ***SW=Surface water

The oxidation of glyphosate (herbicide) by different disinfection chemicals from pilot-

plant studies was reported by Speth (1993). Glyphosate concentration (796 µg/L) was reduced by chlorine (2.1 mg/L) after 7.5 minute contact time to below detection limits (< 25 µg/L). Ozone destroyed glyphosate (840 to 900 µg/L) within 5 to 7 minutes at applied dosages of 1.9 and 2.9 mg/L. In the bench-scale studies, treatments with ClO_2, $KMnO_4$ and H_2O_2 were less successful in pesticide (glyphosate) oxidation.

The effect of chlorination on pesticides was also evaluated at full-scale treatment plants in Ohio (Miltner et al., 1989). Three treatment plants in Tiffin District, Fremont, and Bowling Green, Ohio, generally used up to 13 mg/L Cl_2 (especially during runoff season) and provided in-plant contact time of less than 12 hours. The percent removal data for those pesticides initially present at parts per billion levels (µg/L) are summarized in Table 3.6. For atrazine, cyanazine, simazine, alachlor, metolachlor, and linuron, the removal efficiencies were either zero or extremely low. Slight removal was observed for carbofuran. Up to 98 % removal was reported for metribuzin. However, according to the investigators, this high removal efficiency may be partly attributed to sample preparation in which no reducing agent was added to stabilize the samples. Thus, it was possible that chlorination could have continued for days prior to analysis of the samples collected.

Table 3.6. Removal of Pesticides Associated with Chlorination at Full-Scale Treatment Plants.

Pesticide	Initial Concentration (µg/L)	% Removal
Atrazine	1.59 - 15.5 (SW)	0
Cyanazine	0.66 - 4.38 (SW)	0
Metribuzin	0.10 - 4.88 (SW)	24 - 98*
Simazine	0.17 - 0.62 (SW)	0 - 7
Alachlor	0.94 - 7.52 (SW)	0 - 9
Metolachlor	0.98 - 14.1 (SW)	0 - 3
Linuron	0.47 (SW)	4
Carbofuran	0.13 (SW)	24

From Miltner et al. (1989)
* Metribuzin removal may be the result of sample storage without oxidant quenching. Similar removals in water treatment plants may not be expected.
SW=surface water

3.7(c) Carbon Adsorption

Adsorption water treatment processes are predominately used for control of taste and odor as well as removing synthetic organic compounds, toxic metals, and chlorine.   Sorption is a process of reversible physicochemical binding of the substance on the sorbent (*e.g.*, colloid or activated carbon). Mechanisms controlling sorption are dependent on physical processes such as electrostatic attraction (dipole-dipole interactions, dispersion interactions (van der Waals forces), and hydrogen bonding) or chemisorption (J.M.M. Consulting Engineers, 1985). Non-linear

equilibrium models such as the Langmuir and Freundlich models have been used to predict adsorption potential of organic contaminants. Compounds with a high Freundlich coefficient have sorption affinity to activated carbon. Another approach for predicting adsorption is the Polanyi potential theory.

Granular activated carbon (GAC) and powdered activated carbon (PAC) are common sorbents. Activated carbon is composed of expanded layers of graphite, which leads to an extremely high surface area to mass ratio for sorption (J.M.M. Consulting Engineers, 1985). The main difference between GAC and PAC is the particle size; PAC has smaller particles when compared to GAC. Other less common sorbents are activated aluminum, silica gel, synthetic aluminosilicates, polymeric resins, and carbonized resins. GAC is used as a filter adsorber for taste and odor control, and post-filter adsorbers are designed for synthetic organic removal. In contrast, PAC is added within conventional treatment systems before or during the coagulation/ flocculation and sedimentation treatment process.

The adsorption capacity of activated carbon to remove pesticides is affected by concentration, temperature, pH, competition from other contaminants or natural organic matter, organic preloading, contact time, mode of treatment, and physical/chemical properties of the contaminant. GAC column effectiveness is also a function of the water loading rate and empty bed time, whereas PAC effectiveness is also a function of the carbon dosage. Generally, activated carbon has an affinity for contaminants that are hydrophobic (low solubilities), although other parameters such as density and molecular weight can be important.

Isotherm constants have been reported to be valuable for predicting whether activated carbon adsorbs a particular pesticide (Speth and Miltner, 1990; Speth and Adams, 1993). They reported that, in general, compounds with a Freundlich coefficients on activated carbon greater than 200 ug/g $(L/ug)^{1/n}$ would be amendable to removal by carbon sorption.

3.7(c)1 Powdered Activated Carbon (PAC)

Miltner *et al.* (1987,1989) studied the removal of atrazine and alachlor using PAC. PAC doses were selected to reflect the range commonly used by PWSs for taste and odor control. Both jar and full-scale treatment tests conducted using surface water samples containing other synthetic organic contaminants indicated that atrazine and alachlor could be adequately sorbed to activated carbon. The observed removal was attributed to adsorption because previous studies indicated that conventional treatment was ineffective in removing these pesticides in the raw water. Only the results of the full-scale treatment effects will be presented here. Table 3.7 summarizes the doses, PAC types (WPH Calgon and Hydrodarco), water source, and mean concentrations of the two pesticides. The percent removal ranged from 28% to 87% for atrazine and 33% to 94% for alachlor. As the PAC dose increased, sorption removal efficiencies likewise increased.

Table 3.7. Removal of Atrazine and Alachlor Using PAC during Full-Scale Treatment.

PAC* (dose, mg/L)	Water Source**	C$_o$ (μg/L)		% Removal	
		Atrazine	Alachlor	Atrazine	Alachlor
WPH (2.8)	Sandusky River (C)	7.83	1.67	28	33
WPH (3.6)	Sandusky River (C)	2.61	1.49	38	36
WPH (8.4)	Sandusky River (R)	12.05	2.84	35	41
WPH (11)	Sandusky River (R)	4.43	2.53	41	41
HDB (18)	Maumee River (R)	8.11	8.21	67	62
HDB (33)	Maumee River (R)	2.39	0.97	87	94

From Miltner et al., 1987 and Miltner et al., 1989.
* PAC type: WHP = WHP Calgon and HDB = Hydrodarco, ICI, America
** (C) = Clarified Water; (R) = Raw Water

       The PAC dose required to reduce the pesticide concentration to a predetermined value in a jar test using distilled water could be different compared to using a natural water from a treatment plant. The difference could be due to the presence of other solutes and treatment chemicals in natural water that can compete with the pesticides for sorption sites. Figure 3.1 shows that the activated carbon adsorptive capacity for parathion, 2,4,5-T ester, lindane, and dieldrin in Little Miami River water is more than 50% lower than that in distilled water (Najm et al., 1991).
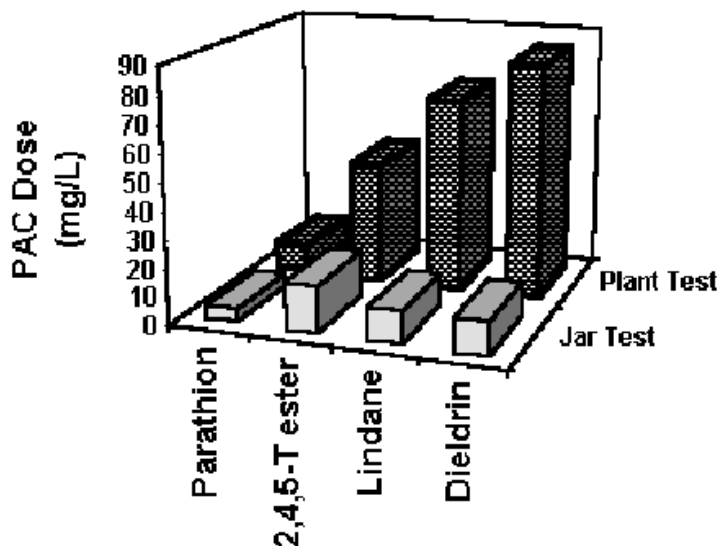
Figure 3.1. PAC Doses Required to Remove 99% of the Pesticide from Jar and Plant Tests. Initial concentration of each pesticide is 10 µg/L (Data from Najm et al, 1991).
Jar Test: PAC dose in jar tests (distilled water) determined from 1 hour contact time.
Plant Test: PAC dose in plant test (river water) determined using conventional treatment and activated carbon sorption.

3.7(c)2 Granular Activated Carbon (GAC)

Like PAC, GAC is also known for adsorbing a wide variety of organic compounds and pesticides. The performance of GAC in removing pesticides from raw water has been demonstrated by the studies of Miltner *et al.* (1989) who used pesticides belonging to triazine, acetanilide, and dinitroaniline classes. The carbon was in operation for 30 months before sampling. As shown in Table 3.8, two types of GAC, Calgon Filtrasorb 300 and Filtrasorb 400, were used. Relative to the initial concentrations of the pesticides, the percent removal of the two acetanilide pesticides (72 - 98%) was higher than those of the triazine pesticides (47 - 62%). The highest removal efficiency (>99%) by Filtrasorb 400 was reported for pendimethalin.

Table 3.8. Removal of Pesticides by Granulated Activated Carbon Adsorption.

Pesticide	GAC	C_o (µg/L)	% Removal
(Triazine)			
Atrazine	Calgon Filtrasorb 300[*]	4.83 (SW)[+]	47

27

Table 3.8. Removal of Pesticides by Granulated Activated Carbon Adsorption.

Pesticide	GAC	C_o (µg/L)	% Removal
Cyanazine	Calgon Filtrasorb 300[*]	1.62 (SW)[+]	67
Metribuzin	Calgon Filtrasorb 300[*]	0.89 (SW)[+]	57
Simazine	Calgon Filtrasorb 300[*]	0.39 (SW)[+]	62
(Acetamilide)			
Alachlor	Calgon Filtrasorb 300[*]	3.70 (SW)[+]	72
Metolachlor	Calgon Filtrasorb 300[*]	5.60 (SW)[+]	56
Pendimethalin (dinitroaniline)	Calgon Filtrasorb 300[*]	0.20 (SW)[+]	>99

From Miltner et al., 1989 & Milner et al.,1987
[*] 30 month-old carbon, bed depth = 1.5 ft, loading = 4 gpm/ft^3, EBCT = 2.81 min.
[+] SW=clarified Sandusky River water (Surface Water)

Based on the data of Miller and Kennedy (1995) for two triazine herbicides and a transformation product in reservoir and drinking waters, activated carbon treatment actually employed in different municipalities could have mixed results. As presented in Table 3.9, GAC adsorption in Creston, Lake Park, and Oscealo, Iowa decreased the concentrations of atrazine, cyanazine, and desethylatrazine in the treated water. But in Fairfield, cyanazine was detected in the drinking water (close to detection limit) but was not found in the water reservoir. In Lake Park, desethylatrazine was detected in the drinking water but not in the reservoir water. It is difficult to know whether the results for Fairfield and Lake Park are somehow related to sampling and analytical deficiencies or possible breakthrough of cyanazine and desethlyatrazine from the GAC column. The sampling time and schedule for the reservoir and drinking waters have to also be considered.

Table 3.9. Water Supply Sources Treated with GAC and Herbicide Concentrations in Drinking Water

City/Town	Water Supply Source	Atrazine* Drinking Water	Reservoir Water	Cyanazine* Drinking Water	Reservoir Water	Desethylatrazine* Drinking Water	Reservoir Water
Creston	Twelve Mile Lake	0.35	0.46	0.11	0.16	0.11	0.16
Fairfield	Fairfield Reservoir/Wells	<0.1	<0.1	0.11	<0.1	<0.1	<0.1
Lake Park	Silver Lake	0.28	0.30	0.22	0.3	0.3	<0.1
Lenox	Lenox East Reservoir/ Twelve Mile Lake	0.27	0.34	0.36	0.68	<0.1	0.10
Osceola	West Lake	1.3	2.4	2.8	4.7	0.22	0.42

* Concentrations in µg/L

3.7(c)3 Biologically Active Carbon (BAC)

BAC is a process of removing soluble organic compounds in raw water through a combination of adsorption to GAC and biological oxidation by the microorganisms present in the activated carbon. The aerobic microbial growth in the activated carbon filters is enhanced by providing sufficient dissolved oxygen into the water ahead of the GAC beds. If organic compounds in the raw water are not readily biodegradable or recalcitrant substances are present, ozone is usually added ahead of the carbon filters. Consequently, preozonation is sometimes used to convert larger, less biodegradable organic compounds into smaller, more easily metabolizable molecules. As a result of biological oxidation, the activated carbon is not rapidly saturated with biorefractory compounds, and thus, the adsorber bed service life is extended. Generally all GAC columns are biofilters because GAC will remove the disinfectant in the top few inches of the bed. No studies or reports were found to provide information on the extent of removal of pesticides passing through BAC adsorber columns. No reference was also found that distinguishes between adsorption and biodegradation.

3.7(d) Membrane Treatment

Membranes are used in water treatment for desalinization, specific ion removal, removal of color, organics, nutrients, and suspended solids.   Membranes are used in reverse osmosis (RO), electrodialysis (ED), ultrafiltration, microfiltration, and nanofiltration (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). Ultrafilitration is considered a filtering technique because it is designed to exclude compounds with molecular weights greater than 500 grams/mole. In contrast, RO and ED are designed to use a semipermeable membrane as a diffusion barrier for dissolved constituents in the water.   Electrodialysis is controlled by electrostatic attraction of ionic compounds to anionic and cationic electrodes across a semipermeable membrane. Reverse osmosis, however, is controlled by hydrostatic pressure (300 to 1000 psi) to drive feedwater through a semipermeable membrane. Membranes are typically composed of cellulose acetate, polyamide membranes, and thin film composites. Membrane configurations for RO are spiral wound and hollow fine fiber membrane. The effectiveness of RO is dependent on membrane composition, physicochemical properties of raw water, pressure, and membrane treatment conditions. Electrodialysis is affected by amount of DC current.

3.7(d)1 Reverse Osmosis (RO)

The use of semipermeable membranes during RO treatment has been demonstrated to remove organic pollutants and pesticides from contaminated water. The membranes normally used in the past were either cellulose acetate (CA) or polyamide. Later, a new type of membrane called thin film composites was introduced. These membranes could be produced from a variety of polymeric materials that were formed in-situ or coated onto the surface of an extremely thin polysulfone support. Examples are NS-100 (cross-linked polyethylenimine membrane), FT-30 (cross-linked polyamide that contains carboxylate group), and DSI (modified polyalkene on a polysulfone base with non-woven polyester backing).

A short-term laboratory test conducted by Chian (1975) demonstrated that NS-100

29

membrane was able to remove 97.8% of atrazine compared to 84.0% removal using CA membrane. Since then, other studies by several investigators (Eisenberg and Middlebrooks, 1986; Lykins et al., 1988; Miltner et al., 1989; Fronk et al., 1990) generally indicated that thin film composite membranes have superior performance in removing pesticides compared to those of CA and polyamide membranes. For instance, as summarized in Table 3.10, the percent removal of linuron from groundwater samples was zero using CA, 57% using polyamide, and 99% using thin film composite DSI. Similar results were obtained for alachlor in surface water samples: 70% removal using CA, 77% using polyamide, and 100% by thin from composite FT-30. The high removal efficiencies for a wide range of initial concentrations (ppb to ppm) are presented in Table 3,10.   The reported data pertain to pesticides belonging to triazine, acetanilide, organochlorine, urea derivative, carbamate, and organophosphorus classes. For individual compounds in each class and others [that include 1,2-dichloropropane, captan, trifluralin.and aldicarb transformation products (sulfoxide and sulfone)], the percent removal data in surface water (SW) and groundwater (GW) are presented in Appendix A.

Table 3.10. Removal Efficiencies of RO Membranes for Different Pesticide Classes

Pesticide Class	Cellulose Acetate (CA)	Polyamide	Thin film Composite
Triazine	23 - 59	68 - 85	80 - 100
Acetanilide	70 - 80	57 - 100	98.5 - 100
Organochlorine	99.9 - 100		100
Organophosphorus	97.8 - 99.9		98.5 - 100
Urea Derivative	0	57 - 100	99 - 100
Carbamate	85.7	79.6 - 93	> 92.9

Membranes operated with a lower pressure can also be used in water treatment plants. Fronk *et al.* (1990) conducted an evaluation of removing certain pesticides from groundwater using thin film composite membranes. The results are shown in Table 3.11. Excellent removal (~100%) of organochlorine pesticides (chlordane, heptachlor and methoxychlor) and an acetanilide compound (alachlor) was obtained. The removal of dibromochloropropane was not high and ethylene dibromide was not removed at all.

Table 3.11. Removal of Pesticides Using Ultrafiltration

Pesticide	Membrane	C_o (ug/L)	% Removal
Organochlorine			
Chlordane	Thin Film Composite	< 100 (GW)	~ 100
Heptachlor	Thin Film Composite	< 100 (GW)	~ 100
Methoxychlor	Thin Film Composite	< 100 (GW)	~ 100

Table 3.11. Removal of Pesticides Using Ultrafiltration

Pesticide	Membrane	C_o (ug/L)	% Removal
VOC			
Dibromochloropropane	Thin Film Composite	< 100 (GW)	19 -52
Ethylene dibromide	Thin Film Composite	< 100 (GW)	~ 0
Others			
Alachlor	Thin Film Composite	< 100 (GW)	~ 100

From Fronk et al., 1990

3.7(d)2 Nanofiltraton (NF)

Another membrane technique is nanofiltration or NF. The membrane employed is somewhat "more loose" and the process is operated with lower effective pressure and without significant changes in water salinity. A pilot plant study reported by Hofman *et al.* (1996) indicated promising removal results, as summarized in Table 3.12. Using four different membranes, up to about 90% of diuron can be removed while more than 90% removal can be achieved for atrazine and simazine. Bentazon had a removal efficiency of 95%, the highest in the study.

Table 3.12. Removal of Pesticides Using Nanofiltration Membranes

Pesticide	Membrane	C_o (µg/L)	% Removal
Atrazine (triazine)	4 different membranes	not given	80-98
Simazine (triazine)	4 different membranes	not given	63-93
Diuron (urea)	4 different membranes	not given	43–87
Bentazone (miscellaneous)	4 different membranes	not given	96-99

From Hofman et al, 1996

3.7(d)3 Integrated membrane/adsorbent systems

Microfiltration (MF) with porosity nominally > 0.1 µm and ultrafiltration (UF) with porosity . 0.01 µm are sometimes combined with adsorbents such as PAC to form an intergrated system that can be effective in removing pesticides. An integrated system UF/PAC system was reported by Anselme et al (1991) to effectively remove some pesticides. Jack and Clark (1998) found that a UF/PAC (10 mg/L PAC) system was capable of removing cyanazine by 70% and atrazine by 61%. With higher PAC levels, better results can be obtained. The removal of atrazine was increased from 57% at 5 mg/L to 89% at 20 mg/L PAC. (Claire et al, 1997).

It would be expected that the integrated membrane/adsorbent system will lead to greater adsorption with increase in the adsorbent time. Other factors that can influence the final degree of

31

adsorption include temperature, pH (for ionizable pesticides), PAC type and dose, and competitive adsorption from dissolved natural organic materials and other contaminants.

3.7(e) Corrosion Control Treatments

Corrosion control is used in water treatment to limit interaction of the treated water with pipes and water conduit systems. The principal processes for corrosion control are regulation of pH and addition of corrosion inhibitors (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). The adjustment of pH through the addition of lime or sodium hydroxide is required by EPA to inhibit metal dissolution (*e.g.*, lead) in finished water. Chemical control agents (such as zinc orthophosphate, silicates, polyphosphates) are added to encourage mineral coating (zinc carbonates or iron silicates) on the surface of the pipes, which prevents corrosion of pipes.

Control of pipe corrosion in potable distribution systems can be achieved by pH or alkalinity adjustment and application of corrosion inhibitors. So far, no studies have been reported nor found that would suggest that pesticides detected in raw or untreated water are removed or reduced during corrosion control operations in the treatment plants. Whether calcium carbonate deposition or calcium reaction with phosphate inhibitors can ultimately lead to removal of pesticides in water remains to be seen. The pH adjustment may have an impact on pesticides susceptible to pH dependent hydrolysis.

3.7(f) Aeration/Air Stripping

Aeration and air stripping are water treatment processes associated with gas transfer in drinking water. These processes have been used to: inject disinfectants (O_3 and ClO_2) in finished water, inject O_2 into feed water to accelerate oxidation, and to remove ammonia (NH_3) and volatile organic compounds (J.M.M. Consulting Engineers, 1985 and USEPA, 1989). Gas exchange is accomplished using gas dispersion methods (bubbling air or mechanical mixing) or specially designed gas-liquid contact equipment (*e.g.*, packed towers, cross-flow towers, and spray towers). The Henry's Law Constant, the ratio of pesticide concentrations between gas and liquid phases at equilibrium, has been used to predict the effectiveness of aeration and air stripping techniques on the removal of organic compounds.

The removal of volatile organic contaminants and pesticides can be accomplished by using packed towers, spray towers, or agitated diffused gas vessels. Qualitatively, the greater the Henry's Law Constant (H) of a chemical or pesticide, the more easily the chemical can be removed from the solution or aqueous phase. Based on a study by McCarty (1987), a chemical with a H value of 1×10^{-3} atm m^3 mole^{-1} is amenable to removal by aeration. Pesticides with H values slightly lower than 1×10^{-3} atm m^3 mole^{-1} may be still be removed, but more energy would be required. In addition, relatively higher towers and greater air/water ratios would be needed if a packed tower stripper is used. Examples of pesticides that could be removed by air stripping are those belonging to volatile organic chemical (VOC) class:

<div align="center">

Pesticide   H (atm m^3 mole^{-1})

</div>

Dibromochlorpropane	2.78×10^{-3}
1,2 - Dichloropropane	1.80×10^{-3}
Ethylene dibromide	0.67×10^{-3}

3.8 Pesticide Transformation Associated with Certain Treatment Processes

Most of the treatment processes that have been demonstrated to significantly remove pesticides from raw water involve physical phase separations in which the pesticides are transferred from the solution phase and then trapped or concentrated in the solid matrix such as filters, activated carbon or membranes. However, certain treatment operations ultimately lead to loss of the parent pesticides through chemical reactions. Thus, the pesticides are converted to another chemical(s) as transformation products. Transformations typically occur when a treatment chemical is introduced and subsequently significantly changes the acid-base character or facilitates the redox processes in the water. During lime softening and disinfection with chemical oxidants, pesticides could be transformed into other process products. Some byproducts resulting from ozonation of certain pesticides have been reported in a recent preliminary literature review on treatment of pesticide-contaminated raw water (Pisigan,1998). In many cases, these transformation are considered important by OPP.

Pesticides are susceptible to microbially-mediated oxidation in terrestrial and aquatic environments. This degradation pathway will ultimately lead to the formation of CO_2 with the formation of intermediate by-products. In many cases these transformation products are identified as part of the OPP risk assessment process since extensive animal, plant, and soil metabolism studies are required to be submitted by the registrant and are reviewed by the Agency. Similar degradation pathways and transformation products are expected from chemical oxidation through the water treatment disinfection process. Preliminary data from the EPA-USGS pilot reservoir monitoring project indicate that water treatment processes have an impact on the recovery of organophosphates and some other pesticides in treated water when compared to spiked raw water samples (personal communication Joel Blomquist at USGS and James Carleton at OPP/EPA). Low or non-existent analytical recoveries of some pesticides (especially organophosphates) occurred in spiked treated water samples, presumably due to oxidation by residual chlorine. However, some oxidative transformation products (oxons, sulfoxides, sulfones, oxon-sulfones, etc.) of certain organophosphates (*e.g.* methyl-paraoxon, ethyl-paraoxon, fenamiphos sulfone, terbufos oxon-sulfone, azinphos-methyl oxon) when spiked into treated water appear to have better analytical recoveries than their respective parent compounds. The preliminary recovery data suggest that organophosphates may be oxidized in treated water to form relatively stable, toxic transformation products.

3.8(a) Transformation Induced by Lime Softening

Basic chemicals such as slaked calcium oxide are added during lime softening to increase the pH of the water to about 10 to 11. At this alkaline condition, pesticides that undergo alkaline hydrolysis would be expected to be transformed. Examples of pesticides that are known to be hydrolytically unstable at high pH values are demeton-S-methyl, carbofuran, captan, and

methomyl. During high lime treatment for 2 hours, van Rensburg *et al.* (1978) observed that demeton-S-methyl was apparently hydrolyzed at pH 10.5 yielding about 70% removal of demeton-S-methyl present in the raw water at an initial concentration of 3100 ug/L. In conducting a study on the adsorption capacity of GAC for synthetic organics, Speth and Miltner (1998) reported that methomyl had to be tested with a pH of 2.8 to maintain stability because methomyl rapidly degraded over a wide pH range. This implies that at highly alkaline conditions methomyl will undergo very fast hydrolysis. According to fate properties summarized in Table 3.13, the pH 9 hydrolysis half-lives of carbofuran and captan are 0.625 day and 0.00056 day, respectively. Carbofuran was found to be 100% removed during water softening at pH 10.9 and 11.1 in a full-scale treatment tests conducted by Miltner *et al.* (1989). Based on Nanogen International (1975), the possible hydrolysis/hydroxylation products are 3-hydroxycarbofuran and carbofuran phenol. Carbofuran has been shown to hydryolze under alkaline conditions to form carbofuran-7-phenol as the major degradation product (USEPA, 1999). Thus, the possible softening reaction involving carbofuran may be represented as follows:

$$\text{carbofuran} \xrightarrow[\text{pH 10-11}]{\text{OH}^-} \text{carbofuran-7-phenol} + \text{3-hydroxycarbofuran}$$
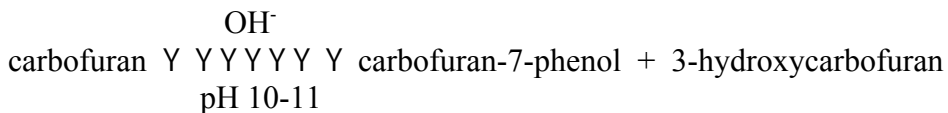
The extent of the alkaline hydrolysis and the formation of other products are expected to be affected by contact time and water quality characteristics.

Other pesticides with short hydrolysis half-lives (< 1 day) at pH 9.0 are: desmedipham, dicofol, iprodione, thiodicarb, and 2-hydroxypropyl methanethiosulfonate. These pesticides potentially can be removed and transformed by basic hydrolysis during softening.

3.8(b) Transformation Caused by Chemical Disinfection/Oxidation

Chemical disinfection is widely applied to destroy disease-causing microorganisms and thus make the treated water safe for human consumption. More than 95% of surface water treatment facilities serving 501 to more than 100,000 persons employ disinfection. For the same ranges of population served, at least 80% of the groundwater treatment plants use disinfection to get rid of pathogenic microbes. The chemicals used as disinfectants are chlorine and chlorine compounds, ozone, iodine, and bromine. The most common form of disinfection practiced in the United States is the addition of chlorine to water. Ozone is a widely used disinfectant in Europe and is also becoming an alternative chemical oxidant and disinfectant in some water treatment facilities in the United States. Both chlorine and ozone are strong oxidizing agents that react with a variety of organic compounds and pesticides and convert the compounds to disinfection by-products that could be present in the treated water.

3.8(b)1 Chlorination Byproducts

Certain pesticides belonging to organophosphate and carbamate classes are susceptible to transformation during chlorination of raw water. Magara et al (1984) have shown that organophosphate pesticides containing P=S bonds were easily degraded by chlorine and produced

34

oxons (P=O bond) as a primary byproduct. In a previous study (Aizawa and Magara, 1992), pesticides with thiono group (-P=S-O-) such as diazinon, chlorpyrifos-methyl, fenthion (MPP), pyridaphenthion. and those containing dithio group (-P=S-S-) such as malathion, penthoate (PAP), and ethyl p-nitrophenyl benzenethionophosphate (EPN) were reported to yield oxons and other chlorination degradation products. For instance, diazinon can be converted to diazoxon which may be further transformed to chlorinated products as shown below:

$$Cl_2$$
Diazinon Y Y Y Y Diazoxon
9
diethyl phosphoric acid
9
dichloroacetic acids
trichloroacetic acids

However, diazoxon may remain stable for some time after it is formed. In an experiment in which chlorine was present at levels above 5 mg/L in an aqueous solution of diazinon (5 µg/L), diazoxon was observed to be highly stable against chlorine even after 48 hours (Magara, 1994).

Organophosphate pesticides may also be transformed to the oxon through biochemical reactions in mammalian tissues. Whether formed in mammalian tissues or introduced directly via drinking water, there is a concern with the formation of oxons because it is widely known that oxon forms of organophosphates are more potent acetylcholinesterase inhibitors than the parent form (Amdur et.al., 1991). The oxon intermediate is readily hydrolyzed in mammalian systems.

Certain carbamate pesticides may also react with chlorine to produce disinfection byproducts. In a chlorination study conducted by Mason et al (1990), both aldicarb and methomyl were demonstrated to be transformed by an electrophillic ionic attack by hypochlorous acid (HOCl), which is formed by chlorine hydrolysis in water. The reaction between methomyl and HOCl was found to be several orders of magnitude faster than the reaction between aldicarb and HOCl. Sodium chloride concentration (reflecting ionic strength) and pH were shown to affect the chlorination rates. The chlorination of aldicarb may be described by the following reaction:

HOCl
Aldicarb Y Y Y Y Y Aldicarb sulfoxide + Aldicarb sulfone

+ Aldicarb Oxime + Aldicarb-sulfoxide Oxime

+ Aldicarb Nitrile + sulfur-containing alcohol

No product analysis was done for the methomyl-HOCl reaction. The result of a preliminary bioassay using Daphnia magna to compare the toxicity of aldicarb and chlorination by-products indicated that the by-products were less toxic.

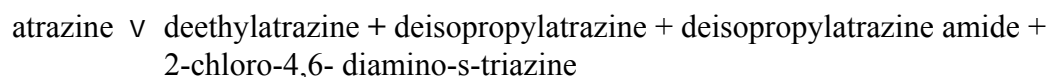A thiocarbamate, thiobencarb, has been reported to be transformed by chlorination during

water purification (Magara et al., 1994). The chlorine reaction with the pesticide present in raw water can be described as:

Thiobencarb Y Y Y Y Chlorobenzyl Alcohol + Chlorotoluene

+ Chlorobenzoic Acids + Chlorobenzyl Chloride

+ Chlorobenzyl Aldehyde

It was further reported that when thiobencarb was detected in raw water, chlorobenzyl chloride (up to 12 µg/L), chlorobenzoic acid, and chlorobenzaldehyde were detected in the filter water of a Japanese purification plant for water supply.

3.8(b)2 Ozonation Byproducts

Ozone is a powerful oxidizing agent that can react in water directly with dissolved organic compounds or generate radical species such as a hydroxy radical (OHQ) which is much more reactive. Experiments were conducted by Adams and Randtke (1992) on the ozonation of atrazine in natural and synthetic waters with a maximum initial concentration of 15 ug/L. Two conditions were used: (a) low pH and high alkalinity, which inhibited the autodecomposition of ozone to the hydroxy radical; (b) high pH and low alkalinity, which favored the production of hydroxy radical from ozone. The natural waters were obtained from Clinton Reservoir, Perry Reservoir, Kansas River and Missouri River. The investigators proposed the following major degradation pathway for the ozonation of atrazine in water treatment processes:

atrazine ∨ deethylatrazine + deisopropylatrazine + deisopropylatrazine amide +
2-chloro-4,6- diamino-s-triazine

The other minor pathway described yielded byproducts such as hydroxyatrazine, 2-amino-4-ethylamino-6-hydroxy-s-triazine, and 2-amino-4-hydroxy-6-ethylamino-s-triazine.

The kinetic formation trends of the products were observed to change as pH increased from 5 to 7, and then 9. Other additional products formed by atrazine reaction with ozone with or without hydrogen peroxide were recently reported by other investigators (Acero et al, 2000; Nelieu et al, 2000).

Due to a growing interest in removal and transformation of pollutants during ozonation, attempts have been made to evaluate the reactivity of pesticides with ozone in water. Hu et al (2000) determined the rate constant of ozone with 4 groups of pesticides (4 phenolic-, 8 organonitrogen-, 8 phenoxyalkylacetic acid-, and 4 heterocyclic – pesticides) under controlled conditions simulating natural waters. The results of the correlation analysis indicated that the reactivity of pesticides can be estimated using the energy of the highest occupied molecular orbital of the chemicals (ε_{HOMO}). A pesticide with a high ε_{HOMO} can be expected to yield a high rate constant of ozonation.

Information on the chemical identities and concentrations of transformation products resulting from chemical disinfection is important in drinking water exposure assessment. Rules pertaining to allowable levels of disinfection by-products have been addressed already in Europe and the United States. The European Union (EU) promulgated a new regulation that establishes not only maximum concentrations of pesticides in drinking water but also includes their degradation products after water treatment (Acero et al, 2000). In the United States, MCLGs and MCLs also have been developed by USEPA for several by-products (trihalomethanes, haloacetonitriles, haloketones, haloacetic acids, etc.) generated from chlorination of dissolved organic compounds in raw water under the D/DBP.

3.9 Assessment of the Relationship Between Environmental Fate Properties and Water Treatment Effects

As part of the pesticide registration process, environmental fate and transport data and physicochemical properties for each pesticide and its toxicologically significant degradation products are required to assess the environmental behavior of the pesticide under specific use conditions and use patterns. The core environmental fate data for most pesticide registrations are: laboratory studies (including abiotic hydrolysis, photodegradation in water and soil, aerobic and anaerobic metabolism in water and soil, batch equilibrium/soil column leaching, volatility from soil, bioaccumulation in fish) and physicochemical properties (including chemical structure, molecular weight, solubility, vapor pressure, Henry's Law Constant, octanol-water partitioning coefficient, and dissociation constants). These data are used in environmental fate models for estimating pesticide concentrations in aquatic environments and drinking water. The range of pesticide properties evaluated in referenced water treatment studies is shown in Table 3.13.

An analysis was conducted to assess possible relationships between pesticide fate properties and removal efficiencies for GAC, PAC, and RO. Based on reviewed data, there were no relationships or trends observed between certain pesticide environmental fate properties (Kow and molecular weight) and removal efficiencies. A major problem with the analysis is associated with the close range of values, which limits defining trends or relationships. Additional data are needed to assess trends and develop regression models for predicting pesticide removal from environmental fate and physicochemical data.

Qualitative water treatment effects, however, may be predicted using environmental fate data. For example, alkaline catalyzed hydrolysis is expected to occur through water softening because of the pH alteration required for $CaCO_3$ and $Mg(OH)_2$ precipitation. This effect has been observed for carbofuran because it hydrolyzes rapidly at pH 9 (Table 3.13). Also, pesticide removal through adsorption on activated carbon can be predicted using physicochemical properties. Compounds exhibiting high Koc, low solubility, and high octanol-water partitioning coefficients are expected to exhibit high binding affinities for activated carbon (Speth and Adams, 1993). Further oxidizability of the pesticide may be inferred from aerobic soil metabolism data. Compounds with short aerobic soil metabolism half-lives are expected to be more prone to chemical oxidation. Finally, functional group analysis as indicated by acid or base dissociation constants provides some basic information on speciation of the pesticide and its possible adsorption potential (cation or anion exchange) on surfaces of colloids, flocs, and activated

carbon. Further research is needed in assessing the quantitative relationship between pesticide fate properties and removal efficiencies.

Table 3.13. Physicochemical and Environmental Fate Properties of Pesticides[1]

	MW	pKa or pKb	log k_{ow}	K_{oc}	Henry's Law Constant [atm-m³/mol]	Vapor Pressure [torr]	solubilty [ppm]	pH 7 hydrolysis half life [day]	pH 9 hydrolysis half life [day]	aqueous photolysis half life [day]	aerobic soil metabolism half life: typical and (range) [day]
2,4,5-T	255.48	2.84 a	3				238				
alachlor	269.77		2.64	190	3.20E-08	2.2 E-05	242	stable	stable	80	17.5 (14-21)
aldicarb	190.26		0.7	30		1.0 E-04	6000	stable			16.7 (1-56)
aldrin	364.91		3.01			7.5 E-05	0.027				
atrazine	215.69	12.3	2.68	88	2.58E-09	3.0 E-07	33	stable	stable	stable	83.5 (21-146)
bentazon	240.3			21	6.30E-12	1.0 E-09	500	stable	stable	<1	38.6 (14-65)
captan	300.59					8.0 E-08	33	0.25	0.005556	stable	4 (1-7)
carbofuran	221.6		1.98	29		5.2 E-07	700	7.28	0.625	stable	130 (21-350)
chlordane	409.78		3.32	1.4E5	9.60E-06	1.0 E-05	600				
cyanazine	240.7	12.9		56	3.17E-12	1.00E-08	171	stable	stable	43	28.5 (10-70)
DBCP	236.36				2.78E-03	10	1000				180
diazinon	304.34		3.01	530	1.40E-06	1.4 E-04	40	stable	stable	34	18 (4-28)
dichloropropene	110.97			36	1.80E-03	27.3	2500	13.5	13.5		33 (12-54)
dieldrin	380.91				8.08E-03	3.1 E-06	0.25				
diuron	233.1		2.81	480	2.26E-08	8.6 E-09	42	stable	stable	43	98 (30-144)
endrin	380.91				4.00E-07	2.0 E-07					
ethylene dibromide	187.85		1.76	22.5	6.73E-04	11.7	4300				
heptachlor	373.32		4.41		4.00E-03	3.0 E-04	0.06				64 (37-112)
heptachlor epoxide	389.3		2.7	220	4.00E-04	3.0 E-04	0.35				
lindane	290.83			1263	3.60E-07	9.4 E-06	10	stable	36	stable	523 (66-980)
linuron	249.1		2.19	863	6.56E-08	1.1 E-05	75	stable	stable	49-76	87.5 (84-91)
methoxychlor	345.65		3.62	8E5			0.1	stable	stable	stable	120
metolachlor	283.8			229	9.16E-09	1.3 E-05	530	stable	stable	70	67
metribuzin	214.29	13	1.6	19	3.50E-11	1.2 E-07	1100	stable	stable	0.179167	73 (40-106)
parathion	291.26			1.8E4		3.8 E-05	24	108			95 (50-140)
pendimethalin	281.31			3.6E4	2.22E-05	2.9 E-06	0.38	stable	stable	17-21	1322
simazine	201.66	12.35	2.51	124	3.20E-10	6.1 E-09	3.5	stable	stable	stable	36
toxaphene	413.81			1E5		0.17	0.037				9
trifluran	335.28		5.07	8000	1.62E-04	1.1 E-04	0.3	stable	stable	0.37	115

1- Data were derived from the EFED One-Liner Data Base.
MW = Molecular Weight
pKa = negative log of acid dissociation constant
pKb = negative log of base dissociation constant
Kow = octanol/water partition constant
Koc = organic carbon sorption coefficient

3.10 Acknowledgments

3.11 Literature Cited

Abel, S. 1992. Drinking water Treatment Processes and Treatment Efficiencies for Organic Contaminants: Utilities Using Surface Water Sources. Sept. 10, 1992 Deliverable 1 for Task No. 3-44 under Contract No. 68-D9-0166 from Versar, Inc.,6850 Versar Center, P.O. box 1549, Springfield,VA.

Acero, J.L., K. Stemmler, and U. Von Guten. 2000. Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment. Environ. Sci. Technol. 34: 591-597.

Adams, C.D. and S.J. Randtke. 1992. Removal of Atrazine from Drinking Water by Ozonation. Jour. AWWA. 84(9): 91-102.

Aizawa, T. and Y. Magara. 1992. Behavior of pesticides in drinking water purification system. Water Malaysia '92. Cited by Magara et al. 1994. Degradation of Pesticides by Chlorination during Water Purification. Wat. Sci. Tech. 30(7): 119-128.

Amdur, PhD, J.Doull, PhD, C.D. Klaassen, PhD, 1991, Casarett's and Doull'sToxicology: The Basic Science of Poisons, 4th Edition, Editors: M.O., pub. McGraw Hill, Inc.)

Anselme, C., J.L. Bersillion, J. and J. Mallevialle. 1991. The Use of Powdered Activated Carbon for the Removal of Specific Pollutants in Ultrafiltration Processes. In Proceedings, AWAA Membrane Processes Conference, March 10-13, 1991. Orlando, FL.

Baier, J.H., B.W. Lykins, Jr., C.A. Fronk and S.J. Kramer. 1987. Using Reverse Osmosis to Remove Agricultural Chemicals from Groundwater. Jour. AWWA. 79: 55-60.

Chian, E. 1975. Removal of Pesticides by Reverse Osmosis. Environ. Sci. Technol. 9(10) (Jan. 1975).

Clark, R.M., C.A. Fronk, and B.W. Lykins, Jr. 1988. Removing Organic Contaminants. Environ. Sci. Technol. 22(10): 1-6.

Calire, D., S. Randtke, P. Adams, and S. Shreve. 1997. Microfiltration of a High-Turbidity

Surface Water with Post-Treatment by Nanofiltration and Reverse Osmosis. In Proceedings, AWWA Membrane Technology Conference. February 23-26, 1997, New Orleans, LA.

Code of Federal Register. 1991. Part II Environmental Protection Agency 40 CFR Parts 141, 142, and 143, National Primary Drinking Water Regulations; Final Rule. Vol 56. No. 20.

DiGiano, Francis A. 1987. Chapter 3: Adsorption of Organic Substances in Drinking Water. In Control of Organic Substances in Water and Wastewater. Bernard B. Berger (editor). Noyes Data Corporation, Park Ridge, NJ.

Edzwald, James K. 1987. In Control of Organic Substances in Water and Wastewater. Bernard B. Berger (editor). Noyes Data Corporation, Park Ridge, NJ.

Faust, S.D. and O.M. Aly. 1999. Chemistry of Water Treatment. 2nd Ed. Lewis Publishers. Boca Raton, FL.

Fronk, C.A. and D. Baker. 1990. Pesticide Removal by Membrane Processes. Paper presented at the 1990 Annual Conference of AWWA. Cincinnati, OH. (June 17-21, 1990).

Fronk, C.A., B.W. Lykins, Jr., and J.K. Carswell. 1990. Membranes for Removing Organics from Drinking Water. Proc. 1990 Amer. Filtration Soc. Annual Meeting, Washington, DC (March 18-22,1990)

Hu, J., T. Morita, Y. Magara, and T. Aizawa. 2000. Evaluation of Reactivity with Ozone Using the Energies of Frontier Molecular Orbitals. Wat. Res. 34(8): 2215-2222.

Jack A.M., and M.M. Clark. 1998. Using PAC-UF to Treat a Low-Quality Surface Water. J. AWWA, 90(11): 83-95.

James M. Montgomery (J.M.M.) Consulting Engineers, Inc.1985. Water Treatment: Design and Design. John Wiley & Sons, New York.

Kobashi, K, R.M. Rompas, T. Maekawa, N. Imada, and Y. Oshima. 1990. Changes in Metabolic Activity of Tiger Shrimp Larvae at Different Stages To Fenitrothion, An Organophosphorus Insecticide. Nippon Suisan Gakkaishi. 56(3); 489-496.

Lytle, Darren A. 1995. How Do I Run A Proper Jar Test Procedures? 1995 AWWA Water Quality and Technology Conference. New Orleans, LA.

Magara, Y., T. Aizawa, N. Matumoto, and F. Souna 1994. Degradation of pesticides by chlorination during water purification. Groundwater Contamination, Environmental Restoration, and diffuse Source Pollution. Water Science and Technology. 30(7): 119-128.

Mason, Y., E. Choshen, and C. Rav-Acha. 1990. Carbamate Insecticides Removal from Water by Chlorination and Ozonation. Wat. Res. 24(1): 11-21.

McCarty, Perry L. 1987. Chapter 4: Removal of Organic Substances from Water by Air Stripping. In Control of Organic Substances in Water and Wastewater. Bernard B. Berger (editor). Noyes Data Corporation, Park Ridge, NJ.

Miller III, J.G. and Kennedy, J.K. 1995. Study of Herbicides in water and Sediment from 19 Iowa Water Supply Reservoirs, January-February, 1995. University Hygienic Laboratory (Limnology Section), University of Iowa, Iowa City, IA. Report No. 95-1, 89 pp.

Miltner, R.J., D.B. Baker, T.F. Speth, and C.A. Fronk. 1989. Treatment of Seasonal Pesticides in Surface Waters. Jour. AWWA. 81: 43-52.

Miltner, R.J., C.A.Fronk, and T.F. Speth. 1987. Removal of Alachlor from Drinking Water. Proc. Nat'l Conference on Environ. Engineering, ASCE. Orlando, FL (July 1987).

Najm, I.N., V.L. Snoeyink, B.W. Lykins, Jr., and J.Q. Adams. 1991. Using Powdered Activated Carbon: A Critical Review. Jour. AWWA. 83(1): 65-76.

Nanogen International (1975) as cited by Miltner, R.J., D.B. Baker, T.F. Speth, and C.A. Fronk. 1989. Treatment of Seasonal Pesticides in Surface Waters. Jour. AWWA. 81: 43-52.

Nelie, S., L. Kerhoas, and J. Einhorn. 2000. Degradation of Atrazine into Ammeline by Combined Ozone/Hydrogen Peroxide Treatment in Water. Environ. Sci. Technol. 34: 430-437.

Pisigan, Jr., R.A. 1998. Treatment of Pesticide Contaminated Raw Water: Importance to Drinking Water Exposure Assessment. Paper Presented at the 19th Annual Meeting of SETAC. Charlotte, NC (November 15-19, 1998).

Rompas, R.M., K. Kobayashi, Y. Oshima, N. Imada, K. Yamato, and Y. Mitsuyasu. 1989. Relationship between Toxicity and Acetylcholinesterase Inhibition of Some Thiono- and Oxo-form Organophosphates in Tiger Shrimp Larvae at Different Stages. Nippon Suisan Gakkaishi. 55(4): 669-673.

Science Applications International Corporation (SAIC). 1999. Geometries and Characteristics of Public Water System. Draft Report prepared for United States Environmental Protection Agency in Washington, D.C., McLean, VA 22102.

Speth, T.F. and J.Q. Adams. 1993. "GAC and Air Stripping Design Support for the Safe Drinking Water Act", *Strategies and Technologies for Meeting SDWA Requirements*. Clark, R. and S. Summers, Eds., Lewis Publishers, Ann Arbor, MI, pp. 47-89.

Speth, T.F. and R.J. Miltner. 1998. Technical note: adsorption capacity of GAC for synthetic organics. Jour. AWWA. 90(4): 171-174.

USEPA NRMRL, Office of Research and Development, Water Supply and Water Resources Division, Treatment Technology Evaluation Branch. Cincinnati, OH.

United States Environmental Protection Agency. 1997. Community Water System Survey Volume I:Overview. EPA 815-R-97-001a.

United States Environmental Protection Agency. 1997. Community Water System Survey Volume II: Detailed Survey Result Tables and Methodology Report. EPA 815-R-97-001b.

United States Environmental Protection Agency. 1989. Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities. EPA/625/4-89/023.

United States Environmental Protection Agency. 1998. Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996. EPA 815-R-98-002.

van Rensburg, J.F.J., P.G. van Rossum, and W.H.J. Hattingh. 1978. The Occurrence and Fate of Organic Micro-Pollutants in a Water Reclaimed for Potable Reuse. Prog. Wat. Tech. 10(1&2): 41-48.

APPENDIX A. REMOVAL OF PESTICIDES USING DIFFERENT REVERSE OSMOSIS MEMBRANES

Class/ Pesticide	Membrane	C_o (µg/L)	% Removal	Reference
Triazine				
Atrazine	Cellulose Acetate	86.5 - 161.3 (GW) 2.46 - 11.75 (SW)	38.5 29	Fronk & Baker (1990) Fronk & Baker (1990)
	Polyamide	86.5 - 161.3 (GW) 2.46 - 11.75 (SW)	68 78	Fronk & Baker (1990) Fronk & Baker (1990)
	Thin Film Composite (FT-30)	2.46 - 11.75 (SW)	100	Fronk & Baker (1990)
	Thin Film Composite (DSI)	86.5 - 161.3 (GW)	80-100	Fronk & Baker (1990)
	CA	1101.7	97.82	Eisenberg & Middlebrooks (1986)
	NS-100	1101.7	84.02	Eisenberg & Middlebrooks (1986)
Cyanazine	Cellulose Acetate	0.0 - 2.53 (SW)	40-50	Fronk & Baker (1990)
	Polyamide	0.0 - 2.53 (SW)	69	Fronk & Baker (1990)
	Thin Film Composite (FT-30)	0.0 - 2.53 (SW)	100	Fronk & Baker (1990)
Metribuzin	Cellulose Acetate	0.0 - 2.53 (SW)	59	Fronk & Baker (1990)
	Polyamide	0.0 - 2.53 (SW)	76	Fronk & Baker (1990)
	Thin Film Composite (FT-30)	0.0 - 2.53 (SW)	100	Fronk & Baker (1990)
Simazine	Cellulose Acetate	86.1 -117.2 (GW) 0.11 - 0.82 (SW)	31 23	Fronk & Baker (1990) Fronk & Baker (1990)
	Polyamide	86.1 - 117.2 (GW) 0.11 - 0.82 (SW)	85 72	Fronk & Baker (1990) Fronk & Baker (1990)
	Thin Film Composite (FT-30)	0.11 - 0.82 (SW)	100	Fronk & Baker (1990)

Class/ Pesticide	Membrane	C_o (µg/L)	% Removal	Reference
	Thin Film Composite (DSI)	86.1 - 117.2 (GW)	99	Fronk & Baker (1990)
Acetanilide				

Class/ Pesticide	Membrane	C_o (µg/L)	% Removal	Reference
	Thin Film Composite (DSI)	86.1 - 117.2 (GW)	99	Fronk & Baker (1990)
Acetanilide				
Alachlor	Cellulose Acetate	0.78 - 6.44 (SW)	70	Fronk & Baker (1990)
	Polyamide	0.78 - 6.44 (SW)	77	Fronk & Baker (1990)
	Thin Film Composite (FT-30)	73.4 - 106 (GW) 0.78 - 6.44 (SW)	100 100	Fronk & Baker (1990) Fronk & Baker (1990)
	Cellulose Acetate	1.65 (SW)	71.4	Miltner et.al.(1989)
	Nylon Amide	1.65 (SW)	84.6	Miltner et.al.(1989)
	Thin Film Composite	1.65 (SW)	98.5	Miltner et.al.(1989)
Metolachlor	Cellulose Acetate	2.73 - 14.61 (SW)	80	Fronk & Baker (1990)
	Polyamide	2.73 - 14.61 (SW)	78	Fronk & Baker (1990)
	Thin Film Composite (FT-30)	30.9 - 111 (GW) 2.73 - 14.61 (SW)	100 100	Fronk & Baker (1990) Frank & Baker (1990)
Urea Derivative				
Linuron	Cellulose Acetate	74.7 - 106.8 (GW) 0.0 - 1.18 (SW)	0 0	Fronk & Baker (1990) Fronk & Baker (1990)
	Polyamide	74.7 - 106.8 (GW) 0.0 - 1.18 (SW)	57 100	Fronk & Baker (1990) Fronk & Baker (1990)
	Thin Film Composite (FT-30)	0.0 - 1.18 (SW)	100	Fronk & Baker (1990)
	Thin Film Composite (DSI)	74.7 - 106.8 (GW)	99	Fronk & Baker (1990)
Organo-chlorine				
Aldrin	CA	142.3	100	Eisenberg & Middlebrooks (1986)

Class/ Pesticide	Membrane	C_o (µg/L)	% Removal	Reference
	NS-100	142.3	100	Eisenberg & Middlebrooks (1986)
Heptachlor	CA	505.4	100	Eisenberg & Middlebrooks (1986)
	NS-100	505.4	100	Eisenberg & Middlebrooks (1986)
Dieldrin	CA	321.3	99.88	Eisenberg & Middlebrooks (1986)
	NS-100	321.3	100	Eisenberg & Middlebrooks (1986)
Organophosphate				
Diazinon	CA	437.7	98.25	Eisenberg & Middlebrooks (1986)
	NS-100	437.7	98.05	Eisenberg & Middlebrooks (1986)
Malathion	CA	1057.8	99.16	Eisenberg & Middlebrooks (1986)
	NS-100	1057.8	99.66	Eisenberg & Middlebrooks (1986)
Parathion	CA	747.3	99.88	Eisenberg & Middlebrooks (1986)
	NS-100	747.3	99.83	Eisenberg & Middlebrooks (1986)
Others				
Captan	CA	668.9	97.78	Eisenberg & Middlebrooks (1986)
	NS-100	668.9	100	Eisenberg & Middlebrooks (1986)
Trifluralin	CA	1578.9	99.74	Eisenberg & Middlebrooks (1986)
	NS-100	1578.9	99.99	Eisenberg & Middlebrooks (1986)
Carbofuran	Cellulose Acetate	14 (GW)	85.7	Lykins et al(1988); Fronk et al (1990)
	Polyamide	14 (GW)	> 92.9	Lykins et al(1988); Fronk et al (1990)

Class/ Pesticide	Membrane	C_o (µg/L)	% Removal	Reference
	Thin Film Composite*	14 (GW)	> 92.9	Lykins et al(1988); Fronk et al (1990)
	Polyamide**	4.3 - 9.8 (GW)	79.6 - 90.0	Lykins et al(1988); Fronk et al (1990)
1,2-Dichloro-propane	Cellulose Acetate	24 (GW)	4.2	Lykins et al(1988); Fronk et al (1990)
	Polyamide	24 (GW)	75	Lykins et al(1988); Fronk et al (1990)
	Thin Film Composite*	24 (GW)	37.5 - 87.5	Lykins et al(1988); Fronk et al (1990)
	Polyamide**	17.5 - 22.2 (GW)	52.6 - 71.2	Lykins et al(1988); Fronk et al (1990)
Aldicarb Sulfoxide	Cellulose Acetate	39 (GW)	> 97.4	Lykins et al(1988); Fronk et al (1990)
	Polyamide	39 (GW)	> 97.4	Lykins et al(1988); Fronk et al (1990)
	Thin Film Composite*	39 (GW)	94.9 - 97.4	Lykins et al(1988); Fronk et al (1990)
	Polyamide**	11.2 - 20.0 (GW)	91.1 - 95.0	Lykins et al(1988); Fronk et al (1990)
Aldicarb Sulfone	Cellulose Acetate	47 (GW)	93.6	Lykins et al(1988); Fronk et al (1990)
	Polyamide	47 (GW)	95.7	Lykins et al(1988); Fronk et al (1990)
	Thin Film Composite*	47 (GW)	93.6 - 95.8	Lykins et al(1988); Fronk et al (1990)
	Polyamide	14.0 - 31.4 (GW)	91.4 - 95.8	Lykins et al(1988); Fronk et al (1990)

* Bench scale studies using spiked groundwater from Suffolk County, NY
** Pilot plant studies in Suffolk County, NY

Appendix B. Questions for Public Comment

1   Do the scientific data demonstrate clear quantitative relationships exist between the physical/chemical properties of particular pesticide classes and specific water treatments processes?

2.   Based on its technical review of the literature on the impacts of different treatment processes on levels of pesticide residues in drinking water, OPP is leaning toward an interim approach which assumes, in the absence of representative pesticide-specific water plant monitoring data, that residues in finished drinking water will be the same as levels in such water prior to treatment. Given the objective of accurately estimating pesticide concentrations in drinking water, do the scientific data support this approach? How would an approach be developed based on the state of knowledge about the impact of treatment on pesticides? Under what circumstances can OPP use data on the impacts of a specific treatment process on several pesticides in a chemical class to support a general conclusion about all pesticide in that class?

3   During disinfection with chlorine, pesticides such as organophosphates can be oxidized to form toxic degradation products. What other classes of pesticides may be transformed by drinking water treatment processes to form toxic byproducts? What issues related to pesticide transformation should OPP be aware of?

4   Laboratory jar tests are often employed to determine if a regulated contaminant, including some pesticides, in raw water can be removed by a given treatment process. What are the advantages and disadvantages of using results of jar tests as the basis of evaluating whether the pesticide will be eventually removed in the actual water treatment plant? How might these results be used to adjust raw water concentrations for use in human health risk assessment? What are the advantages and disadvantages of using other types of data, e.g. paired samples from field monitoring, or pilot plant data.

5   Studies cited in the literature review indicate that many factors, such as raw water composition, water treatment method, and treatment plant conditions, may affect the removal of pesticides. What issues should OPP be considering in determining the potential impact of these factors on the percent removal and transformation of pesticides by different water treatment plants?

6   What additional water treatment data from other studies, which either support or are inconsistent or contradict the data presented in the preliminary literature review, should OPP consider? Please submit any data that would provide information on the impacts of water treatment on additional pesticides or classes of pesticides.

7.   For example, some pesticides, including carbamates and organophosphates, with hydrolysis half-lives of less than 1 day in alkaline (pH 9) water are observed to be "removed" during lime-soda softening (pH 10~11) by alkaline hydrolysis. Can this observation be generalized in predicting whether a pesticide with alkaline abiotic

hydrolysis half-life of less than 1 day will be "removed" through water treatment?

8   The effects of water treatment on pesticide residues in drinking water can be assessed by regression modeling of important parameters with removal efficiency, experimental or laboratory studies, and actual field monitoring. What other approaches or methods can be used to assess water treatment effects? What are the pros and cons of these methods?

9.   What types of data are needed regarding the extent and manner of use of a particular drinking water treatment process in order to use the data on the impact of such method on pesticide concentrations in finished drinking water in a deterministic or probabilistic exposure assessment?