**Progress Report on
Estimating Pesticide Concentrations in Drinking Water
and Assessing Water Treatment Effects
on Pesticide Removal and Transformation:
A Consultation**

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AN OVERVIEW AND UPDATE OF OPP ACTIVITIES**

Overview for Scientific Advisory Panel Consultation
September 29, 2000

**1.1 Purpose of Consultation**

With the passage of the Food Quality Protection Act (FQPA) in August 1996, Congress directed EPA to consider "all anticipated dietary exposures and all other exposures for which there is reliable information" in determining whether pesticide residues in food are safe. Because a number of pesticides have been found in ground water and surface water throughout the United States, EPA considers drinking water to be an anticipated dietary exposure route for certain pesticides. Prior to FQPA, the Office of Pesticide Programs (OPP) did not routinely incorporate drinking water exposure into the quantitative human health risk assessment. Rather, OPP's strategy for managing pesticides which had the potential to contaminate water was to emphasize prevention – requiring mitigation measures such as geographic restrictions on pesticide use and "buffer zones" near water bodies where pesticide use is prohibited. Since FQPA, OPP has routinely considered exposure to pesticides in drinking water as a part of its dietary risk assessments process.

The purpose of this consultation is to update the Scientific Advisory Panel (SAP) on the progress OPP has made to date in improving its drinking water assessment process and to consult with the SAP on two specific issues. The Agency believes it is critical to get the perspective of the SAP as it moves forward with its improvements rather than wait until the entire package is developed. Thus, consultations with the SAP are a part of the development process, allowing OPP to obtain feedback along the way and providing for the opportunity to make mid-course corrections as needed.

This section of the consultation document provides an overview of the Agency's efforts in developing and refining a tiered screening assessment for drinking water and in developing tools and data for use in more advanced drinking water assessments. The sections that follow present specific issues on which EPA would like to consult with this SAP. Section 2.0 is a progress report on regression modeling approaches for estimating pesticide concentrations in drinking water. This is a continuation of efforts first presented to the SAP in March 2000. A review of scientific literature on the impacts of drinking water treatment on pesticide removal and transformations is presented in Section 3.0. This review was initiated on the advice of an earlier SAP.

**1.2 Developing a Tiered Screening Assessment**

With the passage of FQPA, OPP first focused its efforts on developing a series of assessment tools to separate those pesticides which are not expected to be present in drinking water at concentrations that would result in unacceptable risk from those that have the potential

to pose an unacceptable risk. In 1996, OPP had available two mechanistic surface water models that were designed to assess ecological impacts of pesticides and no quantitative ground water screening tool. Initial efforts focused on modifying the available surface water models for use in drinking water assessments and on developing a quantitative ground-water screening model.

The basic concept of the tiered screening approach is to compare estimates of concentrations of a particular pesticide in drinking water sources to a drinking water level of comparison (DWLOC). The DWLOC is pesticide concentration in drinking water associated with the difference between the maximum safe intake of a pesticide and the sum of the exposure from food and residential sources. A more detailed discussion of the screening approach can be found in the drinking water science policy paper released in November 1999 (EPA OPP, 1999b). Figure 1.1 illustrates the general framework used for the drinking water screening process. The intent of the screening approach is to estimate pesticide concentrations in water from sites that are highly vulnerable to runoff or leaching so that the Agency can be confident that any pesticide that "passes" the screening tiers (i.e., the estimated drinking water concentration is less than the DWLOC) poses a low possibility of significant risk to human health. At the same time, the screen should not be so conservative that those pesticides that are truly not expected to pose a risk to human health "fail" the screen.

### 1.2(a) Surface Water Screening Tools

The evolution of OPP's current screening tools for drinking water assessments can be tracked in several FIFRA Scientific Advisory Panel (SAP) reviews:

- *A Set of Scientific Issues Being Considered by the Agency in Connection with Estimating Drinking Water Exposure as a Component of the Dietary Risk Assessment* (December 1997). See EPA OPP (1997) and FIFRA SAP (1997) for details.

- *Proposed Methods for Basin-Scale Estimation of Pesticide Concentrations in Flowing Water and Reservoirs for Tolerance Reassessment* (July 1998). See EPA OPP (1998) and FIFRA SAP (1998) for details.

- *Proposed Methods for Determining Watershed-derived Percent Crop Areas and Considerations for Applying Crop Area Adjustments to Surface Water Screening Models* (May 1999). See EPA OPP (1999a) and FIFRA SAP (1999) for details.

As a result of these consultations, OPP made the following refinements to the initial surface water screening tools:

- an index drinking water reservoir replaced the standard field pond scenario for screening models of surface-water sources of drinking water; and

- screening model results are adjusted with a percent crop area (PCA) factor to account for the area of the watershed that may potentially be in the crop or crops being modeled.

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**FIGURE 1.1. GENERAL FRAMEWORK FOR THE DRINKING WATER SCREENING PROCESS**

**Compare Available Data to Minimum Information and Data Needs**
Are the environmental fate data sufficiently complete to model the fate and transport of the pesticide?
Are application and use information available to model pesticide usage on crops of interest?

No→

**Unable to Continue:**
Request additional data in order to make an assessment.

Yes ↓

**Estimated Drinking Water Concentration (EDWC)**
**Modeling:** Screening models estimate peak and annual average pesticide concentrations at a vulnerable site

**Monitoring:** EDWC compared with available monitoring data. Monitoring data serve as a "lower bound" on the estimate.

**Drinking Water Level of Comparison (DWLOC)**
Calculate the DWLOC value [the difference between the maximum daily intake (the reference dose) and the sum of the exposure from food and residential sources converted to a concentration with assumptions on consumption rates and body weights] for acute short-term, intermediate-term, chronic, and cancer risk assessments.

**Screening Comparison:**
Acute DWLOC values are compared to peak (maximum)concentrations from screening model. Is EDWC $\geq$ acute DWLOC values?
Chronic DWLOC values are compared to average annual concentration from screening model. Is EDWC $\geq$ chronic DWLOC values?

No ↓                                                    Yes ↓

**Assessment Done**
Pesticide concentrations in drinking water, when considered along with other sources of exposure for which OPP has reliable data, is not expected to pose an unacceptable risk for human health.

**Continue to the Next Screening Level**

These revisions improve OPP's initial screening assessments by representing a watershed prone to generating high pesticide concentrations in water that is also capable of supporting a drinking water facility. The PCA factor accounts for the fact that such watersheds are not likely to be covered entirely in one crop.

OPP currently uses two tiers to develop initial estimates of pesticide concentrations in surface-derived sources of drinking water. In the first tier, GENEEC (GENeric Estimated Environmental Concentrations) estimates peak and longer-term average concentrations of

pesticides in water from a few basic chemical parameters and pesticide label application information. In the second tier, the coupled PRZM (Pesticide Root Zone Model) and EXAMS (EXposure Analysis Modeling System) models include more site-specific information in the scenario details regarding application method and temporal distribution with weather, and better accommodates chemical-specific parameters. 'Passing' either of the initial tiers indicates a low possibility of significant risk to human health. 'Failing' the tiers, however, does not necessarily mean the chemical is likely to cause health problems, but rather that there is a need to continue on to the next higher tier of assessment.

### 1.2(a)1 Tier 1 Screening Model

GENEEC, developed as an initial screening tool for ecological impact assessments, models pesticide concentrations in a large (20-million-liter capacity) field pond. The model considers adsorption of the pesticide to soil or sediment, incorporation of the pesticide at application, direct deposition of spray drift into the water body, and degradation of the pesticide in soil before runoff and within the water body. GENEEC is expected to overestimate pesticide concentrations in drinking water for most sites because it uses maximum pesticide application rates, assumes that no buffer exists between the pond and the treated field, simulates runoff from a 6-inch rainfall over a 24-hour period, represents a water body that is smaller than a drinking water reservoir, and assumes that the entire watershed is cropped and the pesticide is applied to the entire crop. A detailed description of GENEEC can be found in EPA OPP (1997).

GENEEC estimates the peak value which occurs on the day of the single large rainstorm and the average value for the next 56 days. The peak value is used for acute exposure assessments and the average value is used for chronic exposure assessments. It is important to note that, if a pesticide "fails" this tier (i.e., either the estimated peak or average drinking water concentration exceeds the appropriate DWLOC), the Agency does not take risk mitigation action. Instead, the assessment moves to the next screening tier. This initial screen provides a rapid, inexpensive assessment that does screen out those pesticides that are not likely to occur in drinking water sources at concentrations that are of concern.

OPP is in the process of revising this screening model to replace the current farm pond with a drinking water reservoir (see section 1.2(a)3). The model will also adjust the estimated pesticide concentrations in drinking water by the maximum fraction of the watershed which would be planted in the crop or crops of concern (see section 1.2(a)4).

### 1.2(a)2 Tier 2 Screening Model

The coupled PRZM and EXAMS models include more site-specific information regarding application method and temporal distribution with weather, and better accommodate chemical-specific parameters. Using best professional judgement and information gathered from USDA extension experts and grower groups, OPP selects a combination of site, soil, management, and weather factors for each modeled crop use that, taken together, represent a vulnerable, but not worst-case, watershed on which the crop is actually grown. As a screening tool, it simulates maximum application rates and frequencies for a vulnerable drinking water reservoir.

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PRZM/EXAMS generates daily pesticide concentrations using actual weather data, typically covering 36 years, from a station representative of use area. This distribution of daily concentrations are analyzed to provide:

- Peak concentrations for each year of simulation: From these yearly peaks, OPP derives the peak concentration from the 1-in-10-year event for use in acute exposure assessments.

- Average annual concentrations for each year of simulation: OPP then derives the 1-in-10-year average annual concentration for use in chronic, noncancer exposure assessments.

- Average concentration over the entire simulation period: The average of the entire distribution of daily values is used in cancer exposure assessments.

Some communities that derive their drinking water from smaller bodies of water with minimal outflow or with more runoff-prone soils would be likely to get a higher drinking water exposure that estimated using the index reservoir. More detail on PRZM and EXAMS can be found in EPA OPP (1997 and 1998). The index drinking water reservoir and the percent crop area adjustment, discussed in the sections that follow, have been applied to the second screening tier.

### 1.2(a)3  Index Drinking Water Reservoir

In order to provide a more realistic screening assessment of surface water sources of drinking water, OPP replaced the "field pond" scenario originally used in its Tier 2 screen with an index drinking water reservoir (EPA OPP, 1998 and 1999a). The index reservoir is based on the properties of Shipman City (IL) Lake, which is representative of a number of reservoirs in the central Midwest that are known to be vulnerable to pesticide contamination. These reservoirs tend to be small and shallow with small watersheds, and frequently have Safe Drinking Water Act (SDWA) compliance problems with atrazine, a herbicide widely used on corn grown in these watersheds. The index drinking water reservoir characteristics have been incorporated into the PRZM and EXAMS models and are implemented in conjunction with percent cropped area adjustment.

While estimates of pesticide concentrations in drinking water based on a Midwestern index drinking water reservoir may not be representative of residue levels in drinking water sources in other parts of the country, the scenario provides an effective screening tool to determine the need for more extensive refinements. The modeling scenarios currently account for region-specific rainfall, soil, and hydrologic/runoff factors. Steps to develop scenarios for regional reservoirs for advanced tiers of modeling have been hampered by the lack of monitoring data outside of the Midwest that is of sufficient quality and extent to develop scenarios for additional reservoirs.

This screening approach assumes that field simulations with the PRZM and EXAMS models reasonably approximate pesticide fate and transport within a watershed that contains a drinking water reservoir. If the models fail to capture pertinent basin-scale fate and transport processes consistently for all pesticides and all uses, small errors can be magnified going from a

field- to a watershed-scale. This may result in overestimates in some cases and underestimates in other cases. Assessments made in the development of the percent cropped area (PCA) suggest that PRZM/EXAMS may not be realistically capturing basin-scale processes for all pesticides or all uses (EPA OPP, 1999a). In some instances, the screening model estimates are more than an order of magnitude greater than the highest concentrations reported in available monitoring data; in a small number of instances, the model estimates are slightly less (generally within the same order of magnitude) than monitoring concentrations.

### *1.2(a)4  Percent Crop Area (PCA) Adjustments*

The PCA is a generic adjustment which represents the maximum percent of any watershed that is planted to the crop or crops being modeled and, thus, may potentially be treated with the pesticide in question. PCA factors are generated from Geographic Information System (GIS) overlays of cropping area and watershed delineations and are applied to estimates of index reservoir surface water pesticide concentration values from the PRZM/EXAMS model. The output generated by these models is multiplied by the maximum decimal fraction of cropped area in any watershed generated for the crop or crops of interest. To be effective as an adjustment to screening model estimates, the PCA should result in estimated concentrations that are closer to, but not less than, actual pesticide concentrations in vulnerable (prone to pesticide-laden runoff) surface water sources. While it moves away from assuming that the entire watershed would be treated at the same time, the PCA is still expected to be a screen because it represents the highest percentage of crop cover of any large watershed in the lower 48 states of the U.S. and it assumes that the entire crop is being treated.

Model outputs are multiplied by the maximum PCA (decimal) for the crop or crops of interest. The SAP felt PCAs were appropriate for the following four major crops, based on comparisons with available monitoring data (FIFRA SAP, 1999).

- •  Corn:  PCA 46% (0.46)
- •  Soybeans:  PCA 41% (0.41)
- •  Wheat:  PCA 56% (0.56)
- •  Cotton:  PCA 20% (0.20)

These PCAs represent the watershed with the highest pct of that single crop. We also have PCAs for the watershed(s) which have the highest percentage of any combination of these crops (e.g., for a corn-soybeans pesticide, the combined PCA is 83%). For other crops, the SAP recommended using a simple screening approach, default PCA or targeted monitoring for other crops (FIFRA SAP, 1999). This year, we added an interim default adjustment factor of 87% for other crops and are collecting data to develop and evaluate additional PCA factors. The default value represents the watershed which had the greatest percentage of all combined agricultural lands.

The PCA adjustment is only applicable to pesticides applied to agricultural crops. Contributions to surface waters from non-agricultural uses such as urban environments are not well-modeled. Currently, non-agricultural uses are not included in the screening model assessments for drinking water.

### 1.2(b)  Ground Water Screening Tools

When FQPA was enacted, OPP had no screening tool that could provide quantitative estimates of pesticide concentrations in ground water. SCI-GROW (Screening Concentration In GROund Water) was developed using data from perspective ground water monitoring studies to provide screening estimates of pesticide concentrations in shallow, vulnerable ground-water (EPA SAP, 1997; EPA OPP, 1999b). This regression model estimates ground water concentrations arising from labeled uses at a vulnerable agricultural site using the chemical's adsorption (soil/water partition coefficient) and persistence (soil metabolism half-life). The model assumes pesticide application at the maximum label rate to a field that has rapidly permeable soils overlying shallow ground water. Pesticide concentrations estimated by SCI-GROW are expected to represent high-end values because the model is based on ten prospective ground-water monitoring studies which were conducted by applying the pesticide at maximum allowed rates and frequency to hydrogeologically-vulnerable sites (i.e., shallow aquifers, sandy, permeable soils, and substantial rainfall and/or irrigation to maximize leaching). SCI-GROW uses different criteria than PRZM/EXAMS for chemical-specific input parameters because the model is based on a regression analysis with those specific parameters. The conservatism in SCI-GROW comes from the vulnerable sites from which the regression is derived.

OPP does not currently have a tier 2 ground water model. If a pesticide does not pass the initial screen for ground water, OPP relies on monitoring data to make a refined assessment of the potential impact of the pesticide in ground water on human health. If adequate monitoring data are not available, the Agency will request that targeted monitoring studies, such as prospective ground water monitoring studies, be conducted. In FY2001, OPP plans to evaluate existing ground water models and begin to develop a procedure for a second tier assessment of pesticides in ground water.

### 1.2(c)  Monitoring Data

During the screening stage, OPP compares the model-estimated drinking water concentrations with available monitoring data. Typical sources of monitoring data include USGS's NAWQA, NASQAN, and Toxic Substances Hydrology programs (USGS, 2000), EPA Office of Water's STORET database (EPA OW, 1998), OPP's Pesticides in Ground Water Data Base (EPA OPP, 1992), and the National Pesticide Survey (EPA, 1990). Chemical-specific monitoring studies are also evaluated, if available. If monitoring data show concentrations greater than the estimated model values, then the monitoring value will be incorporated into the screening process. Otherwise, the estimated model values will be used. In some instances, the monitoring data will serve as a "lower bound" on the screening estimates while the estimated model values serve as the "upper bound." A more detailed discussion on the use of monitoring data in drinking water assessments is presented in EPA OPP (1999b).

### 1.2(d)  Advanced Screening Tools

If the pesticide "fails" the Tier 2 screen, i.e., model estimates exceed the DWLOC, then OPP assumes that the pesticide may have some potential to reach surface- and/or ground-water sources of drinking water at levels of concern to human health.  Additional steps taken to reduce the uncertainty in the drinking water estimates include requesting chemical or usage information to refine model estimates, more fully analyzing existing monitoring data, or requesting additional monitoring data that can be related to drinking water sources.  Monitoring studies targeted toward a specific pesticide, when available, are valuable in evaluating and reducing the uncertainty in the drinking water component of the exposure assessment.  Such efforts to reduce the uncertainty in estimates of pesticide concentrations in drinking water have been chemical-specific, driven by the nature of the chemical, the available data, and the usage patterns.

In the past year, OPP evaluated the effectiveness of its existing screening process and is considering adding an additional tier to its surface water screening approach.  Such a tier would allow us to further narrow our focus to potential problem pesticides while still retaining a protective screen.  This tier would take advantage of the fact that, for surface water, our models provide a distribution of daily pesticide concentrations.  Daily water concentrations would be loaded into HED's DEEM (Dietary Exposure Evaluation Model) along with the food to generate a probabilistic distribution of aggregate exposure estimates.  This would be compared to the Population Adjusted Dose for screening.  We are now evaluating this with case studies and plan to present this for public comment in an upcoming new policy/guidance paper on establishing a multi-tiered drinking water assessment process.

## 1.3  Advanced Tools for Use in Aggregate Exposure Assessments

Some pesticides are not going to pass the screening process.  For those pesticides which do not pass the screening tiers, OPP is evaluating a combination of tools that will allow us to develop reasonable approximations of distributions of drinking water concentrations for direct use in human health aggregate exposure and risk assessments.  These tools would add spatial and temporal distributions of drinking water concentrations for use in aggregate exposure assessments.  A combination of available monitoring data, modeling, usage information, and geographically-distributed site and climate data would be used to identify areas of the country where a particular pesticide is likely to be found in surface-water sources of drinking water, and at what levels or range of levels.  These estimates would  be combined with population estimates for use in a national assessment.  In the non-use or non-occurrence areas, drinking water does not contribute to the aggregate exposure, so the aggregate exposure estimate would be based solely on food intake and residential exposure.  In the other parts of the country, drinking water may contribute to exposure, resulting in localized areas and subpopulations with higher aggregate exposure.  Because drinking water is local, the national exposure assessment for drinking water must address localized areas of the country where unacceptable aggregate exposure may occur due to drinking water contamination.

Recent SAPs highlight the preliminary progress OPP has made in tool development:

- *Consultation on the Development and Use of Distributions of Pesticide Concentrations in Drinking Water for FQPA Assessments* (March 2000). See EPA OPP (2000a) and FIFRA SAP (2000a) for details.

- *Monitoring Strategies for Pesticides in Surface Derived Drinking Water* (June 2000). See EPA OPP (2000a) and FIFRA SAP (2000a) for details.

### 1.3(a)  Available Monitoring Data

Relatively few studies have sufficient monitoring data and ancillary information to allow for the development of a national exposure assessment for more than a handful of pesticides. Many monitoring studies provide variable data quality and broad ranges in limits of detection. For national-scale studies, such as USGS' NAWQA (USGS, 2000), data are not available for all pesticides, especially degradates. For a given pesticide, spatial coverage is often inadequate to represent its full use range. Nontargeted monitoring data may not represent the actual pesticide use area. The sampling frequency for most studies is not enough to capture peak concentrations which are important in acute exposure assessments. Monitoring data may not represent actual or potential drinking water sources. Additional discussion on acquiring and interpreting drinking water monitoring data can be found in EPA OPP (1999b).

NAWQA study results have found that those pesticides detected in agricultural streams are predominantly herbicides while those in urban areas have a wider scatter of pesticides. Some pesticides are detected year-round in water while others are more seasonal in nature (USGS, 2000). All of this information has given us a better understanding of the likelihood of pesticide occurrence in drinking water sources: enough to know that a number of pesticides have the potential to be found in at least some drinking water sources at concentrations that may be of potential concern. It has also pointed to the need for better data and tools to make informed risk assessments and management decisions.

In 1999, USGS, with EPA support, undertook a pilot monitoring project designed to fill in some holes, specifically on pesticide occurrence in drinking water reservoirs. This pilot study monitored pesticide concentrations at 12 reservoirs in order to evaluate sampling-frequency schemes in reservoir systems, provide preliminary monitoring data for reservoirs, link drinking water concentrations with raw sources and take a first cut at comparing treatment effects, and link concentrations in reservoirs with watershed and reservoir characteristics (USGS, 1999). The results of the first year of the study are still being analyzed and a preliminary report is expected by the end of the year. In the meantime, the study is continuing into its second year.

### 1.3(b)  Regression Modeling for Quantitative Risk Assessment Purposes

While OPP continues to acquire additional monitoring data and works to develop a national multi-pesticide monitoring effort, we also need tools to interpret available data and to allow us to develop reasonable approximations of pesticide concentrations in drinking water for

use in quantitative risk assessments. Monitoring data often give us scattered dots (or snapshots) in time and space. Some recent regression modeling efforts have shown promise in being able to help us make the best use of what available data we have. USGS's recent work in developing regression models based on monitoring may give us a needed tool to connect the dots and extend the value of limited data in completing quantitative risk assessments. Two ongoing modeling efforts were presented to the SAP in March and we received very positive feedback from the panel on the concept and encouragement to continue (EPA OPP 2000a, FIFRA SAP, 2000a). A report on progress made in the regression modeling effort since March follows this section. The ultimate endpoint we hope to get from these models is a reasonable approximation of pesticide concentrations at drinking water intakes for use in quantitative human health risk assessments.

The USGS regression modeling effort has identified certain critical information gaps and data needs. We need additional monitoring data to improve the models. The more data we have on a variety of pesticides, the broader we can apply this approach and the better the estimates will be. The models have been developed using stream/river data. We have less data on reservoirs, lakes, and ground water sources of drinking water. Pesticide usage is a driving factor. Agricultural pesticide usage is reported on a county-basis and "average" rates are derived by dividing county-wide sales, in pounds of active ingredient per acre (lb a.i./A), by total county acreage. However, actual single applications can range from a minimum efficacious rate to maximum application rates; applications may be intensive in areas of high pest pressure and non-existent where the pest does not occur. Such variations are not captured in averaging data based on sales and total county acreage. While the USGS work and other studies have shown that pesticides used in urban or other nonagricultural settings are being detected in surface- and ground-water, practically no data are available on urban usage of pesticides.

Work is in progress on identifying the locations of all of the community drinking water system intakes, delineating and characterizing the basins that drain into these intakes. As OPP moved forward, we discovered how few drinking water intake locations are identified. We've been working with EPA's Office of Water and USGS to complete the database for all intakes. We have begun preliminary efforts to develop a GIS tool that would pull all of this information together for use in monitoring study design as well as for model development. Such data needs will be addressed in this SAP, as well as in planned future consultations with the SAP.

### 1.3(c) Acquiring Additional Monitoring Data

For pesticides that have not been cleared by available drinking water assessment methods, data call-ins are being used to gather targeted, pesticide-specific monitoring data for use in drinking water assessments. Work is also continuing on the design of a national-scale, multi-pesticide drinking water monitoring program since the June consultation with the SAP (EPA OPP, 2000b; FIFRA SAP, 2000b). Since the SAP, OPP has refocused the objective of "national-scale multi-pesticide monitoring" to gather data to advance regression model development (in addition to gathering data for use in pesticide-specific risk assessments). The Agency has had follow-up meetings with representatives from EPA, USGS, USDA, and ACPA regarding coordinated efforts to collect data.

EPA, USGS, USDA, and ACPA share a common interest in (1) improving drinking water assessments under FQPA for use in both quantitative human health risk assessment and risk management decison-making, (2) making such improvements as soon as possible, and (3) making the best use of available government and private resources in a cooperative and coordinated manner to take advantage of their combined technical expertise and funds. They have agreed to a common vision of organizing to focus their efforts on advancing the development and validation of more refined predictive tools (regression-based models). The immediate objective of this effort is to determine what monitoring data and other information need to be collected and by whom to most efficiently and effectively advance the development of higher-tiered regression-based drinking water assessment models.

Representatives of EPA, USGS, and USDA agreed to form an intra-governmental FQPA drinking water steering committee, with committee representation from USDA, USGS, and EPA. Representatives of ACPA and other interested public groups would be invited to sit in as observers of these meetings. The steering committee would establish the necessary scientific and technical working groups, provide guidance, direction, and oversight for these working groups, review and comment on their work products, and identify policy issues which may require broader input. Initially, two working groups have been proposed: a monitoring/modeling working group and an ancillary data working group.

## 1.4 Considering Drinking Water Treatment Effects

Drinking water treatment can have an impact on the nature and degree of human exposure to pesticides. At present, if a particular pesticide still exceeds the DWLOC after OPP's screening and refinement assessments based on raw water are completed, the Agency notes in is human health risk assessment that the assessment has not taken into account the potential effects of drinking water treatment implying that the treatment is expected to have some impacts in terms of risk reduction. However, there has been little effort made to date to determine whether such a risk reduction does indeed exist and, if so, to what degree risk may be reduced. In order to assess these potential effects and to determine whether OPP needs to change how it addresses treatment issue in the human health risk assessment, OPP has worked with EPA's Office of Research and Development (ORD) and others to research available scientific literature to prepare a paper that is intended to succinctly capture the state-of-the-science on the impact of drinking water treatment on pesticides. This draft paper is included in this briefing document and is a major part of this particular consultation with the SAP.

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**2.0 PROGRESS REPORT ON REGRESSION MODELING APPROACHES ESTIMATING PESTICIDE CONCENTRATIONS IN DRINKING WATER FOR FQPA EXPOSURE ASSESSMENTS**

**2.1 Synopsis of March 2000 SAP Consultation**

This progress report is to serve as an update on the SAP presentation entitled "Development and Use of Distributions of Pesticide Concentrations in Drinking Water for FQPA Exposure Assessments: A Consultation" which was presented on March 3, 2000. (A copy of the presentation and the response of the panel is attached). That presentation focused on two potential multi-site computer modeling approaches for estimating population-weighted distributions of pesticide concentrations at the intakes to community water systems (CWS). Both approaches utilize, at least in part, regression equations and are based upon a large quantity of monitoring data as well as pesticide usage and nationally available soils, hydrologic and hydrographic data and other drainage-basin characteristics.

**2.1(a) Modeling Approaches Presented**

The first of the approaches presented was developed by Larson and Gilliom at the US Geological survey. Regression models were developed for estimating pesticide concentration distributions for streams. Individual regression models were developed for stream concentrations of the herbicides alachlor, atrazine, cyanazine, metolachlor, and trifluralin. Regression equations were derived using measured concentrations of the four herbicides as the response variable and nationally available agricultural use data and physiographic basin characteristics as predictor variables. Concentration data for the herbicides are from 45 streams sampled as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program during 1993-95. Separate equations were developed for each of six percentiles ($10^{th}$, $25^{th}$, $50^{th}$, $75^{th}$, $90^{th}$, and $95^{th}$) of the annual distribution of stream concentrations, and for the annual time-weighted mean concentration.

The second of the approaches is the SPARROW (SPAtially Referenced Regression On Watershed Attributes) model which was also developed by the USGS and has been widely used for nutrient assessment. The SPARROW method uses spatially referenced regressions of contaminant transport on watershed attributes to support regional water-quality assessment goals, including descriptions of spatial and temporal patterns in water quality and identification of the factors and processes that influence those conditions. The method is designed to reduce the problems of data interpretation caused by sparse sampling, network bias, and basin heterogeneity. The regression equation relates measured transport rates in streams to spatially referenced descriptors of pollution sources and land-surface and stream-channel characteristics. Spatial referencing of land-based and water-based variables is accomplished via superposition of a set of contiguous land-surface polygons on a digitized network of stream reaches that define surface water flow paths for the region of interest.

SPARROW's digital framework (derived from EPA's river reach file RF-1) provides a nationally consistent method for segmenting large pollutant source areas. Although additional calibrations are required to account for targeted contaminants, the model can be used to address a

variety of questions, including travel times, probabilities of exceedance of concentrations for contaminants at selected locations within the source-area watersheds, and relative contributions of different sources and sub-basins to contaminant concentrations near the locations of drinking water utility intakes.

### 2.1(b)  Questions To and Responses From the March SAP

**Question Summary.** The Agency asked the SAP members to comment on the OPP assumption that population-based, regional (or national) distributions of pesticide concentrations in drinking water are the most appropriate representation for incorporation into aggregate and cumulative risk assessment as defined by FQPA.  It also asked whether the USGS regression approaches presented were sufficiently rigorous and promising to warrant further developmental efforts.  In addition it asked if the panel would support an effort to build a level of predictive capability into the regression approaches presented, based upon adding pesticide use and important environmental fate properties as additional regression variables.

**SAP Response Summary.** The panel responded in the affirmative to all of the questions. (Full text of presentation and SAP response are included in the documents attached). In summary, the panel stated:

" The use of population-based regional (or national) distributions to represent pesticide residues (concentrations) in drinking water is very appropriate and the Agency is commended for trying to find ways to move beyond point estimates of drinking water exposure to pesticides.  We support a realistic approach that incorporates the diversity of biophysical conditions in the U.S. and addresses the variable exposure and risk associated with various subpopulations in various regions and at various time intervals.  This is perhaps a complex approach, but given the diversity of conditions and populations, it is necessary to evaluate true exposure risks.  It reduces the level of conservatism which is necessary to deal with uncertainty when point estimates are used.  An important additional benefit is the better understanding that is gained of the complexity of exposure risk by incorporating the diversity issues.

"A question that needs to be addressed as this work progresses is the level of quality and representation of the monitoring data that are available for this effort, especially as it relates to water quality monitoring data for limited-use compounds.  The examples presented to the FIFRA SAP involved mostly high-use pesticides that are widely applied and for which extensive monitoring data are available.  The Agency needs to move forward with this approach but, along the way, needs to remain aware and critical of the appropriateness of the procedures, and the level of confidence associated with estimates of pesticide exposure.  This especially relates to the higher-percentile estimates of pesticide distributions for short-term exposure assessment of minor-use or new pesticides and is especially important when using logarithmic values in regression models.  Ultimately, it is important that estimates are bound by real-world exposure levels.  It is apparent that the Agency is aware of this issue.

"The idea of 'building a level of predictive capability' into the regression approaches has merit and should be explored further. Included should be chemical properties and management factors. It is recommended to recognize the limitations of extrapolation, especially for geographically-targeted minor-use chemicals. The process should allow for recognition of the fact that the exposure cannot be reasonably estimated and the emphasis may need to be on targeted intensive monitoring of the chemical. With regards to the usefulness of adding additional regression predictor variables, it will be important to look for predictor variables that would be available for all CWSs in the U.S."

**Organization of this Update**

This report is comprised of four parts: (1) Formation of institutional support infrastructure for the developmental work, (2) Ongoing technical work designed to support the modeling, (3) Intermediate progress in pesticide modeling and (4) Evolving plans for the immediate future.

**2.2 Formation of Institutional Support Infrastructure for the Developmental Work**

Following the receipt of the response to the March 3, 2000, SAP presentation and an additional SAP presentation of a drinking water monitoring design in June 2000, the Agency was told by both the American Crop Protection Association (ACPA) and the US Department of Agriculture (USDA) that they wished to join EPA and USGS in partnership in the project to develop these regression-equation based models. ACPA also expressed a desire to redirect the focus of an industry initiative to gather monitoring data toward support of the data needs of regression models.

In response to this evolving common vision, initial meetings were held between EPA, USGS, USDA and ACPA to discuss methods and design an institutional structure to work on the further advancement of the regression modeling approach and support the collection of the additional monitoring data needed for model development. As discussed in the overview [section 1.3(c)], initial plans call for a government planning and oversight group and formation of from two technical groups that will address such issues as monitoring design and development of pesticide usage estimates.

**2.2 Ongoing Technical Work Designed to Support the Modeling**

A number of projects are underway that support components of the modeling tools and methods that will be used to estimate distributions of pesticide concentrations in surface water. These projects include verification of locations of community water system (CWS) intakes, delineation of the boundaries of the watersheds that route water to these intakes, location of dams and reservoirs on GIS overlays and development of time-of-travel and flow velocity for stream reaches.

**2.3 Intermediate Progress in Pesticide Regression Modeling**

Progress in multi-site regression modeling since results presented to the SAP in March

2000 includes the following: (1) further regression analysis of atrazine and other common herbicides in streams based on newly available monitoring data, (2) preliminary analysis for selected insecticides and (3) technical developments in enhancing the capabilities and accuracy of the SPARROW model.

### 2.3(a)  National Regression Model for Atrazine in Surface Water

As presented at the March Science Advisory Panel meeting, regression models were developed for stream concentrations of the herbicides alachlor, atrazine, cyanazine, metolachlor, and trifluralin.  The regression equations were derived using measured concentrations of the five herbicides as the response variable and nationally available agricultural use data and physiographic basin characteristics as predictor variables.  Separate equations were developed for each of six percentiles (10th, 25th, 50th, 75th, 90th, and 95th) of the annual distribution of stream concentrations, and for the annual time-weighted mean concentration. The 45 model development sites were selected from NAWQA stream sites sampled primarily during 1993-94 (1991 Study Units). A journal article on this work has been completed and is being submitted to the Journal of the American Water Resources Association.

#### 2.3(a)1  Verification Testing of Regression Models

The regression models developed from data for the 1991 Study Units data were applied to two additional groups of stream sites where concentrations of the herbicides have subsequently been measured: 38 NAWQA stream sites sampled primarily during 1996-97 (1994 study unit data), and 23 NASQAN sites on larger rivers sampled primarily during 1996-97.  These two additional groups of sites have been be used as verification data sets for the models developed from the 1991 study unit data.

Two examples illustrating the agreement between predicted and actual values for atrazine are shown in Figure 2.1. The error in the concentrations predicted from the regression equations for both the model development sites and the verification sites can be evaluated by examining residuals (measured concentration minus predicted concentration). Residuals for the upper percentiles (50th, 75th, 90th, and 95th) and for the annual mean concentration are shown in Figures 2.2 - 2.5.

In most cases, variability among the residuals was greater for the 1994 study unit data than for 1991 study unit data.  In other words, the predicted concentrations were generally closer to the actual values for the model development sites than for the 1994 study unit sites.  This is expected because the model was fit to the 1991 study unit data.  Variability among the residuals for the NASQAN sites was similar to or lower than variability among the 1991 study unit sites. This is somewhat surprising because the NASQAN data are from the same period of time as the 1994 study unit data (rather than the 1991 study unit data), and the NASQAN sites generally represent much larger river systems than the sites sampled in the 1991 study units.  However, the large size of these rivers makes them less variable in terms of characterizing concentration distributions and reduces the influence of annual variability in use and weather in localized areas.

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The residual data shown in Figures 2.2 - 2.5 may be used to assess the accuracy of the predicted concentrations. Residual values of 1 and -1 in Figures 2.2 - 2.5 correspond to predicted concentrations equal to 1/10 and 10x the actual concentration, respectively. Most predicted values were within a factor of 10 of the actual values for all four of the compounds.

Figures 2.1 - 2.5 include data only for sites with uncensored actual concentration values (i.e., the actual concentration statistic was greater than the reporting limit for the compound), because residuals can not be calculated for cases in which the actual value is censored. For these four compounds, the regression models correctly predicted the concentration as less than the reporting limit in 87% of the 363 cases in which the actual value was censored in the 1994 study unit data, and in 95% of the 218 cases in which the actual value was censored in the NASQAN data.

The boxplots in Figures 2.2 - 2.5 show that the predicted concentrations for some compounds were biased either high or low for the 1994 study unit sites, the NASQAN sites, or both. The Wilcoxon signed rank test was applied to each set of residuals to determine whether the median of the residuals was significantly different than zero. This non-parametric test was used because not all of the sets of residuals are normally distributed. Medians significantly different than zero (p<.05) are indicated in Figures 2.2 - 2.5 with an asterisk below the boxplot.

For atrazine, none of the medians were significantly different than zero for any of the percentiles for the 1991 study unit sites, the 1994 study unit sites, or the NASQAN sites. For alachlor, all of the medians of the residuals for the NASQAN sites and the 50th percentile values for the 1994 study unit sites were biased high (low predictions). For metolachlor, nearly all of the medians for the NASQAN and 1994 study unit sites were biased slightly high. For cyanazine, medians of 1994 study unit residuals were biased high. Whether the bias seen for alachlor, metolachlor, and cyanazine predictions is significant in a practical sense is a matter of judgement; the values shown in Table 2.1 indicate that nearly all predicted values for these compounds are within a factor of 10 of the actual values.

Table 2.1. Comparison of predictor variables for regressions using 1991 NAWQA sites and regressions using 1991 & 1994 NAWQA sites.

+ Significant positive effect
- Significant negative effect

| Predictor variables | 91 Study Unit Sites | | | 91 & 94 Study Unit Sites | | |
|---|---|---|---|---|---|---|
| | 50$^{th}$ %ile | 95$^{th}$ %ile | Annual mean | 50$^{th}$ %ile | 95$^{th}$ %ile | Annual mean |
| Log (use/drainage area) | + | + | + | + | + | + |
| Dunne overland flow | - | - | - | not significant | not significant | not significant |
| Log (drainage area) | + | + | + | + | + | + |
| AWC | + | + | + | + | + | + |

Table 2.1. Comparison of predictor variables for regressions using 1991 NAWQA sites and regressions using 1991 & 1994 NAWQA sites.

+ Significant positive effect
- Significant negative effect

| Predictor variables | 91 Study Unit Sites | | | 91 & 94 Study Unit Sites | | |
|---|---|---|---|---|---|---|
| | 50th %ile | 95th %ile | Annual mean | 50th %ile | 95th %ile | Annual mean |
| %HGC + %HGD | + | + | + | + | + | + |
| % SILT | not significant | not significant | not significant | + | + | + |
| R-squared | 0.82 | 0.88 | 0.91 | 0.70 | 0.80 | 0.80 |

Statistical tests were also done to determine whether the residuals for the 1991 study unit sites, the 1994 study unit sites, and the NASQAN sites were significantly different from each other. The nonparametric Kruskal-Wallis test indicates that the medians of the three groups of residuals for atrazine were not significantly different from each other ($p<.05$) for any of the percentiles. For alachlor, the 50th percentile residuals were significantly lower for the 1994 study unit sites and the 90th percentile residuals were significantly higher for the NASQAN sites. For metolachlor, residuals for both the 1994 study unit sites and the NASQAN sites were significantly higher than residuals for the 1991 study unit sites for all but the 90th percentile. For cyanazine, medians for the three groups of residuals were not significantly different except for the 50th percentile, for which the NASQAN site residuals were lower (high predictions) than the residuals for the 91 and 1994 study unit sites. Again, whether these differences are significant in a practical sense is a matter of judgement.

The most critical factors that cause greater variance in residuals for the 1994 study unit streams are probably year-to-year variability in pesticide use and weather conditions. Especially for small basins, annual variability can be high in both use and runoff conditions. Work is also underway to investigate approaches for accounting for these sources of variability.

### 2.3(a)2  New Model for Atrazine from Combined Data

For atrazine, we have refit the regression models to the combined 1991 study unit and 1994 study unit NAWQA data. In most respects the new models are similar to the original, although variance explained by the new models is somewhat lower and the significance of predictor variables changed somewhat, as shown in Table 2.1. We are investigating the properties of several highly influential sites that cause the Dunne overland flow variable to be insignificant for the combined model (see Figure 2.6).

### 2.3(b)  Preliminary Analysis for Selected Insecticides

Work is under way to expand regression analysis to include both old and new monitoring data for two selected insecticides as a step toward developing methodologies for cumulative,

aggregate exposure assessment. A pilot exposure assessment is to be presented to a meeting of the Science Advisory Panel in December 2000. The biggest issue to address is availability of estimates of urban pesticide use. The preliminary analysis will have to use indirect measures such as urban area and population density.

### 2.3(c) Development of Surrogacy Methods

Also under way is development of methods to estimate distributions of pesticide concentrations for chemicals for which there is little or no monitoring data. This work will use atrazine as a conservative surrogate and attempt to develop environmental fate property-based adjustment factors which can be used in simulation of distribution of concentrations of other chemicals. It is believed that atrazine may serve as an ideal benchmark due to the abundance of monitoring data, its long half-life and its high mobility in relationship to many other chemicals. This approach will also begin by using monitoring data from the same two selected insecticides identified in section 2.3(b) above. This work will also investigate use of cropping areas and label rates to represent pesticide usage when better data is not available. The results of this work also will be presented to a meeting of the Science Advisory Panel in December 2000.

### 2.3(d) Refinements to the SPARROW Model

A number of efforts are also underway to further refine the SPARROW model which was presented to the March 2000 SAP meeting. The following is a list of enhancements which are ongoing or have been completed.

1)      An investigation is underway of pesticide variability within the SPARROW framework. This will allow identification of sources of variability.

2)      Addition of a one kilometer resolution digital elevation model (DEM) will facilitate better land-to-water routing of pesticides and enhance watershed delineation.

3)      Data from more monitoring networks (NAWQA, NASQAN and district stations) is being added to the model. This will increase the statistical power of the estimates and reduce the estimated error of the predicted concentration values.

4)      Locations of up to 75,000 reservoirs and dams are being added to the stream routing network. This will improve the time-of-travel estimates for movement of pesticides through the stream network and improve the accuracy of predictions for systems that are located on lakes and reservoirs.

5)      A separate SPARROW model is being developed to estimate the quantity of stream flow using the same technique as the one used to estimate the pesticide mass. This should provide a more consistent basis to calculate pesticide concentration estimates.

6)      New methods of contaminant load estimation will accommodate censored data. Serial correlation will be addressed through simulated maximum likelihood estimation.

7)      An algorithm has been developed to better distribute spatially aggregate source data. This will improve predictions of monitoring locations and enhance characterizing of prediction error for water quality and source distributions.

8)      New methods of SPARROW calibration have also been finalized. These include development of a multi-contaminant model, capacity for sequential rather than full-path in-stream delivery and cross-basin correlation of residuals.

9)      SPARROW will be fully implemented using only ARC/INFO and Statistical Analysis System (SAS) software. Improved code will make model specification and prediction easier.

## 2.4  Near to Mid-term Goals (3-6 months)

1)      A pilot project is underway to develop a cumulative, aggregate exposure assessment for selected insecticides.  We plan to present this to the SAP in December.

2)      OPP will continuing working with the newly formed oversight group and working groups to develop the work-plan for collection of new monitoring data and others use data to allow further enhancement of modeling tools.

3)      OPP will continue to work with the developers of spatial, hydrologic, and GIS databases; the National Hydrography Database (NHD) which is under development by USEPA; and the E2RF1 which is under development by USGS for interim use until the NHD is ready for use. This will assure these databases have maximum utility to this modeling effort.

4)      OPP will continue to support that ancillary projects to develop modeling components (delineation of watershed boundaries location of dams and reservoirs, etc).

## 2.5  Questions for the SAP

2.1     What new directions or approaches for modeling are suggested by the new results presented here?

2.2     Do the model enhancements being undertaken present useful steps forward in the model development process?  What other enhancements can the panel identify that would further improve the accuracy or usability of the models under development?

2.3     What recommendations does the panel have concerning issues regarding the design of a monitoring program to collect data to advance regression model development? What issues of selection of pesticides, soil types, region, weather, timing, etc., merit special attention?

2.4     What level of accuracy is reasonable for the Agency to generally expect from distributions of concentrations predicted by regression-equation based computer models after further

development? Is it unreasonable to expect that we will be able to be within a factor of 2 for individual sites or for the entire distribution?  What level of accuracy might we realistically expect ?
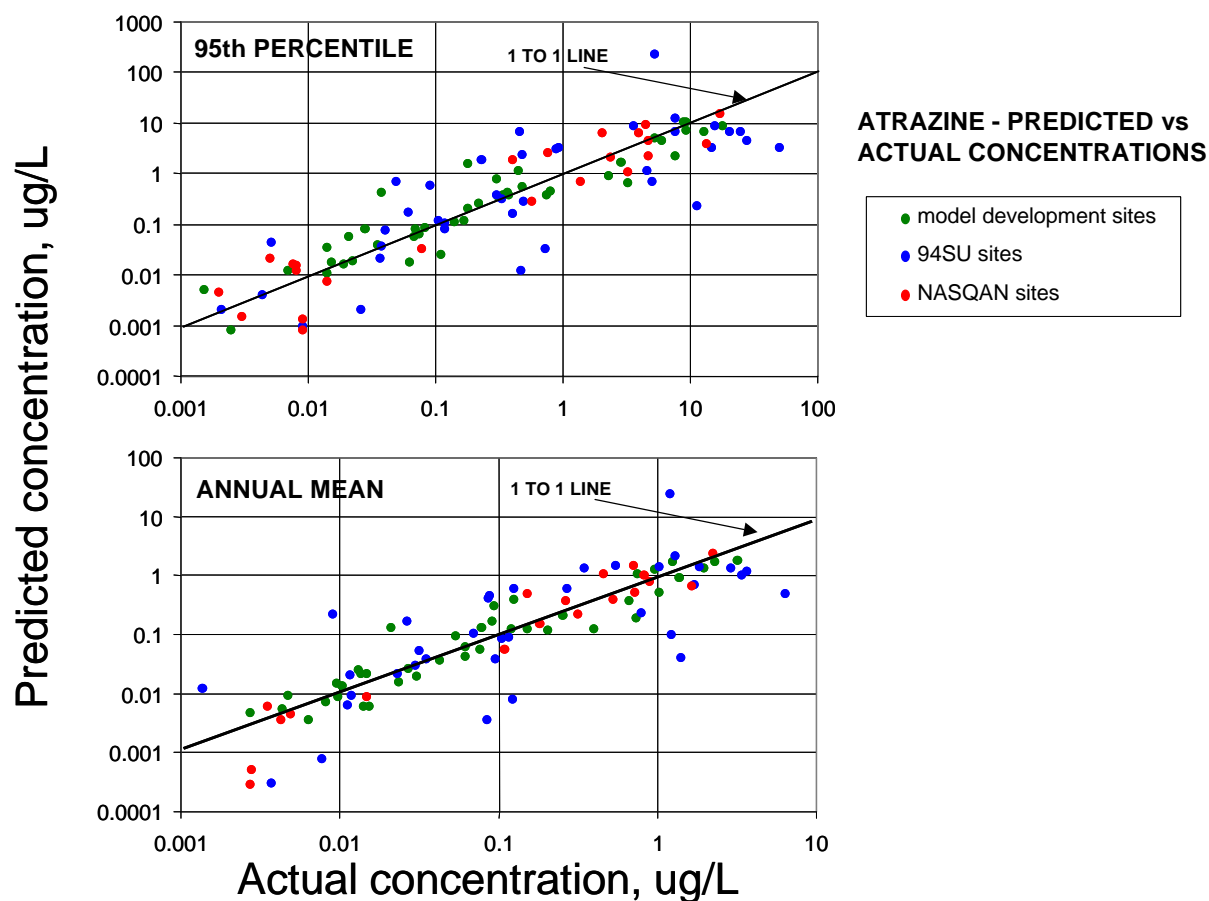
**Figure 2.1.** Predicted vs Actual Concentrations of Atrazine, Atrazine Regression Model.  Source: B. Gilliom, USGS.

# ATRAZINE
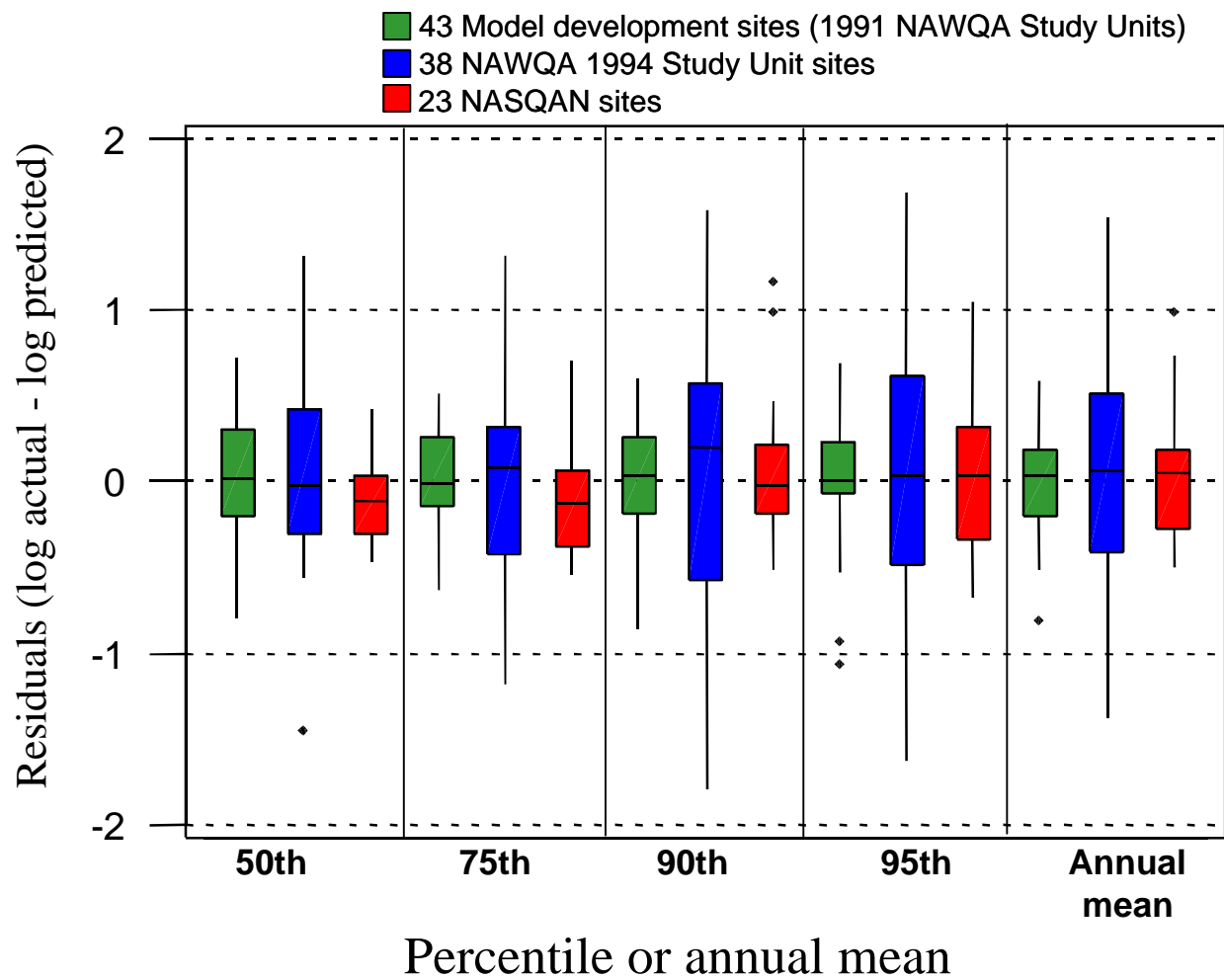
**Figure 2.2.** Residual error in concentrations predicted from the regression equations for atrazine.  Source: R. Gilliom, USGS.
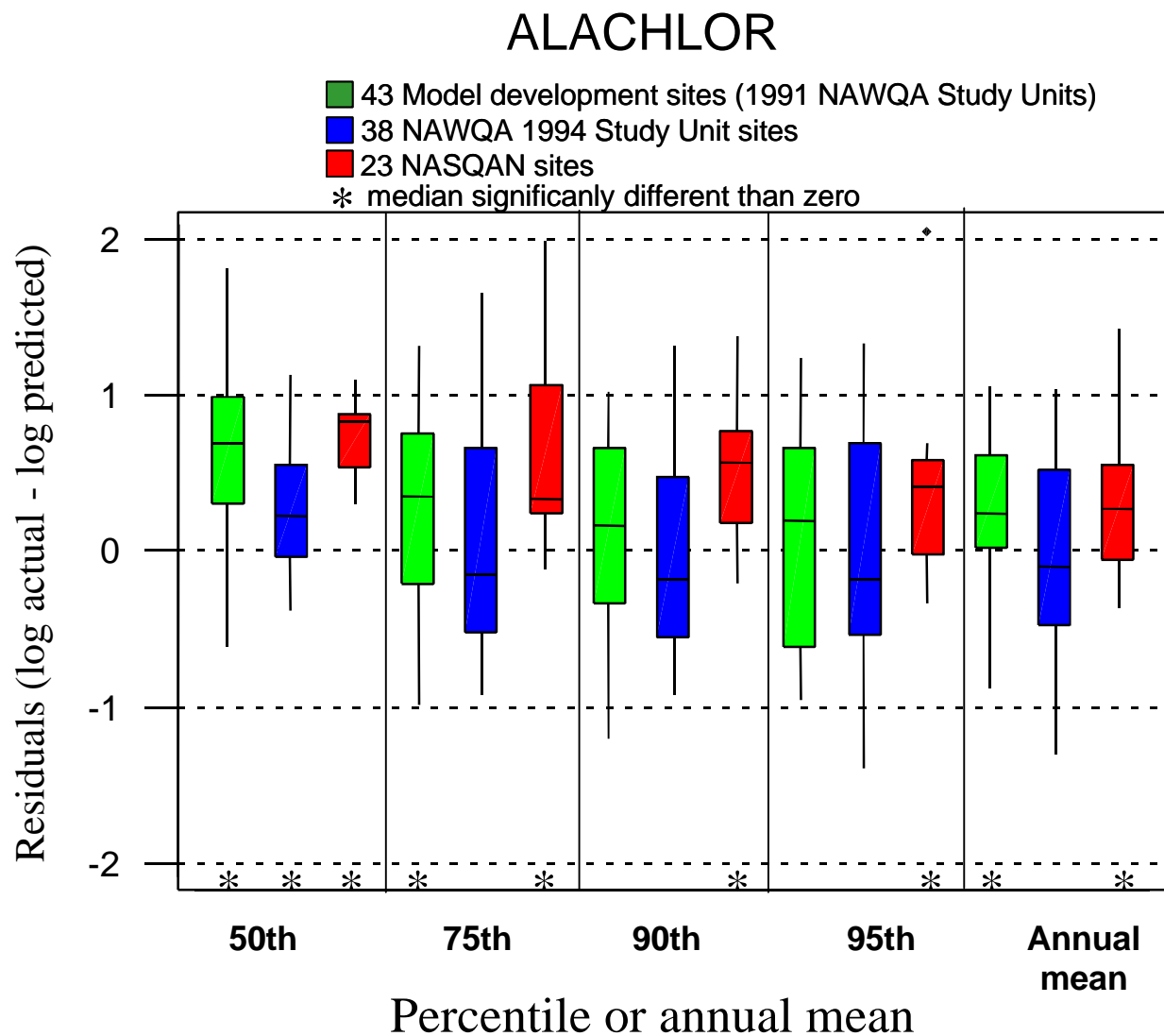
**Figure 2.3.** Residual error in concentrations predicted from the regression equations for alachlor.  Source: R. Gilliom, USGS.

# METOLACHLOR



■ 43 Model development sites (1991 NAWQA Study Units)
■ 38 NAWQA 1994 Study Unit sites
■ 23 NASQAN sites
∗ median significanly different than zero

**Figure 2.4.** Residual error in concentrations predicted from the regression equations for metolachlor.  Source: R. Gilliom, USGS.
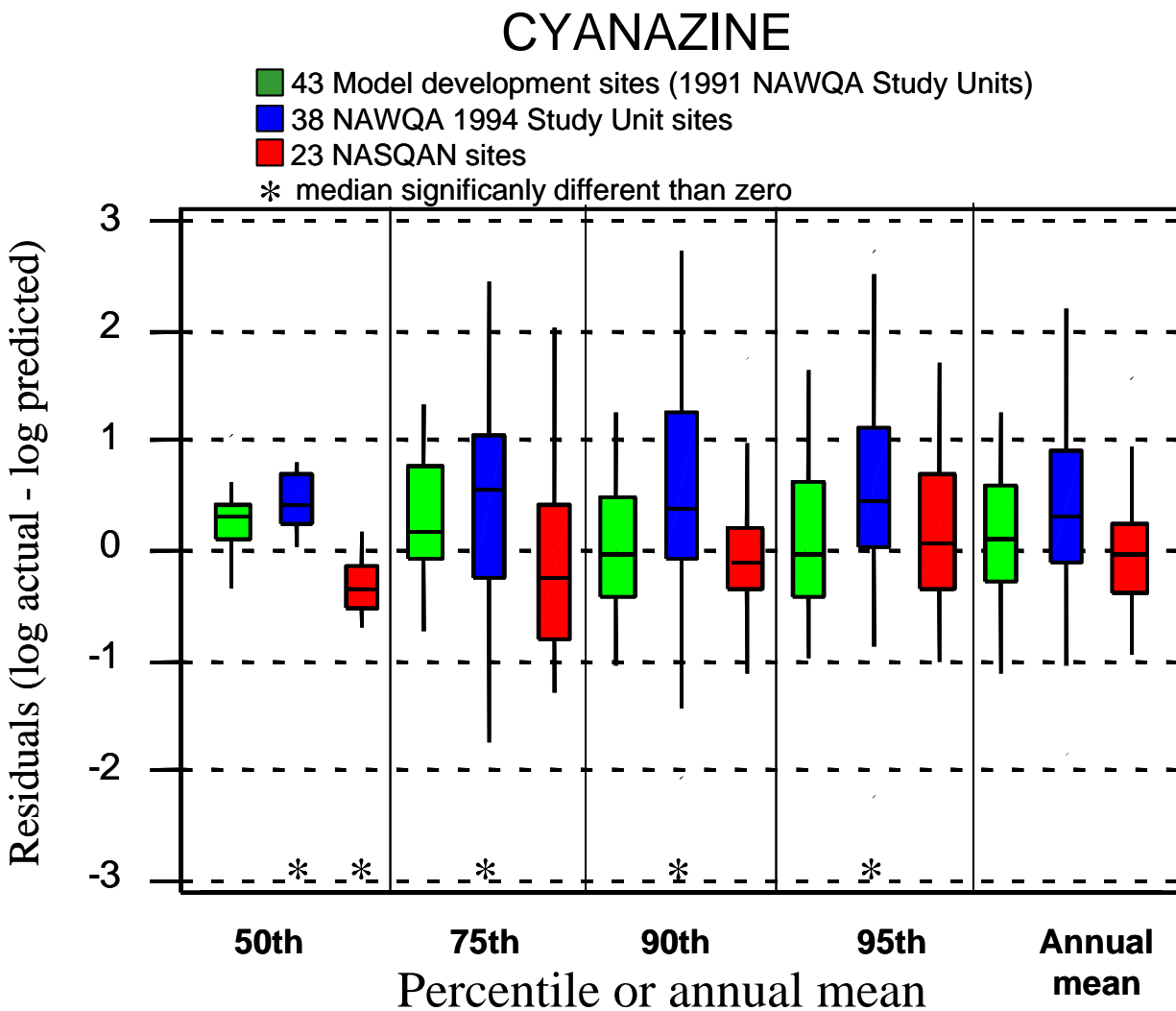
**Figure 2.5.** Residual error in concentrations predicted from the regression equations for cyanazine.  Source: R. Gilliom, USGS.
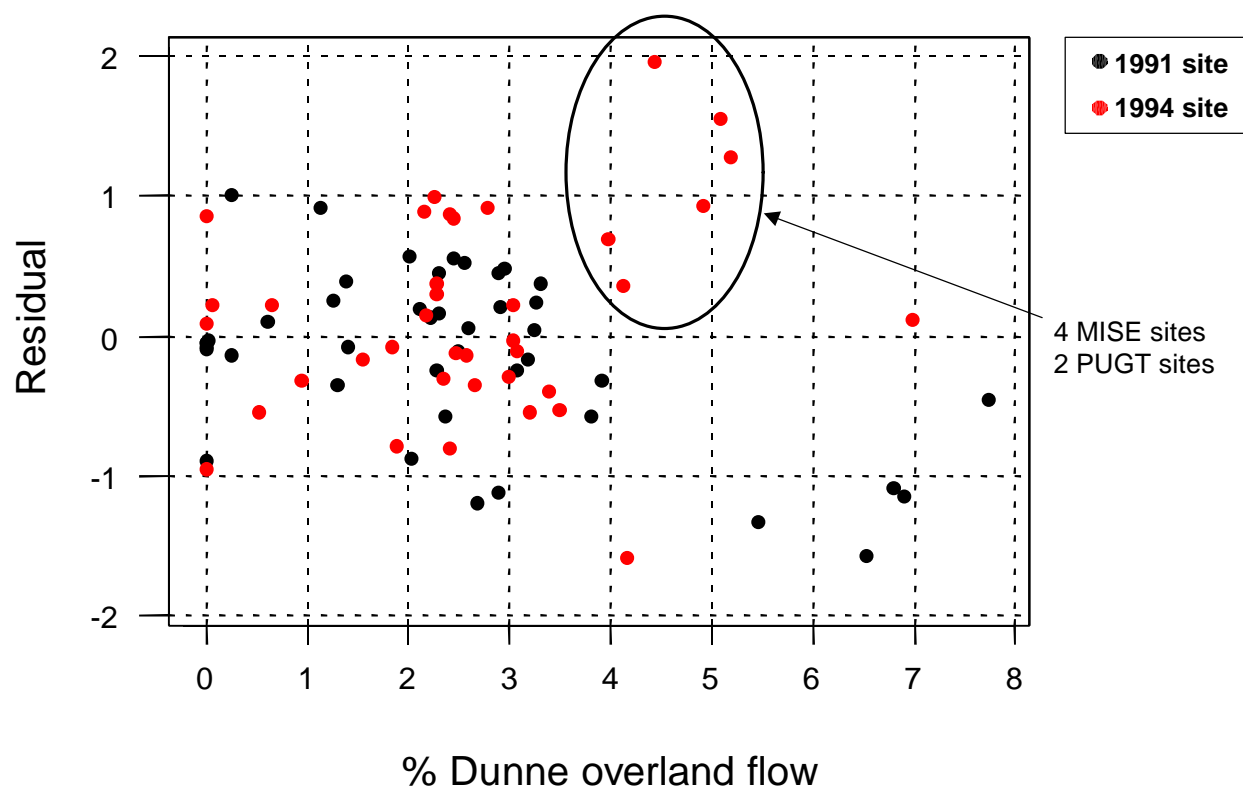
**Figure 2.6**. Residuals from regression of atrazine 95th%ile and atrazine use intensity vs Dunne overland flow values. Source: R. Gilliom, USGS.

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

## 3.1 Overview

### 3.1(a) Introduction

The Office of Pesticide Programs (OPP) wants to produce reliable and accurate estimates of pesticide concentrations in drinking water for use in Food Quality Protection Act (FQPA) aggregate human health risk assessments.  For most pesticides, measurements of pesticide levels in finished water are not available.  Instead, model-based estimates or measurements of pesticide concentrations in raw drinking water are available.  OPP recognizes that some  water treatment technologies  may effectively reduce concentrations of certain pesticides in raw water. OPP also recognizes that pesticides may be transformed and/or transformation products may be formed as a result of treatment.  In these cases, what people are exposed to in the "glass" from which they drink may be different from what is present in raw water.

The objective of this paper is to conduct a preliminary assessment of the impact of water treatment processes on pesticide removal and transformation in treated drinking water derived from ground water and surface water.  This assessment would serve as the technical foundation for the new OPP policy on how to factor the impacts of water treatment into drinking water exposure assessment under FQPA.

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

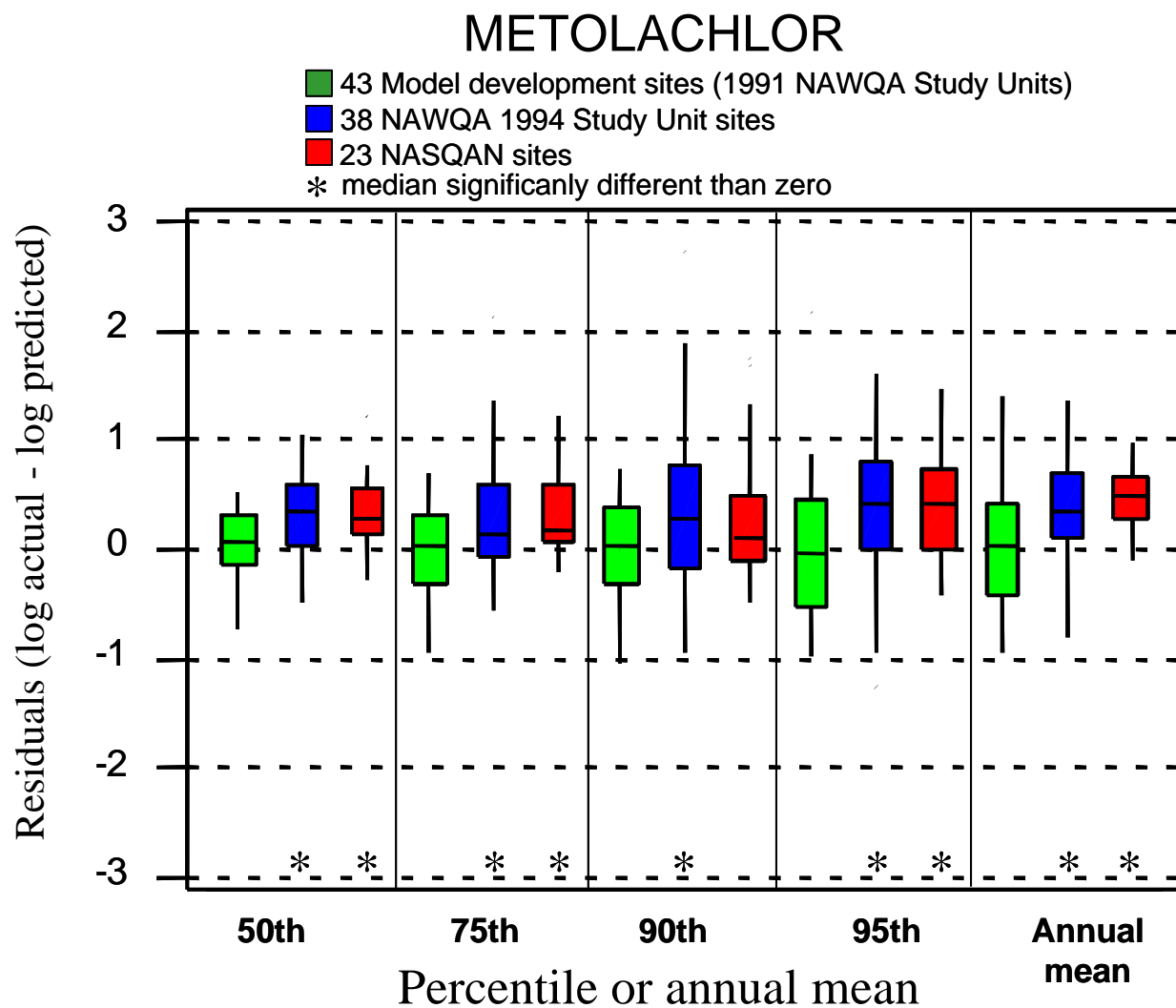OPP's conclusions from the preliminary literature review indicates that, in general,  water treatment at most CWS, specifically coagulation-flocculation, sedimentation, and conventional filtration, does not appear to facilitate pesticide removal and transformation in finished drinking water.  This finding is  important because these are commonly used treatment processes at CWSs in the United States.  Disinfection and water softening, which also routinely occur at CWSs can, however, facilitate pesticide transformation and, in some cases, facilitate pesticide degradation.  Chemical disinfection has been shown to form pesticide degradation products.  There is, however, limited information on the nature and toxicological importance of pesticide disinfection by-products.  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 water treatment processes for removal of organic chemicals, including certain pesticides (primarily acetanilide herbicides), but specific removal data on most pesticides are not available.  Also, air stripping is only effective for volatile pesticides or those with a high Henrys 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 would be amenable to removal by carbon sorption.

## 3.2  Background

The Food Quality Protection Act (FQPA) of 1996 requires that all routes of pesticide exposure be considered in aggregate and cumulative dietary human health exposure assessments for pesticide tolerance reassessment.  Because drinking water is a potential route of dietary exposure, it is factored into FQPA dietary exposure assessments.  FQPA drinking water exposure assessments are based on screening models (*e.g.*, GENEEC and PRZM/EXAMS), pesticide occurrence data in ambient waters [*e.g.*, NAtional Water Quality Assessment (NAWQA)], and when appropriate pesticide occurrence data in drinking water are available on these data. This approach generally does not allow for 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.

Linkage of  the pesticide concentrations between ambient water and treated water for FQPA exposure assessment requires an understanding of the removal efficiency for various pesticides and treatment processes, as well as an understanding on the spatial and temporal distribution of treatment systems within potential pesticide use areas.  Assessment of treatment processes is  complicated because each water treatment system is uniquely designed to accomodate 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

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 were reviewed 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. Hence, the tabulated removal efficiencies of pesticides tend to answer the question "What happens to pesticides as they move through the treatment train in drinking water purification facilities?"

When appropriate and 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 dealing with 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. 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 as possible to the maximum contaminant level goal (MCLG). Once the MCL is established for a contaminant, the contaminant is included on the list of regulated contaminants. There are 14 currently registered pesticides on this list.

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. They may be required to filter their water if certain water quality criteria (*e.g*., turbidity, removal of *Giardia* cysts and viruses, compliance of 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 activiated carbon (GAC) under the SDWA  is the best available technology (BAT) for removing synethic organic chemicals (SOC).  Other recommended BATs are aeration technologies for dibromochloropropane and chlorination or ozonation for glyphosate.

The Disinfectants/Disinfection By-Products Rule (D/DBP) was initially published in 1991 and has been rewritten and is planned to be enforced in different stages. 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 set a new regulation that sets not only a maximum concentration of pesticides in drinking water, but also inlcudes the pesticides degradation products after water treatment (Acero et al, 2000)

### 3.4(a)  Pesticides Currently Regulated Under the SDWA

Under the current SDWA, the allowable levels of some pesticides should not exceed their MCLs.  These MCLs are established to be protective of human health and must be "feasible." The 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 ($\mu$g/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 at 60 days out of the year.  A PWS is either a

community water system (CWS) or non-community water system.  Non-transient non-community water systems are defined as water systems that serve less than 25 of the same people for a six months period.  An example of non-transient 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 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 non community-based systems (*e.g.*, very small surface water-based sources).  The remaining 252 million people in the United States obtain their drinking water from a 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  physicochemical 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, 85% of  CWSs are  small systems serving 3,300 or fewer people (USEPA, 1997).  Medium (serving 3,301 to 50,000 people) and large (serving > 50,000 people) CWSs account for only 13% and 2% of CWS population, respectively.

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

The percentage of CWSs  using no water treatment technologies has decreased from 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 very small percentage (0.9 to16%) of the population of CWSs.  With the exception of  the small CWSs (serving < 500 people) using surface water, all CWSs on 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.  The main purpose of water treatment processes are disinfection, iron/manganese removal, flocculation/coagulation, filtration, organic removal, and corrosion control.  Disinfection is the most common treatment process for CWSs using only groundwater (Table 3.1).  In contrast, the predominate 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 mixtures of ground and surface waters generally use similar treatment technologies as are used for the predominate source water type (USEPA, 1997).   The major difference between the treatment strategies for ground water and surface water is associated with the treatment for turbidity.

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 PWS 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, filtration, softening, recarbonation, and chlorination (Miltner, et al. 1989). Water treatment design, however, is dependent on several factors including, seasonal changes/requirements, water quality, watershed properties, population served, economics, and the selected water treatment process. 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 needs to be considered in 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 literature review for this paper covered pesticides which generally had similar environmental fate properties. 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. This 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; dose of coagulants; 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 the jar test as method for determining impacts of conventional treatment on pesticides are that they typically do not permit evaluation of how characteristics of the raw source water (*e.g*., turbidity or pesticide concentration)-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 studies 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.

## 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 (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.

### 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 to 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 (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 [$Al_2(SO_4)_3 \cdot 14H_2O$: 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 for materials and particulates with densities greater than water (1 g/cm$^3$) (J.M.M. Consulting Engineers, 1985), which will 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 microrganisms (*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 refer to the 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). 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).   Physical disinfection process is the use of ultraviolet radiation (UV), which encourages photodegradation of nucleic acids in microorganism (USEPA, 1989). This process is conducted at wavelengths ranging 250 to 270 nm (USEPA, 1989).  Other chemical disinfectant systems 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).

Primary disinfection is the process of disinfection  prior 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 acheive 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 (higher 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 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 require a higher disinfectant concentration because of disinfectant demand exerted by the particulates.  Bench-scale studies 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 organic 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.

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 chemical oxidation results as a function of the 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. A 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.

### 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 and 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.

Activated carbon adsorption capacity 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 are valuable for knowing whether activated carbon adsorbs a particular pesticide (Speth and Miltner, 1990; Speth and Miltner, 1998). They reported that, in general, compounds with a Freundlich coefficients on activated carbon greater than 200 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. The doses of PAC were selected to reflect the range commonly used for taste and odor control. Both jar and full-scale treatment tests conducted in 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 summarize the doses, PAC types (WPC Calgon and Hydrodarco), water source, and mean concentrations of the two pesticide. The percent removal range from 28% to 87% for atrazine and 33% to 94% for alachlor. As the PAC dose increased the 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 |
| WPC (2.8) | Sandusky River (C) | 7.83 | 1.67 | 28 | 33 |
| WPC (3.6) | Sandusky River (C) | 2.61 | 1.49 | 38 | 36 |
| WPC (8.4) | Sandusky River (R) | 12.05 | 2.84 | 35 | 41 |
| WPC (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: WPC = WPC 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 using a natural water in a plant test. 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).

## PAC Dose for 99% Removal of Pesticides (Co=10 ug/L)
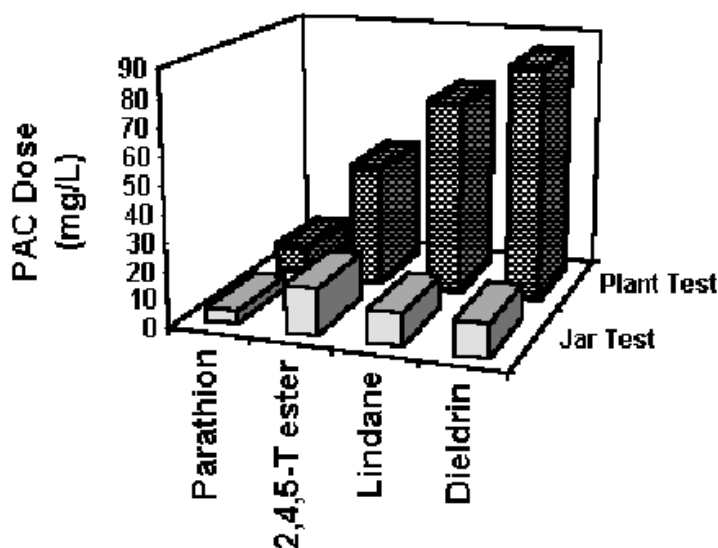


**Figure 3.1**. PAC Doses Required to Remove 99% of the Pesticide from Jar and Plant Tests. Initial concentration of each pesticide is 10 μg/L (Data from Najm et al, 1991).
**Jar Test**: PAC dose in jar tests (distilled water) determined from 1 hour contact time.
**Plant Test**: PAC dose in plant test (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. 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 better 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 |
| 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 400[*] | 3.70 (SW)[+] | 72 |
| | Calgon Filtrasorb 300[**] | 20 (SW)[++] | 95 |
| | Calgon Filtrasorb 300[**] | 50 (SW)[++] | 98 |
| | Calgon Filtrasorb 300[**] | 10 (SW)[++] | 90 |
| Metolachlor | Calgon Filtrasorb 300[*] | 5.60 (SW)[+] | 56 |
| Pendimethalin (dinitroaniline) | Calgon Filtrasorb 400[*] | 0.20 (SW)[+] | >99 |

From Miltner et al., 1989

[*] bed depth = 3 ft, loading = 4 gpm/ft$^3$, Empty Bed Contact Time (EBCT) = 5.62 min.

[**] bed depth = 1.5 ft, loading = 4 gpm/ft$^3$, EBCT = 2.81 min.

[+] clarified Sandusky River water

[++] Filtered Ohio River 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 decreased the concentrations of atrazine, cyanazine, and desethylatrazine in the treated water. But in Fairfield, cyanazine was detected in the drinking water 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 related to analytical methodology or possible breakthrough of cyanazine and desethlyatrazine from GAC column. The sampling time and schedule for the reservoir and drinking waers have to be considered also. Table 3.9 also shows that PAC adsorption removes pesticides present in surface waters in the different municipalities.

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 |

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 |
|-----------|---------------------|----------|----------|----------|----------|----------|----------|
| Fairfield | Fairfiled 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, an ozone is usually added ahead of the carbon filters. Consequently, preozonation is sometimes done to convert larger, less biodegradable organic compounds into smaller, more easily metabolizable molecules. As a result of the 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 reviewed to provide information on the extent of removal of pesticides passing through BAC adsorber  columns.

### 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 reserve osomsis (RO), electrodialysis (ED), and ultrafiltration (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 anonic 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.

45

### 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 membranes 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 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 3.6, 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 under 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 |

### 3.7(d)2 *Ultrafiltration (UF)*

Membranes operated with a lower pressure can also be used in water treatment plants. The process involved is called ultrafiltration or UF.  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 |
| 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)3  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.  An excellent result was obtained for bentazon, with more than 95% removal efficiency.

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 |
| Simzine (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(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 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 corrosion of pipes used 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 calcuim 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 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, a ratio of a pesticide between gas and liquid phases at equilibrium, has been used to predict the usefulness 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 tower, 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 the study of McCarty (1987), a chemical with a H value of $1 \times 10^{-3}$ atm $m^3$ $mole^{-1}$ would be amenable to removal by aeration.  Pesticides with H values slightly lower than $1 \times 10^{-3}$ atm $m^3$ $mole^{-1}$ may be still be removed, but more energy would be required.  In addition, relatively higher tower 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:

| Pesticide | H (atm $m^3$ $mole^{-1}$) |
|---|---|
| Dibromochlorpropane | $2.78 \times 10^{-3}$ |
| 1,2 - Dichloropropane | $1.80 \times 10^{-3}$ |
| Ethylene dibromide | $0.67 \times 10^{-3}$ |

**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. The transformation is typically caused when a treatment chemical is introduced and subsequently significantly changes the acid-base character or facilitate 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).

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.  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 in these conditions. 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 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 X, 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:

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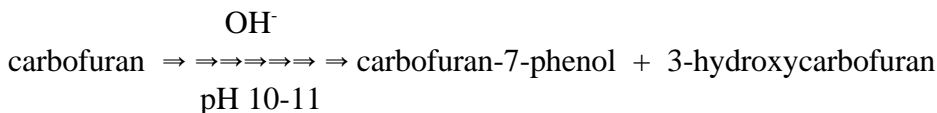
The extent of the alkaline hydrolysis and the formation of other products are expected to be affected by the contact time and water quality characteristics.

Other pesticides with short hydrolysis half-lives (< 1 day) at pH 9.0 are desmedipham, dicofol, iprodione, thiodicarb, and 2-hydroxypropyl methanethiosulfonate. These pesticides can be potentially removed and transformed by basic hydrolysis during softening.
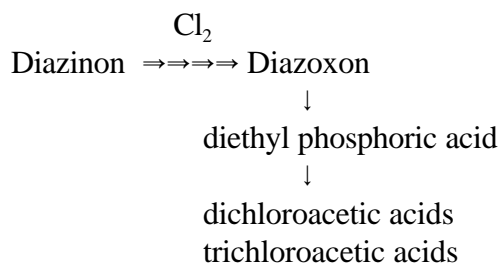
### 3.8(b)  Transformation Caused by Chemical Disinfection/Oxidation

Chemical disinfection is widely applied to destroy disease-causing microorganism 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 employs disinfection. For the same ranges of population served, at least 80% of the groundwater treatment plants uses 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 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, fenthon (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 transformed to chlorinated products as shown below:

$$Cl_2$$
Diazinon  $\Rightarrow\Rightarrow\Rightarrow\Rightarrow$ Diazoxon
↓
diethyl phosphoric acid
↓
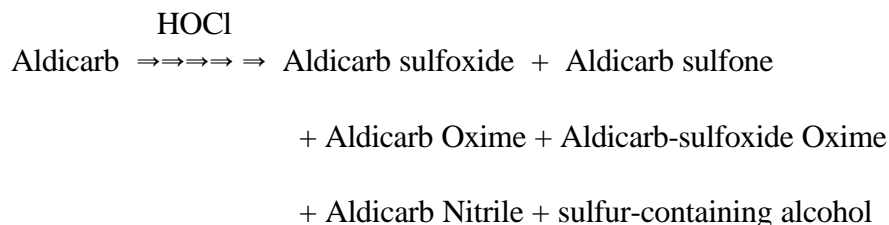dichloroacetic acids
trichloroacetic acids

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 a aqueous solution of diazinon (5 μg/L), diazinon was observed to be highly stable against chlorine even after 48 hours.

There is a concern with the formation of oxons because oxons are known to interfere with acetylcholinesterase reaction. Based on toxicity experiments using tiger shrimp larvae, oxon has been reported to be more toxic than the parent organophosphate pesticide (Rompas et al, 1989; Kobayashi et al, 1990). For example, the 24-hr $LC_{50}$ values of fenitrothion during the shrimp larval stage range from 0.32 to 1.84 mg/L compared to 0.0066 to 0.0076 mg/L when exposed to fenitrooxon, about two orders of magnitude lower. In the acetylcholinesterase inhibition tests, the $I_{50}$ values (concentration producing 50% inhibition) of fenitrooxon were about 12000 times lower than those of fenitrothion in all the larval stages. The $I_{50}$ values of diazinon were about 1000 times lower than those of diazoxon, indicating the stronger inhibition action of the by-product oxon relative to the parent compound.

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  $\Rightarrow\Rightarrow\Rightarrow\Rightarrow \Rightarrow$  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  ⇒⇒⇒⇒  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 (OH•) 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 was described to yield 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 was 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 on 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 highest occupied molecular orbital of the chemicals ($\mathring{a}_{HOMO}$). A pesticide with a high $\mathring{a}_{HOMO}$ 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) has set a new regulation that establishes not only a maximum concentrations of pesticides in drinking water but also includes their degradation products after water treatment (Acero et al, 2000). In the United States, MCLG and MCL also have been developed by USEPA for several by-products (trihalomethanes, haloacetonirtiles, 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 toxicological significant degradation products are required to assess the environmental behavior of the pesticide under specific use conditions 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 X). 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, 1998). 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-m$^3$/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 Questions for the SAP**

3.1     Coagulation-flocculation, sedimentation, and filtration processes in conventional water treatment are not effective in removing certain pesticides belonging to triazine, acetanilide, carbamate, and urea derivative classes.  What relationships exist between the physical/ chemical properties of other pesticide classes and these water treatments?

3.2     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?  What  other classes of pesticides may be removed or transformed by water softening and in what manner?

3.3     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 disinfection processes to form toxic byproducts?  What issues related to pesticide transformation should OPP be aware of?

3.4     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?

3.5     Many factors, such as raw water composition, water treatment method, and treatment plant conditions, can affect the removal of pesticides.  What issues should OPP be considering in determining whether it is possible to accurately predict the percent removal and transformation of pesticides among different water treatment plants?

3.6     The preliminary literature review indicates that coagulation-flocculation, sedimentation, and conventional filtration are not effective in pesticide removal for many types of classes of pesticides.  Effective removal of some pesticides has been observed with activated carbon adsorption (GAC and PAC), softening, disinfection, membrane treatments, and in some cases air-stripping.  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?

3.7     Based on this technical review, OPP is leaning toward an interim approach to address the impacts of water treatment on a case-by-case, pesticide-specific basis in its human health risk assessment.   OPP expects that for most pesticides, however, available data will not be sufficient to establish the impacts of treatment.  Accordingly, as a practical matter it is very likely that until pesticide-specific treatment data are generated, OPP will be using raw or untreated drinking water estimates in human health risk assessments under FQPA.

Given the objective of estimating pesticide concentrations in drinking water, does the SAP believe that the state-of-the-science supports this approach? If not, how would an approach be developed based on the state of knowledge about the impact of treatment on pesticides?

3.8    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?

## 3.11  Acknowledgments

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**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)<br>2.46 - 11.75 (SW) | 38.5<br>29 | Fronk & Baker (1990)<br>Fronk & Baker (1990) |
| | Polyamide | 86.5 - 161.3 (GW)<br>2.46 - 11.75 (SW) | 68<br>78 | Fronk & Baker (1990)<br>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)<br>0.11 - 0.82 (SW) | 31<br>23 | Fronk & Baker (1990)<br>Fronk & Baker (1990) |
| | Polyamide | 86.1 - 117.2 (GW)<br>0.11 - 0.82 (SW) | 85<br>72 | Fronk & Baker (1990)<br>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 | | | | |
| 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