I. Preliminary OP Cumulative Risk Assessment

E. Water OP Cumulative Risk

1. Introduction: Incorporating Water Exposure Into the OP Cumulative Assessment

FQPA, passed in 1996, imposed an expansion of the risk assessments for food use pesticides by requiring that the Agency perform cumulative risk assessments, i.e., that the Agency assess the risks from different pesticides having a common mechanism of action and focusing on the likelihood that a person will be concurrently exposed to multiple pesticides from multiple sources (food, drinking water, and residential uses). Ideally, data to support the water side of this exposure calculation would provide information on multiple pesticides, and their transformation products, collected from drinking water sources, both surface and ground water, throughout the U.S. at a sufficient frequency to reflect daily and seasonal patterns of pesticide occurrence in water. However, due to the great diversity of geographic-, climatic-, and time-dependent factors impacting water contamination with pesticides, this approach is not possible. For the organophosphorous (OP) pesticides cumulative assessment, the Office of Pesticide Programs (OPP) must rely on both available monitoring data and modeling to develop sufficient data for use in the exposure assessment.

This chapter will focus on methods used in the preliminary cumulative drinking water assessment to estimate organophosphorous pesticide residues (concentrations) in water over time in watersheds in 12 regions of the United States. Because drinking water is local, the national exposure assessment for drinking water must address localized areas of the country where exposure to OPs may occur due to drinking water contamination. In order to estimate concentrations in these locations, pesticide movement from application on the land in a watershed to a drinking water source in the watershed will be predicted. The methods described in this chapter account for the fact that pesticide concentrations found in drinking water are not random, but are in large part determined by the amount, method, timing and location of pesticide application, the physical characteristics of the watersheds in which the community water systems (CWS) are located, and other environmental factors (such as rainfall) which cause the pesticide to move from the location where it was applied.

OPP is using a probabilistic, calendar-based approach to appropriately match and subsequently combine estimates of pesticide residues in food with estimates of pesticide residues in drinking water to determine reasonable approximations of the amount of OP pesticides ingested in the diet on a daily basis. This approach looks at each individual day of the year and allows appropriate temporal matching of exposures through food and drinking water on a daily basis. Each single day assessment serves as a “building block” for the construction of multiple consecutive day average exposures. This method accounts for the temporal aspect of exposure to OPs due to expected seasonal pulses and seasonal use-patterns.

To realistically estimate exposures, the assessment must take into account which OPs can and do occur together in time and place to account for co-occurrence. Only those exposures which are likely to occur in the same location, in this case a watershed, are combined. Those exposures that are likely to occur on different days and in different locations will be separated. Although multiple OP pesticides may be registered for use on the same site, they may not necessarily be used at the same time.

Risk is a function of both hazard and exposure, and estimation of the exposure portion of the equation for drinking water requires data on the concentrations of the pesticides in the drinking water and the consumption of drinking water for different demographic populations on a daily basis. Food is distributed nationally and pesticide residues on food are more constant over time despite their location. Drinking water is locally derived and concentrations of pesticides in source water fluctuate over time and location for a variety of reasons. Pesticide residues in water fluctuate daily, seasonally, and yearly as a result of the timing of the pesticide application, the vulnerability of the watershed to pesticide runoff, spray drift and leaching, and changes in the weather. Changes in concentrations also result from the method of application, the location and characteristics of the sites where a pesticide is used, the climate, and the type and degree of pest pressure. Given the data needs and the number of variables that can affect the outcome of the predictive model, it is apparent that the development of daily distributions of concentrations of co-occurring OPs in drinking water for various regions of the US is far-reaching in scope and complexity.

The goal of the drinking water exposure assessment is to provide estimates of distributions of residues (concentrations in drinking water) for use in probabilistic exposure assessment that account for

- ☐ daily and seasonal variations in residues over time due to time of application(s) and runoff/leaching events

- ☐ year-to-year variations due to weather patterns

- ☐ variability in residues from place to place, resulting from the source and nature of drinking water and from the regional / local factors (soil, geology, hydrology, climate, crops, pest pressures, usage) that affect the vulnerability of those sources

☐ the potential for co-occurrence of more than one OP in location and time only when this is likely to happen

The section that follows discusses briefly what we know about OP occurrence in drinking water sources from available monitoring data and how OP residues in drinking water may be affected by conventional drinking water treatment processes. Based on the needs of the probabilistic cumulative exposure assessment and the information gained from this assessment of monitoring data, OPP designed a drinking water assessment that provides multiple years of daily residue concentrations from drinking water sources in twelve regions across the country. These methods, and a characterization of the results of this assessment, follow the monitoring assessment.

2. What We Know About OP Occurrence in Drinking Water from Monitoring Data

The drinking water exposure assessment for the OPs would ideally be performed using direct drinking water data, or at least using extensive surface- and ground-water monitoring data as a surrogate. With few exceptions, the quantity, quality and relevance of available monitoring data analyzed in each of the individual OP risk assessments were considered inadequate to support a drinking-water exposure assessment. In some cases, such as those of chlorethoxyfos and phostebupirim, no monitoring data are available. For other OPs, such as acephate and oxydemeton-methyl, no detections were reported from a limited monitoring set, but it is unclear whether these non-detects signify a lack of transport, or insufficient or non-targeted sampling. In preparing the cumulative assessment, OPP will rely primarily on the assessment of the monitoring data described in the individual OP assessments.

In some cases, monitoring data were used for a screening-level assessment, but may not be complete enough for use in the cumulative assessment. For instance, in the case of azinphos-methyl, ground-water contamination measured in wells from a Virginia karst area were used for the screening assessment. At best, such data might be used to calculate exposure to azinphos-methyl in the karst regions of the Mid-Atlantic and Southeast U.S., but data from this very vulnerable scenario will not be applied to all regions of the country.

The first part of this section briefly summarizes available surface-water and ground-water monitoring studies that included multiple OP pesticides. Additional monitoring data that focused only on a single OP pesticide are summarized in the individual chemical risk assessments (available through the Office of Pesticide Programs web site at http://www.epa.gov/pesticides/op/status.htm). This is followed by a review of published literature and registrant-submitted studies on the effects of water treatment on OP residues in drinking water. The section concludes with an evaluation of the extent to which the monitoring data fulfill the needs of the cumulative water exposure assessment.

a. Surface Water

Available monitoring has shown that OP insecticides contaminate surface-water resources from both agricultural and urban use. Maximum contaminant levels (MCLs) under the Safe Drinking Water Act have not been developed for the OP pesticides, and OPs will be included on the Unregulated Contaminant Monitoring List for the first time in 2002. As a result, States and public water supplies (PWS) have not often included OPs in surface-water monitoring. Therefore, with the exception of preliminary results from the pilot USGS-EPA Reservoir Monitoring Study, few studies include analyses of OP insecticides in raw and finished drinking water.

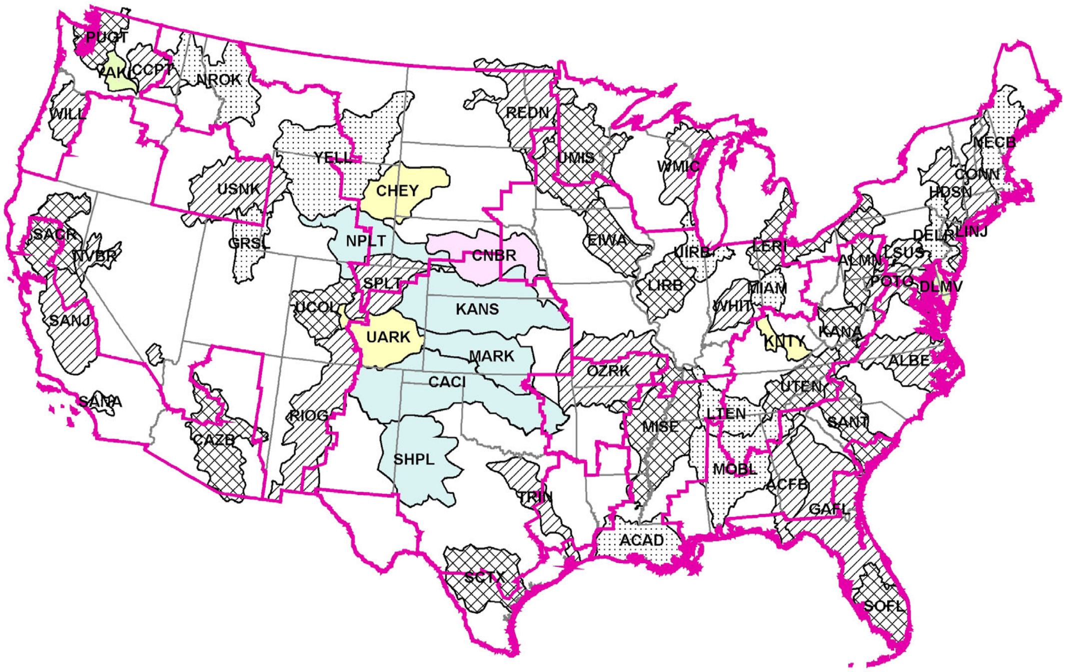
Available surface-water monitoring for OPs represents a range of surface-water bodies, from agricultural drainage ditches to outflow samples from the largest rivers in the nation. Monitoring data from bodies such as small streams may not represent direct drinking water sources, but can give an indication of possible surface-water concentrations in high OP-use areas. Sampling from streams that are used for drinking-water supply gives an indication of possible concentrations in drinking water. Without direct data at a drinking water intake downstream, however, a risk assessor cannot assume potential exposure at concentrations above or below that detected.

i. Sources of Surface-Water Data

Although the number of “ambient” surface-water monitoring studies which have included OP pesticides as analytes is extensive, extensive monitoring data is not available for all OPs. This is mainly true because the largest available source of surface-water monitoring for OPs, the **USGS NAWQA Program**, includes only nine active OPs: chlorpyrifos, diazinon, malathion, phorate, methyl parathion, disulfoton, terbufos, azinphos-methyl and ethoprop. Also included are fonofos and parathion, both of which have been voluntarily cancelled.

The NAWQA program includes monitoring data for 76 pesticides, including 11 OP pesticides, and covers “more than 50 major river basins and aquifers covering nearly all 50 states” (http://water.usgs.gov/nawqa/nawqa_home.html). Currently available NAWQA data, which does not include those from the 15 study units begun in 1997, include 2,800 stream sites and 5,000 wells, and a total of 15,000 pesticide samples (http://infotrek.er.usgs.gov/pls/nawqa/nawqa.home). Results of the individual NAWQA study units are described in the appropriate regional assessments. Appendix III.E.1, Summary of OP Occurrence in Ambient Waters from the USGS NAWQA Program, provides additional tabulations of OP monitoring results from each of the NAWQA study units.

Figure I.E-1 Location of NAWQA study units. Monitoring data are available for the study units in hatch and cross-hatch. Monitoring is ongoing in the units with dotted shading, but no data are available. Monitoring has not started in the other units.



The USGS **National Stream Quality Assessment Network (NASQAN)** program monitors water quality in the Rio Grande, Mississippi, Columbia, and Colorado Rivers, four of the nation's largest rivers. This study monitors for the same OPs included in NAWQA. NASQAN was designed to measure the mass flux of constituents such as pesticides and nutrients in these rivers, and so the 41 sampling stations are located at the mouths of these rivers, at the confluence of tributaries entering the rivers, and at the intake and outflow of reservoirs along their path. Detection of OPs in these studies is significant (diazinon, for example, has been detected in all four), because detection in such large water bodies indicates that a large mass of the pesticide has run off to surface water. The relatively small number of stations and relatively infrequent sampling make it more difficult to connect detections in this study to specific OP uses.

State surface-water monitoring programs are most likely to include analytes required by the Safe Drinking Water Act, but may include OPs if consistent with budget priorities and local needs. When available, State monitoring programs are important additions to NAWQA data for a full understanding of possible OP exposure in drinking water. State programs are described in detail in the individual regional assessments.

The USEPA Office of Pesticide Programs (OPP), USEPA Office of Ground Water and Drinking Water (OGWDW), and USGS National Water Quality Assessment (NAWQA/USGS) initiated a **reservoir monitoring project** to assess pesticide concentrations in untreated and finished drinking water derived from surface water reservoirs. Twelve drinking water reservoirs were selected from a list of candidate drinking water reservoirs which were potentially vulnerable to pesticide contamination. Vulnerable reservoirs are considered to be located in small watersheds with high pesticide use areas and high runoff potential. A summary of the results of this study occurs later in this section. Appendix III.E.3, Preliminary Analysis of the USGS-EPA Pilot Reservoir Monitoring Project, provides a detailed analysis of the study and its results.

ii. Completeness of the Surface-Water Monitoring Data Set

Monitoring data is most extensive for chlorpyrifos, diazinon and malathion, the three OP pesticides most frequently detected in agricultural and urban surface water. States that did include more OPs generally did so as part of a wider screen, using a multi-analyte method, rather than specifically monitoring for the OPs in specific areas of OP use. The Agency has not identified any monitoring studies which included chlorethoxyfos, phostebupirim, or tribufos.

Many of the OP parent compounds not included in broad surface-water surveys are short-lived, and degrade by aerobic soil metabolism, photolysis or hydrolysis to longer-lived transformation products. Some of these short-lived compounds transform into degradates of toxicological concern that are more persistent and mobile than the parent compounds. The transformation of disulfoton to its sulfoxide and sulfone degradates is an example. Unfortunately, the toxic transformation products are, by and large, not included in monitoring studies.

Detection of pesticides in surface water is most likely when the sampling corresponds at least roughly to the timing and location of pesticide use. Several monitoring studies which include OPs illustrate this well:

- ☐ A series of studies by the California Department of Pesticide Regulation (CDPR) and the USGS investigated OP contamination from winter use as a dormant spray to tree fruits and tree nuts. The frequency and concentrations of OP detections in these studies were both relatively high. Among OPs detected in these studies were methidathion and dimethoate, which are rarely included in other monitoring programs.

- ☐ Diazinon and chlorpyrifos in urban streams represents the OP contamination most frequently detected in NAWQA surface water, followed by detection of malathion in urban streams. Since urban uses of these pesticides can occur year-round, and every NAWQA study monitored streams in watersheds dominated by urban or mixed land use, these studies were targeted to the timing and location of these uses.

- ☐ A study in the USGS San Joaquin River Basin (SJRB) further confirmed the importance of timing of sampling. Sampling three times per week in this study was more likely to detect higher concentrations than once per week. Sampling once per week was more appropriate for determining the median concentration.

iii. Effects of Study Design

In general, the surface-water studies which included OP pesticides as analytes were not specifically designed to correspond with times and locations of agricultural OP use. For instance, the same suite of nine OPs was included in NAWQA sampling programs nationwide. Azinphos-methyl was detected in surface water in the NAWQA Lower Susquehanna River Basin study unit, an area where azinphos-methyl is used in orchards. NAWQA also included azinphos-methyl as an analyte in three

Heartland study units that it identified as part of the “Corn Belt.” Surface-water sampling in the Lower Illinois River Basin study was specifically targeted to “two watersheds with greater than 90 percent row-crop agriculture and the basin inflow and outflow sites.” Azinphos methyl is not used on corn, and it was not detected in any surface-water samples from these three study units. The USGS notes this effect of design in its analysis of OP occurrence in surface water and ground water from 1992 to 1997, reporting that azinphos methyl and ethoprop were not widely distributed in NAWQA and NASQAN studies, but that they “were detected in 43 and 69 percent, respectively, of samples from a few small agricultural watersheds in western irrigated valleys.”

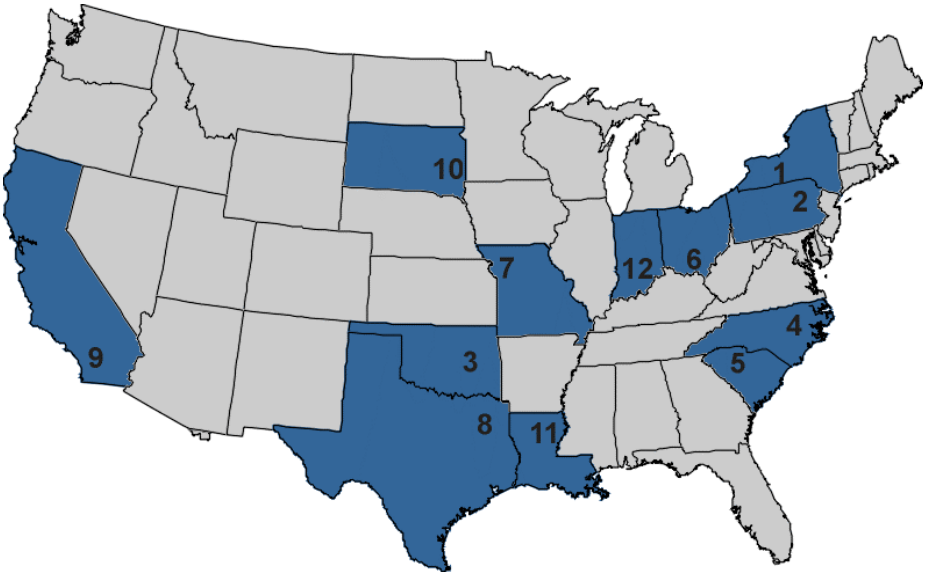
The design of the available programs determines their utility for the cumulative drinking water exposure assessment. The NAWQA program includes sampling from almost all states in the nation, but a good number of the studies were designed to answer locally important questions for each river basin, and were therefore not uniform. The USGS Pesticide National Synthesis Project web page elaborates on why the studies are not specifically designed to produce a statistically representative analysis of national water-quality conditions. This page can be found at http://wwwdwatcm.wr.usgs.gov/ccpt/pns_data/data.html .

As mentioned above, NASQAN has by comparison relatively few sites and samples each year, and is designed to allow an assessment of mass flux from some of the largest rivers. State studies were even more limited. Due to funding limitations, and knowledge of which pesticides were the most common surface water contaminants, States were most likely to include diazinon and chlorpyrifos in monitoring programs, if OPs were included at all. States that did include more OPs generally did so as part of a wider screen, using a multi-analyte method, rather than specifically monitoring for the OPs in specific areas of OP use.

iv. USGS-EPA Reservoir Monitoring Project

The USGS-EPA Reservoir Monitoring Study was designed to evaluate potential concentrations of OPs and transformation products in untreated and treated drinking water derived from reservoirs. The pilot study includes twelve reservoirs covering a range of pesticide use areas across twelve states (Figure I.E-2). Monitoring included 27 OP parent compounds and 19 OP transformation products. The sampling frequency was designed to focus sampling during the period of the year with highest pesticide runoff vulnerability and variability in the post pesticide application season. Each reservoir was sampled quarterly for one year, as well as biweekly for a 4 month post-application period. Two sites were sampled at weekly intervals for 6 months post-application-season to improve the estimate of peak concentrations for short-lived compounds. Ancillary data also were collected for each site to obtain information on watershed properties, water treatment information, and reservoir characteristics.

Figure I.E-2 Location of reservoirs in the USGS-EPA Reservoir Monitoring Project



While both untreated (raw) and treated (finished) water samples were taken at each sample time, the sampling scheme does not account for the travel time of the pesticide and its transformation products through the water treatment plant. Therefore, the occurrence and magnitude of pesticides in raw and finished waters cannot be directly correlated. This will likely exaggerate variability in removal efficiencies and limit direct linkage of degradation and formation patterns of pesticides during water treatment.

The pilot reservoir monitoring study provides two years of sampling, with 602 to 626 samples for each of 31 active OP parent and transformation products that are included in this cumulative assessment. This pilot program included some OPs rarely included in monitoring studies, such as tribufos, phostebupirim, profenofos and dichlorvos. It also included some toxicologically significant, but rarely analyzed transformation products.

Thirteen of these 31 compounds were detected in either raw or finished drinking water samples, in spite of extreme drought conditions in the northeastern United States in 1999 (see Appendix III.E.2 for results of this analysis). Diazinon, the most frequently detected, was found in 35% of 323 raw water samples analyzed, but in none of the 227 finished water samples. Although the data do not represent a set of paired raw and finished water samples, the fact that this frequently detected chemical was not detected at all suggests that it is removed by the treatment process. However, the likely transformation product diazoxon was not included as an analyte in the pilot program.

Monitoring results for other OPs also strongly suggest that parent OP compounds are transformed during water treatment. For instance, malathion was only detected in 6 of 323 raw water samples (2%), while malaoxon was only detected in 11 of 220 finished water samples (5%). Chlorpyrifos was detected in 5.3% of raw water samples; neither chlorpyrifos nor its oxygen analog were detected in finished water. Azinphos-methyl and its oxon were both found in raw and finished water. The difference between the number of detections for each is not enough to draw conclusions on treatment effects, especially since azinphos methyl and its oxon were only found in the same reservoir once (Missouri in 2000). While the actual transformation process is difficult to assess because raw and finished water samples were not temporally paired, the conversion of some OPs to oxon transformation products is consistent with published data and recent studies submitted by OP registrants.

A small number of detections of other transformation products are consistent with expectations based on the environmental fate properties of the parent chemicals. Fenamiphos and disulfoton were not detected in this limited sampling program, but both the longer-lived sulfoxide and sulfone transformation products were detected in one or two samples each. While their detection in raw water is an indication that drinking water contamination is possible, detections were few enough that the lack of detections in finished water is not a clear indication of removal by treatment.

Diazinon was detected in 10 of 12 reservoirs, and chlorpyrifos was detected in six, which likely reflects their widespread use. No other OP was detected in more than three reservoirs in this limited sampling. Azinphos-methyl had the highest concentration detected of all parent products, a detection of 0.114 ug/l in South Carolina raw water. Azinphos-methyl was found in 46% and 32% of samples taken in South Carolina in 1999 and 2000. Azinphos-methyl oxon was detected at a maximum concentration of 0.263 in Oklahoma, and was detected in 20% of samples in New York and Missouri in 2000. Malaoxon had the highest concentration detected of all analytes with maximum detections in Louisiana of 0.556 ug/l in 2000, and 0.204 ug/l in 1999.

Phostebupirim, which is very rarely included in any monitoring studies, was detected in 10% and 8% of 1999 raw water samples in Missouri and Pennsylvania, respectively. The concentrations were low (0.003 to 0.007 ug/l), but serve as a reminder that OPs may be transported to surface water bodies, even if few monitoring data are available to confirm this.

Although the reservoir monitoring study has only progressed through the pilot stage, it included more OPs than any previous study. Therefore, it is particularly useful for considering the possibility of exposure to multiple OPs. Of 314 *intake samples* considered, 137 (44%) had one or more detectable OPs. Of the 137 with detectable OPs, 16 (12%) had more than one OP detected. Of 67 *outfall samples* considered, 17 (25%) had one or more detectable OPs. Of the 17 with detectable OPs, 2 (12%) had more than one OP detected. Of 218 *finished samples* considered, 24 (11%) had one detectable OPs. None of the finished samples considered here had more than one OP detected.

The pilot reservoir monitoring program confirmed the utility of sampling for a wide range of OPs and transformation products in drinking water, using low levels of detection. Continued and expanded monitoring should improve understanding of potential drinking water exposure, and of the effects of degradation in the field and from drinking water treatment.

v. Industry's Six-OP Monitoring Study

On October 24, 2001, the Agency received a drinking monitoring study conducted by a consortium of registrants entitled, "Drinking Water Monitoring for Six Organophosphate Insecticides and Four Oxons in 44 Community Water Systems on Surface Water in the United States" (Tierney et al., 2001). The study looked for 6 organophosphorous pesticides – acephate, azinphos methyl, chlorpyrifos, diazinon, malathion, and methamidaphos – and four oxon degradates – azinphos methyl oxon, chlorpyrifos oxon, diazoxon, and maloxon. The stated purpose of the study was "to generate reliable information on OP pesticide levels, if any, from targeted surface water source community water supply facilities (CWS) in watersheds with product use in the United States." The intent was to collect drinking water data "to assess whether or not concentrations exceed acceptable levels of cumulative human health risk under existing HALs under the SDWA or drinking water levels of concern under FQPA." The Agency previously reviewed the protocol in July 2000. However, the study was initiated before EPA received the protocol, so Agency comments were not considered in the conduct of the study. The Agency concluded that:

"After a review of the protocol, site selection document, and associated amendments, our conclusion is that the study will provide little relevant information on occurrence of the target OP pesticides because the sampling frequency is too low for acute exposures, the duration of the proposed study is too short, the number of CWS monitored is very limited, and the vulnerability of those CWS to contamination is questionable. Unfortunately, it also appears that processes which result in high concentrations in surface water (e.g. usage intensity and precipitation) cannot be identified as a result of this study because ancillary data needed to provide this information will not be collected.”

The Agency has not yet completed a formal review of the study, but a preliminary review has identified substantial additional concerns related to QA/QC beyond those identified in the protocol review. In the study, 39 samples contained at least one target analyte representing a total of up to 70 pesticide measurements. However, the study authors conclude that as many as 64 of the 70 detects were due to cross-contamination caused by the auto sampler during analysis. In addition, only 6 field spikes in duplicate were taken from two facilities during the study. This limited number of quality control samples seriously limits the ability to maintain and evaluate the data quality. Furthermore, a large number of samples was apparently held longer than the 40 days detailed in the protocol. Information on the number of samples that exceeded the 40 days and the length of the storage times for these samples was not included in the report, so it is not possible to determine whether this deviation affected the study results. The Agency is concerned that these issues, in combination with those detailed in the protocol review, render the data unusable for exposure assessment.

b. Ground Water

Due to the chemical properties of most of the OP insecticides, drinking-water exposure through contamination of surface-water resources is generally more likely than through contamination of ground water. However, even in regions where surface water is the predominant source of drinking water for most of the population, a significant portion of homes derives drinking water from relatively shallow domestic wells. In some areas of the country, where soils are especially permeable and depth to unconfined ground water particularly shallow, domestic wells represent some of the drinking-water sources most vulnerable to pesticide contamination.

Most OPs were described as unlikely to leach to ground water in the individual risk assessments completed over the last few years. This is due mainly to the relatively short aerobic soil-metabolism half-life of many OPs. However, there are some important exceptions. Several OPs are described as having the potential to contaminate ground water, but lack the data to sufficiently evaluate the magnitude of this risk.

Fenamiphos and its degradates, fenamiphos sulfoxide and fenamiphos sulfone, are the best examples of this problem. These chemicals have been detected at high levels in ground-water studies conducted in Florida, and to a lesser extent in California. Concentrations of fenamiphos and its transformation products detected in the Central Ridge area of Florida ranged as high as 246 ppb (204 ppb fenamiphos sulfoxide) in a retrospective ground-water study. Such detections led to the phase-out of fenamiphos use on citrus in this portion of the State.

However, recent ground-water monitoring which includes fenamiphos is scarce. The USGS undertook a fenamiphos ground-water study at seven golf courses in Florida, and reported maximum detections of < 1.0 ug/l each for fenamiphos and its transformation products. The State of Florida reports that its database includes only two wells with detections of fenamiphos sulfoxide in its ground-water database. California collected samples from 40 drinking water wells in fenamiphos use areas during the early and mid 1990s, but did not detect fenamiphos (another round of sampling is currently underway). Hawaii, Michigan and North Carolina report that fenamiphos was not detected in a total of fewer than 100 drinking water or monitoring wells, and fenamiphos is not included among analytes in the NAWQA program. Therefore, while fenamiphos has been detected in vulnerable to very vulnerable soils in Florida and California, sufficient data is not available which could allow a more detailed monitoring assessment for other areas of the country.

i. Sources of Recent Ground-Water Monitoring Data

The Agency contacted **pesticide lead agencies and other agencies in all 50 States** to inquire whether OPs were included in surface-water or ground-water monitoring (either ambient or drinking water) programs over the last decade. OPP requested recent data since 1) earlier data are more likely to be included in the aggregate assessments of individual OPs, 2) recent data are more likely to reflect current use rates and use areas, and 3) such data are more likely to be in electronic format, accessible either over the Internet or as an e-mail attachment. Government scientists in nearly all States offered to describe or provide summaries of current monitoring programs, or directed the Agency to data which are available online.

As a result of the relative non-persistence of most OPs in soil and the limits on funding for monitoring in State and Federal programs, few OPs are included in ground-water monitoring programs conducted over the last decade. Chlorpyrifos, diazinon and malathion are the OPs most commonly included as analytes in State ground-water monitoring programs. In some States, multiple OPs are included as part of a general screen under EPA methods 507 or 525.5. In such cases, the levels of detection are often higher than in more chemical-specific analyses.

The voluntary cancellation of non-agricultural uses of chlorpyrifos and diazinon affects the ground water assessment for these chemicals. While many of the agricultural uses remain, the Agency believes that most of the ground water monitoring detections of these chemicals are associated with uses that have been cancelled. The termiticide use of chlorpyrifos, which is currently being phased out, represents the use that has led to the highest known concentrations of any OP in ground water. The concentrations of chlorpyrifos measured in wells affected by the termiticide use ranged as high as 2090 µg/l, significantly higher than concentrations found in agricultural areas, which generally are below 1 µg/l.

The **USGS NAWQA program** is the other major source of ground-water data for the OPs. NAWQA has conducted ground-water monitoring in more than 50 study units that include part of nearly every State in the Union. While the NAWQA program has provided a very valuable ground-water data set, it has several important limitations with respect to the cumulative OP drinking water assessment:

- ☐ Only nine OPs that are eligible for reregistration are included as analytes.

- ☐ Many NAWQA ground-water studies included only a single sample of each well in the network. Even if wells in such studies were located in OP use areas, the monitoring was not timed to correspond specifically to account for pest pressure and OP application for that particular year.

- ☐ A number of land-use studies in the program were focused on urban areas. The phase-out of homeowner uses of chlorpyrifos and diazinon renders such data less useful for our assessment.

Finally, the design of the ground-water studies differs between each study unit, reflecting the local aspect of ground-water quality that was being investigated in each monitoring program. For instance, monitoring in the Eastern Iowa Basins study unit included 65 domestic wells in order to assess the water-quality of the most heavily used aquifers in the study unit. By contrast, one of the ground-water studies in the Ozark Plateaus study unit was designed to evaluate water-quality in domestic wells in cattle and poultry-producing regions. One of the studies in the Southern Florida study unit included wells less than 15 feet deep and located in the drip line of citrus trees, where the depth to the water table was 2 to 4 feet below the land surface. In addition, a study in the Central Arizona Basins study unit included domestic, public supply, and other wells that draw older water (at least pre-1953) from a confined aquifer, which to this point is considered to have had very little hydraulic connection with potentially contaminated shallower ground-water above the confining layer. **The differing design among the different ground-water monitoring studies limits the applicability of statistical methods to the combined**

NAWQA ground-water dataset for a national OP drinking-water assessment.

Some OPs are not included in any ground-water monitoring supplied to the Agency, such as phostebupirim, chlorethoxyfos and tribufos. Other OPs have only very limited monitoring data from the 1980s in which a small number of ground-water detections are reported. One example is methamidophos, which was detected in four wells near a Maine potato field in 1986 at concentrations up to 10 ug/l. Such data may not well represent current use or use rates, but may also have underpredicted possible ground-water contamination due to higher analytical detection limits. Older studies which revealed ground-water contamination indicate that exposure to rarely analyzed OPs is possible. However, the lack of extensive, recent ground-water data for compounds such as methamidophos make it very difficult to quantify the potential risk nationwide.

With few exceptions, ground-water monitoring programs which include OPs are surveys which are not targeted specifically to assess the effects of OP use on ground-water quality. Examples of exceptions include chlorpyrifos termiticide use studies and fenamiphos studies near Florida golf courses. The results of survey studies give some indication of the possible exposure to populations as a whole. However, since survey studies usually include sampling of wells in areas where OPs are not used, they are less useful for quantifying potential drinking-water exposure in OP use areas.

An additional uncertainty is introduced by the possibility that OPs are transformed into daughter products through primary drinking-water treatment. Available data indicate that many OPs are transformed to their oxygen analogs through chlorination. Organophosphorous pesticide residues in water from untreated domestic wells may be in the form of the originally applied “parent” compound. The implications of this disparity depend on the relative toxicity of the OPs and their oxon transformation products.

Few ground-water studies include OP transformation products as analytes. The fenamiphos prospective ground-water studies and the USGS golf-course study mentioned above are rare exceptions. Lack of monitoring for transformation products might be important for other OPs which form sulfoxide and sulfone degradates, such as disulfoton, phorate and terbufos. If these OPs follow the same pattern as fenamiphos, the sulfoxide moieties of these chemicals may be a greater concern for ground-water contamination than the parent compound.

3. Effects of Drinking Water Treatment on OP Pesticides

The weight of evidence from open literature, registrant-sponsored data, ORD/EPA laboratory data and USGS-EPA monitoring data show parent OP pesticide residues in water are likely to be reduced during finished drinking water treatment. The most probable pathway is transformation by oxidation through chlorination and not physical removal. Oxidative transformation products of toxicological concern, such as sulfones, sulfoxides, and oxons, have been detected in finished water samples from actual water-treatment plants. Laboratory data indicate oxons can be relatively stable in chlorinated drinking waters for 48 hours. Although the detection frequencies of oxidative degradation products were low in the reservoir monitoring data, they were more frequently detected in finished water than in raw water, as described above. These data suggest oxidative degradation products such as oxons, sulfones, and sulfoxides have a high likihood of occurrence in finished drinking water.

This section only very briefly summarizes the available data on removal and transformation of organophosphorus pesticides and certain degradation products through water treatment. The review was conducted as an extension of the OPP water treatment literature review (http://www.epa.gov/scipoly/2000/September/sept-00–sap-dw-0907.pdf). Documents in this report include open literature, registrant-sponsored water treatment data, and the USGS-OPP pilot reservoir monitoring data.

Available information indicates that two common water-treatment methods lead to transformation of some OPs:

☐ Treatment of water by **chlorine and chlorine compounds for disinfection** can result in transformation of parent OP compounds. The P=S bond of OPs can be oxidized to a P=O bond leading to the formation of oxon transformation products. According to Magara et al (1994), several OPs are transformed to their corresponding oxons in this manner. For instance, diazinon is oxidized to diazoxon, which is relatively stable in chlorinated water for at least 48 hours. In a laboratory study at EPA-ORD's AWBERC facility in Cincinnati, Ohio, about 90% of chlorpyrifos-methyl was removed by chlorine treatment. The removal was most probably due to oxidation of the insecticide to oxons and other products.

☐ In areas where **water softening treatments** add lime and soda ash to reduce calcium and magnesium levels in water, the pH can increase to about 10 - 11. This high pH can lead to base-catalyzed hydrolysis of the OPs which are susceptible to hydrolysis under alkaline conditions. In the ORD treatment study, more than 99% of malathion was removed during softening treatment. The effects of softening may not be so dramatic for all OPs;

although phorate has a 3-day hydrolysis half-life at pH 9, lower removal (20%) of phorate was observed.

Appendix III.E.4, Effects of Drinking Water Treatment on Organophosphorous Pesticides, provides more detail on the effects of water treatment on OPs, and the resulting pathways of transformation.

a. 2001 Syngenta Study of Chlorination Effects on Six OPs and Four Oxons

The Agency very recently (October 24, 2001) received a registrant-sponsored jar test study on the potential effects of chlorination on six OP pesticides and four oxons (Tierney, et al., 2001). A preliminary review revealed incomplete information on the experimental procedures. Additional information required to complete the Agency's assessment include:

- ☐ Water quality data, which will affect pesticide fate and treatment effects
- ☐ The impact of sodium thiosulfate on water chemistry
- ☐ Data on storage stability data
- ☐ Pesticide concentrations above the limit of detection and below the limit of quantification

Despite the lack of information on experimental methods, the data indicate organophosphorus pesticides (acephate, azinphos-methyl, chloropyrifos, diazinon, malathion, and methamidaphos) are degraded in chlorinated drinking water. Chemical oxidation of the organophosphorus compounds led to the formation of oxons for azinphos-methyl, chloropyrifos, diazinon, and malathion. The oxons were more stable than their parent organophosphorus pesticides in independent degradation studies. Degradation of oxons was attributed to non-chlorine degradation processes and/or hydrolysis. Chloramines were formed during the experiment, and because chloramines have lower oxidizing potential than hypochlorus acid, the extent of degradation and formation of oxidative degradation products (oxons) may be different under conditions of higher free chlorine concentrations.

4. Summary of Monitoring Information

Evidence from the available monitoring studies confirms that OP pesticides do occur in drinking water sources. The frequency of detections is generally low, except for chlorpyrifos, diazinon, and, in some instances, malathion, and the magnitude generally ranges from sub-parts per billion to a few parts per billion. Significantly greater frequencies of detection occur in the limited number of targeted monitoring studies.

These OP pesticides can occur together in the same water source at the same time. Chlorpyrifos, diazinon, and malathion are the three OP pesticides most likely to occur together. However, other OP pesticides may also occur with one or more of these three in local areas. The USGS NAWQA study detected multiple OP pesticides in the same water samples at the same time in almost all of its study units. In some instances, up to 7 of the 11 OP pesticides included in the monitoring study were detected together (see Appendix III.E.1).

In general, surface water sources are more likely to be vulnerable to OP contamination than are ground water sources. OP pesticides are found in streams draining through predominantly urban/residential as well as agricultural watersheds. Chlorpyrifos, diazinon, and malathion are frequently detected in urban streams. While the residential uses of chlorpyrifos and diazinon are being cancelled, residential uses for malathion remain.

Although monitoring for OP pesticides in treated drinking water is very limited, the weight of evidence from available studies is that chlorination may transform the OPs to oxons, sulfoxides, and sulfones, which are of toxicological concern. A few studies indicate that the oxon transformation product will be stable in chlorinated water for at least 24 to 48 hours after treatment.

5. Suitability in Meeting Cumulative Assessment Needs

While the available monitoring studies provide a profile of OP occurrence in water, critical limitations preclude basing the cumulative water exposure assessment solely on monitoring. In particular, the monitoring studies were not designed to characterize daily concentration profiles and are not robust enough to provide daily distributions. Nor have the studies been conducted over a long period of time (typically less than three years) necessary to characterize year-to-year fluctuations due to weather patterns. While the NAWQA study units coincide with a number of high OP-use areas, not all of the major OP use areas have monitoring data. Lack of monitoring for some compounds make it difficult to completely assess co-occurrence. Finally, monitoring provides a snapshot in time and does not reflect recent mitigation actions, such as lower application rates and fewer applications or cancellation of certain uses or chemicals, initiated for individual chemicals during the risk management phase.

Despite these limitations, water monitoring will be used in the cumulative assessment to help identify vulnerable surface water sources, characterize OP residues in ground-water sources, compare relative impacts of OP use on water resources in different locations across the country, and provide a baseline comparison for estimated OP concentrations used in the probabilistic exposure assessment. Estimated OP concentrations are compared with available local monitoring. Where notable differences occur, OPP investigates the potential reasons for these differences. If no explanation, such as changing use patterns or unusual nature of the monitoring location, is found, then OPP evaluates the estimation parameters and makes adjustments as needed and supported by real-world information.

a. Limitations on Use of Surface-Water Monitoring for the Cumulative Assessment

With the publication of data from the nationwide set of NAWQA study units, more surface-water data for the OPs is available than ever before. However, the cumulative OP drinking-water exposure assessment requires the estimation of simultaneous daily drinking-water exposures to multiple pesticides, which is something that has never been attempted before. Although the available data is extensive, the cumulative drinking-water exposure assessment cannot be solely based on monitoring for the following reasons:

- ☐ **Incompleteness of the data:** As mentioned above, even the NAWQA program included only nine active OPs, and most of the others included in the cumulative assessment were rarely included in surface-water monitoring programs, if ever.

- ☐ **Design of available studies:** Next year, a number of OPs will be included on the EPA Office of Water's Unregulated Contaminant Monitoring List. Until then, little drinking water data for the OPs and their transformation products are available beyond the USGS-EPA Reservoir Monitoring Program.

  As useful as the NAWQA data is for the cumulative drinking-water risk assessment, the amount of data is not sufficient to allow estimation of daily drinking-water exposures across the nation. The majority of the sampling in each NAWQA study occurred over a two or three-year period, which is not a sufficient amount of time to account for climatic differences that would make surface-water runoff more or less likely than average. More importantly, the most intensive sampling schedule for surface water studies was on a weekly basis during the growing season, and biweekly or monthly otherwise. Even weekly sampling is not sufficient to ensure detection of peak concentrations for an acute exposure risk assessment, and less so for estimation of daily drinking water exposures.

Furthermore, as noted by the USGS, the survey design of the NAWQA program can lead to the underestimate of possible contamination in particular regions, because sampling timing and location will not correspond to the use patterns for all pesticides included as analytes.

❑ **Lack of monitoring data for transformation products:** As indicated above, the short persistence of some of the OPs suggests that monitoring for their transformation products would be more appropriate. However, surface-water data for transformation products is very scarce. Exceptions include very recent studies such as the USGS-EPA Reservoir Monitoring Program, and California DPR dormant-spray studies.

In addition, available surface-water monitoring does not include transformation products which are not so much formed in the environment as by water treatment.

Therefore, the daily drinking water exposure estimates have been generated using the simulation models PRZM and EXAMS. A description of the use of these models for the cumulative OP drinking water exposure assessment follows, below. The use of models allows estimation of possible concentrations of OPs not included in monitoring programs, or in areas for which monitoring for locally important OPs was not available. As described in the Risk Characterization section, peak values from the modeling are not always as high as some seen in small streams in the NAWQA program. However, the models allow the Agency to estimate a cumulative exposure assessment for **all** OPs used in representative scenarios for each region, even if they do not consistently match all the highest detections for each individual chemical.

6. Drinking Water Assessment Methods

The goal of the cumulative assessment is to aggregate exposure from the 24 organophosphorous (OP) pesticides over multiple routes of exposure (food, drinking water, residential) in a manner that is consistent in time (i.e., those exposure routes that are likely to occur on the same day are combined; those that are not likely to occur on the same day are not combined) and in location (i.e., only those exposures that may potentially occur in the same location are considered together). The Agency needs reasonable approximations of daily distributions of OP residues (concentrations) in drinking water to combine with food and residential exposures using a probabilistic, calendar-based approach (CALENDEX).

This cumulative risk assessment represents the first attempt to quantify possible drinking water exposure to multiple chemicals at the same time.

Available surface-water monitoring is not sufficient to allow estimation of potential daily drinking water exposure to the OPs included in this assessment. No currently-available model is specifically designed to simulate the simultaneous application and transport of multiple pesticides in a watershed. Therefore, the Agency looked to available tools to provide these daily exposure estimates for consideration with food and residential exposures.

Because drinking water is local, the national exposure assessment for drinking water must address localized areas of the country where exposure to one or more OPs may occur due to drinking water contamination. The consideration of OP use in specific regions of the country will facilitate the assessment of potential co-occurrence of different OPs in drinking water, leading to a cumulative assessment of OPs in drinking water on a regional basis.

The sections that follow describe the steps OPP has taken to generate regional drinking water exposure assessments as a part of the cumulative OP assessment.

a. Chemicals and Uses Included in the Cumulative Assessment

i. Parent Chemicals and Uses

The drinking water exposure assessment includes those OP pesticides with registered outdoor uses that may potentially impact surface- or ground-water sources of drinking water. Those pesticides or pesticide uses that are being cancelled and/or phased out as a result of agreements between the Agency and the specific OP registrants, and those OPs with uses that are unlikely to reach drinking water were not included in the water exposure assessment. Those agreements in place as of October 9, 2001, were considered in this preliminary assessment. Later phase-outs will be included in the revised assessment.

ii. Transformation Products

Those OP transformation products identified as being of toxicological concern will be included in the cumulative drinking-water risk assessment when environmental fate studies indicate that these products may be formed in the environment or may form as a result of water treatment. The main transformation products of toxicological concern are the oxons and sulfoxide/sulfones. The sulfoxide/sulfone products are generally found in the environmental fate studies; many are often more persistent and mobile than the parent compounds. While the oxon products are generally not found at significant levels in the environment, available studies suggest they are being formed by water treatment – in particular, through chlorination of the parent OP, as noted earlier.

Consideration of transformation products will require EPA to reconcile different assessment approaches in the individual OP risk assessments. For instance, the environmental fate profile for OP transformation products is rarely adequate, and the decision whether to estimate concentrations of transformation products depended greatly on the available data. Some OP risk assessments did not consider the transformation products quantitatively because no environmental fate data was available, while others assumed that the characteristics of the transformation products were equivalent to that of the parent, or combined limited data with conservative assumptions for a screening assessment.

Because full environmental fate profiles are not available for any of the OP transformation products, including these chemicals in the cumulative assessment will still require that some assumptions be made about their physicochemical properties. The method used for disulfoton and its sulfone and sulfoxide provides a likely example. All three disulfoton species were modeled using PRZM-EXAMS as “total disulfoton”. The formation and decline curves from an aerobic soil-metabolism study allowed the assessment team to fit a single modeling half-life for the combined residues. However, this required the assumption that all three chemicals were equally toxic, and that the sulfone and sulfoxide had the same soil-water partitioning coefficient as parent disulfoton. When such assumptions must be made, the Agency will attempt to describe the effect of the assumptions on the conservativeness of the risk assessment.

iii. List of Parent Chemicals and Transformation Products

Table I.E-1 lists the parent OP, transformation product(s) of toxicological concern, and approach for considering the contributions of the transformation products to the cumulative water exposure. Detailed chemical-specific inputs, based on environmental fate studies submitted by the OP registrants, are documented in Appendix III.E.5, Chemical-Specific Inputs Used in the Drinking Water Exposure Assessment. These inputs are based on the individual chemical assessments that were published in the REDs.

Table I.E-1 OP Pesticides and Toxic Transformation Products Included in the Cumulative Water Exposure Assessment

Pesticide	Transformation Products of Toxicological Concern	Approach for Including Transformation Product
Acephate	Methamidophos	Conversion from parent to product; max rate based on fate studies
Azinphos Methyl	Oxon	Formed by treatment
Bensulide	Oxon	Formed by treatment
Chlorethoxyfos	Oxon	Formed by treatment
Chlorpyrifos	Oxon	Formed by treatment
Diazinon	Diazoxon, Hydroxy-diazinon	Formed by treatment
Dichlorvos (DDVP)	None	
Dicrotophos	Monocrotophos	Not in field studies
Dimethoate	Oxon	Formed by treatment
Disulfoton	Sulfone, Sulfoxide	Combined residues
Ethoprop	SME, OME, M1	Not modeled; negligible residues; parent relatively stable
Fenamiphos	Sulfone, Sulfoxide	Combined residues
Malathion	Malaoxon	Formed by treatment
Methamidophos	None	
Methidathion	None	
Methyl Parathion	Methyl Paraoxon	Formed by treatment
Naled	Dichlorvos (DDVP)	Conversion from parent to product; max rate based on fate studies
ODM	Sulfone	Not modeled; negligible residues
Phorate	Sulfone, Sulfoxide	Combined residues
Phosmet	Phosmet Oxon	Formed by treatment
Phostebupirim (also known as Tebupirimphos)	Oxon	Formed by treatment
Profenofos	None	
Terbufos	Sulfone, Sulfoxide	Combined residues
Tribufos	None	

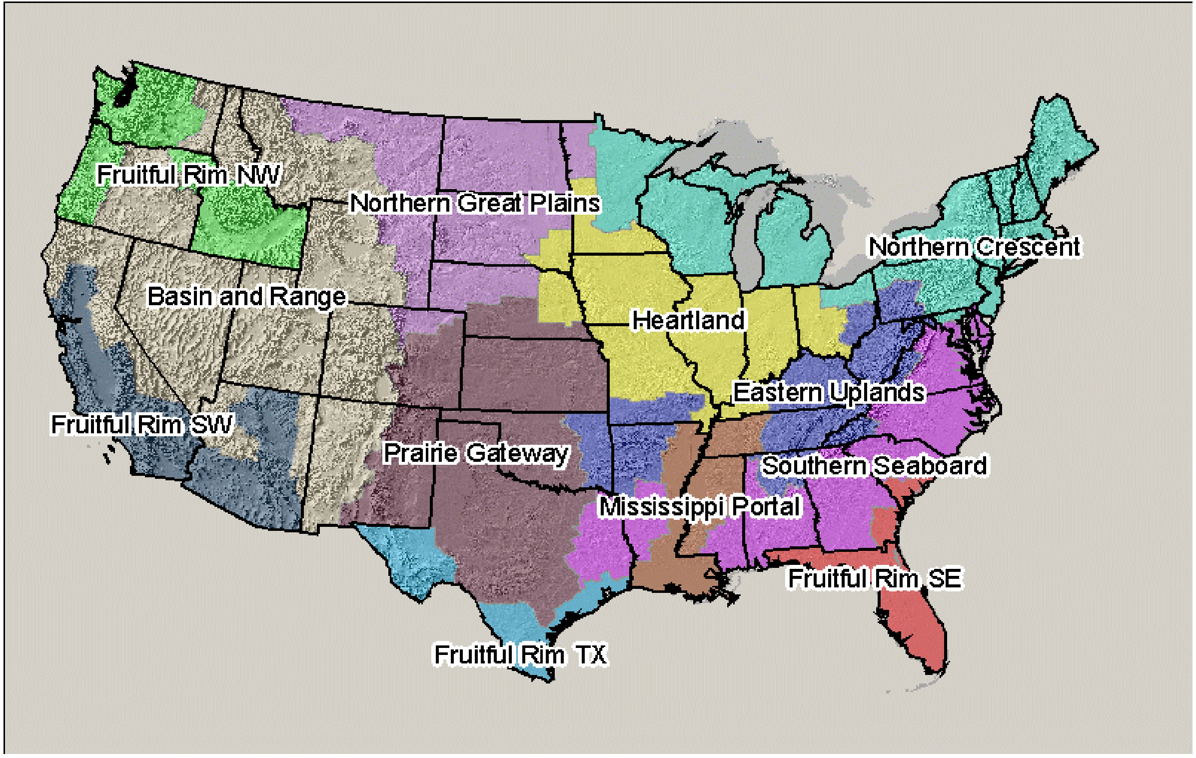
b. Regional Approach for the Cumulative Water Exposure Assessment

It is not feasible to conduct assessments for every watershed in the US. Therefore, locations were selected for areas where OPs in surface water and/or ground water are likely to be of concern. The farm resource regions facilitate the selection of locations by making it easier to rank the locations according to concerns regarding drinking water exposure. By design, there are many similarities within a particular region, such as crops grown, application timing (use season), percent of area treated, and application rates. There are also many similarities in key environmental factors affecting runoff, such as precipitation, irrigation practices, soil types, and average slopes. If a region is too large such that agronomic practices differ considerably across the alternative locations, then it would be much more difficult to identify one location as having greater concern or priority over another location. These farm resource regions provide a framework for identifying one or more locations which represent an area of the greatest concern for drinking water exposure in each region. In this way, the Agency can choose a set of locations which will represent drinking water exposure throughout the US.

i. Selecting and Defining Regions

As depicted in Figure I.E-3, the 48 contiguous states are divided into twelve Farm Resource Regions. These twelve regions were recently developed by the U.S. Department of Agriculture, Economic Research Service (ERS) to depict geographic specialization in the production of U.S. farm commodities (Heimlich, 2000). In constructing these regions, USDA identified areas with similar types of farms, intersected with areas of similar physiographic, soil, and climatic traits, as reflected in the USDA Land Resource Regions (Kellogg, 1998). A cluster analysis of U.S. farm characteristics, indicate that a few commodities tend to dominate farm production in specific geographic areas that cut across State boundaries. The climate, soil, water, topography, pest problems, and economic factors in localized geographic areas tend to constrain the types of crops and livestock that will thrive there. USDA conformed these intersecting areas to follow the boundaries of USDA Crop Reporting Districts, which are aggregates of counties (Sommer and Hines, 1991). The USDA ERS intends to utilize the twelve Farm Resource Regions in their future publications, and we intend to utilize the Farm Resource Regions to help in defining, characterizing, and conducting the EPA organophosphorous (OP) pesticide cumulative drinking water assessments. These Farm Resource Regions also may be applicable to future cumulative and aggregate assessments.

Figure I.E-3 Map of the Farm Resource Regions



Unlike the old ten Farm Production Regions, which had to follow state boundaries, these twelve Farm Resource Regions cut across state boundaries. The USDA has been able to use these new regions to display statistical information on agricultural production, since there are more specific data available at the county level. Since Crop Reporting Districts are generally composed of several counties, Geographical Information Systems (GIS) capability is not required to conduct data analyses using these regional statistics.

ii. Consistency with US Environmental Protection Agency Residue Crop Production Regions

EPA has extensively utilized Agricultural regions in developing the US EPA Crop Production Residue Crop Field Trials (EPA, 1995, Subdivision O: Residue Chemistry Test Guidelines. OPPTS 860.1500). Crop field trials need to be conducted to determine the magnitude of the pesticide on raw agricultural commodities in order to establish a tolerance level that reflects the specific application rates and timing, crop growth stages, use season, irrigation, cultural practices such as tillage, agronomic and horticultural practices, climatic (temperature and rainfall) and soil differences, and specific use directions to control pests in a food and/or feed crops. These regional crop field trials are used to establish tolerances for specific food and/or feed commodities as well as for Crop Group tolerances (40 CFR 180.41). The EPA Crop Production Regions are established in thirteen specific regions and are based on natural geography, climatic boundaries, and crop acreage within each region, and their borders are defined by either state boundaries or by major Interstate highways intersecting a state. Generally, the USDA Farm Resource Regions are in most cases consistent with the established US EPA Crop Production Regions. For example, EPA Crop production Region IV is fairly consistent with the Mississippi Portal Farm Resource Region, as well as EPA Region III (FL) is consistent with the SE Fruitful Rim (FL). The advantage of the USDA Farm Resource Regions is the ability to construct an agricultural region to specific county borders.

iii. General Region Descriptions

Table I.E-2 depicts the total acres planted for selected crops in each of the 12 regions. Overall, there are approximately 309 million acres of cropland in the US. The Heartland, Region 1, accounts for almost one third of that cropland, or nearly 100 million acres, with corn (43.5 million acres) and soybeans (42 million acres, not shown) being the principal crops in terms of acres planted. A brief description of the twelve Farm Resource Regions follows and includes a list of major commodities and livestock in the region, with references to previous names utilized by researchers in describing these regions.

- ☐ **Region 1. Heartland:** The primary crops in the Heartland region are corn, soybeans, alfalfa, and winter wheat. In addition to corn and soybeans, hog and beef cattle production is widespread in this region. This region is the classical Corn Belt Region, and the Land Resource Region called Central Feed Grains and Livestock Region.

- ☐ **Region 2. Northern Crescent:** Dairy cattle producers are widespread throughout this region. Apples are produced in Michigan and New York. Cherries are produced in Michigan. There is a concentration of snap beans production in southern Michigan, small vegetable farms and nurseries are scattered along the mid-Atlantic and northeastern states. The region also grows significant amounts of soft winter wheat, potatoes, grapes, forage crops, sugar beets, and sweet corn. This region is also known as the Hay and Dairy Region, and includes the Land Resource Regions called Northern Lake States Forest and Forage Region, Lake State Fruit Truck and Dairy Region, and the Northeast Forage and Forest Region.

☐ **Region 3. Northern Great Plains:** The Northern Great Plains contains a considerable amount of wheat, and small grains, and oilseeds including sunflower and canola. Potatoes and sugar beets are also grown along the Red River Valley area in both Minnesota and North Dakota. Beef cattle and sheep are also raised in this region. Dry beans and peas are also produced. This region is also known as the Spring Wheat Region, and includes the Land Resource Regions called Northern Great Plains Range and Irrigated Region and Western Great Plains Spring Wheat Region.

☐ **Region 4. Prairie Gateway:** The Prairie Gateway has a considerable amount of wheat and grain sorghum in north Texas, Oklahoma and Kansas. There is a concentration of cotton production in west Texas, with cattle and other livestock (sheep) in the southwestern area of Texas. Peanuts are grown in Oklahoma, and Texas is a major watermelon producing state. This region is also known as the Central Great Plains Region, and includes the Land Resource Regions called Central Great Plains Winter Wheat and Range Region and Southwestern Prairie Cotton Rangeland and Forage Region.

☐ **Region 5. Eastern Uplands:** There is a considerable amount of tobacco production in Kentucky, and parts of northeastern Tennessee, and bordering counties in Virginia and North Carolina. There are some poultry farms in West Virginia, Tennessee, Alabama and in Arkansas. Small general farms are characteristic of this region. Other crops important to this region are winter wheat, corn, and alfalfa. This region is also known as the Corn and Winter Wheat Belt Region, and includes the Land Resource Region called East and Central Farming and Forest Region.

☐ **Region 6. Southern Seaboard:** There are poultry farms in DelMarva peninsula (Delaware, Maryland, Virginia), and south including North Carolina, South Carolina, Georgia, Alabama, Mississippi, Louisiana, Arkansas and Texas. Blueberries are important in New Jersey. This region is a mix of small and large farms with corn, soybean, sweet potato, wheat, tobacco, cotton, pecans, peaches, and peanuts being important crops. This region is also known as the Cotton Belt Region and includes the Mid-Atlantic Fruit and Truck Crop Region; and includes the Land Resource Regions called South Atlantic and Gulf Slope Cash Crops Forest and Livestock Region and part of the Atlantic and Gulf Coast Lowland Forest and Crop Region.

- ☐ **Region 7. Southeast Fruitful Rim, CA\AZ:** There is a considerable amount of cotton, rice, and alfalfa production in California. A considerable amount of citrus and subtropical fruits and tree nuts (almond and walnut) also are produced throughout the Central Valley. Other important crops include apricots, plums, sugar beets, grapes, and ornamental crops. There is considerable degree of vegetable production throughout California and Arizona, including broccoli, lettuce, onions, tomatoes, and peppers. Extensive dairy and beef cattle production exists in this region. This region is also known as the Pacific Subtropical Crop Region and includes the Land Resource Regions called California Subtropical Fruit Truck and Speciality Crop Region and parts of the Western Range and Irrigation Region.

- ☐ **Region 8. Basin & Range:** There is a considerable amount of land area used for grazing and irrigated crops. Major commodities in this region are wheat and grain sorghum and cattle. This region is also known as the Grazing and Irrigated Crops Region and includes the Land Resource Regions called Western Range and Irrigated Region.

- ☐ **Region 9. Mississippi Portal:** Cotton, soybeans, and rice are the major crops in this region. Sugarcane production is important in Louisiana. Poultry and hogs are important. This region is also known as the Mississippi Delta and Delta Region and includes the Land Resource Regions called South Atlantic and Gulf Slope Cash Crops Forest and Livestock Region, Mississippi Delta Cotton Feed Grains, and part of the Gulf Coast Prairie Region.

- ☐ **Region 10. Northwest Fruitful Rim:** There is a considerable amount of apples and pears produced in central Washington. Several grass, legume, and vegetable seed crops are grown in Willamette Valley, Oregon. In western Washington, there is a considerable amount of bushberries grown. Potatoes, sugar beets, dry peas and dry beans are major crops in Idaho. This region is also known as the Northwestern Pome Fruit and Wheat and includes the Land Resource Regions called Northwestern Wheat and Range Region and the Northwestern Forest Forage and Speciality Crop Region.

- ☐ **Region 11. Southwest Fruitful Rim (Texas):** A considerable amount of vegetables are produced in the Lower Rio Grande Valley (LRGV) area of Texas. Cotton and grain sorghum are major crops, and land is grazed by beef cattle. This region is also known as the Southwestern Plateau and Plains Region and includes the Land Resource Regions called Western Range and Irrigated Region and Southwestern Plateaus and Plain Range and Cotton Region.

☐ **Region 12. Southeast Fruitful Rim (Florida):** There is a considerable amount of citrus (oranges, grapefruits, limes, etc.) and tropical and subtropical fruit grown in Florida. Sugarcane is a major crop in southern Florida. Fresh tomatoes and other vegetables are grown in Florida. Various vegetable farms are located along the Georgia and South Carolina coast. This region is also known as the Humid Subtropical Crop Belt and the Florida Specialty Crop Region and includes the Land Resource Regions called Florida Subtropical Fruit Truck Crop and Range Region and parts of the Atlantic and Gulf Coast Lowland Forest and Crop Region.

Table 1.E-2 Total Acres Planted for Selected Crops, by USDA Farm Resource Region

	Total Acres Planted Selected Crops, By USDA\ERS Farm Resource Regions (1,000)												
Selected Crops	1	2	3	4	5	6	7	8	9	10	11	12	Grand Total
Alfalfa Hay	3,641	4,445	4,779	2,024	819	110	979	3,061	11	1,350	26	2	21,248
Field seed/grass seed	72	11	38	15	48	6	12	117	4	492	<1	11	825
Corn for grain or seed	43,517	8,713	3,250	8,614	991	2,315	291	80	1,358	107	280	195	69,712
Cotton	388	<1	<1	4,734	130	2,679	1,360	13	2,958	<1	688	216	13,166
Peanuts	<1	<1	<1	319	6	894	<1	<1	2	<1	30	84	1,336
Potatoes	25	244	138	11	7	26	32	148	<1	550	9	37	1,227
Sugar beets	104	227	668	28	<1	<1	97	99	<1	210	<1	<1	1,433
Tobacco	53	14	<1	<1	288	448	<1	<1	14	<1	<1	19	836
Sugarcane	<1	<1	<1	<1	<1	<1	<1	<1	26	<1	<1	15	41
Dry edible beans	43	387	855	104	<1	<1	63	72	<1	119	<1	<1	1,643
Wheat	4,430	1,312	21,524	21,206	492	1,733	669	3,279	1,173	2,841	41	61	58,760
Land in orchards	37	355	<1	212	87	253	2,610	90	22	373	63	990	5,091
Almonds	<1	<1	<1	<1	<1	<1	539	<1	<1	<1	<1	<1	540
Apples	17	196	<1	2	28	28	46	20	<1	213	<1	<1	551
Pears	<1	4	<1	<1	<1	<1	16	17	<1	37	<1	<1	74
Cherries	<1	55	<1	<1	<1	<1	20	14	<1	30	<1	<1	119
Peaches	3	24	<1	5	8	35	76	5	2	4	<1	<1	163
Plums and prunes	<1	2	<1	<1	<1	<1	148	1	<1	4	<1	<1	154
Lemons	<1	<1	<1	<1	<1	<1	72	<1	<1	<1	<1	<1	72
Oranges	<1	<1	<1	<1	<1	<1	234	<1	<1	<1	8	755	997
Berries	2	63	<1	<1	2	5	23	<1	<1	20	<1	2	117
Grapes	<1	62	<1	1	2	2	853	21	<1	47	<1	<1	989
Land used for Vegetables	277	800	20	87	59	271	1,169	96	16	338	75	253	3,463
Asparagus	<1	19	<1	<1	<1	<1	31	2	<1	20	<1	<1	72
Lettuce	<1	4	<1	2	<1	<1	292	2	<1	<1	<1	2	303
Snap beans	15	118	<1	4	14	24	7	<1	<1	28	<1	28	237
Cantaloups	4	3	<1	2	<1	6	75	<1	<1	<1	4	2	99
Sweet corn	121	288	4	2	10	38	26	18	<1	140	<1	38	685
Tomatoes	13	22	<1	<1	6	8	307	<1	1	<1	<1	40	399
Mint	30	14	<1	<1	<1	<1	<1	19	<1	86	<1	<1	149
Total (all crops) Cropland	99,715	30,856	46,014	53,525	11,845	15,495	9,071	11,312	16,341	8,572	3,274	2,937	308,956
Pct of Total Cropland	32%	10%	15%	17%	4%	5%	3%	4%	5%	3%	1%	1%	100%

c. Selecting Regional Water Exposure Assessment Locations

Even within the regions, drinking water exposure will vary locally due to OP usage, agricultural practices, nature and vulnerability of drinking water sources, and weather patterns. Thus, the preliminary water exposure assessment focuses on one or more specific geographic areas within each region in a manner that would engender a distribution which would be realistically protective of all sites within the region.

The selection of a specific location for regional drinking water assessments involves several steps. First, OPP identified the high OP usage areas and high agricultural intensities within each region; these are shown on a national scale in Figure I.E-4. Next, in each high usage area within the region, OPP determined the types and locations of drinking water sources. The final step in choosing a location is to assess the vulnerability of drinking water sources within the high usage area within the region. OPP adapted vulnerability schemes proposed by Kellogg and others at USDA for this purpose. Locations of surface drinking water intakes overlain on runoff vulnerability maps (Figure I.E-5) were compared with the OP use areas to determine whether potentially vulnerable surface water sources of drinking water coincided with high use areas. For ground water, OPP compared OP use areas with a pesticide leaching vulnerability map (Figure I.E-6).

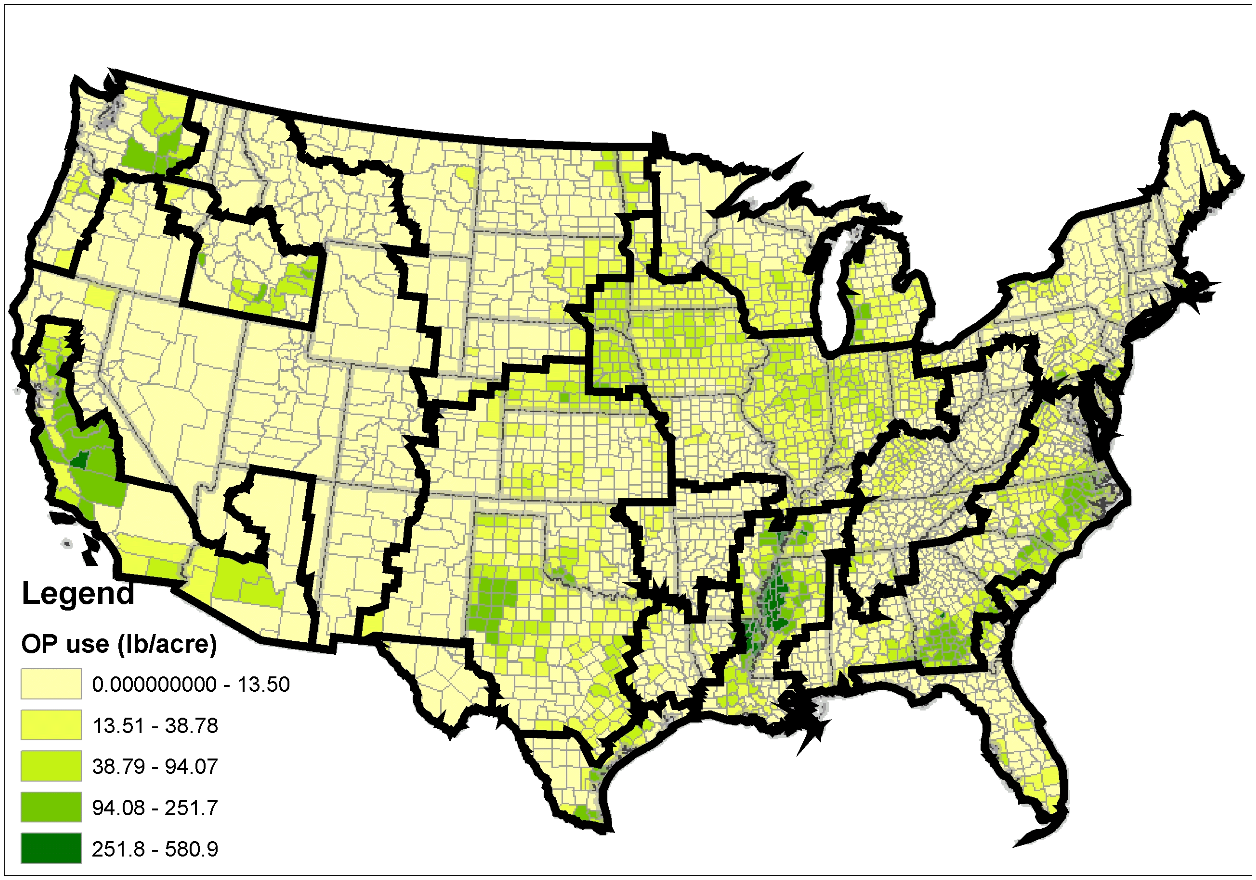


Figure I.E-4 Total organophosphorous (OP) pesticide usage on an area-weighted basis

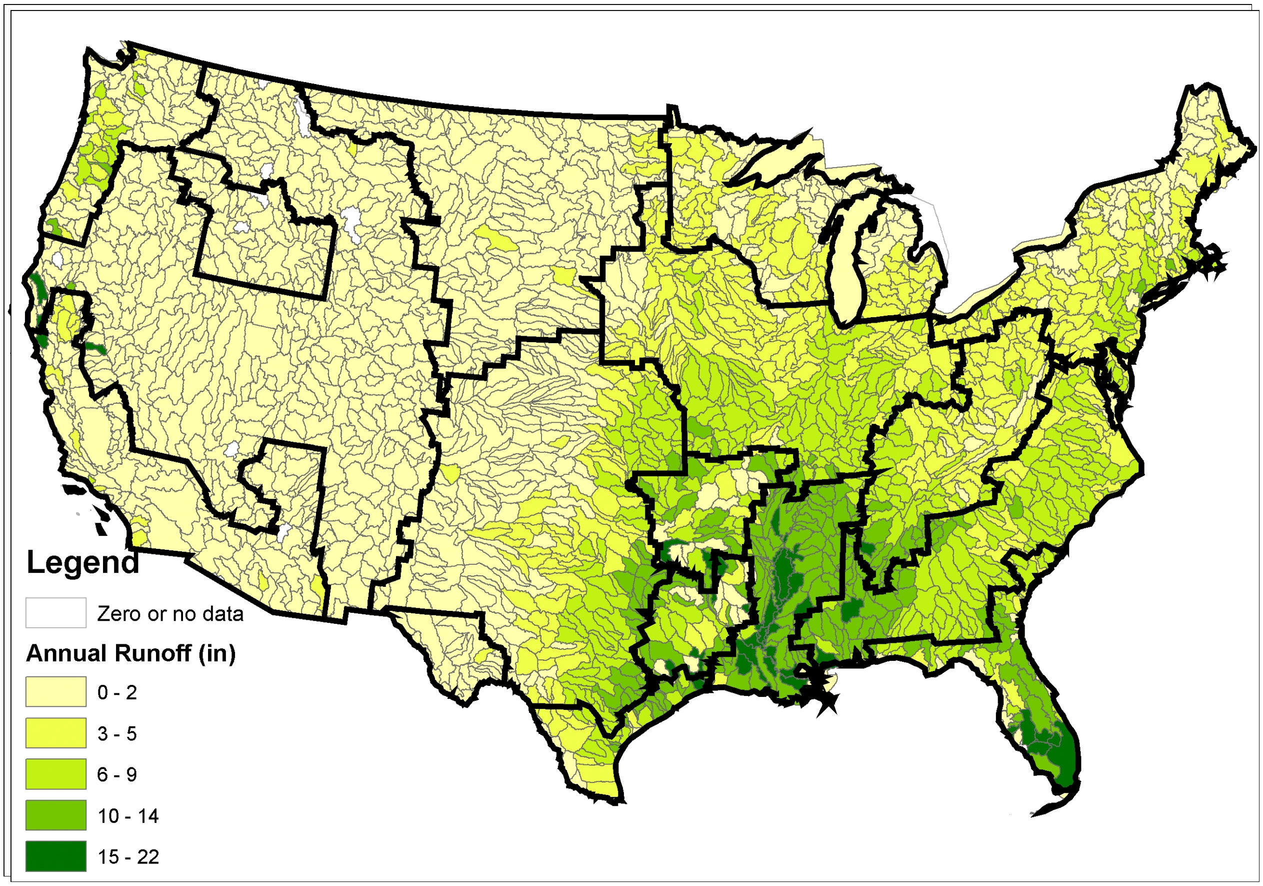


Figure I.E-5 Runoff vulnerability (in/year), adapted from USDA (Kellog, 1998)

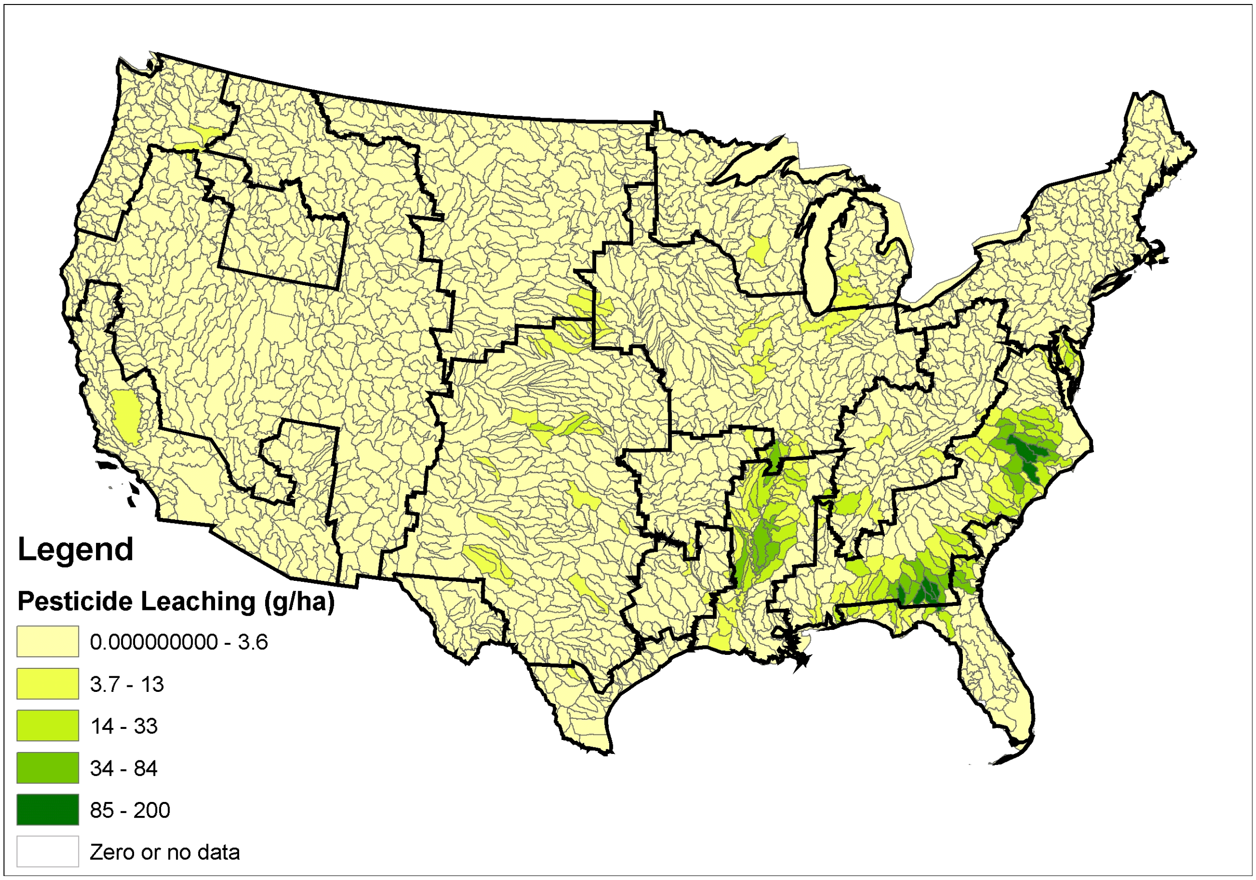


Figure I.E-6 Pesticide leaching vulnerability, adapted from USDA (Kellogg, 1998)

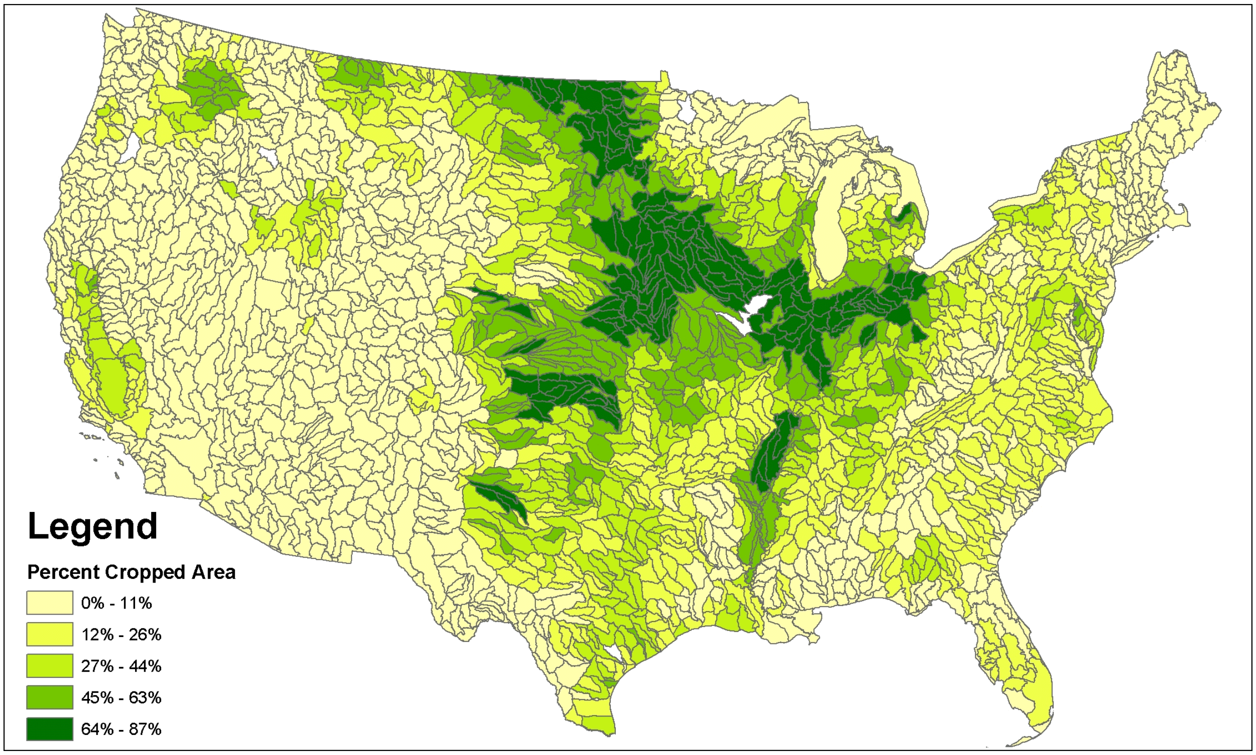


Figure I.E-7 National map w/ PCAs by 8-digit HUC, region lines

Details of this process are provided in each regional assessment. The Northwest Fruitful Rim provides an illustration of this process. Three high OP-use areas occur in the Northwest Fruitful Rim (Figure I-E-4): Yakima County and eastern Washington are the highest OP use area (predominantly on orchards) and highest percent crop area (Figure I-E-7). The Snake River Valley in Southeast Idaho is the second highest use area (predominantly on potatoes, sugar beets). The Willamette Valley, Oregon, is the third high-use area, with a mix of OP uses. We find predominantly ground-water sources of drinking water in Idaho and eastern Washington, with vulnerability to leaching potentially higher in eastern Washington. A few surface-water intakes occur in the Yakima County area; the Willamette Valley has more surface water intakes and is more vulnerable to runoff. Available monitoring from NAWQA study units in Willamette Valley, Snake River Basin, and Pugett Sound suggest that Willamette Valley will be more vulnerable to OP contamination with a higher potential for co-occurrence of multiple pesticides.

OPP based its surface water assessment for the Northwest Fruitful Rim on the Willamette Valley in Oregon. We also looked at potential impacts of OP pesticides on ground water resources in eastern Washington and southeast Idaho, relying largely on ground-water monitoring available through the USGS NAWQA program and state monitoring programs.

d. Estimate Pesticide Concentrations in Drinking Water Sources Within Each Region

After considering several predictive tools, the Agency adapted its paired PRZM and EXAMS models for the Index Reservoir (PRZM-EXAMS IR) to estimate a daily concentration of drinking water concentrations that could be used for multiple chemicals over several years of predictions across the country. PRZM-EXAMS IR has been modified to calculate concentrations in a small drinking water reservoir in a primarily agricultural watershed. PRZM-EXAMS has the capability of predicting water concentrations over a number of years based on collected historical weather data for the sites which are being modeled. Using the same weather inputs from the chosen watershed, the model was run for each chemical:crop combination reported to be used in the counties selected for watershed modeling. The model outputs were modified with the regional specific Cumulative Adjustment Factors of Total Acres Treated described below. The modified output was then normalized to methamidophos equivalents and the normalized output for each chemical:crop combination was summed day by day to give a single distribution of potential combined water residues for the region.

The PRZM component of the model is designed to predict the pesticide concentration dissolved in runoff waters and carried on entrained sediments from the field where a pesticide has been applied into an adjoining edge-of-field surface water body. The model can simulate specific site, pesticide, and management properties including soil properties (organic matter, water holding capacity, bulk density), site characteristics (slope, surface roughness, field geometry), pesticide application parameters (application rate, frequency, spray drift, application depth, application efficiency, application methods), agricultural management practices (tillage practices, irrigation, crop rotation sequences), and pesticide environmental fate and transport properties (aerobic soil metabolism half-life, soil:water partitioning coefficients, foliar degradation and dissipation, and volatilization). OPP selects a combination of these different properties to represent a site-specific scenario for a particular pesticide-crop regime.

The EXAMS component of the model is used to simulate environmental fate and transport processes of pesticides in surface water, including: abiotic and biotic degradation, sediment:water partitioning, and volatilization. Currently, OPP is using an index reservoir as the benchmark surface water body for drinking water exposure assessments.

For each component, the values used are derived from real world data. Pesticide environmental fate properties used in the modeling come from registrant-submitted data used for pesticide registration or reregistration. The values used for soil properties and site characteristics are chosen from real world databases appropriate for the sites on which the pesticide may be used. For example, if the pesticide is approved for use on cotton, OPP uses data reflecting the soil types in the Cotton Belt. The index reservoir being modeled is based on and represents an actual, small flow-though reservoir used for drinking water. Finally, the weather inputs for the model are taken from regional specific weather data, based on the USDA Major Land Resource Areas. PRZM modeling is generally simulated for 20 to 36 years in order to calculate a return frequency of concentration in surface water body. Further information on how the Index Reservoir model is used for screening-level drinking water assessments of individual pesticides can be found in the EPA Environmental Fate and Effects Division's pesticide science policy paper, "Guidance for Use of the Index Reservoir Guidance for Use of the Index Reservoir in Drinking Water Exposure in Drinking Water Exposure Assessments."

Running the assessment with historical data for several years provides more confidence that variations due to weather have been considered in the assessment. Having the historical weather data, pertinent site information and reported use histories allows the Agency to factor regional variations into the assessment. With this method, multiple chemicals which have varying uses and application factors are assessed and co-occurrence is realistically accounted. Since the day by day component is retained, this distribution can easily be paired with residues resulting from residential applications.

The PRZM-EXAMS/IR tool has been used in many of the individual assessments to predict a reasonable high end screening concentration to factor into the aggregate assessment. However, the cumulative assessment focuses on the probability or likelihood a person will be concurrently exposed to multiple pesticides from food, water, and residential use. The method which was used in the aggregate assessments has been modified in several ways to focus on the probability of co-occurrence from the various routes.

The most significant change in terms of predicted exposure is that the entire range of PRZM-EXAMS/IR output is used for the probabilistic distribution. In other words, instead of choosing a single value at the upper end of the distribution to represent the exposure, all daily concentration values are used in the CALENDEX runs.

Also, a very important factor is that the cumulative assessment modeling is done using "typical rates" with "typical numbers of applications" instead of labeled maximum rates and maximum numbers of applications which were used in the individual chemical assessments. While this is reflective of the "typical" condition, it does not reflect potential concentrations that may occur when the pesticide is used at maximum rates because of pest pressure.

The drinking water assessments for cumulative are regional in nature. This allows EPA to make informed judgements about when compounds co-occur and when they compete. Overall, the assessment is much more realistic on a regional basis. Scenarios chosen for regional assessments are reflective of regional differences in cropping and pesticide use as well as differences in run-off and leaching vulnerability.

The regional estimate will also allow for a Cumulative Adjustment Factor (CAF) based on the total reported numbers of acres which receive OP applications. In the aggregate assessments, the adjustment factor used for compound with multiple use sites was the default Percent Cropped Area (PCA) of 0.87 which represents the highest percentage of agriculture in any watershed in the US. We know that regions with less intense cropping will have lower estimated concentrations based on a regional CAF compared to the national PCA.

In summary, the PRZM-EXAMS IR modeling tool is being used to generate a daily distribution of residues which may occur in drinking water from multiple crop:chemical combinations on a regionalized scale.

i. Cumulative Adjustment Factors for Crop Area and OP Use

The CAF accounts for the percent of the location area that is planted to crops and treated with the corresponding OPs that are being assessed. While the CAF is a fairly straightforward concept, it is based on several different data sources. The Agency used the USGS 8-digit Hydrologic Unit Codes (HUCs) to delineate watersheds, and the National Agricultural Census for 1997, reported on a county basis, to identify areas planted to agriculture. This procedure is detailed in the 1999 SAP [Reference] and 2000 draft science policy paper [Reference]. Percent crop area values were calculated for each region. To determine the total acres planted for each crop within the selected location, the Agency used the most recent county level production statistics, generally taken from USDA publications. And finally, to calculate the area treated by the various OPs, the most recent percent of crop treated estimates, generally taken from USDA\NASS publications were applied.

In addition to primary USDA publications, various other data sources (California Department of Pesticide Regulation, Pesticide Use Reporting Data, academia publications) were used to obtain acres planted and acres treated estimates.

The following example illustrates how CAFs are calculated and applied. Suppose, that after reviewing the various data (drinking water source, vulnerability, crop production, pesticide use, and monitoring data), a location (one or several counties) is identified around which the drinking water assessment is conducted. The total area for this location is 800,000 acres; agricultural cropland accounts for 600,000 acres of this total area, and 320,000 acres of the agricultural cropland are planted to four crops (corn, alfalfa, beans and apples) that are treated with OP pesticides:

		Acres	Percent of area	PCA
Total Area		800,000		
Crop Area, All Agricultural Uses:		600,000		75%
OP Uses in Region:	Corn	200,000	25%	
	Alfalfa	80,000	10%	
	Beans/legumes	16,000	2%	
	Apples/pome fruit	24,000	3%	
Total OP Use Area		320,000		40%

Further, suppose that 4 different pesticides are used on each of the 4 crops (some pesticides are used on more than one crop). Acres treated represent the total number of acres of the crop that were treated with each pesticide (may represent more than one application). Following the numerical example above, if 60,000 acres of field corn were treated with pesticide A, then the CAF for this particular use (field corn-pesticide A) is 0.075, or:

$$\begin{aligned} \text{CAF}_{\text{Corn-OP(A)}} &= (\text{Total Acres Planted}_{\text{All OP Crops}} / \text{Total Acres}) \\ &\quad \times (\text{Acres Treated}_{\text{Corn-OP(A)}} / \text{Acres Planted}_{\text{All OP Crops}}) \\ &= (320{,}000 / 800{,}000) \times (60{,}000 / 320{,}000) = 0.075 \end{aligned}$$

Crop	Pesticide	Acres Treated	Cumulative Adjustment Factor
Corn	A	60,000	.075
Corn	B	1,000	.00125
Corn	C	500	.000625
Corn	D	40,000	.05
Alfalfa	A	16,000	.02
Alfalfa	B	4,000	.005
Alfalfa	E	10,000	.0125
Alfalfa	F	8,000	.01
Apples	A	10,000	.0125
Apples	F	15,000	.01875
Apples	G	6,000	.0075
Apples	H	6,000	.0075
Beans	B	16,000	.02
Beans	E	1,000	.00125
Beans	I	16,000	.02
Beans	J	2,000	.0025

Again, these CAF are applied to the model is run for a particular chemical:crop combination. In this manner, since the use statistics come from reported data, competing and compatible uses are accounted for by summing the appropriate distributions across days after the RPFs are applied.

e. Pesticide Usage Information

For regions exclusive of the Southwestern Fruitful Rim, the primary sources of information for percent crop treated, number of applications, and amount of active ingredient applied are USDA National Agricultural Statistics Service (NASS) Agricultural Chemical Usage summaries. These documents provide data for selected crops in selected states; they are published annually for field crops and biennially for vegetables and for fruits and nuts. Vegetable chemical usage summaries are reported for even years; fruit and nut chemical summaries are reported for odd years. The years 1997-2000 were reviewed for field crops, 1998 and 2000 for vegetables, and 1997 and 1999 for fruits/nuts. The most recent summary data is cited for state/crop combinations appearing in the cumulative surface water assessments. Citations follow the format: "NASS, 2000 Vegetable Summary."

In a given NASS summary, specific OP pesticides may be noted, by use of an asterisk, as being applied to a crop but no usage data is provided. This situation arises where the number of individuals reporting use of the specific OP is so small (i.e., fewer than five) that respondent confidentiality could be compromised through data disclosure. In such instances, an earlier summary has been consulted. The NASS data for OP use on corn in the Heartland (Illinois) illustrates this procedure:

Agricultural Chemical	Area Applied (percent)	Applications (number)	Rate per Application (pounds)	Year
Chlorethoxyfos	4	1	0.08	1999*
Chlorpyrifos	13	1	1.2	2000**
Terbufos	4	1	1.4	2000**
Tebupirimphos	3	1	0.1	1999*

*NASS Field Crops 1999
**NASS Field Crops 2000

In the example cited above, both chlorethoxyfos and tebupirimphos were reported as being used on corn in Illinois in 2000; however, usage data was not disclosed. The 1999 NASS survey provided the most recent NASS estimates for these two OP pesticides on corn in Illinois.

NASS data was not available for all specific chemical/state/crop combinations examined. In some cases, additional survey instruments were consulted. All usage data sources are documented at their occurrence in the regional summaries.

An application window has been established for each of the OP pesticides reported. This window represents an approximate beginning and ending date for the use of the pesticide on a particular crop. Delineation of these windows was based on review of crop profiles and other relevant crop production publications; surveys such as the Doane Marketing Research, Inc. Agrotrak^{tm} reports on agronomic, row and specialty crops; and on consultations with field experts. Unless otherwise noted, the default planting and harvesting dates for crops were taken from the following USDA documents:

- ☐ United States Department of Agriculture, Crop Reporting Board, Statistical reporting Service. 1977. Usual Planting and Harvesting Dates for Fresh Market and Processing Vegetables. Agriculture Handbook No. 507.
- ☐ United States Department of Agriculture, National Agricultural Statistics Service. 1997. Usual Planting and Harvesting Dates for U.S. Field Crops. Agricultural Handbook No. 628.

These USDA handbooks also provide "most active" periods during the planting and/or harvesting windows. The mid-point of the most-active period was selected as the application date for a pesticide applied at the "planting" stage of crop production. A case in point is the data input for terbufos on corn in the Eastern Upland (North Carolina):

Pesticide	Stage	Application Date	Range	Most Active
Terbufos	Planting	April 17	April 1 - May 20	April 10 - April 25

A similar procedure was followed with the OP defoliant tribufos used as a harvest aid for cotton. Here is the data input for this OP in the Prairie Gateway (Texas):

Pesticide	Stage	Application Date	Range	Most Active
Tribufos	Harvest	November 1	August 10 - December 28	October 1 - December 2

When most active periods are not provided, the single application date for a pesticide is the beginning of the crop stage window. Multiple applications, such as OP cover sprays for tree fruits, are placed at the beginning and equidistant within the application window. The following example is for three cover sprays of phosmet on apples in the Northern Crescent (Pennsylvania):

Pesticide	Stage	Application Dates	Range
Phosmet	Foliar	May 1 June 18 August 5	May 1 - September 21 May 1 - September 21 May 1 - September 21

A most likely, or predominant, application method is also designated for each pesticide. The choice is simply “air” or “ground.” Review of NASS and proprietary data bases, crop production profiles, as well as consultation with field experts, informed these application method determinations.

For each location examined, the total cropland of the inclusive counties was derived from the county acreages reported in the USDA NASS 1997 Census of Agriculture. Total acres for targeted crops was based on the most recent state-level information. These figures were typically the 2000 data listed in state agricultural statistic service (SASS) publications. Sources are noted in the text for each region examined.

For the Southwestern Fruitful Rim, the California Department of Pesticide Regulation, Pesticide Use Reporting (PUR) data was used to determine both the acres treated and the application dates. The PUR contains detailed information on every commercial pesticide application made within the State of California. Since the two locations identified and assessed in this region were located in the State of California, the Agency used the PUR data base to calculate the total area treated by each pesticide, on each crop for each date. For some uses, growers reporting making applications on numerous dates (>50 days) throughout the Calendar year. For data management purposes, five application dates were selected for each crop-OP use to be used in the assessment; each application date represents 20% of the total acre treatments made for that particular use.

In summary, the NASS and other published survey instruments provided the bases for the OP usage patterns described for all regional surface location examined. These state-level snapshots of pesticide practice are, of necessity, limited in time and scope. Usage patterns change continually to reflect OP label amendments and the availability of alternatives which include other, non-OP classes of pesticides and cultural, non-pesticidal control options. Moreover, state survey data is at a level of refinement somewhere between maximum label rates and frequencies and actual agronomic practice in specific location. And, of course, surveys are only as good as the number and quality of responses that educate the derived estimates. With these reservations in mind, this approach was undertaken to provide transparent modeling scenarios using the best currently available data.

f. Incorporate the Drinking Water Exposure Estimate into the Cumulative Assessment

In summary, within each region, a residue file was generated by PRZM-EXAMS/IR for each pesticide:crop combination which was reported in the county or counties selected for assessment. This day-by-day residue file was modified by the CAF specific to that pesticide:crop combination and the relative potency factor for that pesticide. Then, the modified residue files for all pesticide:crop combinations for that location were summed across days to give a distribution of combined daily residues in drinking water.

This distribution of combined daily residues can then be used as an input file for the CALENDEX model which is discussed elsewhere in this document. CALENDEX allows the Agency to combine OP concentrations from water and residential exposures which are time and location dependent with food exposures which are not time and location dependent.

The distribution of daily residues can also be compared to any water monitoring data available for the chemicals and region being examined. Plots of the daily distributions can be analyzed to ascertain which uses may be expected to contribute significant exposures. The comparison of monitoring data and the understanding of which uses contribute to exposure are important aspects of risk characterization of the water portion of the OP cumulative risk assessment.