

I. Revised 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 that affect pesticide contamination in water, 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.

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. 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 for drinking water requires data on concentrations of the pesticides in the drinking water and consumption of drinking water for different demographic populations on a daily basis. 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

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. For many of the OPs, limited or no monitoring data are available. For some OPs, 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.

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. 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 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 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.

b. Surface Water Monitoring

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 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. 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. Two other OPs – fonofos and parathion – included in the study have been voluntarily cancelled.

The NAWQA program includes monitoring data for 76 pesticides and covers “more than 50 major river basins and aquifers covering nearly all 50 states” (Figure I.E-1) (http://water.usgs.gov/nawqa/nawqa_home.html). Results of the individual NAWQA study units are highlighted in the appropriate regional assessments and in more detail in Appendix III.E.1.

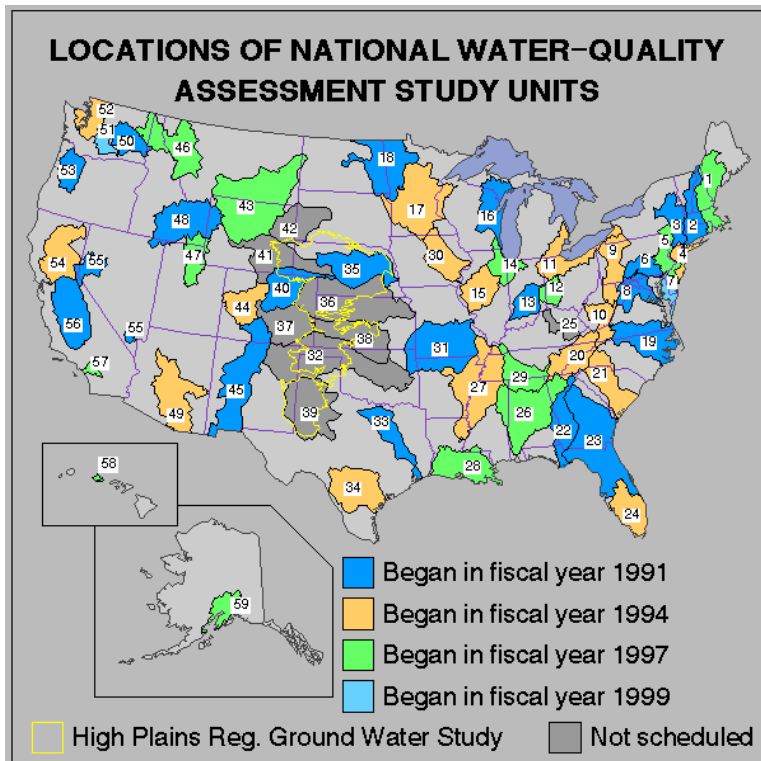


Figure I.E-1. Location of USGS NAWQA study units (Source: USGS).

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

ivers, and at the intake and outflow of reservoirs along their path. Any detection of OPs in these studies is significant 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 Appendix III.E.2.

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 and in more detail in Appendix III.E.3.

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 waters. 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.

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 illustrate this:

- ❑ 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 (SJR) 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 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. While the NAWQA program samples in almost all states, a good number of the studies were designed to answer locally important questions for each river basin, and are not uniformly designed. The USGS Pesticide National Synthesis Project elaborates on why the studies are not specifically designed to produce a statistically representative analysis of national water-quality conditions (http://www.dwatcm.wr.usgs.gov/ccpt/pns_data/data.html).

In comparison to NAWQA, NASQAN includes 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, and 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 (Blomquist et al., 2001; available through the USGS web site at http://md.water.usgs.gov/nawqa/OFR_01-456.pdf) was designed to evaluate potential concentrations of a variety of pesticides and transformation products in untreated and treated drinking water derived from reservoirs. This study included twelve reservoirs covering a range of pesticide use areas across twelve states (Figure I.E-2). The study focused 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. Additional data collected for each site provided information on watershed properties, water treatment information, and reservoir characteristics.

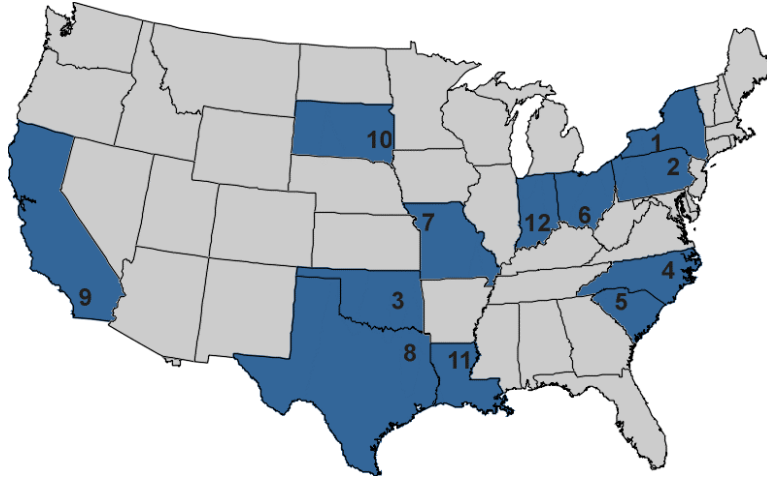


Figure I.E-2. Location of reservoirs in the USGS-EPA Reservoir Monitoring Project

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 included in this cumulative assessment. This program included some rarely-monitored OPs, such as tribufos, phostebupirim, profenofos and dicrotofos, and 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 6 of the 12 watersheds in 1999 (see Appendix III.E.3 for details). Diazinon, the most frequently detected OP, was found in 35% of 323 raw water samples but in none of the 227 finished water samples. Although the lack of truly paired raw and finished water samples precludes definitive conclusions, these results suggest that diazinon may be removed by the treatment process. However, the likely transformation product, diazoxon, was not included as an analyte in the pilot program.

Results for other OPs suggest that parent OP compounds are transformed during water treatment. For instance, malathion was detected in raw water samples (2%) while malaoxon was detected in finished water samples (5%). Chlorpyrifos was detected in 5% 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 but the difference between the number of detections for each is insufficient 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 6, 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 (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 ug/l 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 was not specifically targeted to high OP-use areas, it included more OPs than any previous study. Therefore, it is 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%) included more than one detected OP. Of 67 *outfall samples* considered, 17 (25%) had one or more detectable OPs, two of those samples (12%) having more than one OP detected. Of 218 *finished samples* considered, 24 (11%)

had one detectable OPs, and 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.

c. Ground Water Monitoring

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.

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 $\mu\text{g/l}$, significantly higher than concentrations found in agricultural areas, which generally are below 1 $\mu\text{g/l}$.

The **USGS NAWQA program** is the other major source of ground-water data for the OPs. 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 included in this cumulative assessment are included.

- ❑ Many NAWQA ground-water studies included only a single sample of each well in the network. Even if wells 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 some compounds makes 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.

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.

d. Effects of Drinking Water Treatment on OP Pesticides

The weight of evidence from open literature, a registrant-sponsored study, an ORD/EPA laboratory study, and the USGS-EPA reservoir monitoring program show parent OP pesticide residues in water are likely to be transformed during 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 water-treatment plants. Although not all oxons were tracked, the USGS-EPA reservoir study suggests that malathion may have been converted to malaoxon as a result of treatment.

Studies have shown oxons to be relatively stable in chlorinated drinking water for at least 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. These data suggest oxidative degradation products such as oxons, sulfones, and sulfoxides have a high likelihood of occurrence in finished drinking water.

Appendix III.E.4 provides additional detail on removal and transformation of organophosphorus pesticides and certain degradation products through water treatment. The review extends 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.

A complete review of a registrant-sponsored jar test study on the potential effects of chlorination on six OP pesticides and four oxons (Tierney, et al., 2001) was hindered by incomplete information on the experimental procedures (particularly, water quality data, the impact of sodium thiosulfate on water chemistry, storage stability, and clarification regarding 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, chlorpyrifos, diazinon, malathion, and methamidaphos) are transformed in chlorinated drinking water. Chemical oxidation of the organophosphorus compounds led to the formation of oxons for azinphos-methyl, chlorpyrifos, diazinon, and malathion. Chloramines were formed during the experiment, and because chloramines have lower oxidizing potential than hypochlorous acid, the extent of degradation and formation of oxidative degradation products (oxons) may be different under conditions of higher free chlorine concentrations.

e. 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 was 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. Appendices III.E.1 and III.E.2 compare estimated OP concentrations with available local monitoring. Significant trends between estimated concentrations and monitoring are highlighted in the regional assessments in Part II.

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.

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. 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.

3. Drinking Water Assessment Methods

The goal of the cumulative assessment is to aggregate exposure from the 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.

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

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. 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	na
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
Malathion	Malaoxon	Formed by treatment
Methamidophos	None	na
Methidathion	None	na
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	na
Terbufos	Sulfone, Sulfoxide	Combined residues
Tribufos	None	na

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 (Table I.E.1). 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 May 1, 2002, were considered in this assessment. Revisions since the preliminary assessment in December 2001 include exclusion of fenamiphos and azinphos methyl use on cotton, both of which are being voluntarily cancelled.

ii. Transformation Products

Those OP transformation products identified as being of toxicological concern (Table I.E.1) were 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. 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.

Sulfoxide and Sulfone Products: The sulfoxide/sulfone products of disulfoton, phorate, and terbufos are often more persistent and mobile than the parent compounds. Full environmental fate profiles are not available for the sulfoxide/sulfone transformation products, requiring some assumptions to be made about their physicochemical properties. The parent OP and two transformation products were modeled as “total toxic residues”. Formation and decline curves from aerobic soil-metabolism studies 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.

Oxon Products: Table I.E.1 identifies ten OP pesticides which form oxon transformation products. While the oxons are generally not found at significant levels in the environment, available studies suggest they are formed by water treatment – in particular, through chlorination of the parent OP, as noted earlier. Based on the available studies, OPP assumed that oxons were not formed in the environment and, for the most part, would not be found in significant levels in untreated drinking water sources. This assumption was supported by the results of the USGS-EPA reservoir monitoring study, in which oxons were detected in the treated water samples but not in samples taken at the drinking water intake.

Transformation To Another Active OP: Acephate transforms to methamidophos and naled transforms to diclorvos (DDVP). For these pesticides, OPP assumed a conversion from one OP to the other based on the maximum percent transformation from available environmental fate studies. Thus, OPP assumed that 25% of applied acephate transformed

into methamidophos and 20% of applied naled transformed into DDVP. The transformed OP as modeled separately, with an application rate that reflected the appropriate percent conversion of the parent OP (with adjustment for differences in molecular weights). The timing of the simulated “application” was off-set by one half-life period. In the case of acephate, this amounted to two days (e.g., the timing of the formation of 25% methamidophos was simulated as occurring 2 days after acephate was applied). Because the half-life for naled was less than 1 day, the 20% DDVP load was assumed to form on the same day as application.

iii. Accounting for Water Treatment By-Products

Limited scientific evidence (section I.E.d) suggests that many parent OP pesticides may be transformed during drinking water treatment, primarily by oxidation through disinfection. The oxidative transformation products of toxicological concern – sulfones, sulfoxides, and oxons – have been detected in treated water. Limited data suggest that these treatment by-products may be stable for sufficient periods of time (for least 24 to 96 hours) to move through the distribution system.

The information is not sufficient to make quantitative adjustments to the cumulative exposure estimates. OPP estimated maximum potential impacts to determine whether additional information is needed by assuming that all OP parents that form oxons, sulfoxides, or sulfones (see Table I.E.1) are completely transformed into those products as a result of oxidation. Where the transformation is less than complete, and where non-toxic products are also formed, the such an assumption will overestimate drinking water exposure. For a preliminary evaluation, OPP did not assume removal of any of the other OP parent pesticides. OP assumed that the sulfoxide and sulfone products are equal in toxicity to the parent and that the oxon products are ten times more toxic than the parent. A comparison of the RPFs for dimethoate (0.32) and omethoate (0.96), the oxon of dimethoate, suggests that this assumption would be protective. The impacts are addressed in the risk characterization (I.G).

b. Regional Approach for the Cumulative Water Exposure Assessment

The Agency used a regional approach as a first step in addressing the impacts of regional and localized variability in site, environmental, and management practices that effect pesticide concentrations in water. The USDA Farm Resource Region map (Heimlich, 2000) provided a framework for focusing the cumulative assessment (see Appendix III.E.10). By providing general groupings according to similarities in key environmental factors affecting runoff and leaching, such as precipitation, irrigation practices, and soil types, 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 chose a set of locations to represent drinking water sources throughout the US.

Within the regions, drinking water exposure will vary locally due to OP use, agricultural practices, nature and vulnerability of drinking water sources, and weather patterns. Thus, the water exposure assessment focused on one or more specific geographic areas within each region in a manner that would be realistically protective of all sites within the region. OPP selected locations where OPs in drinking water sources are likely to be of concern. If OP levels in water from these vulnerable sites are not major contributors to the total regional cumulative OP exposure, then the Agency can reasonably conclude that drinking water exposures will not be a concern in other, less vulnerable, portions of the region. If drinking water exposure from one or more of these vulnerable sites is a significant contributor to the total cumulative exposure, then additional assessments are necessary to characterize the extent of the potential exposure.

Based on results of the preliminary cumulative risk assessment, OPP has condensed the twelve farm regions into seven regions (Figure I.E-3). Table I.E-2 compares the combined regions with the original regions.

Table I.E-2. New and Old Regions and Representative Vulnerable Sites Used in the Cumulative Water Exposure Assessment

New Region	Old Region	Representative Vulnerable Site
A - Florida	Fruitful Rim, SE (12)	West Palm Beach Co (FL) *
B - Northwest	Fruitful Rim, NW (10)	Willamette Valley (OR) *
C - Arid/Semiarid West	Fruitful Rim, SW (7)	Central Valley (CA) counties of (a) Merced, San Joaquin, Stanislaus * (b) Fresno, Tulare, King, Kern
	Basin & Range (8)	none (Red R. Valley surrogate)
D - Northeast/ Northcentral	Northern Great Plains (3)	Red River Valley (ND/MN) *
	Heartland (1)	Central IL
	Northern Crescent (2)	Southcentral PA
E - Humid Southeast	Southern Seaboard (6), east	Coastal Plain, northern NC *
	Eastern Uplands (5), east section	Western NC
F - Lower Midwest	Prairie Gateway (4)	Central TX Hills *
	Fruitful Rim, TX (11)	Central TX Hills (surrogate)
G - Midsouth	Mississippi Portal (9)	Northeast LA, west-central MS *
	west sections of E. Uplands, S. Seaboard	none

* Scenario used to represent new region in revised OP cumulative risk assessment.

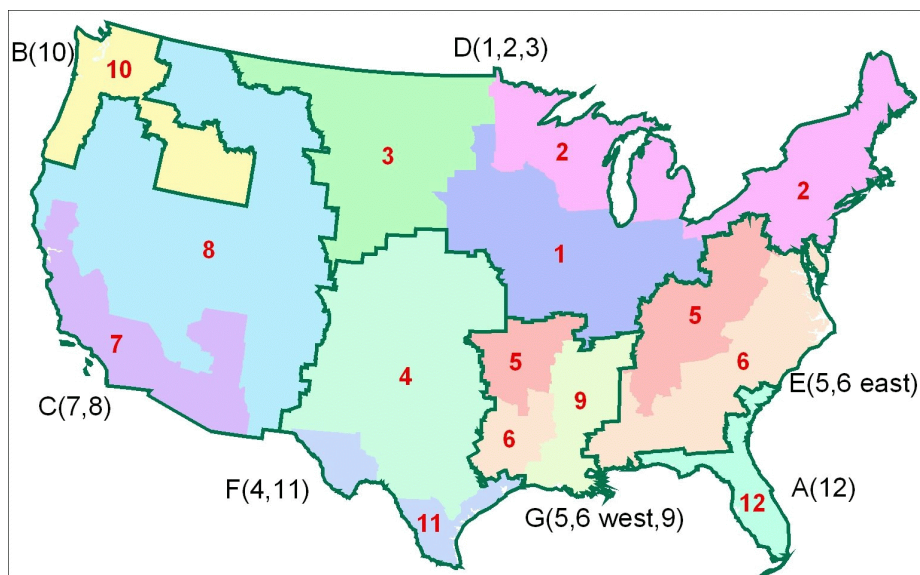


Figure I.E-3. Regions used in OP Cumulative Risk Assessment, based on USDA Farm Resource Regions

c. Selection of Regional Water Exposure Assessment Locations

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).

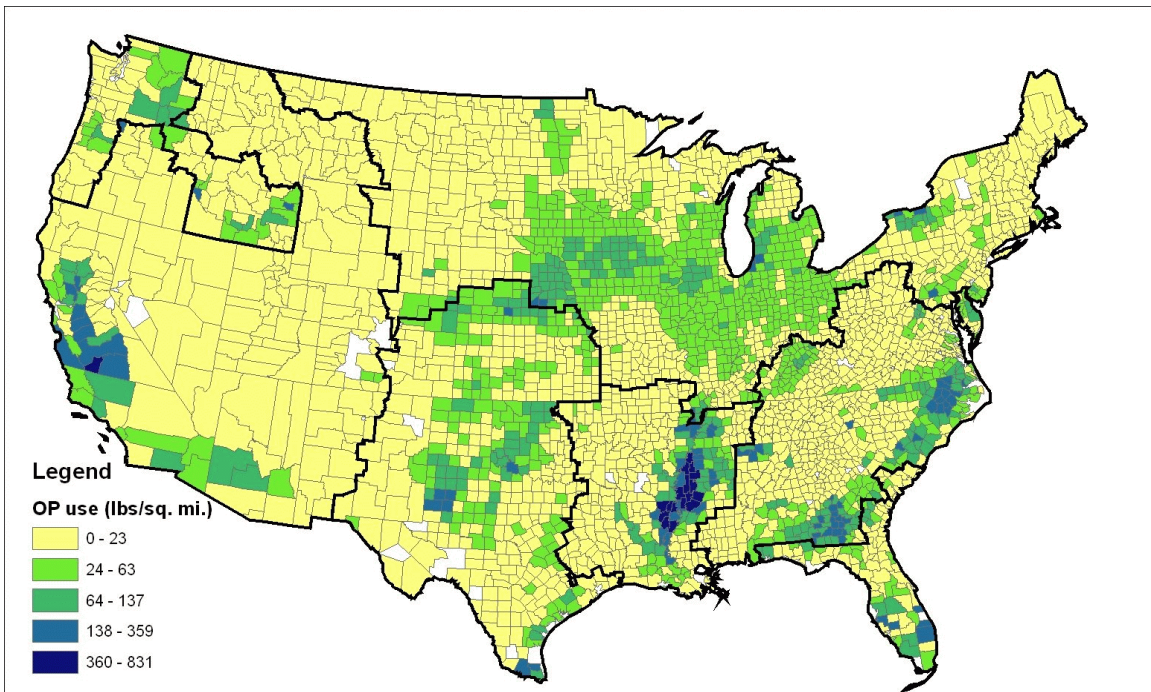


Figure I.E-4. Total organophosphorous (OP) pesticide usage on an area-weighted basis, showing high-use areas in each region.

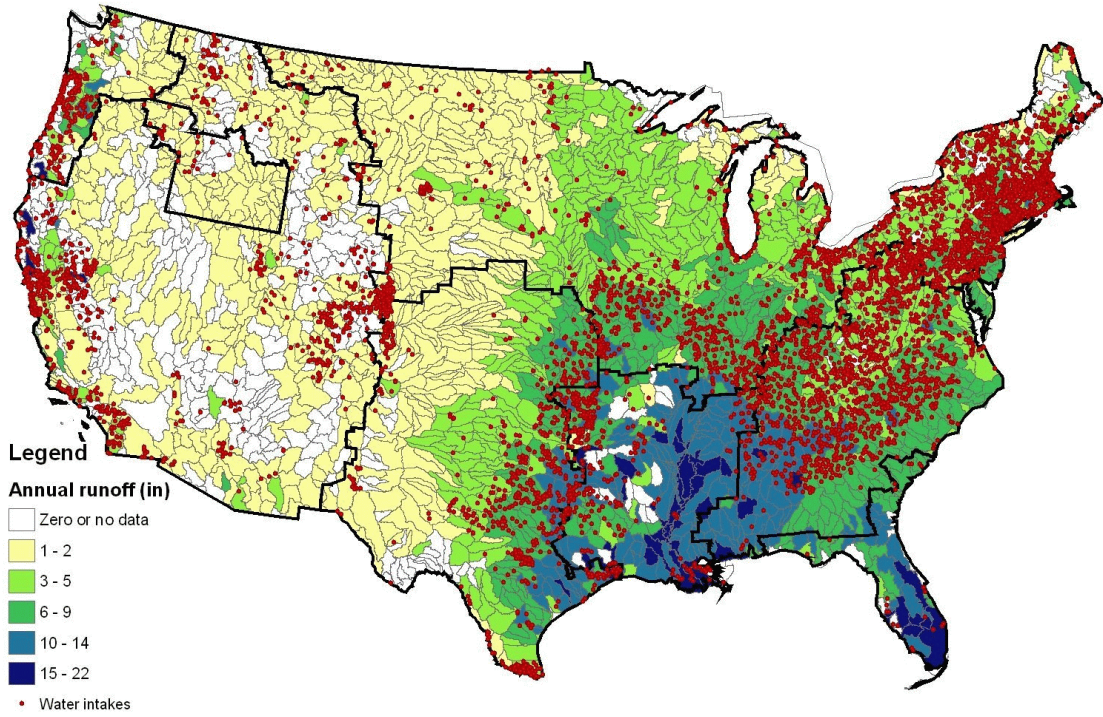


Figure I.E-5. Runoff vulnerability (in/year), adapted from USDA (Kellogg, 1998)

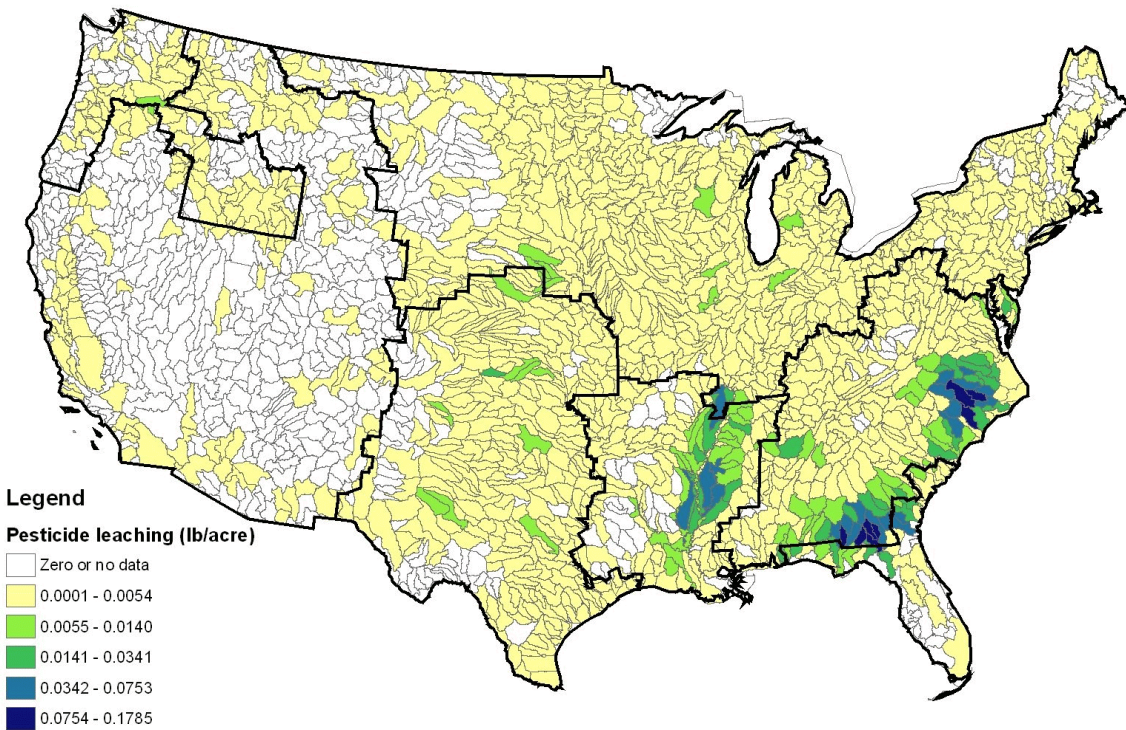


Figure I.E-6. Pesticide leaching vulnerability, adapted from USDA (Kellogg, 1998)

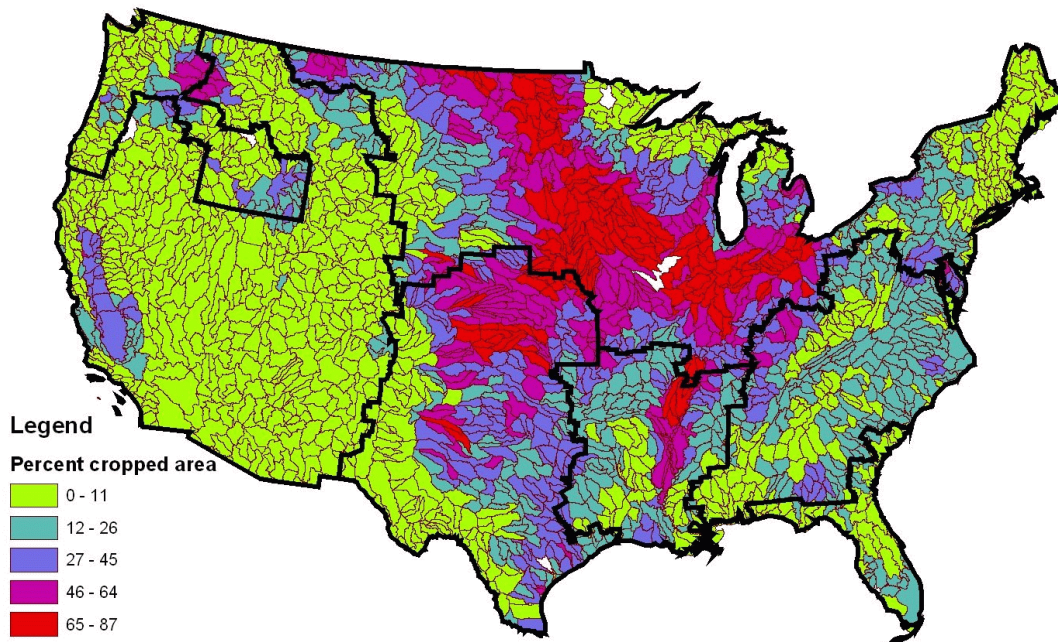


Figure I.E-7. National map w/ Percent Crop Areas by 8-digit HUC

Details of this process are provided in each regional assessment. The Northwest region (Region A) illustrates this process. Three OP-use areas stand out in the region (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. Ground water is the predominant source 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 region in 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.

In the preliminary cumulative risk assessment, OPP selected eleven vulnerable drinking water sources for the drinking water exposure assessment (Table I.E.2). Each of the 12 USDA regions had a representative vulnerable site except for the Prairie Gateway and Texas Fruitful Rim, which shared the same Central TX Hills site, and the Basin and Range, where no

vulnerable sites were identified. In the Central Valley (CA), two sites were identified: (a) Fresno County and south, where OP usage is among the highest in the country, and (b) north of Fresno County, where total OP usage is lower, but surface water sources are more vulnerable to runoff, particularly during the dormant season.

This revised cumulative risk assessment combines several of the regions (Table I.E.2). However, only two combined regions include more than one of the original vulnerable sites. The Northeast/ Northcentral Region (D) includes the original Northern Great Plains (Red River Valley), Heartland (Central IL), and Northern Crescent (Southcentral PA) sites. The Humid Southeast includes the original Southern Seaboard (Eastern NC) and Eastern Uplands (Western NC) sites. OPP compared the estimated cumulative distributions, NAWQA monitoring results, and OP usage to select a single representative site for each of these new regions. Because of the influence of the relative potency factors (RPF) in the cumulative OP loads in water, sites with significant usage and monitoring detections of the higher-RPF pesticides, such as terbufos and phorate, were selected over sites which had higher uses and monitoring detections of lower-RPF pesticides such as chlorpyrifos, diazinon, and malathion. These comparisons are discussed in the regional assessments in Part II.

d. Estimate of 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 distribution of daily 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.

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-through 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.

The cumulative assessment modeling used “typical” application 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.

i. Cumulative Adjustment Factors for Crop Area and OP Use

PRZM is a field-scale model, while the OP cumulative water assessment focuses on watershed-scale impacts (i.e., the contributions of multiple OP uses on multiple crops occurring in multiple fields in a watershed). In individual chemical assessments, PRZM is used to simulate a watershed. In the OP cumulative assessment, the Agency used PRZM to model multiple fields in a watershed. While this approach provides a more realistic depiction of multiple chemical usage in a watershed, it still has limitations. PRZM can simulate multiple fields, but provides no spatial context for those fields. It also assumes that the runoff from each of those fields goes into the reservoir. In other words, each field is assumed to be uniformly distributed in the watershed, with no distinction made between those fields located in the upper reaches of the watershed and those near the reservoir.

To adapt PRZM for this watershed approach, OPP must adjust the estimated pesticide concentrations to account for the portion of the watershed that is treated by a particular OP. This was done using a Cumulative Adjustment Factor (CAF), which accounts for the percentage of the watershed that is planted to a particular crop and the fraction of those acres which receive OP applications.

The CAF accounts for the percent of the location area planted to crops and treated with the corresponding OP pesticides. The CAF 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 was presented to OPP Science Advisory Panel (available through the Agency web site at http://www.epa.gov/scipoly/sap/1999/may/pca_sap.pdf) and is described in an OPP science policy paper (available through the Agency web site at <http://www.epa.gov/oppfead1/trac/science/reservoir.pdf>). 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 (Table I.E-3) 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:

Table I.E-3. Cumulative Adjustment Factor Illustration: Deriving Cumulative OP Percent Crop Area

		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:

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

Table I.E-4. Cumulative Adjustment Factor Illustration: Individual Crop-Pesticide Factors Used for Conversions.

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.

ii. Relative Potency and Safety Factor Adjustments

The resulting CAF-adjusted concentrations for each OP-crop combination must be converted to a concentration equivalent for an index chemical. Once this is done, the concentrations can be combined into a single set of daily distributions (spanning multiple years) for each region. The concentrations were normalized to methamidophos equivalents using the relative potency factor (RPF) and safety factor. This 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.

Factors to convert from individual to cumulative distributions:

$$C_{v(OPx,CROPz)} = C_{(OPx,CROPz)} \times CAF_{(OPx,CROPz)} \times RPF_{(OPx)} \times SF_{(OPx)}$$

where

$C_{v(OPx,CROPz)}$ is the converted concentration for OPx on CROPz

$C_{(OPx,CROPz)}$ is the raw PRZM/EXAM daily concentration

$CAF_{(OPx,CROPz)}$ is the cumulative adjustment factor

RPF is the Relative Potency Factor

SF is the FQPA Safety Factor

e. Pesticide Usage Information

The estimated OP cumulative distributions in each region are based on typical application rates and numbers of applications (taken as the average of rates reported in pesticide usage summaries). The timing of pesticide applications was based on label specifications (e.g., apply at plant, at harvest, at blossom) and locally-derived windows of use based on crop profiles.

USDA National Agricultural Statistics Service (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.

i. Typical Pesticide Use (Rate and Frequency)

For regions exclusive of the Arid/Semiarid West, the primary sources of information for percent crop treated, number of applications, and amount of active ingredient applied are 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.

NASS data were 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.

OPP used the average application rate reported in the NASS summaries to represent the typical application rate for each OP-crop combination in a region. Likewise, OPP used the average number of applications to determine how many times the OP pesticide would be applied to the crop in a particular year. These rates were frequently less than the maximum allowable application rates and frequencies specified on the label. A comparison of OP cumulative distributions estimated by typical and maximum label rates in three regions found that use of all maximum rates generates concentrations that are one to four times greater than those estimated using typical rates (see I.G. and Appendix III.E.11 for detailed analysis). In reality, it is unlikely that all OP pesticides would be used on all crops at maximum rates in the same year. Thus, the difference between OP cumulative loads in a "typical" year and in a year when intense pest pressure requires maximum label rates for one or more OP pesticide on one or more crops is likely to be less than the one- to four-times estimated.

ii. Timing of Pesticide Application(s)

An application window has been established for each of the OP pesticide crop uses reported in each region. 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. Agrottrak™ 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 North Carolina:

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

When most active periods are not provided, the single application date for a pesticide is set at 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 Northeast (Pennsylvania):

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

Because the application dates are held constant through a series of years of weather patterns, variations in the selected date may affect the estimated peak concentrations. Relatively high pulse loads from runoff may occur if application events are closely followed by runoff-producing

rains. However, a comparison of OP cumulative distributions resulting from varying the application dates found that notable differences only occur at the very highest concentrations that distributions at the 99th percentile only vary by a factor of 2 or less (see I.G. and Appendix III.E.11 for discussion).

OPP assumed that the entire application of a given pesticide on a given crop occurred on the same day. Except in Region C, where detailed pesticide use reports from California Department of Pesticide Regulations were available, sufficient usage information was not available to split applications. While this is likely to result in conservative (health-protective) estimates, the assumption is not unreasonable in the smaller, more vulnerable watersheds represented by the index reservoir. A comparison of estimated OP cumulative distributions using split- and single-applications in Region C found a difference of less than a factor of two across the distribution profile (see I.G and Appendix III.E.11 for discussion).

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.

iii. Use of CDPR Use Information in Region C

For the Central Valley (CA), used in Region C, 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.

Evaluations of CDPR and NASS usage information in California found no routine under- or over-estimation of pesticide usage from the survey methods used by NASS. A comparison of OP cumulative distributions generated using both data sources found that the distributions generated with the more complete CDPR information were greater than those generated with the NASS survey data by a factor of 3 (see Appendix III.E.11 for comparison).

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.

For each vulnerable site, OPP developed a site-specific scenario for each crop group with reported OP usage (see Appendix III.E.7a and b for a description of scenario development and documentation). Thus, the site and soil characteristics are representative of those that actually occur in the region and support that particular crop growth.