

Comparison of Regulatory Estimates of Drinking Water Concentrations with Monitoring Data

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Currently, regulatory practice in the United States is to estimate potential concentrations in drinking water from surface water by using an index reservoir scenario. This approach extrapolates results from the modeling of a single field with maximum application rates to the watershed scale, based on a percent crop area estimate. Since 1998, Bayer CropScience and its predecessor companies have conducted drinking water monitoring studies with a number of different compounds. The results from these studies show that the index reservoir scenario greatly overpredicts residues in surface water. The most important factor is the overestimation of use within a watershed. Other factors contributing to the overestimation of concentrations are the conservative procedures used to obtain the chemical fate related input parameters and the simplified hydrology. A new procedure based on the USGS WARP model, being developed by a group of scientists from the EPA, USGS, USDA, and industry, will provide more realistic estimates of concentrations of pesticides and their metabolites in drinking water.

KEYWORDS: Modeling; drinking water; aldicarb; bromoxynil; carbaryl; ethoprophos

INTRODUCTION

In 1997 Rhône-Poulenc Ag Co. (a predecessor company to Bayer CropScience) began evaluating the expected dietary exposure of a number of its compounds to prepare for the re-registration process. The results of these assessments indicated that the standard EPA assessments for estimating the contribution of drinking water from surface water were overly conservative, often filling the risk cup, and at this time EPA began requiring drinking water studies as a condition of re-registration. Therefore, a number drinking water monitoring programs of community water systems drawing from surface water have been initiated in the past six years. This paper compares the results of four of these monitoring studies with EPA estimates of potential exposure produced via surface water modeling during re-registration.

MATERIALS AND METHODS

The drinking water monitoring studies were conducted with four compounds: aldicarb, bromoxynil, carbaryl, and ethoprophos. Each of the studies involved regular collection of raw and finished water samples from community water systems using surface water. Finished samples were analyzed when detectable concentrations were found in the raw water samples (or in the bromoxynil study, when concentrations exceeded the level of quantitation). In some limited instances, finished water samples were analyzed when residues were not found in raw water, for example, as part of quality assurance programs.

Registrant sales data were used to select community water systems with the highest use intensity watersheds in various regions.

Aldicarb. This three-year study was initiated at 28 community water systems (**Table 1**) in December 2000 through the spring of 2001 (depending on the location) and was conducted voluntarily by the registrant. Samples were collected weekly during and after the application season and monthly at other times of the year.

Bromoxynil. This two-year study was initiated at 16 community water systems (**Table 2**) in the spring of 1998. The study was started voluntarily by the registrant, but the EPA later made it a condition of re-registration. Samples were collected every two weeks during and after the application season and monthly or quarterly at other times of the year.

Carbaryl. This three-year study was initiated at 20 community water systems (**Table 3**) in 1999 and was conducted voluntarily by the registrant. Sixteen of the community water systems had watersheds located in agricultural use areas, whereas four of the community water systems had watersheds draining urban and suburban areas in the south, where the intensity of homeowner use is highest. Samples were collected from the agricultural sites weekly during and after the application season and then monthly at other times of the year. The urban sites were sampled weekly throughout the year.

Ethoprophos. This three-year study was initiated at five community water systems (**Table 4**) in 2002, and the first two years of results are included in this paper. The study was conducted as a condition of re-registration. Samples were collected weekly during and after the application season and then monthly at other times of the year.

In the bromoxynil and carbaryl studies, analyses were for parent compound. In the aldicarb study, the analyses were for the three carbamate compounds (aldicarb, aldicarb sulfoxide, and aldicarb sulfone). The analytical method for ethoprophos included parent and four metabolites; however, the metabolites will not be discussed in this paper because the EPA did not model the concentrations of these four metabolites in drinking water from surface water. Analytical methods (HPLC-MS/MS for aldicarb, carbaryl, and ethoprophos; and GC-MS

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Table 1. Summary of Results for the Aldicarb Monitoring Study by Sampling Location

site	major uses	max concn ^a (ppb)						TWA concn ^b (ppb) in finished water		
		raw water			finished water			1999	2000	2001
		1999	2000	2001	1999	2000	2001			
Belle Glade City, FL	citrus	ND ^c	ND	ND	NA ^d	NA	NA	0.012	0.012	0.012
Bradenton City, FL	citrus	0.098	0.063	0.059	0.092	0.075	0.075	0.041	0.036	0.036
Okeechobee City, FL	citrus	ND	ND	ND	ND	NA	NA	0.012	0.012	0.012
Punta City, FL	citrus	0.333	0.221	0.223	0.241	0.156	0.137	0.068	0.068	0.050
West Palm Beach, FL	citrus	ND	ND	ND	ND	NA	NA	0.012	0.012	0.012
Alva City, FL	citrus	0.149	0.072	0.150	0.091	0.048	0.019	0.026	0.015	0.012
Robert Lee, TX	cotton	ND	e	e	NA	e	e	0.012	e	e
Spur, TX	cotton	ND	ND	ND	ND	NA	NA	0.012	0.012	0.012
Waynesboro, GA	peanuts, cotton	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Port Wentworth, GA	peanuts, cotton	ND	ND	ND	ND	NA	NA	0.012	0.012	0.012
Enfield, NC	peanuts, cotton	0.170	ND	0.047	0.062	NA	0.039	0.013	0.012	0.012
Greenville, NC	peanuts, cotton	0.263	0.022	0.676	0.118	0.016	0.177	0.018	0.012	0.019
Wilson, NC	peanuts, cotton	0.042	0.030	0.622	0.032	0.031	0.127	0.013	0.013	0.016
Lumberton, NC	peanuts, cotton	0.019	ND	0.050	0.019	NA	0.026	0.017	0.012	0.012
Hanahan, SC	cotton	ND	ND	ND	NA	NA	ND	0.012	0.012	0.012
Bennettsville, SC	cotton	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Florence, AL (Wilson Lake)	cotton	0.028	0.092	0.030	0.018	0.030	0.018	0.012	0.012	0.012
Florence, AL (Cypress Creek)	cotton	0.018	ND	0.019	0.024	NA	0.016	0.012	0.012	0.012
Weiser, ID	potatoes	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Hermiston, OR	potatoes	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Richland, WA	potatoes	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Norfolk, VA	peanuts	ND	ND	0.083	NA	NA	0.024	0.012	0.012	0.013
Monroe, LA	cotton	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Ferriday, LA	cotton	ND	ND	0.018	NA	NA	ND	0.012	0.012	0.012
Newellton, LA	cotton	ND	ND	ND	NA	NA	ND	0.012	0.012	0.012
Brentwood, CA	potatoes	0.015	ND	ND	ND	NA	NA	0.012	0.012	0.012
Lynda Shaw, VA	peanuts	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012
Albert Montilla, CA	cotton	ND	ND	ND	NA	NA	NA	0.012	0.012	0.012

^a Sum of concentrations measured for aldicarb, aldicarb sulfoxide, and aldicarb sulfone. Values of each analyte below the detection limit were considered to be half the detection limit. Therefore, a sample with no detectable residue was considered to have a concentration of 0.0115 ppb (rounded to 0.012 ppb in this table). ^b Annual time-weighted concentration; finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit. ^c Not detected. ^d No finished samples analyzed due to aldicarb carbamate residues not being detected in raw water samples. ^e Samples were collected for only one year at this location.

Table 2. Summary of Results for the Bromoxynil Monitoring Study by Sampling Location

site	major uses	max concn (ppb)				TWA concn ^a (ppb) in finished water	
		raw water		finished water		1998	1999
		1998	1999	1998	1999		
Juliaetta, ID	small grains	0.033	0.006	0.007	NA ^b	0.005	0.002
Ontario, OR	small grains	0.018	0.020	NA	0.011	0.004	0.003
Valley City, ND	small grains	0.112	0.010	ND ^c	NA	0.005	0.004
Mayville, ND	small grains	0.030	0.078	0.011	0.110	0.004	0.009
Park River, ND	small grains	0.059	0.011	0.041	0.005	0.011	0.003
Des Moines, IA	corn	0.083	0.089	0.019	0.028	0.005	0.005
Winterset, IA	corn	0.383	0.067	0.019	ND	0.002	0.002
Elgin, IL	corn	0.012	0.009	NA	ND	0.003	0.002
Hudson, IL	corn	0.010	0.020	NA	0.008	0.002	0.003
Horton, KS	corn	0.133	0.023	0.005	0.014	0.004	0.003
Ferriday, LA	cotton	0.011	0.019	NA	ND	0.003	0.003
Gramercy, LA	cotton	0.029	0.026	NA	0.006	0.005	0.003
Monroe, LA	cotton	0.009	ND	NA	NA	0.003	0.002
Newellton, LA	cotton	0.006	0.012	NA	NA	0.002	0.003
Greenville, NC	cotton	0.005	0.006	NA	NA	0.002	0.002
Wilmington, NC	cotton	0.007	ND	NA	NA	0.003	0.002

^a Annual time-weighted concentration, finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit. ^b No finished samples analyzed due to bromoxynil residues not being above the limit of quantitation in raw water samples. ^c Not detected.

for bromoxynil) were developed that allowed detection of all of these compounds at concentrations below 0.01 $\mu\text{g/L}$. Detection limits of the specific analytes are provided in **Table 5**. When compounds were not stable in raw or finished water due to the impact of pH or chlorine, additives were added to stabilize the samples.

In the processing of data, all values above the limit of detection were considered to be the actual values. However, larger uncertainty is associated with values below the limit of quantification. Analytical

results below the limit of detection were considered to have nondetectable residues (below the limit of detection, residues cannot be reliably distinguished from baseline noise). In the calculation of time-weighted values, nondetectable residues were considered to have a concentration of half the detection limit. An analysis at a specific sampling time was considered to represent the time interval starting halfway between the previous sampling time and the sampling time until halfway between the sampling time and the following sampling

Table 3. Summary of Results for the Carbaryl Monitoring Study by Sampling location

site	major uses	max concn (ppb)						TWA concn ^a (ppb) in finished water		
		raw water			finished water			1999	2000	2001
		1999	2000	2001	1999	2000	2001			
Manatee, FL	citrus	0.009	0.003	0.025	0.011	ND ^b	0.019	0.001	0.001	0.003
West Sacramento, CA	orchards, nuts	0.003	0.024	0.014	0.003	0.010	0.009	0.001	0.001	0.001
Lodi, CA	orchards, nuts	0.012	0.031	0.004	0.004	0.007	ND	0.001	0.001	0.001
Riverside, CA	grapes, tree crops	0.008	ND	ND	ND	NA ^c	NA	0.001	0.001	0.001
Lake Elsinore, CA	citrus	ND	0.003	0.006	NA	NA	ND	0.001	0.001	0.001
Corona, CA	citrus	ND	ND	ND	NA	NA	NA	0.001	0.001	0.001
Beaumont, TX	various agricultural	ND	ND	ND	NA	NA	NA	0.001	0.001	0.001
Point Comfort, TX	rice, tree crops	0.018	0.005	ND	ND	ND	NA	0.001	0.001	0.001
Penn Yan, NY	grapes, apples	ND	0.023	ND	NA	ND	NA	0.001	0.001	0.001
Westfield, NY	grapes, apples	0.021	0.005	ND	ND	0.009	NA	0.001	0.001	0.001
Jefferson, OR	vegetables, strawberries	ND	0.010	0.004	NA	ND	ND	0.001	0.001	0.001
Coweta, OK	pecans	0.004	ND	ND	ND	NA	NA	0.001	0.001	0.001
Pasco, WA	apples, potatoes	0.002	0.003	ND	ND	ND	NA	0.001	0.001	0.001
Manson, WA	apples	ND	ND	ND	NA	NA	NA	0.001	0.001	0.001
Deerfield, MI	vegetables	0.010	0.004	0.022	0.160	ND	0.004	0.005	0.001	0.001
Brockton, MA	cranberries	0.031	0.027	ND	ND	0.003	NA	0.001	0.001	0.001
East Point, GA	home and garden	0.018	0.018	0.013	0.003	0.008	ND	0.001	0.001	0.001
Midlothian, TX	home and garden	0.014	ND	0.014	ND	NA	ND	0.001	0.001	0.001
Cary, NC	home and garden	0.004	ND	ND	ND	NA	NA	0.001	0.001	0.001
Birmingham, AL	home and garden	0.023	0.035	0.040	ND	ND	0.032	0.001	0.001	0.002

^a Annual time-weighted concentration; finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit. ^b Not detected. ^c No finished samples analyzed due to carbaryl residues not being detected in raw water samples.

Table 4. Summary of Results for the Ethoprophos Monitoring Study by Sampling Location

site	major uses	max concn (ppb)				TWA concn ^a (ppb) in finished water	
		raw water		finished water		2002	2003
		2002	2003	2002	2003		
Jefferson, OR	vegetables	ND ^b	ND	NA ^c	NA	0.002	0.002
Ontario, OR	potatoes	ND	ND	NA	NA	0.002	0.002
Lodi, CA	potatoes	ND	ND	NA	NA	0.002	0.002
Franklin, LA	sugar cane	ND	ND	ND	ND	0.002	0.002
Wilson, NC	tobacco, sweet potatoes	0.009	0.012	ND	ND	0.002	0.002

^a Annual time-weighted concentration; finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit. ^b Not detected. ^c No finished samples analyzed due to the absence of ethoprophos residues in raw water samples.

Table 5. Sensitivity of the Analytical Methods Used in the Drinking Water Monitoring Studies

analyte	limit of detection ($\mu\text{g/L}$)	limit of quantitation ($\mu\text{g/L}$)
aldicarb	0.007	0.021
aldicarb sulfoxide	0.009	0.027
aldicarb sulfone	0.007	0.021
bromoxynil	0.004	0.030
carbaryl	0.002	0.030
ethoprophos	0.003	0.009

time. Because the source of dietary exposure is finished drinking water, time-weighted averages have been calculated with the concentrations measured in finished water. At time points when finished samples have not been analyzed, values for raw water have been used.

RESULTS

The results of the four monitoring studies are summarized by sampling location in **Tables 1–4**, and overall statistics are summarized in **Table 6**. Although residues of the target compound were found in all four studies, the concentrations are substantially below guideline levels [maximum contaminant level (MCL) or health advisory level (HAL)] or, in the absence of guidelines, concentrations that could cause any health effects [based on a drinking water level of comparison (DWLOC)]. In

general, concentrations in finished water were equal to or less than concentrations in raw water. However, in some cases residues in finished water were higher than in raw water due to rapidly changing concentrations in raw water and the residence time in the treatment system.

DISCUSSION

Daily concentrations are applicable for risk assessments for aldicarb, carbaryl, and ethoprophos, whereas annual time-weighted concentrations are applicable for bromoxynil. However, this paper compares regulatory predictions and monitoring results for both daily values and annual time-weighted averages for each of the four compounds.

Regulatory estimates come directly from assessments performed by the EPA for the compounds as part of the re-registration process. These assessments were based on the EPA's standard index reservoir scenario, which is evaluated using PRZM and EXAMS. The index reservoir is a reservoir of specified dimensions, independent of location. Pesticide inputs are determined on the basis of a simulation of a single field of a vulnerable soil type in the use area being evaluated, assuming worst-case spray drift assumptions (unless the product is applied as a granule). The compound is assumed to be applied at the maximum application rate and for the maximum number of applications with the minimum spacing between applications.

Table 6. Overall Summary of Results for the Monitoring Studies

	aldicarb	bromoxynil	carbaryl	ethoprophos
no. of sites in study	28	16	20	5
no. of sites with residues in raw water	12	16	17	1
no. of sites with residues in finished water	10	10	8	0
no. of raw water samples ^a	2120	495	2186	233
no. of raw water samples with detectable residues ^a	287	166	168	2
no. of raw water samples with residues greater than LOQ ^a	177	23	5	2
max concn observed in raw water samples (ppb)	0.68	0.38	0.040	0.012
no. of finished water samples ^a	306	48	183	30
no. of finished water samples with detectable residues ^a	255	26	38	0
no. of finished water samples with residues greater than LOQ ^a	164	3	2	0
max concn observed in finished water samples (ppb)	0.24	0.11	0.16	ND ^b
max TWA concn ^c (ppb)	0.07	0.01	0.005	0.002

^a Replicate samples and analyses are not included. ^b No residues detected in finished samples. ^c Annual time-weighted concentration; finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit.

Table 7. Comparison of EPA Predictions with Monitoring Data

compd	max concn (ppb)		maxi TWA concn ^a (ppb)	
	predicted ^b	obsd	predicted ^b	obsd
aldicarb	0.95–17	0.24	0.17–5.8	0.07
bromoxynil	11	0.11	0.2	0.01
carbaryl	47–745	0.16	1.9–31	0.005
ethoprophos	15–127	ND (<0.003)	2.6–13	ND (<0.003)

^a Annual time-weighted concentration; finished values substituted for raw water values when available. Values below the detection limit were considered to be half the detection limit. ^b Predictions based on the index reservoir scenario. The range of values represents the maximum for different crops.

The mass flow at the edge of the field is directly introduced into the reservoir, after adjustment for the percent area of the watershed considered to be planted to the relevant crop. The default value used for minor crops is 87%, with a somewhat lower value used for major crops such as corn, soybeans, and cotton.

In some of the assessments for the four compounds, the EPA made nonstandard assumptions that reduced the calculated concentrations. For example, for bromoxynil the EPA calculated the 30 year time-averaged value rather than the 90th percentile of 30–40 yearly time-weighted average concentrations. For aldicarb, the EPA reviewer decided to use degradation rates based on the extensive field data rather than the considerably slower degradation rates obtained in laboratory studies.

Table 7 compares the daily and yearly time-weighted average concentrations predicted using the index reservoir scenario with the concentrations measured in the monitoring studies. In general, the regulatory estimates are 1–4 orders of magnitude higher than observed in the monitoring study. The overestimation is not limited to the maximum concentration, but extends to a major portion of the distribution curve of daily values. For example, the index reservoir scenario predicts detectable residues of carbaryl in about half of the samples, whereas detectable residues were observed in raw water <10% of the time and in drinking water <5% five percent of the time (**Table 8**). Because the distributions from the monitoring studies were not corrected to account for the increased sampling frequency during times when residues were most likely to be present, these distributions overestimate the percent of time that residues are present.

One of the most important causes of overprediction of residues using the index reservoir scenario is the regulatory assumption of use in the watershed. The area of the crop in the watershed is assumed to correspond to the watershed with the highest percent of the specific crop in the region. The market share of the product is assumed to be 100% (that is, all of the

Table 8. Carbaryl Residue Distributions of Daily Values for Predicted and Observed Concentrations

case	concn (ppb) at designated percentile					
	50	70	90	95	99	max
predicted for oranges ^a	<0.001	0.018	20.4	44.6	140	745
predicted for apples ^a	0.002	0.040	3.22	7.66	14.6	66.2
observed in raw water	ND ^b	ND	ND	0.003	0.017	0.040
observed in raw and finished water ^c	ND	ND	ND	ND	0.005	0.16

^a Predictions based on the index reservoir scenario. ^b Not determined. ^c Finished values substituted for raw water values when available.

crop in the watershed is treated). Also, all applications are assumed to be at the maximum rate and maximum number of applications permitted on the label. As a consequence of these assumptions, use estimates >2 orders of magnitude higher than actual values are often assumed in the regulatory estimates. Use intensity (mass of active ingredient applied divided by watershed area) is one of the most important variables affecting concentrations in surface water (*I*), so an overestimation of the use intensity results in a corresponding overprediction in the concentration estimates.

Overprediction of residues also results from other sources. The compound environmental fate parameters used in the index reservoir scenario are conservative, and high values are assumed for spray drift, including that the edge of the reservoir is assumed to be 1 m from the edge of the field. Spray drift input is maximized by assuming applications occur on the same day throughout the watershed, and all drift is assumed to be toward the reservoir, regardless of the direction of the wind. The index reservoir uses a simplified hydrology, which assumes that all edge of field runoff is directly and immediately introduced into the reservoir, so field margins do not reduce runoff and no degradation occurs in the streams and ditches leading to the reservoir. Also, the regulatory estimates assume no losses occur during the water treatment processes.

Recognition of the overprediction of residues in drinking water from surface water has resulted in a desire to develop a procedure that will result in more realistic estimate for parent compounds and their metabolites. Therefore, a new procedure based on the USGS WARP model (*I*) is being developed by a group of scientists from the EPA, USGS, USDA, and industry.

WARP is a regression model based on data mainly from the USGS NAQWA program, but also includes a few data sets from academia and industry monitoring programs. A variety of single-compound and multiple-compound models have been developed. For the example in this paper, a multichemical model based on

Table 9. Comparison of 95th Percentile Concentrations Estimated with the Index Reservoir Scenario and WARP with the Concentrations Observed in the Carbaryl Monitoring Study

case	95th percentile value for carbaryl (ppb)
index reservoir scenario	8–45 ppb ^a
WARP	0–0.66 ppb ^b
all values from monitoring study	ND ^c
individual sites in the monitoring study	ND–0.008 ppb ^d

^a Range of values represent the maximum for different crops. ^b Range of values represent the maximum for different watersheds. ^c One value for each sample date per location; finished values substituted for raw water values when available. ^d Range of the 95th values at each of the 20 sites; one value for each sample date per location; finished values substituted for raw water values when available.

the atrazine single-compound model was used. The model provides equations for estimating the mean values for the annual time-weighted average concentration, 5th, 10th, 15th, 25th, 50th, 75th, 85th, 90th, and 95th percentiles of the concentration distribution along with the standard deviation around the mean (this reflects both temporal and spatial variability). Currently, WARP is applicable only to flowing streams and rivers, but an extension to reservoirs is being considered.

The implementation of WARP into risk assessment includes a number of associated features:

- a procedure for estimating use of specific compounds in specific watershed;
- watershed boundaries for 1600 community water systems drawing water from flowing streams; and
- procedures for estimating daily values of parent compounds and metabolites for aggregate and cumulative dietary assessments.

One of the main advantages of the WARP procedure over the index reservoir is that watershed-specific estimates can be made for each of the 1600 flowing stream watersheds using watershed-specific estimates of product use. Another advantage is that the model is regression-based, so the values should be in the range of what is actually observed. Using a regression-based model eliminates the need for the simplified hydrology assumed in the index reservoir scenario.

A comparison of the predictions of WARP with those of the index reservoir scenario and the observed results of the carbaryl

monitoring study is shown in **Table 9**. The WARP predictions used in this comparison were the individual estimates for the 1600 flowing stream watersheds. This comparison indicates that the WARP estimates are considerably lower than those obtained from the index reservoir scenario but that they are higher than those actually observed in finished drinking water. One factor contributing to the higher values from WARP is that WARP does not consider losses during drinking water treatment. Therefore, WARP seems to be a more realistic approach than the index reservoir scenario but still conservative with respect to actual finished water monitoring data.

CONCLUSIONS

A comparison of regulatory modeling predictions with results of drinking water monitoring show that regulatory modeling procedures overestimate residues in drinking water, usually by 1–4 orders of magnitude.

The magnitude of the overprediction resulting from current modeling procedures shows the importance of developing and implementing improved tools and modeling procedures. One example of a promising approach is the implementation of the WARP model for developing daily values for drinking water.

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