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**REPORT:**

**FIFRA Scientific Advisory Panel Meeting, September 29,  
2000, held at the Sheraton Crystal City Hotel,  
Arlington, Virginia**

*Session VI- A Set of Scientific Issues Being Considered by  
the Environmental Protection Agency Regarding:*

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

**Mr. Larry Dorsey**  
**Designated Federal Official**  
**FIFRA/Scientific Advisory Panel**  
**Date:\_\_\_\_\_**

**Mary Anna Thrall, D.V.M**  
**Session Chair**  
**FIFRA/Scientific Advisory Panel**  
**Date:\_\_\_\_\_**

**Federal Insecticide, Fungicide, and Rodenticide Act  
Scientific Advisory Panel Meeting  
September 29, 2000**

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

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**PUBLIC COMMENTS**

**Oral statements were received from:**

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None

## **INTRODUCTION**

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), Scientific Advisory Panel (SAP) has completed its review of the set of scientific issues being considered by the Agency regarding the review of issues pertaining to estimating pesticide concentrations in drinking water and assessing water treatment effects on pesticide removal and transformation. Advance public notice of the meeting was published in the Federal Register on September 5, 2000. Agency presentations were made by Nelson Thurman, Dr. James Hetrick, Dr. Rodolfo Pisigan and Dr. Ronald Parker. The review was conducted in an open Panel meeting held in Arlington, VA, on September 29, 2000. The meeting was chaired by Mary Anna Thrall, D.V.M. Larry Dorsey served as the Designated Federal Official.

## **The Charge to the Panel**

### **REGRESSION MODELING**

- Question 1.1** What new directions or approaches for modeling are suggested by the new results presented here?
- Question 1.2** Do the model enhancements being undertaken present useful steps forward in the model development process? What other enhancements can the panel identify that would further improve the accuracy or usability of the models under development?
- Question 1.3** What recommendations do the panel have concerning issues regarding the design of a monitoring program to collect data to advance regression model development? What issues of selection of pesticides, soil types, region, weather, timing, etc., merit special attention?
- Question 1.4** What level of accuracy is reasonable for the Agency to generally expect from distributions of concentrations predicted by regression-equation based computer models after further development? Is it unreasonable to expect that we will be able to be within a factor of 2 for individual sites or for the entire distribution? What level of accuracy might we realistically expect ?

## DRINKING WATER TREATMENT EFFECTS

- Question 2.1** Coagulation-flocculation, sedimentation, and filtration processes in conventional water treatment are not effective in removing certain pesticides belonging to triazine, acetanilide, carbamate, and urea derivative classes. What relationships exist between the physical/ chemical properties of other pesticide classes and these water treatments?
- Question 2.2** Some pesticides, including carbamates and organophosphates, with hydrolysis half-lives of less than 1 day in alkaline (pH 9) water are observed to be “removed” during lime-soda softening (pH 10~11) by alkaline hydrolysis. Can this observation be generalized in predicting whether a pesticide with alkaline abiotic hydrolysis half-life of less than 1 day will be “removed” through water treatment? What other classes of pesticides may be removed or transformed by water softening and in what manner?
- Question 2.3** During disinfection with chlorine, pesticides such as organophosphates can be oxidized to form toxic degradation products. What other classes of pesticides may be transformed by disinfection processes to form toxic byproducts? What issues related to pesticide transformation should OPP be aware of?
- Question 2.4** Laboratory jar tests are often employed to determine if a regulated contaminant, including some pesticides, in raw water can be removed by a given treatment process. What are the advantages and disadvantages of using results of jar tests as the basis for evaluating whether the pesticide will be eventually removed in the actual water treatment plant? How might these results be used to adjust raw water concentrations for use in human health risk assessment?
- Question 2.5** Many factors, such as raw water composition, water treatment method, and treatment plant conditions, can affect the removal of pesticides. What issues should OPP be considering in determining whether it is possible to accurately predict the percent removal and transformation of pesticides among different water treatment plants?
- Question 2.6** The preliminary literature review indicates that coagulation-flocculation, sedimentation, and conventional filtration are not effective in pesticide removal for many types of classes of pesticides. Effective removal of some pesticides has been observed with activated carbon adsorption (GAC and PAC), softening, disinfection, membrane treatments, and in some cases air-stripping. What additional water treatment data from other studies, which either support or are

inconsistent or contradict the data presented in the preliminary literature review, should OPP consider?

**Question 2.7** Based on this technical review, OPP is leaning toward an interim approach to address the impacts of water treatment on a case-by-case, pesticide-specific basis in its human health risk assessment. OPP expects that for most pesticides, however, available data will not be sufficient to establish the impacts of treatment. Accordingly, as a practical matter it, is very likely that until pesticide-specific treatment data are generated, OPP will be using raw or untreated drinking water estimates in human health risk assessments under FQPA. Given the objective of estimating pesticide concentrations in drinking water, does the SAP believe that the state-of-the-science supports this approach? If not, how would an approach be developed based on the state of knowledge about the impact of treatment on pesticides?

**Question 2.8** The effects of water treatment on pesticide residues in drinking water can be assessed by regression modeling of important parameters with removal efficiency, experimental or laboratory studies, and actual field monitoring. What other approaches or methods can be used to assess water treatment effects? What are the pros and cons of these methods?

## **PANEL RESPONSE TO THE CHARGE**

### **REGRESSION MODELING**

**Question 1.1** What new directions or approaches for modeling are suggested by the new results presented here?

The Panel was in general agreement that the regression modeling approach being used by EPA and USGS is fundamentally sound. The following suggestions for improvements were offered:

1. There is a use for modeling in the type of decision-making being done by OPP. The Agency is to be commended for exploring the possibilities of improving models. However, there is a point where one has to admit that the data needed to make the model more realistic is unlikely to arise from work that will be submitted for approval.

Clearly, to improve on the present circumstance, models have to be developed on a watershed basis. Pesticides are applied locally, not nationally. Weather patterns that mobilize these pesticides to a drinking water source will vary by locality. The drinking water systems that draw water from those sources may also vary considerably in the treatment processes that they employ, particularly if the sources are rivers. Furthermore, there is the possibility of preferential flow in reservoirs at different localities in different times of the year, so that the assumption of uniform mixing could result in low estimates rather than high estimates.

The behavior of the Index Water Reservoir in two different years illustrates this point. In Figure 1 (see addendum) the concentrations of atrazine found in reservoirs in Table 1 of Document #2 are plotted against the drainage area/normal capacity ratio. The first point is that there is no consistent relationship here. The second is that the Index Reservoir had one of the lowest mean concentrations in 1995 (Table 11), while it had the highest in 1996. Clearly, there is something about the use of atrazine (amounts or patterns), the weather patterns in this watershed, the rate at which the reservoir water was turning over (i.e., residence time), or some other variables that are not being taken into account or that influenced these results. Clearly, there is more scatter in these data at the lower ratios, and that is what needs to be taken into account. If it were not for one extreme point, one could have easily made the conclusion that it is the large reservoirs that should be used in these models.

The main concern is that models will be “corrected” on the basis of monitoring that is too limited to capture the variation. There seems to be no discussion of why these levels varied so much between these two consecutive years of measurement. Without an attempt to identify the sources and/or the extent of this variability, deviating from a conservative model could create some surprises for the local water plant operators.

How are the monitoring data to be obtained for more extensive modeling? The exercise provided indicates that the Agency must go to unusual lengths to obtain some relevant data. These data on the Shipman reservoir (the Index Reservoir) relied on measurements of finished drinking water. The differences attributed to the Index Reservoir could be entirely the result of a change in treatment. It was assumed that it was higher in the Lake, a “safe” assumption. However, there was no indication of the kind of treatment that was used in the water treatment plant to even make an intelligent guess as to what the concentration might have been. It is clear that the Agency must either devote the needed resources to collect those data or have a way of getting it done by registrants.

2. The Panel recommends the continued use of water flow patterns and geographical information to model pesticide loads and concentrations. It is also a good idea to model multiple pesticides jointly. Particularly in the regression approach, joint modeling can help make better predictions for the individual compounds. Different data sets were used for the various regression analyses. These data sets exhibited different mean levels and different variabilities.

Such behavior is common when data sets are collected under different conditions. The statistical methodology of hierarchical modeling can help to combine analyses of similar variables collected from different data sets. Hierarchical modeling can also help when trying to model compounds for which only limited data are available. It is recommended that the Agency take a serious look at using hierarchical models to aid in the modeling of pesticide concentrations.

3. It appears that the results presented point toward incremental development along already established directions, not new departures. The most important next steps are to let these approaches reach their potential.

4. Reconsider the log transformations. The regression estimation procedure should serve the questions posed by physical modeling (physical modeling should dictate basic form of relationships) rather than being distorted for the convenience of satisfying regression estimation assumptions. Consider linear models with log errors minimized in optimization and points weighted by inverse variance of log observations.

Reconsider the separate modeling of pre-specified percentiles. Consider the possibility of having the dependent variable(s) be the parameters of a unimodal log-normal or a mixture of two or more log-normals. This would provide a more complete distributional characterization, allowing tentative projection of estimates of very high percentiles of the distributions. Some variables could conceivably affect mean results and some might affect variability more strongly.

Explore ways to remove the spreading effects of measurement error from the observations or from the fitted distributions.

5. The modeling effort is consistent with the state of regression modeling science. It would be helpful if the state of the science could be advanced by:

--Improving the representation of the mathematical relationship between flow and concentration. It may not be appropriate to assume a simple negative linear correlation, but it also may be inappropriate to assume a negative linear relation between logs of concentration and flow. These data points need to be weighted appropriately to their variance.

--Improving the statistics related to the probability band of interest--it may not always be at, say, 95%. Ideally, the model should address the entire distribution of the dependent variable. It appears that the SPARROW model is headed in this direction.

--Concern about the real truth about the variation of the concentrations. The spread is affected not only by the real variation in concentration, but also by the measurement error. Ideally, attempts should be made to remove the effects of measurement error from the estimates of concentration.



**Question 1.2 Do the model enhancements being undertaken present useful steps forward in the model development process? What other enhancements can the panel identify that would further improve the accuracy or usability of the models under development?**

(Also, see responses to Question 1.1)

The Panel was in general agreement that the steps being taken to develop the regression models are appropriate and useful. The following suggestions for other enhancements were offered:

1. Several Panel Members expressed concern about using the Mid-West reservoir as a default. Other systems are much more dynamic. Water quality in semi-arid areas is affected not only by storm events but also where the storm occurred. For example, in the Santa Ana drainage in Orange County California, the USGS has developed a considerable database that indicates that water quality differs significantly depending upon whether rain is in an agricultural area or in an urban area where different pesticides are frequently used because of different problems.

The lack of watershed models (p. 31 of document #2) is a particularly critical shortcoming. National or regional models do not describe the factors that affect flow in a particular location.

2. Refinements to the SPARROW model all appear to be logical developments, but their importance cannot be determined until some results from the model are available for evaluation. In this sense the SPARROW model developments represent very much a work in progress, and further comment on it seems premature. One Panel Member noted that it would be useful if the development of the SPARROW hydrology model resulted in the load model being converted to instantaneous concentrations, which then could be used to estimate time-weighted mean concentrations.

3. The most important step forward in the Larson and Gilliom regression models is the verification testing using data other than that used to develop the model. The results are generally promising in that the predictions for the non-calibration datasets are not drastically poorer than those for the calibration dataset. Application of this modeling approach to insecticides and development of surrogacy methods for pesticides lacking data are also appropriate developments, but as with the SPARROW model the results are not yet available.

4. Some of the regression model results are disturbing, particularly the results for alachlor. One Panel Member noted that he did not understand why the distributions derived by running the model with the calibration dataset show such consistent and often substantial bias. He said that he would expect these distributions to be symmetric about 0. The alachlor model is also the least successful when applied to the NASQAN stations. Perhaps one of the most useful steps in developing these regression models further is to determine why the models fail when they do,

be it systematically as in the case of alachlor or in specific cases (outliers) in the case of atrazine. Insights gained in this way may lead to improvements in the models, for example, by indicating other variables that need to be included. Some issues that should be investigated:

- Consistent biases, especially alachlor
- Consistent differences in prediction success for NASQAN and new NAWQA data, especially alachlor and cyanazine
- Variables not included, e.g., impact of major storm events

5. As a result of the Information Collection Rule (ICR), EPA now has a national database that includes the specific treatment train at each water plant in the country. It was suggested that the Agency consider using these data for these modeling efforts. Tied to the above would be consideration of using data on raw and finished water to develop regression models on performance of specific treatment trains with respect to specific pesticides and herbicides.

6. Care should be taken when using average conditions, especially average weather conditions, in simulating pesticide concentrations, which seem to respond largely to extreme events.

7. One new direction that could be helpful is using either a mixture model or an extreme-value approach that is part statistical, part mechanistic. New developments to incorporate sensor data will be helpful, but we need to be careful about adding a new source of uncertainty, derived from the sensor measurement process.

8. The models should use the most recent available land-use/ land-cover data, such as the 1992 MRLC data. Similarly, they should use the most recent available soils data. A fallback mechanism is needed for situations where models do not provide an adequate simulation. An example of this situation could include watersheds with variable amounts of land in buffer strips.

**Question 1.3 What recommendations do the panel have concerning issues regarding the design of a monitoring program to collect data to advance regression model development? Which issues of selection of pesticides, soil types, region, weather, timing, etc., merit special attention?**

The Panel felt all of the above-mentioned issues are worthy of attention, with the most important being timing. The following specific suggestions were offered:

1. It is important to have repeated measurements. This includes measurements at the same location but at different times. (There was some suggestion in the documents that some sensible proposals in this direction were being pursued.) It also includes measurements at different

sources in the same system, multiple measurements at the same source, and even multiple analyses of the same sample. These types of multiple measurements will help to partition the variability in observed concentrations among its various sources. Of course one does not need to take all of the aforementioned multiple measurements at each monitoring epoch, but one should have a good sampling of the various levels of repeat measurement throughout the sampling plan.

2. One issue that has not received much attention is the difference in the temporal variance of concentrations in rivers and streams as opposed to lake and reservoirs. Runoff events dominate concentration variability in flowing waters but are much less important in many lakes and reservoirs. Interestingly, several presentations from the Agency seem to reflect a reservoir perspective, while USGS data are mostly from rivers and streams. The two kinds of systems will probably require different sampling strategies and different numbers of samples to obtain results of comparable precision.

3. The most useful monitoring efforts are best targeted for the most abundantly applied pesticides and herbicides and their respective degradation products. The aggregate usage data is a good predictor of pesticide availability in the environment to be transported into streams, lakes, and aquifers and eventually into drinking sources. As for regions, the focus should be on areas where pesticide/herbicide usage is prevalent and may have demonstrated a history of pesticide or herbicide contamination in the past. Timing, sampling frequency, and longevity of sample programs are important to capture the true impact on pesticide entering the aquatic environment. An understanding of the herbicide or pesticide's intended use in the environment and the times it is applied and if it is available for transport in water are important factors in designing monitoring programs to capture meaningful exposure data. Frequent sampling allows the capture of enough data points to define events and estimate maximum concentrations and to calculate mass transfer more accurately. Pesticide application amount, application timing, and the timing and intensity of the first rains after applications are major factors affecting the resulting pesticide runoff levels and mass. Year-to-year weather variability affects transport to rivers and streams. Rain in non-contributing river basins dilutes pesticide containing streams.

4. The hydrographic dataset for monitoring and modeling should be as detailed as possible, to help represent the small watersheds.

5. Stratified random sampling should be incorporated on an oversampling basis to verify that the high end of the concentration curve is being adequately stimulated.

6. It also would be desirable to associate treatment-in-place data with monitoring data. This can be useful in reducing uncertainty about treatments in place. It would be very useful to observe both raw and finished water at the same site, preferably in before/after treatment form. But even simultaneous measurement would be useful. This would enable the fitting of a treatment efficiency model. Occasionally, randomly selected sites that are not part of the

monitoring plan should also be sampled, if for no other reason than validation of the fitted model.

7. In reservoir monitoring programs, consider including the simplest kind of reservoir model in your effort, namely stratification into two layers and estimating the time of turnover (also could just base it on latitude and time of year or perhaps likelihood of a certain magnitude wind storm) . Tied to the above would be to consider sampling not just reservoir effluent but also the vertical profile of the reservoir (above and below thermocline).

8. The basic guidance is to stratify the sample by the independent variables that are most strongly predictive of contaminant levels, particularly high percentiles of contaminant levels.

9. Data are lacking in upland (headwater) watersheds. Monitoring programs do not need to be completely reinvented but more attention should be paid to these watersheds.

**Question 1.4 What level of accuracy is reasonable for the Agency to generally expect from distributions of concentrations predicted by regression-equation based computer models after further development? Is it unreasonable to expect that we will be able to be within a factor of 2 for individual sites or for the entire distribution? What level of accuracy might we realistically expect ?**

The Panel generally felt that expecting consistent results within a factor of 2 would be unrealistic, but that such results could probably be achieved for a fair proportion of the time, around 50-75 percent. Furthermore, the panel noted several complicating factors affecting the determination of model error, as described in the following comments:

1. Figure 1 of the background document indicates a 10-fold variation with the smaller drainage area/reservoir capacity ratio. The goal needs to be specified in terms of how frequently it would fall into a certain variation, not an absolute factor (e.g., 2). From the data provided, it would be surprising if the 5<sup>th</sup> to 95<sup>th</sup> percentiles would be within a factor of 2 of one another, which would suggest that a factor of 2 is probably not realistic.

2. How closely concentrations can be estimated depends on several factors. First, the model must be a good approximation. The model must account for most of the important features. The models discussed seem to be doing a good job of addressing this concern. Second, lots of data are needed. Third, model results will suffer from variability. These last two factors are related. The more highly variable the data you can get, the more of it you will need in order to obtain good estimates. However, if data are sufficiently variable, no matter how much you get, there will be significant limitations on the precision of predictions. There are methods for estimating how well you can hope to do with “perfect” data. Also, there are methods for estimating how much data you will need in order to make predictions and estimates with a desired degree of precision.

For example, if the Agency contemplates additional observations and/or additional sites at which observations will be collected, they can perform the following "pre-data" calculation. Include the independent variables (predictors) associated with the additional observations and/or sites together with the existing data, and compute the variances of estimators that would be obtained if the additional data were collected. (Estimates of the variances of the various noise terms in the model will have to be substituted for the unknown variances in order to compute values that do not involve unknown parameters.) These variances can then be used to see how large the confidence intervals and the prediction intervals would be if the additional data were to be collected. A reverse method is also available when there exist closed-form expressions for the variances of estimators. In this case, one can first decide how wide one wishes the confidence interval or prediction interval to be (e.g., a factor of 2 translating to  $\pm \log(2)$  on a logarithmic scale). Then write the width of the interval in terms of the variance of the appropriate estimator.

Finally, use the expression for the variance of the estimator to solve for the features of the regression design that will be required to achieve the desired interval width. Use of methods such as these can help the Agency decide how much reduction in uncertainty can be achieved from a proposed increase in sampling effort. These methods can also help to determine the size of the sampling effort required to achieve a desired reduction in uncertainty. The Agency should use methods such as these if it is concerned about whether or not a given data collection scheme will be able to reach a desired goal.

3. A factor of two would be hopeful for small river systems. The complexity of larger systems may be more difficult to capture.

4. There is a need to distinguish between accuracy and precision. Accuracy is the ability of a process to come up with the right answer. Precision is the ability of a process to come up with the same answer in trial after trial. Accuracy is primarily reflected by the mean or median, and precision by the variance of the distribution of results from the process. A process that is not accurate is biased. A process that is not precise is, well, imprecise. Obviously, when the process at hand is monitoring of a natural water body, precision includes natural variability, which is generally not the same from trial to trial.

Many of the box plots for the regression residuals have boxes that extend about  $\log(2)$  units on either side of the median (although some show a substantially wider spread). This means that 50% of the regression results are within a factor of two of the median result. However, to varying degrees, the median result is biased. If the sources of bias can be determined and corrected, then the results will be within a factor of two of the correct answer in about 50% of the cases (sites). It is not clear what development steps can be undertaken to increase this precision substantially.

It is unrealistic to hope that the regression models can deliver results that are always within a factor of two, and even achieving a factor of two 50% of the time may be out of reach for some compounds. Results that rely on surrogacy approaches because of the lack of direct

observations for a compound may well be both more biased and less precise; the biggest problem is that there may be no way to determine whether or not this is the case.

Being within a factor of two for the whole distribution would seem to translate to being within a factor of two for the median. The atrazine and metolachlor models accomplished this for the datasets tested; the alachlor and cyanazine models did so for about half the tests or more. If sources of bias are systematic and not just quirks of the particular datasets tested, if they can be understood, and if corrections can be incorporated into the models, it should be possible to considerably improve results for the entire distribution. As SPARROW continues to be developed these ideas need to be tested.

5. This question is difficult to answer, particularly because it is not as fully specified as it might have been. How often does the Agency want to be within a factor of 2? 50% of the time? 90% of the time? And do you care differently about the predictions that are made at the high end of the distribution, relative to the accuracy of predictions of the mean or median? In any event if the goal is to be, for example, within a factor of 2 for the high percentiles 90% of the time, this will be a challenge. It would be easier for the Agency to make predictions by keeping track of the quantitative improvement in prediction accuracy (by some consistent metric) over time with successive innovations in methods and improvements in input data.

6. There are also some errors inherent in basin characteristics, such as chemical use-data and ground-water infiltration rates.

7. Perhaps the Agency could track the accuracy of the model predictions over time to show the effect of improvements.

## DRINKING WATER TREATMENT EFFECTS

**Question 2.1 Coagulation-flocculation, sedimentation, and filtration processes in conventional water treatment are not effective in removing certain pesticides belonging to triazine, acetanilide, carbamate, and urea derivative classes. What relationships exist between the physical/ chemical properties of other pesticide classes and these water treatments?**

The Panel agreed that all these processes are designed to reduce turbidity, that is to remove the particles from the water that make it appear cloudy. They are effective in removing solids-associated contaminants and in preparing the water for downstream processes such as oxidation or disinfection, but they do not affect many anthropogenic organic chemicals. Activated carbon is the treatment process that appears to have the greatest removal efficiency for pesticides. Activated carbon can be added in a powder form (PAC) to the coagulation processes or in a



granular form (GAC) as part of the filtration process.

If a chemical were to have physical/chemical properties that cause it to be normally associated with the suspended solids in the water column (lipophilic or hydrophobic), then it could be expected to respond to these treatments. PAHs and PCBs might be examples of such compounds. The major difficulty is whether this behavior can be predicted with confidence in different water treatment systems that use different processes and different water sources. Very high molecular weight is probably the property most easily identified. Most pesticides are not that hydrophobic. Most pesticides have relatively low molecular weights (100 AMU to 500 AMU). Wilfred Periera of USGS investigated transport of herbicides dissolved in water and adsorbed on sediment in the early 1990's on Mississippi River tributaries. This work is worth reviewing to determine pesticide transport on solids.

One problem with determining the efficiency of removal of hydrophobic pesticides is that particle-associated pesticide molecules would not be measured in the filtered water samples used for measurement of raw water concentrations. Many pesticides are ionizable, rather than molecular, in water. It is possible that charged pesticide ions may undergo some removal.

One Panel Member mentioned that utilities are monitoring the removal efficiencies for the Mississippi River. They are finding no significant removal. They are not publishing these data, but are willing to make them available.

**Question 2.2 Some pesticides, including carbamates and organophosphates, with hydrolysis half-lives of less than 1 day in alkaline (pH 9) water, are observed to be “removed” during lime-soda softening (pH 10~11) by alkaline hydrolysis. Can this observation be generalized in predicting whether a pesticide with an alkaline abiotic hydrolysis half-life of less than 1 day will be “removed” through water treatment? What other classes of pesticides may be removed or transformed by water softening and in what manner?**

The Panel agreed that it might be reasonable to assume that such compounds will be removed in many softening plants, but there are several dangers here:

- b. Not all systems use lime
- a. Most water supplies are not softened
- c. Not all lime softening plants operate at such high pHs
- d. Softening is sometimes done with processes that don't elevate the pH (ion exchange, membrane softening, RO and ED). Some also re-carbonate or perform an acid addition to lower pH. The length of time pesticides have to react may vary. Detailed treatment operation plans would be necessary to predict transformations

The Panel Members were not aware of other pesticides that undergo such hydrolysis.

Extrapolation to other groups of pesticides is not warranted; data should be collected on a case-by-case basis.

**Question 2.3 During disinfection with chlorine, pesticides such as organophosphates can be oxidized to form toxic degradation products. What other classes of pesticides may be transformed by disinfection processes to form toxic byproducts? What issues related to pesticide transformation should OPP be aware of?**

The Panel agreed that this question is rarely addressed before the fact. Only very limited research has been conducted on the disinfection by-products of pesticides in drinking water treatment and essentially no risk assessments have been done on the health effects of these compounds from exposure to drinking water.

The Agency should have organic chemists, familiar with water treatment techniques, to predict the behavior of pesticides in water treatment processes. This task should include identification of potential products that could be formed and the conditions under which they might be formed. At present someone accidentally finds something in finished water that was not in the raw water and then must go through the puzzling process of identifying how the unknown product was formed.

The Panel noted several potential transformations. This following list is probably not exhaustive:

1. In general, stronger oxidants such as ozone will form a greater number of pesticide disinfection by-products with ozone > chlorine dioxide > chlorine > chloramines. A considerably large research effort would be required to identify these pesticide byproducts and determine their level of occurrence and health significance.
2. It would appear that pesticides of the dialkyldithiocarbamates have the potential to yield nitrosamines with chlorination. This has been clearly demonstrated with thiram, where NDMA is seen to form at about a 0.2% yield (Graham et al., 1996). Apparently it is also formed from DDC, ferban, and ziram. A logical extension of this would be formation of diethylnitrosamine from the diethyldithiocarbamates such as disulfiram, but this has not apparently been studied. It is important to distinguish formation of NDMA from this source vs. others including endogenous sources. It is also quite clear that formation of NDMA is favored with one disinfectant over others at different times and with different water conditions. Consequently, dealing with this issue would require a wide-ranging study of varying conditions that would occur in a water supply from the source water to the finished product water.
3. In general aromatic rings are subject to chlorination, particularly those with electron donating groups, such as phenolic groups. For example the aromatic ring on captan is relatively easily chlorinated. In some cases amino groups can be converted to chlorinated



amines.

4. Not all systems use chlorine. Do we know what happens if a system using combined chlorine with a longer contact time to avoid disinfection by-product formation would degrade the organophosphates as quickly as free chlorine? The issue of concentration versus contact time needs to play into any dependence on disinfection to remove pesticides. For example, ozone has a short half-life in water. How important is reaction time with respect to all the other substrates ozone is acting on in the water.

5. Only a small amount of work that has been done on oxidation of pesticides. Based on that work, it would not be prudent to accept oxidation as an adequate treatment alternative for any pesticide unless the byproducts of that oxidation have been identified and their toxicity determined.

6. The Stage 1 DBP Rule becomes effective December 2001, and utilities have been adjusting to minimize trihalomethane (THM) formation. Use of chlorine in combination with chloramines is increasing to moderate THM formation. Chloramines are a weaker oxidant and are less reactive. We do not know if chloramines are reactive enough to oxidize organophosphates.

7. Additional research is needed on the occurrence and health effects of pesticide transformation products and on analytical methods for those that currently lack appropriate methods.

8. The question is not whether by-products will be formed but what by-products will be produced and how toxic they will prove to be, since all disinfectants are oxidants. Some good research should be available from Japan and Europe, where concern over pesticide disinfection by-products is high.

**Question 2.4 Laboratory jar tests are often employed to determine if a regulated contaminant, including some pesticides, in raw water can be removed by a given treatment process. What are the advantages and disadvantages of using results of jar tests as the basis of evaluating whether the pesticide will be eventually removed in the actual water treatment plant? How might these results be used to adjust raw water concentrations for use in human health risk assessment?**

The Panel agreed that jar tests are an excellent way to estimate the impact of conventional water treatment practices on a chemical through processes such as coagulation, flocculation and sedimentation, and adsorption on PAC. On the other hand, jar tests are run in batches and full-scale plants are real-world continuous flow operations. Jar test results will typically exceed conventional flocculation/sedimentation plant results due to the difference in flow characteristics

and short-circuiting. On the other hand, jar test results will be significantly worse when compared to up-flow sludge blanket clarifiers because the jar test cannot simulate the effects of the sludge blanket. When jar tests are successful, pilot and full-scale results are generally necessary before a reliable estimate of full-scale removal can be obtained.

Another important consideration is that the removal that can be achieved by processes that are easily evaluated by the jar test is generally very sensitive to the quality of the specific water used in the test, including temperature variations from 32° to 90° Fahrenheit, and the pesticides that may be dissolved or adsorbed to particles. As a result, jar tests conducted in one location are not easily extrapolated to another location. Setting the scale-up issue aside, generalizations suitable for risk assessments can only be made after the analysis of test results from several locations.

The use of jar tests to estimate national average pesticide removal in drinking water through the use of PAC will suffer from the inability to simulate site specific treatment plant conditions as well as those variables indicated above for PAC: seasonal use, PAC type, PAC dosage, source water characteristics, PAC suspension time, and interference from other treatment chemicals employed in the clarification process.

Given the high degree of uncertainty about what causes what to be removed from water, it is relatively unlikely that jar tests will provide anything more than suggestions about what treatments will remove which pesticides. These suggestions can be used to form prior distributions over the parameters of removal efficiency models. This will help stabilize predictions during the early stages of analysis when there might not be much on-site data.

**Question 2.5 Many factors, such as raw water composition, water treatment method, and treatment plant conditions, can affect the removal of pesticides. What issues should OPP be considering in determining whether it is possible to accurately predict the percent removal and transformation of pesticides among different water treatment plants?**

The Panel agreed that this is an important question. Water conditions vary significantly from one source to another. Simple differences in water pH, temperature, turbidity, dissolved organic matrix, and competition for absorptive surfaces with other organic material in the water make broad scale prediction difficult at best. Even if this variation in source water can be accounted for, varying conditions within plants using the same source water, such as plant flow rate, mixing, filter rate, and treatment chemicals, also may affect pesticide removal efficiency. In general, conventional water treatment does little to remove pesticides. Efficient removal depends upon the installation of treatment processes that are tailored to the pesticide of concern.

**Question 2.6 The preliminary literature review indicates that coagulation-flocculation, sedimentation, and conventional filtration are not effective in pesticide removal for many**

types of classes of pesticides. Effective removal of some pesticides has been observed with activated carbon adsorption (GAC and PAC), softening, disinfection, membrane treatments, and in some cases air-stripping. What additional water treatment data from other studies, which either support or are inconsistent or contradict the data presented in the preliminary literature review, should OPP consider?

The Panel agreed that most available data support the preliminary conclusion of little removal by conventional treatment. The following suggestions were offered regarding pesticide removal and additional treatment data:

1. PAC is usually added to remove taste and odor and can vary in effectiveness in removing pesticides. PAC is manufactured in various ways for special uses. Competition from background NOM can reduce effectiveness. NOM is usually in the milligram-per-liter range, while pesticides are in the microgram-per-liter range. When removing lower and lower levels of pesticide the required dosage of PAC increases exponentially. PAC application policy varies between utilities. Some just use it for taste and odor, some feed it to lower pesticide levels below MCLs, some aggressively apply it to remove of any measurable levels of pesticides. When activated carbon is used for pesticide removal, utilities often monitor atrazine to determine when to use or add GAC/PAC. If atrazine concentrations in the raw water fall, so may GAC/PAC use, and other pesticides may face less removal.
2. The principle processes known to address compounds of this type are adsorption, oxidation, and membrane treatment. High pH processes and air stripping are effective in a few instances. Other advanced oxidation processes that might be considered are: UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, or Fenton's reagent reactions, etc. But none of these are common in water treatment practice today.
3. Consider effects of riverbank filtration as a pre-treatment option.
4. The use of the isotherm equation to estimate carbon dosage in real treatment processes is flawed. An extrapolation process may be more accurate.
5. Jefferson Parish, in Louisiana, has over ten years of weekly raw and finished water data that indicate that there is no removal of major agricultural herbicides by conventional treatment. Current priority pesticide reductions in source water concentrations have resulted mainly from the use of PAC, GAC or both. PAC has traditionally been employed to combat taste and odor. In recent years, CWSs have been forced to implement PAC as a more economic alternative to GAC, the BAT for atrazine. This has resulted in significant reductions in atrazine MCL violations over the last several years. (historical SDWIS data)

PAC is used seasonally to remove taste and odor with the typical T & O season being late

summer corresponding to low flow, warm water temperatures, and strong sunlight conditions. PAC is also used seasonally to maintain the priority drinking water regulated pesticide(s), e.g., atrazine, below the MCL. Usage is based on historical trends and monitoring by plant operators using immunoassay tests specific for the priority pesticide(s), e.g., the triazines. If a particular pesticide is not monitored, it will not be addressed by seasonal PAC treatment unless its occurrence coincides with the regulated pesticide(s) being removed, i.e., the PAC treatment goal.

Seasonal use of PAC will affect drinking water concentrations of non-drinking water regulated pesticides only if non-drinking water regulated pesticide runoff coincides with PAC use, and effectiveness will vary with the treatment goal for PAC use.

T & O use of PAC is unlikely to be effective for non-drinking water regulated pesticide removal unless application/runoff events coincide with seasonal T & O. This is not the case for most agricultural pesticides used in the central US which exhibit peak runoff in the spring while T & O events typically occur in late summer.

The use of PAC for pesticide removal targets one or more priority drinking water regulated pesticides. PAC use on non-drinking water regulated pesticides will be ineffective unless application and runoff events coincide with those of the priority drinking water regulated pesticide(s). Except for the large CWSs with analytical laboratories, monitoring for non-regulated pesticides is not likely to be conducted by treatment plant operations personnel. Therefore effective PAC treatment for non drinking water regulated pesticides with a use pattern differing significantly from the priority regulated pesticide is unlikely.

A number of events can cause the current level PAC use for pesticide removal in the central U.S. to be significantly reduced:

- 1) Agricultural use of the current priority regulated pesticide (atrazine) decreases because it is determined to be carcinogenic and becomes a restricted use pesticide; or, it is replaced in the Ag market with a non-drinking water regulated pesticide.
- 2) A total triazine MCL of 20 ug/L is set in the future resulting from the manufacturer's petition under the triazine Special Review.
- 3) The increased use of Best Management Practices in the watershed by the agriculture industry may result in significantly lower levels of the priority drinking water regulated pesticide(s) in source waters.

Along with seasonal use, PAC effectiveness for pesticide removal is also affected by PAC type, PAC dosage, source water characteristics, PAC suspension time, and possible interference from other treatment chemicals employed in the clarification process.

The reasons for GAC use are similar to those of PAC. While the use of GAC filtration is

typically continuous throughout the year due to the use of GAC in a filter-absorber mode, a number of variables will impact pesticide loading rates:

GAC type, filter design and hydraulic loading (EBCT), the prior loading of the priority pesticide(s), and presence and prior loading of other competing organics in the source water. Pesticides, including possible biodegradates, will also desorb from GAC when the peak runoff concentration decreases in the source water.

GAC bed life can exceed several years and is usually dependent upon the prior loading of the priority regulated pesticide and its peak concentration in the source water. Thus, if the source water concentration of the priority pesticide significantly decreases, frequent replacement (or reactivation) of GAC will no longer be a requirement.

Many CWSs that employ GAC also use PAC to lengthen GAC bed life and lower GAC replacement costs. PAC use is seasonal and is adjusted based on the source water concentrations of regulated pesticides and the removal efficiency of the GAC filters.

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The effectiveness of the use of GAC on non-drinking water regulated pesticides is affected by the same variables as indicated for PAC. Comment on information presented in "Water Treatment Introduction", regarding the significance of the presence of GAC, PAC, and oxidation processes at a given treatment site: The data summaries prepared to date appear to categorize plants by the presence or absence of certain unit operations: e.g., coagulation, GAC, PAC, etc. Where the use of GAC, PAC, and oxidation are concerned, these data may be misleading, for the

following reasons:

a. In the case of GAC, because the design and operation of these plants varies over such a wide range, from plants such as Cincinnati that have post filter absorbers that are regenerated at some regular frequency to many plants that have put a layer of GAC on top of their filter sand several years ago and make no attempt at regeneration.

b. In the case of PAC and oxidation, because these processes are not always in operation. Many plants go several years without using their PAC capability.

c. On the other hand when pesticides co-occur with pesticides that are regulated, the likelihood that treatment will be in place is much greater.

**Question 2.7 Based on this technical review, OPP is leaning toward an interim approach to address the impacts of water treatment on a case-by-case, pesticide-specific basis in its human health risk assessment. OPP expects that for most pesticides, however, available data will not be sufficient to establish the impacts of treatment. Accordingly, as a practical matter, it is very likely that until pesticide-specific treatment data are generated, OPP will be using raw or untreated drinking water estimates in human health risk assessments under FQPA. Given the objective of estimating pesticide concentrations in drinking water, does the SAP believe that the state-of-the-science supports this approach? If not, how would an approach be developed based on the state of knowledge about the impact of treatment on pesticides?**

The Panel agreed that this is the only feasible approach. Until adequate research is conducted, it would be prudent for the Agency to take a conservative approach by assuming that the finished water pesticide concentration is the same as that estimated for the raw water source. Exceptions might be made for two or three pesticides if the Agency's review demonstrates that removal due to chlorination or hydrolysis can be relied upon. It is also prudent to assume that the health effects of pesticide treatment transformation and disinfection byproducts are similar to those of the parent pesticides.

A water treatment operator will have to treat drinking water removal of pesticides when and if they are found in the source water at concentrations above established MCLs. Therefore, any exceedence in source water imposes an economic burden on a drinking water treatment plant beyond the costs of simple conventional drinking water treatment. The operation of a responsible water system may require monitoring for pesticides used on its watershed even if there is not an established MCL, especially if consumers of that drinking water are aware it is being used and suspect the possibility of contamination.

Adjustments for pesticides based on water treatment should be undertaken only if a broad-



scaled monitoring program were initiated which carefully evaluated the effectiveness of drinking water treatment methods to dependably remove those pesticides that are frequently found in water. Such a monitoring effort would have to be aimed at the questions of how different unit processes contributed to removal. It would need to be focused on developing a set of criteria for pesticides that fall into particular chemical and physical classes. It would necessitate developing enough data that the statistical confidence of the estimated removal can be stated with some accuracy with clear description of the conditions that were in existence at each plant. This is a situation where inadequate data could be dangerous. Therefore, such a study should not be undertaken lightly. Paired sampling monitoring programs would provide better data.

There is a longer-term approach that could address issues of variability (not necessarily solve them) that should be considered. Manufacturers of pesticides could be required to develop chemical-specific methods for treating water intended for human consumption that might exceed an allowable limit. That information should be compiled and made available to water plant operators in the event of imprecise predictions based on models that do not capture the variables that could be encountered in a specific location. This is more than a health issue; it is a question of how much confidence people can/will place in their local sources of drinking water. Applications of material on a watershed should not be done without the knowledge of systems drawing water from the bodies of water affected.

The Panel's concurrence with the Agency proposal is offered primarily because of the absence of information. It should not be taken as an endorsement for the absence of a serious program monitoring field-scale treatment performance. Monitoring the drinking water levels of those pesticides that have been shown to occur in raw water supplies should be among EPA's highest priorities.

One Panel Member noted that, looking to the future, there is a potential for a more accurate estimate of the levels of pesticides in drinking water treatment in the future on a national basis. This could be enabled by three factors: 1) further development of the models for estimating pesticide concentrations in raw water, 2) the emergence of a national database on our water treatment plants and the process train each plant uses, and 3) more extensive characterization of empirical performance of these treatment trains in removing specific pesticides. The time may not be far off when models such as those shown today project the distribution of pesticide densities in the environment at large. It also seems that data collected on pesticides in raw and finished water could be used, along with the specific treatments used to produce finished water at each site, to produce similar models characterizing the removal of these pesticides in treatment. Finally, the results of both of these models could be combined with the national water treatment plant database to produce national estimates of exposure. Such an effort would seem to be in character with the scope of the OPP modeling effort that we have already seen presented today.

The current state of the science does support using raw-water data to estimate treated-water concentrations. However, this must result in large error bars, owing to the wide range of removal rates and rates of production of transformation products, some of which may be 20 times

as toxic as the parent compound. EPA should put a high priority on additional research on the effects of drinking-water treatment on pesticide and degradate concentrations. Case-by-case studies of individual pesticides are prone to ignore the risk posed by exposure to mixtures of various pesticides, degradates, and other contaminants.

**Question 2.8 The effects of water treatment on pesticide residues in drinking water can be assessed by regression modeling of important parameters with removal efficiency, experimental or laboratory studies, and actual field monitoring. What other approaches or methods can be used to assess water treatment effects? What are the pros and cons of these methods?**

Water treatment processes are designed with specific unit operations designed to accomplish specific transformations of components of the water matrix that have been identified as important to the safety and palatability of the water supply. We know what each unit process is intended to do. The problem with pesticides is essentially two-fold: a) contemporary water treatment processes are not designed with their removal as an objective and b) we have not systematically studied the removal of pesticides commonly found in raw waters. The Panel agreed, nevertheless, that intelligent application of regression techniques to modeling performance of these processes using real data on raw and finished water and that state-of-the-treatment at specific sites may lead to useful estimates of treatment effects. These estimates could then be integrated with the rest of the OPP effort through models taking advantage of the strengths of both SPARROW and the Larson-Gilliom Model. Therefore, regression modeling based on a respectable body of relevant experience in different kinds of treatment systems seems the best approach.

Because of the variables involved with the use of activated carbon for the removal of organic substances, EPA (Office of Water) has typically relied on full-scale and pilot-scale study data to set national regulations and should continue to do so. Bench scale studies, such as jar tests, do not accurately portray full-scale treatment processes and should not be employed to estimate national average pesticide removal in drinking water. The full-scale studies should involve timed, paired sampling to characterize the same slug of water as it moves into and through the plant. Variations in treatment processes should be considered, such as duration and timing of PAC/GAC use.



