July 6, 2021

Dr. Katrina White
Environmental Fate and Effects Division
Office of Pesticide Programs
Environmental Protection Agency
1200 Pennsylvania Ave. NW
Washington, DC 20460-0001
Submitted via regulations.gov:

Re: Analysis of Subsurface Metabolism in Groundwater Modeling; EPA-HQ-OPP-2021-0241

Dear Dr. White:

Established in 1933, CropLife America (CLA) represents the developers, manufacturers, formulators, and distributors of pesticides and plant science solutions for agriculture and pest management in the United States. CLA represents its members by, monitoring legislation, federal agency regulations and actions, and litigation that impact the pesticide and pest control industries and participating in such actions when appropriate as well as communicating the benefits of pesticides to a variety of audiences. CLA's members produce, sell, and distribute virtually all the pesticide and biotechnology products used by American farmers.

CLA's comments are presented as a cover letter followed by an executive summary and specific comments to the analysis of subsurface metabolism in groundwater modeling released in the EPA-HQ-OPP-2021-0241 docket.

CLA appreciates the opportunity to comment on the Agency's effort to address longstanding concerns with the degree of conservatism within groundwater assessment tool. Should you have any questions or comments, please feel free to contact me at mbasu@croplifeamerica.org or (202) 296-1585.

Sincerely,

Manojit Basu, PhD
Managing Director, Science Policy
CropLife America

Executive Summary

The development of the groundwater framework to reflect the technical understanding is a positive step towards ensuring that predicted exposure estimates reflect actual exposure. CLA finds the Agency's effort commendable and supports the changes in the methodology for estimating pesticide concentrations in groundwater. To help with the Agency's request for feedback, specific comments are provided on the following topics:

- **Aerobic Soil Metabolism (ASM) Zone**. CLA supports the modification of the groundwater framework to account for the ASM zone at depths greater than 1m and recommends the inclusion of ASM declining to zero at 3m as the new screening level option.

- **Background Metabolism**. CLA agrees with EPA's position that chemicals with no measurable hydrolysis, under typical environmental conditions, can undergo degradation via processes other than aqueous hydrolysis. CLA supports the use of a background metabolism rate 1/10 that of the surface ASM rate for chemicals that do not undergo hydrolysis.

- **Use of Terrestrial Field Dissipation (TFD) Studies in PWC Groundwater Modeling**. CLA requests EPA to reconsider using TFD data for potential refinement of groundwater modeling and subsequent risk assessments. A TFD study represents the ability to evaluate the actual fate and transport of compounds under realistic agronomic practices, and as noted in the report, can form an important line of evidence in the understanding the compound's behavior.

- **Comparison between Prospective Groundwater (PGW) Studies and PWC Modeling Results**. Some PGW studies were not included in the analysis since the field areas did not correspond with the current six groundwater scenarios for PWC. CLA would like EPA to consider a strategy to employ more of the field data in this analysis, as most PGWs are conducted in vulnerable regions and could provide useful information.

- **Water Quality Portal (WQP) Monitoring Versus Modeling for Pesticides**. CLA considered the comparative assessment that EPA conducted between WQP data and Pesticide Water Calculator-Groundwater (PWC-GW) modeling. We agree with the overall assessment of the comparison results except for chemicals with low mobility. CLA supports the modification of the groundwater framework proposed by the Agency since it more accurately reflects real-world conditions.

- Besides the improvement in subsurface metabolism, which is mainly algorithm based, EPA can also extend current general scenarios to more specific scenarios for groundwater modeling.

CLA would like to request a timeline on when the specific concepts addressed in this document can be implemented to the groundwater exposure assessment. CLA supports the effort to improve the PWC model to reflect the science of fate and transport of crop protection products more accurately in the subsurface. A more robust tiered groundwater risk assessment approach is still needed which allows for potential refinement based upon scientific data (for instance, by using probabilistic techniques), like the framework in place for evaluating the food contributions to the dietary risk assessment. In addition to specific comments, CLA has highlighted areas of the report that require correction, modification and has proposed additional scenarios and methodologies for consideration.

1. Aerobic Soil Metabolism (ASM) Zone

CLA supports the modification of the groundwater framework to account for the ASM zone at depths greater than 1m and recommends the inclusion of ASM declining to zero at 3m as the new screening level option.

The development of the groundwater framework to reflect the technical understanding of the change in degradation with depth is a positive step towards ensuring that predicted exposure estimates are not overly conservative. It is well acknowledged, as the Agency has shown, that microbial activity in the subsurface extends to deep layers of the soil; thus, extending the ASM to greater than the currently assumed 1m depth has the potential to provide improved chemical behavior representation.

Most of the data presented show measurements within the top 2m zone; therefore, the expectation is that the new tier 1 default for the ASM zone will be extended to 2m or 3m. Except for the cases where the ASM rates are relatively fast, the model prediction at the 2m ASM reflect only marginal change in Estimated Drinking Water Concentrations (EDWCs). Given the fact that “on occasion, EDWCs are orders of magnitude higher than concentrations observed in non-targeted monitoring data[1]”, marginal changes in the EDWCs produced when the ASM zone is shifted to 2m does not adequately move the model predicted and monitoring data closer into alignment.

Though differences between the ASM declining to zero at 2m (2m0x) and 3m (3m0x) are not substantially different, the 3m0x refinements result in greater separation from the current default (1m0x), which, as shown in the analysis, often results in large overestimation in comparison to monitoring data. Therefore, CLA recommends the use of the ASM declining to 3m as the new default.

2. Background Metabolism

On page 11, Section 3.2[2], EPA states that:

> The data quality objectives of the evaluation of the subsurface modeling assumptions is to minimize over and underprediction of the majority of pesticides, especially those that are a major concern for GW contamination (i.e., mobile and persistent pesticides). This fulfills the need for the model to be reasonable in predicting potential concentrations in GW. For the model to be conservative, it is generally desired that modeled/predicted concentrations will be higher than measured concentrations but not by a large amount.

[1] EPA. 2021. Analysis of Subsurface Metabolism in Groundwater Modeling. Page 5, Section 2
[2] EPA. 2021. Analysis of Subsurface Metabolism in Groundwater Modeling

CLA appreciates EPA's research efforts by using experimental data that might justify the modification of the current groundwater modeling approach to address instances in which the model, i.e., Pesticide Water Calculator-Groundwater (PWC-GW), provides exposure estimates that exceed what is considered "reasonably conservative."

Potential modifications that the Agency considered to accomplish the goal of achieving reasonable exposure estimates were focused on changes to the conceptual model, rather than the currently available refinements that focus on alternative model inputs. The two options considered were increasing the zone of metabolism and assuming a background degradation rate throughout the soil profile. These comments refer to the latter approach, that is currently utilized for the use of hydrolysis half-lives in the subsurface below 1m.

CLA agrees with EPA's position that chemicals with no measurable hydrolysis, under typical environmental conditions, can undergo degradation via processes other than aqueous hydrolysis. This is a plausible explanation for the subsurface degradation in 56% of the considered chemicals that did not undergo hydrolysis. As an attempt to improve predicted EDWCs for active ingredients that did not undergo hydrolysis and degraded in the subsurface, EPA considered the use of a background metabolism rate $^{1}/_{10}$ that of the soil surface rate. This approach is based on assumption of a rate much lower than the soil surface rate. As shown in Figure 6, page 19[3], the choice of a factor of 10 is reasonably justified by the data and still protective since most subsurface metabolism half-life values are within a factor of 10 of the surface ASM.

The use of the background metabolism rate resulted in a smaller reduction in EDWCs than did changing the depth to which ASM is assumed to occur. For chemicals observed to degrade in the field and are stable to hydrolysis, the inclusion of the background rate in this fashion is a modeling refinement that is potentially meaningful and justified by the data summarized by EPA (E.g., Table 2 and Figure 9).[4] The assessment revealed that in most cases, the use of the 3m10x parameterization resulted in EDWCs that are more conservative than the PGW maximum concentrations. The inclusion of the background metabolism rate resulted in a modest decrease in EDWCs. However, this potential modeling refinement is an additional option that should be considered for inclusion in the groundwater modeling framework. It is anticipated that the additional option would only be necessary for chemicals that do not undergo hydrolysis.

3. Use of Terrestrial Field Dissipation in PWC Groundwater Modeling

On page 94[3], Appendix I, EPA stated that:

> It was anticipated that the terrestrial field dissipation half-lives would most often be faster than the ASM input with the potential for double counting loss via other mechanisms other than ASM; therefore, the maximum terrestrial field dissipation half-life was used as the ASM half-life when the terrestrial field dissipation data were readily available.

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[3] EPA. 2021. Analysis of Subsurface Metabolism in Groundwater Modeling
[4] EPA. 2021. Analysis of Subsurface Metabolism in Groundwater Modeling

> Contrary to what was anticipated, in 41% of 42 chemicals, the terrestrial field dissipation half-lives were often longer than the ASM half-life, though the range generally included the values of the ASM half-lives (Figure I2).

CLA acknowledges the effort to assess the use of TFD half-life as the ASM half-life input in PWC groundwater modeling. We recognize the EPA's findings that the ASM half-life value derived from laboratory studies is not necessarily always conservative and may fall within the range of the TFD half-lives. However, for the given chemicals, the maximum TFD half-lives used in the EPA's analysis may not represent the large number of available TFD studies that have been collected over several decades. Selecting only the maximum field dissipation (DT_{50}) for comparison may not provide an accurate reflection of the field data, leading to an incomplete assessment of the fate and transport of a compound in the environment. It would be useful to revisit this analysis with inclusion of data from the additional TFDs conducted for the compounds included in the analysis to represent the full range of field observations, to compare the field dissipation values more accurately with the ASM determined from the laboratory studies.

A TFD study represents the ability to evaluate the actual fate and transport of compounds under realistic agronomic practices, and the use of TFD data should be further considered in future improvements to the prediction of leaching.

In contrast to prospective groundwater (PGW) studies that are conducted only for compounds with very high leaching potential, field dissipation studies are conducted for all registered active ingredients as part of a standard data submission requirement. This provides a rich dataset for comparison with PWC modeled results. In cases where the PWC does not accurately predict the fate and transport of a compound in the field environment, higher tier modeling could be conducted to investigate the impact of various model input parameters. If sufficient data exist to support it, input parameters could be modified, as appropriate for model refinement or a weight of evidence approach could be used. In addition, with proper study design and calibration of the behavior of soil water dynamics, methods are available to estimate intrinsic degradation rates via reverse modelling techniques.

4. Comparison between Prospective Groundwater Studies and PWC Modeling Results

EPA should consider allowing registrants to choose to use existing field data, when available, from PGWs to refine drinking water risk assessments if needed. Use of these data could provide a more accurate evaluation of model capability to characterize fate and transport of crop protection products.

PGW studies for 10 chemicals, representing four of the six PWC scenarios, were examined. However, model runs were set up to replicate the conditions of the PGW study, without modifying the underlying model parameterization aside from metabolism depth (p. 23).

The comparison between modeled data and field data from guideline PGW studies is a useful strategy for evaluating model performance. CLA would like to request more details on how this analysis was conducted and how the PGW conditions were replicated. Did the simulated depth in the model correspond to reported well depths with the maximum reported concentrations? Were the maximum concentrations reported from the PGW studies obtained only from wells, or were residues from lysimeter samples also included in the comparison?

The modeling results were higher than the maximum PGW concentration measured 63% to 77% of the time. While it is important not to underpredict exposure, it is also important not to overpredict exposure. Overpredictions of more than 10x occurred for four pesticides for the 1m0x and 1m10x assumptions, and three pesticides with the 2m0x, 3m0x, 4m0x, 2m10x, 3m10x, and 4m10x assumptions (p. 28; Figure 8 p. 29).

The comparison between maximum concentrations reported for various active ingredients from PGW studies and PWC modeling results included a detailed assessment on the few cases where the model underpredicted the field results; in most cases, clear evidence was available that explains the discrepancy. A detailed analysis for the compounds where the model significantly overpredicted the groundwater concentrations by >10x was not provided; as there were more frequent situations where the model overpredicted the actual concentrations observed in the field, it would be useful to understand why this happens. For pesticides that are not adequately characterized by the PWC model, even with the proposed modifications to the ASM and hydrolysis assumptions and a modified application schedule, further refinement options or reliance upon weight of evidence would be necessary. There are a significant number of PGW studies that were not included in the analysis, as the field areas did not correspond with the current six groundwater scenarios for PWC. EPA should consider a strategy to employ more of the field data in this analysis, as most PGWs are conducted in vulnerable regions and could provide useful information.

5. Water Quality Portal Monitoring Versus Modeling for Pesticides

The results of EPA’s comparison of Water Quality Portal (WQP) monitoring data with modeling using PWC-GW provides justification for modifying the model. The Agency’s assessment indicates that an appropriate balance between conservatism and realism could be achieved by assuming that aerobic metabolism is operative in soils to a depth of 2 meters and including a 10X constant degradation factor in its model to account for processes other than hydrolysis that reduce pesticide concentrations in groundwater. With review of the assessment comes the realization that data is sparse for properly assessing degradation of pesticides in soil below a depth of 2 meters; and that more research in this area is warranted.

In the context of utilizing the WQP monitoring data in its assessment, CLA agrees with the Agency’s assertion that:

> Samples may be from urban or agricultural wells, may not reflect areas vulnerable to GW leaching, may not be representative of drinking water wells, likely do not represent the conceptual model assumed in PWC modeling, and may not have been collected in an area where the pesticide was used.

However, the use of the highest measured concentration of a chemical within a WQP monitoring dataset leads to results that are not representative of the bulk of the dataset and may reflect a false positive finding or a measurement with origin associated with product misuse. Although the

Agency did assess the sensitivity of using the highest concentration value by also assessing the mean of the top five WQP results, such an assessment should be made using a geometric mean to characterize the population of results more appropriately. Also, recognizing that the WQP monitoring datasets typically contain greater than 10,000 samples, solely making modeling comparisons using the 100th percentile result is highly conservative and would be bolstered by furthering the analysis. For example, by also considering modeling comparisons using the 99th and 99.9th percentiles, a more informative assessment could be made as these percentiles better reflect the overall data distribution.

The EPA's assessment considered the results for pesticides with a K_{OC} > 1966 L/kg-organic carbon with throughputs less than one (i.e., those that did not achieve complete breakthrough). The fact that all PWC modeled EDWCs were lower than the highest WQP measured concentration (even with a 100-year simulation) can be interpreted as evidence that the highest WQP in general may not be reflective of a chemical's true propensity for leaching. The Agency postulated that these WQP concentrations may be due to mechanisms of transport not simulated in the PWC such as macropore transport. It is more likely that such findings are evidence that the highest WQPs do not adequately reflect leaching causation by the physicochemical and biological properties of the monitored pesticides. The findings may instead be associated with such factors as lack of integrity in a well casing or a false positive due to an unknown factor occurring in the analytical laboratory.

Contrary to EPA's findings for pesticides with low mobility, CLA has found several cases where the PWC modeled groundwater EDWCs were higher than the highest WQP measured concentrations by two to three orders of magnitude[5][6]. The K_{OC} values for those compounds range from 1000 to more than 2000 L/kg, and the modeled EDWCs were compared to summaries of 30 years of WQP well monitoring data for the respective compound. These examples provide additional evidence that the PWC-GW model in its current form is generally overly conservative for both mobile and immobile compounds.

CLA considered the comparative assessment that EPA conducted between WQP data and PWC-GW modeling. The overall effort is well conceived, and the assessment of the results is suitable. However, the datasets that considered ASM below 2 meters are limited. When the modeled PWC for the selection of chemicals was compared to the highest WQP, in 54% of the cases, the modeled results were greater than 10x higher. In contrast, in only 4% of the cases were the highest WQPs greater than the modeled results. These findings support use of this modeling paradigm since it would appear more realistic than current modeling practices used by EPA for groundwater modeling.

6. Additional Scenarios and Considerations

CLA supports the efforts to improve the PWC model to reflect the fate and transport of crop protection products more accurately in the subsurface. A more robust tiered groundwater exposure assessment approach is still needed which allows for potential refinement based upon

[5] EPA-HQ-OPP-2015-0378-0024
[6] EPA-HQ-OPP-2014-0782-0020

scientific data, like the framework currently in place for the food inputs to the dietary risk assessment.

6.1. Development of Additional Groundwater Scenarios

The Guidance for Using PWC-GW in Drinking Water Exposure Assessments[7] involves a tiered system in which Tier 1 involves assessing the upper-bound pesticide concentration produced from the six standard scenarios located in highly vulnerable areas in the United States. Tier 2 suggests consideration of "well-setbacks, developing representative scenarios, considering additional fate inputs such as subsurface degradation, etc." EPA has done a thorough analysis of the impact of subsurface degradation which was a potential refinement in Tier 2. We assume that the extension of subsurface degradation to 3m will become Tier 1. For higher tiered assessment, it may be useful to incorporate the option of exploring depths lower than 3m if the registrant has data to support it.

While EPA has moved science forward with their analysis of subsurface metabolism with depth in groundwater modeling, the Tier 2 refinement of developing representative scenarios still lacks defined guidance. Some registered products are not used where the PWC-GW standard scenarios are located. While it is understood that the goal of the groundwater assessment framework is to give a conservative view of potential pesticide exposure to groundwater drinking water sources, the spatial extent of the existing six scenarios, located in the eastern and upper midwestern parts of the country, does not adequately cover labelled uses and major agricultural areas. For example, Padilla et al. (2017)[8] highlighted the fact that grain crops, such as wheat (grown primarily in central west and western parts of the country), are not represented in standard scenario list. Furthermore, spatial representation of scenarios commensurate with regional agronomic conditions should form part of the screening assessment as is the case for surface water exposure assessment. At a minimum, if it is expected that registrants will develop scenarios as a refinement option, a guidance document for developing new scenarios should be provided for consistency across registrants. Such a guide could include the changing the weather station or using field data from a PGW. However, it is recommended that standard scenarios should be developed by EPA for each Hydrologic Unit Code (HUC) 2 region such that groundwater exposure concentrations predicted from the most highly vulnerable locations do not over- or under-represent potential exposure to groundwater sources based on representative, realistic use patterns.

In their work to expand the footprint of groundwater standard scenarios to include wheat, Padilla et al. (2017)[8] described a methodology to develop vulnerable groundwater scenarios which can be modified to represent major crop growing areas and HUC 2 region intersection. The first step in the approach is to overlay crop data with soil, weather, and shallow well locations. This is like the newly developed surface water scenarios.

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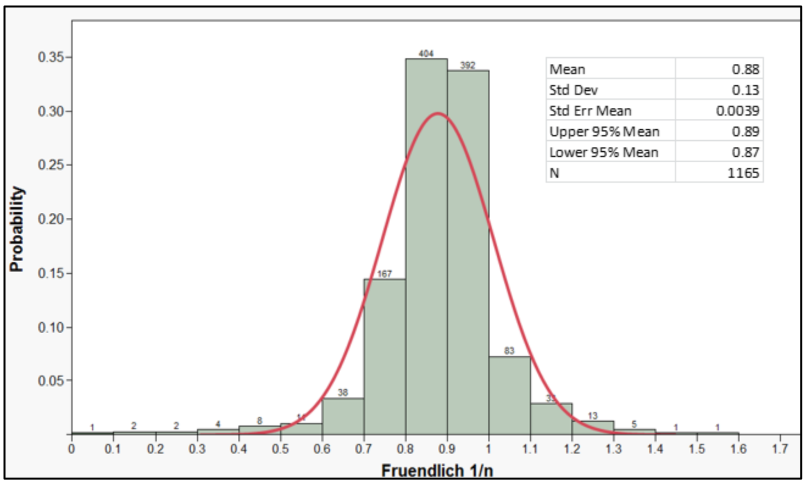
[7] US EPA (2012). PRZM-GW Version 1.07 - Guidance for Using PRZM-GW in Drinking Water Exposure Assessments. https://archive.epa.gov/epa/pesticide-science-and-assessing-pesticide-risks/przm-gw-version-107-guidance-using-przm-gw-drinking.html. Accessed May 10, 2021

[8] Padilla, L., Winchell, M., Peranginangin, N. and Grant, S. (2017), Development of groundwater pesticide exposure modeling scenarios for vulnerable spring and winter wheat-growing areas. Integr Environ Assess Manag, 13: 992-1006. https://doi.org/10.1002/ieam.1925

EPA can also extend current general scenarios to more specific scenarios for groundwater modeling. EPA's current groundwater modeling scenarios mainly focus on field crops, but there are no specific scenarios for non-crop uses, including turfgrass. The agronomic properties of turf are quite different than field crops. Therefore, directly adopting EPA's groundwater scenarios for turf use compounds may result in quite unreasonable exposures in groundwater. The perspectives in turf groundwater scenarios can include improvements in thatch layer representation, suitable plant growth parameters, and irrigation information for turf grasses.

6.2. Non-linear sorption

In a presentation to EPA, CLA summarized two independent sets of adsorption study data for more than 1000 compounds (Figures below). The two independent datasets demonstrated a remarkably consistent result: same mean 1/n (0.89) of the Freundlich parameter in two very different sample sizes in the data. Clearly, sorption nonlinearity (i.e., 1/n≠1) is a shared property by many compounds. Given the availability of the measured 1/n values in the guideline adsorption studies (835.1230), CLA strongly recommends the PWC to adopt the nonlinear isotherm throughout the soil/subsurface profile for all groundwater assessments.



6.3. Anaerobic metabolism

Although aerobic soil metabolism is commonly recognized as a major route of microbial degradation of pesticides in soil, anaerobic metabolism can be significant for some compounds in the subsurface environment where oxygen is absent or limited. For compounds where data supports anaerobic metabolism, CLA recommends that the PWC-GW model use such valid mechanism of degradation in the subsurface in addition to hydrolysis for compounds on a case-by-case basis. This can be parameterized as a simple lumped rate constant of both hydrolysis and anaerobic metabolism without embarking model modification.

6.4. Aged Sorption

As a consideration for higher tiered refinement options for groundwater risk assessment, CLA recommends the use of time-dependent sorption, aged sorption, kinetic sorption, or non-equilibrium sorption as a model input whenever experimental data is available or submitted to the Agency. This increase in sorption slows the downward movement of compounds through the soil profile. The modeling of this process has been largely developed in Europe and was first introduced as an option for regulatory modeling in Europe in 2000. The Pesticide Emission Assessment at Regional and Local Scales (PEARL), Pesticide Leaching Model (PELMO), macropore flow model (MACRO), and Forum for the Coordination of Pesticide fate models and their Use (FOCUS) PRZM models all can simulate time-dependent sorption. Time-dependent sorption is also an option available in the EPA PWC, but it is not activated nor used in regulatory modeling. The use of time-dependent sorption brings predicted values closer to the monitoring data, so the predictions are more reflective of actual exposure[9]. The use of time-dependent sorption should be an option, but only when experimental data are available to derive the descriptive parameters. In the United Kingdom, the Chemicals Regulation Division of the Health and Safety Executive recently released a final guidance document for conducting aged sorption studies, deriving aged sorption parameters for use in regulatory models and the conduct of environmental exposure assessments using these parameters[10]. The guidance reflected European Food Safety Authority recommendations.

6.5. Kinetics

CLA would like to highlight that similar improvement and further guidance and discussion around modeling degradation pathways, metabolites, and improvements over the Total Toxic Residue (TTR) approach used in exposure modeling would be welcome. Several recent assessments have used pathway modeling and PWC has this capability to improve on TTR approaches, but further guidance on selecting modeling parameters from pathway kinetics would remove uncertainties and open a discussion of best practices.

7. General Comments

Timeframe for Implementation

CLA would like to know the timeframe on when the specific concepts addressed in this document can be implemented as refinement to the groundwater exposure assessment.

Modeling Method Evaluation

CLA would strong request that EPA provide the modified PWC model, a PWC input dataset and instructions on enabling PWC to accommodate the changes to the groundwater modeling approach evaluated in the analysis. This will help CLA and other stakeholders to reproduce and validate the methodology and results presented in the analysis.

Corrections

A few areas in the report require minor editing. Although the overarching conclusions may not be impacted, CLA would like the Agency to exercise care when selecting information for the report. As an example, on page 39, Table 4, the K_{OC} for glyphosate is shown as 157 while it

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[9] CropLife America. 2017. Refined Drinking Water Assessments. 2017 CLA and RISE Regulatory Conference. Series II: Screening Approaches for Drinking Water Assessments.

[10] Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments (2021). https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_ppp_app-proc_guide_fate_aged-sorption.pdf. Accessed May 2021

should be 175 (mL/g). This error was a carryover from the risk assessment document that EPA failed to correct.

There seems to be an inconsistency between Table 2 (page 27) and its graphic representations (Figures 7 and 9). As an example, in Table 2, the "Max PGW" concentration for fenamiphos is 0.58 ug/L, while the axis in Figure 7 (yellow bar) suggests that the concentration value is greater than 1. CLA would like to encourage EPA to review the data used to generate the graphs in the report.

On page 39, Table 4, the "Count Peak PWC below WQP Dissolved" for azinphos-methyl is 31, which is greater than the total number of detections (23). CLA requests that EPA review and clarify the discrepancy.

On page 41, Table 5, the "Mean of Top 5 WQP Dissolved" for dacthal is 53.6, despite the fact that "Max WQP Dissolved" is not available. For chlorothalonil and linuron, the "Mean of Top 5 WQP Dissolved" is greater than "Max WQP Dissolved." CLA requests that EPA review and clarify the discrepancy.

8. Conclusion

Again, CLA appreciates the opportunity to comment on the Agency's effort to address longstanding concerns with the degree of conservatism within groundwater assessment tool. The development of the groundwater framework to reflect the technical understanding is a positive step towards ensuring that predicted exposure estimates reflect actual exposure. CLA finds the Agency's effort commendable and supports the changes in the methodology for estimating pesticide concentrations in groundwater.

Should EPA have any questions or wish to discuss these issues further, please do not hesitate to contact us. Thank you for your consideration of these comments.