Response to Water Board Water Quality Criteria Excerpts – Adsorption/Desorption Details

Paul Hendley. Phasera Ltd. Bracknell, UK. November 30th 2015.

At a recent meeting between PWG and Water Board Staff it was mentioned that PWG had some detailed observations regarding generally minor errors in the document that accompanied draft water quality criteria documentation for six pyrethroid AIs released to the public around May 29, 2015 via
http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/central_valley_pesticides/pyrethroid_tmdl_bpa/index.shtml

Draft reviewed - "Excerpt On Alternatives Considered And Recommendation For Water Quality Objectives Chapter 5 And Appendix C"

Observations relating to adsorption/desorption aspects in the excerpt (separate documentation will address other topics):

a) Generally, the document applies the key principles of equilibrium partitioning correctly and makes highly scientifically supportable statements regarding the importance of differentiating between freely available and total measures of pyrethroid present in samples. PWG has strongly advocated for the application of EqP principles for regulatory purposes at both the State and Federal levels for many years.
b) However, we believe there are errors in some of the tables abstracted from other references and that some improbable numbers have been included in the analysis. These detract from the quality of the remainder of the document and should be corrected in the interests of using best science.

Specific Comments:

1) The document specifies that relevant adsorption data are derived from studies with sediment to water ratios of <2:100. PWG strongly supports this for the interpretation of monitoring sample data where the fractions of suspended sediments and DOC/TOC found are very low. PWG will shortly be reporting some data that indicates that adsorption measurements made at much higher ratios of sediment to water can differ significantly from those generated at low ratios (e.g. <2:100) thus highlighting the importance of the recommendation made in the excerpt.
2) As mentioned above, PWG has consistently advocated the adoption of EqP approaches and we were therefore encouraged to see that the excerpt properly applies those principles. However, since EqP is a well-established principle referred to frequently across a wide range of chemistries in the ecological peer reviewed literature, we recommend that a short paragraph or two be introduced to the document to indicate to local stakeholders that the discussion and recommended approaches are following well established and accepted scientific thinking. Citing the seminal references for EqP (e.g. Di Toro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. "Technical basis for establishing sediment quality criteria for non-ionic organic chemicals using equilibrium partitioning". Environ. Toxicol. Chem. 1991, 10, 1541-1583), and a couple of examples of EPA regulations that already use it would help establish that these proposed criteria do not reflect unusual application of adsorption data.
3) The excerpt mentions that freely dissolved concentrations are best obtained from samples filtered using the USGS approach of rapid filtration (Hladik et al. 2009) allied with regular analytical methodology and DOC measurement. PWG believes that the use of SPME

analytical approaches using D6 internal standards (in addition to the measurement of DOC as confirmation) is a preferable, and direct, methodology.

4) The reference to "….Yang et al. (2006a)" on page 12 actually appears to refer to reference Yang 2006b (dealing with Ceriodaphnia) rather than 2006 a which addresses Daphnia? The references to data derived from the Kd values in Yang 2006b in table 5-1 are correct. The reference to Yang et al. 2006a, on page 11 referring to it as the source for SPME data is not correct as this paper does not use the term SPME (although it does report on using PDMS fibers). We believe that page 11 should have cited Yang 2006 b and c and Yang 2007)
5) Table 5-2 contains a number of apparent errors we cannot interpret from the cited literature. Firstly, the value of 6.9% in the %OC column is incorrect – Table 5 in Chickering 2014 (supplied earlier) makes it clear that this value is %OM not %OC. The TOC numbers in table 5-1 for the Cui paper match the numbers in the publication.
6) As far as we can tell the K_{DOC} numbers reported in Table 5-2 do not tie up with the numbers in Table 4 of Cui et al 2013 using the organic carbon contents column in 5-2 as the tie across (via the TOC data in Table 1 of Cui et al). For example, given the %OC value of 0.5%, which ties up to the SC sediment, Table 5.2 reports a K_{DOC} of 43,440,000 for the SC sediment whereas Cui et al report 600,000. It should be noted that the coefficients appear to be mostly correct but badly jumbled, and some of the numbers simply cross-refer to the wrong sediments. This table needs reworking to match up with the literature values. In practice, the table should name the sediments since the OC% is absolutely unrelated to the estimation of KDOC and is liable to mislead readers. If the table used the sediment name and the DOC measurement, it would be more informative and would also allow the reader to match the values obtained from the GCP sediment by Cui et al and by the PWG.
7) Table 5-2 includes a number of Kdoc values of over 12,000,000. PWG believes that these are highly improbable values and, although potentially "helpful" for estimating pyrethroid ambient freely available (bioactive) concentrations in monitoring study samples, they are sufficiently unlikely as to not represent best-available science positions. As mentioned in the May 8, 2015 email from Dr. Hendley to Ms Fojut, PWG strongly recommends that ONLY the PWG $K_{OC\text{-}SPME}$ data be used for regulatory purposes because:
    a. it is consistent across chemicals,
    b. it uses the same sediments across AIs,
    c. it uses the "staggered injection" approach to minimize the standards problem,
    d. it standardized as many variables as possible across all AIs.

    PWG believes that the results >12,000,000 are improbable for reasons outlined in the attached table which lists the results from a recent K_{OW} experiment conducted for all the PWG AIs (Dix et al, 2014) in response to suggestions from an EPA Science Advisory panel (Dorsey and Kendall, 1999) and a peer review group at the Oak Ridge National Laboratory (Armstrong et al. 2000). The table compares the historic values summarized by Laskowski (Laskowski, 2002) with the recent values measured at the same time for all AIs under conditions recommended for highly hydrophobic molecules (slow-stir technique) by Dix et al (2014). It shows that the more recent, more comparable study results are more closely bunched as would be expected for a chemical class as similar to

one another as the pyrethroids. When these high quality recent measurements are inserted into the algorithm for estimating K_{OC} from the K_{OW} coefficient used in the QWASI fugacity model, the maximum theoretical value for K_{OC} is just over 12,000,000. As mentioned in the email to Ms. Fojut, PWG research has strongly suggested that the anomalously high results in Cui et al and transferred to table 5-2 in the excerpt may be due to analytical anomalies associated with SPME analyses. Chickering et al 2014, discussed the probable reason for those problems and how the PWG study took steps to avoid these errors.

Table 12. Historical and recently measured octanol-water partition coefficients along with estimates of corresponding theoretical maximum K_{OC}.

Pyrethroid	Laskowski (2002) LogP[a]	Dix (2014) log $P_{OW,AV}$[b]	Theoretical K_{OC}[c]
Bifenthrin	6.4	7.48 (0.0302)	12,100,000
Cyfluthrin	5.97	6.86 (0.0495)	2,970,000
Cypermethrin	6.54	6.81 (0.0434)	2,650,000
Deltamethrin	4.53	6.99 (0.0153)	3,740,000
Esfenvalerate	5.62	7.17 (0.0220)	6,060,000
Fenpropathrin	6.00	6.40 (0.00650)	1,030,000
Lambda-cyhalothrin	7.00	7.06 (0.0104)	4,820,000
Permethrin	6.1	7.08 (0.00960)	5,040,000
Tefluthrin	NA	6.55 (0.0146)	1,454,735

[a] Logarithmic expression of K_{ow}; collected measured values (Laskowski 2002).

[b] Octanol-water partition coefficients of pyrethroid AIs (expressed as log P_{OW}, equivalent to log K_{OW}) using a weighted average from three replicates (with the variance in parentheses) as recommended in OECD guideline 123 (Dix 2014).

[c] Estimated theoretical K_{OC} values obtained from measured log P_{OW} values using the regression equation employed in the QWASI fugacity model (Mackay 2001; Mackay et al. 1983). The regression is K_{OC} = 0.41*(10^LogP).

8) The attached spreadsheet indicates that we managed to duplicate the reported K_{DOC} coefficients that are reported in the excerpt for the PWG studies. As explained in an email sent to Ms. Fojut from Dr. Hendley on May 8, 2015, we had not reported the K_{DOC} value in our batch adsorption study because we did not have reliable DOC measurements for every AI. However, since the PWG studies were run with replicate batches of the same two sediments extracted using the same equipment under identical conditions, we believe that each experiment was a replicate in terms of DOC generation (i.e. the pyrethroid AI added was the only difference between tests and would not have influences the DOC concentration). Therefore, PWG strongly recommends that, in order to remove uncertainty related to the variation in DOC analysis, the K_{DOC} coefficients should be calculated for each AI using the mean DOC across all replicates for that sediment rather than the individual measurements made for each AI. One immediate advantage of using this approach is that K_{DOC} may be estimated for all the AIs rather than just for those with individual DOC measurements. The spreadsheet contains the appropriate values obtained for the freshwater natural sediment (GCP) using this approach for your reference.
9) PWG believes that Table 5-4 probably contains several errors – firstly, the Log K_{DOC} values in the 20th and 50th percentile columns appear to have been swapped. Secondly, it seems unlikely (but technically possible) that the 50th and 20th percentiles for cypermethrin would be identical.

10) In table 5-21 we were unable to reproduce the 0.05 ng/L value for cyfluthrin at Pleasant Grove Creek using the numbers available to us. We could approximate most of the other estimates in this table.
11) PWG noted that the review failed to mention the extensive documentation in the peer reviewed literature that, as residues age in sediment, substantial portions become bio-inaccessible. Experiments have shown that pyrethroids also demonstrate decreasing levels of bio-accessibility with time (You et al 2006, Xu et al, 2008). A simple concept to explain this is that the pyrethroid parent AI diffuses deeper into organic matter particles so that it is unable to exchange with aqueous systems at the surface of the particles. Equivalent behavior is seen with other extremely hydrophobic molecules (e.g. Fang et al, 2014) indicating that these results are not surprising for molecules like pyrethroids. While this factor would be difficult to build into WQC directly, it should be mentioned in the report as another reason why calculations based on 100% of the measured residue in sediments are likely to be even more conservative than expected.

References:

Armstrong A, Jones D, Lyon B. 2000. Review of Pyrethroid Working Group's (PWG) probabilistic risk assessment for synthetic pyrethroids. Oak Ridge National Laboratory. Oak Ridge, TN

Dix M. 2014. Determining the partitioning coefficient (n-octanol/water) of nine pyrethroids by the slow-stirring method following OECD guideline 123. PWG Report - PWG-ERA-04a. MRID 49314702. Smithers Viscient. Wareham, MA.

Dorsey L, Kendall R. 1999. FIFRA scientific advisory panel meeting, February 23-24, 1999, held at the Holiday Inn, Arlington, Virginia. Arlington, VA: FIFRA/Scientific Advisory Panel. 13 p.

Fang J, Bao L-J, Crago D, Schlenk D & Gan J. "Use of Isotope Dilution Method To Predict Bioavailability of Organic Pollutants in Historically Contaminated Sediments." Environ. Sci & Technol. 48.14 (2014): 7966-7973

Laskowski D. 2002. Physical and chemical properties of pyrethroids. Rev. Environ. Contam. Toxicol. 174:49-170.

Mackay D. 2001. QWASI model of chemical rate in a lake. In: Mackay D, editor. Multimedia environmental models: The fugacity approach - second edition Boca Ration, FL: CRC Press. p. 201-213.

Mackay D, Joy M, Paterson S. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. Chemosphere. 12:981-997.

You J., Landrum P. F., & Lydy M. J. (2006). Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. Environ. Sci. Technol, 40(20), 6348-6353.

Xu Y., Gan J., Wang Z. & Spurlock F. Effect of aging on desorption kinetics of sediment-associated pyrethroids. Environ. Toxicol. Chem. 2008, 27 (6), 1293−1301.