PENTACHLOROPHENOL TASK FORCE

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By Electronic Mail at Paula.wilson@deq.idaho.gov

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Re: **Water Quality: Docket No. 58-0102-1201 - Proposed Rule**

Dear Ms. Wilson:

These comments are submitted on behalf of the Pentachlorophenol Task Force which represents the North American registrant of pentachlorophenol (PCP). Our comments concern the proposed Idaho human health criteria for the wood preservative pentachlorophenol (PCP). We understand that Idaho has relied in part on the bioaccumulation factor (BAF) values for PCP as calculated by the U.S. Environmental Protection Agency (US EPA) in connection with US EPA's 2015 final updates to its national 304(a) criteria, recommendations to states and tribes, for protection of human health. However, as explained below, US EPA made an error in its calculation of the BAF values for PCP. Specifically, EPA used a log Kow of 5.12 as the denominator in the equation for the Food Chain Multiplication (FCM) factors in the model used to derive the BAFs for each of the three tropic values. This log Kow is incorrect as the log Kow for PCP is pH dependent. The correct log Kow at environmentally relevant pH is no higher than 3.69 and this value should have been used in the BAF calculation. A log Kow of less than 4.0 would result in a FCM of 1.0 rather than the higher FCM used by U.S. EPA in deriving the BAFs for PCP. We urge the Idaho Department of Environmental Quality to rerun the modeling used to derive the BAFs for PCP with the correct log Kow as Idaho cannot simply adopt U.S. EPA's calculations in its rulemaking without independently assuring the correctness of those calculations.

<u>The Kow for PCP is pH Dependant</u>

The octanol-water partition coefficient (Kow) is a physicochemical parameter that quantifies the hydrophobicity of an organic compound. It is typically represented by the following equation.

$$K_{ow} = \frac{[HA_o]}{[HA_w]} \qquad (1)$$

where, $[HA_o]$ = concentration of the protonated acidic compound in the octanol phase
$[HA_w]$ = concentration of the protonated acidic compound in the water phase

For ionizable hydrophobic compounds, like pentachlorophenol (PCP), the Kow will depend on the pH (speciation) and ionic strength of the aqueous solution as well as the formation of ion pairs. For ionizable acidic compounds the apparent partition coefficient is typically represented as a distribution ratio, D, based on the total concentration.

$$D = \frac{[HA_o]+[A_o^-]+[MA_o]}{[HA_w]+[A_w^-]+[MA_w]} = K_{ow} \qquad (2)$$

where, $[A_o^-]$ = concentration of deprotonated acidic compound in octanol phase
$[MA_o]$ = concentration of ion pair acidic compound in octanol phase
$[A_w^-]$ = concentration of deprotonated acidic compound in water phase
$[MA_w]$ = concentration of ion pair acidic compound in water phase

Several laboratory studies have investigated the Kow of PCP. Most of these studies determined the Kow at low pH values (pH < pKa) and high ionic strengths in order to assess the neutral form of the compound (Table 1). A few of these studies looked at Kow as a function of pH and ionic strength.

Table 1. Measured log Kow values under low pH conditions (NR = Not Reported).

log Kow	pH	Ionic Strength (μ)	Source
5.04	2	0.05 M $NaHCO_3$	Xie et al. (1984)
5.24	2	0.01 M HCl	Schellenberg et. (1984)
5.01	NR	NR	Callahan et al. (1979)
5.12	NR	NR	Hansch et al. (1995)
4.72	2.4	NR	Kaiser and Valdmanis (1982)
4.74	2.1	0.1 M KCl	Nowosielski and Fein (1998)

Kaiser and Valdmanis (1982) measured the Kow of PCP as a function of pH (pH 1.2 to 13.5); however, the pH of the aqueous phase was measured only at the start of the experiment and not after the octanol-water system had reach equilibrium. In addition, Kaiser and Valdmanis (1982) did not control ionic strength over the pH range, which could also affect the final results. The log Kow was relatively constant over the pH range 1.2 to 4.7 ranging from 4.84 to 4.57. At pH > 5, the log Kow decreased due to the ionization of this weak acid (pKa = 4.8; Jafvert et al., 1990). The log Kow values were relatively constant over the pH range 9.3 to 11.5 ranging from 1.45 to 1.3. They also demonstrated that an increase in ionic strength increased the Kow.

Jafvert et al. (1990) measured the octanol-water distribution, D, of PCP as a function of pH and ionic strength. The pH was measured after equilibrium in these experiments. The pH dependent experiments were conducted at a constant ionic strength (0.1 M KCl). They found the neutral species to dominate both phases when the pH < pKa and the D value to be independent of pH (log Kow ≈ 5). When pH > pKa, the neutral species dominated in the octanol phase and the anionic species dominated in the aqueous phase, causing D to be pH dependent. At pH > 9 the anion dominates both phases and the D is independent of pH (log Kow ~ 1.8), but dependent on ionic strength. In experiments at pH = 12, the log

D = 1.75 for 0.2 M KCl and 1.4 for 0.05 M KCl, demonstrating an increase in partitioning with an increase in ionic strength.

Westall et al. (1985) also demonstrated that log D for PCP is dependent on pH and ionic strength of the aqueous phase. They found that for high aqueous pH values and ionic strengths the dominant species in the octanol phase were the chlorophenolate ions in association with K^+ counter ions. Also, they found that at pH = 11 the log D was a function of ionic strength with a log D = 1.9 for 0.2 M KCl, log D = 1.2 for 0.02 M KCl, and log D = 0.6 for 0.002 M KCl.

Nowosielski and Fein (1998) evaluated the log Kow of PCP as a function of pH and ionic strength. Experimental log Kow results had significant differences between the initial and equilibrium pH values when the pH > pKa (Table 2). They also found a pH dependence in log Kow over the range pKa – 1 < pH < pKa + 3. At lower and higher pH values the behavior was independent of pH (Table 2). The increase in Kow at pH > 11 most likely was due to ionic strength effects from adding a large concentration of base.

Table 2. pH dependent log Kow for PCP, and pH values at test initiation and at equilibrium.

Initial pH	Equilibrium pH	log Kow	Ionic Strength (M)
2.1	2.1	4.74	0.1
3.1	3.1	4.74	0.1
4.1	4.1	4.70	0.1
5.0	4.7	4.60	0.1
5.7	5.0	4.54	0.1
6.1	5.4	4.27	0.1
6.6	5.7	4.08	0.1
7.2	5.9	3.69	0.1
8.0	6.0	3.59	0.1
8.5	6.1	3.45	0.1
9.2	6.2	3.25	0.1
10.1	6.9	2.30	0.1
10.9	7.1	2.07	0.1
11.6	11.6	1.79	0.11
12.2	12.1	1.84	0.13
12.4	12.4	1.87	0.16
13.0	12.9	2.00	0.69
13.3	13.2	2.18	1.02

Nowosielski and Fein (1998) also develop an empirical model to predict the log Kow for acidic compounds as a function of pH and ionic strength. Inputs for the model are log Kow at low pH (pH < pKa) and the acidity constant (pKa). The model was built with data generated for PCP at an ionic strength of 0.1 M (Table 2).

$$\log K_{ow(pH/0.1M)} = \log K_{ow(n)} - \Delta(\log K_{ow}) \cdot \frac{1}{10^{(1.4+pKa-pH)}+1} \quad (3)$$

where, $\log K_{ow(pH/0.1M)}$ = log Kow at the pH of interest for a 0.1 M reference solution

$\log K_{ow(n)}$ = log Kow of the neutral species

$\Delta(\log K_{ow})$ = change in log Kow from the neutral species to the anionic species (2.9 for PCP)

The model was expanded to include an ionic strength (μ) adjustment:

$$\log K_{ow(pH/\mu)} = \log K_{ow(pH/0.1M)} + (slope\ term) \cdot (\log \mu - \log \mu_{0.1\ M\ reference\ solution}) \quad (4)$$

where, $\log K_{ow(pH/\mu)}$ = log Kow at the pH and ionic strength of interest

$\log K_{ow(pH/0.1M)}$ = value determine by equation (3) at pH of interest and μ = 0.1 M

$\log \mu$ = ionic strength of interest

$\log \mu_{0.1\ M\ reference\ solution})$ = log (0.1) = -1.0

The slope term was determined by performing a regression analysis on log Kow verse log μ values for PCP (using data from Nowosielski and Fein, 1998; Westall et al., 1985) over a range of pH values > pKa and μ values of 0.001 to 1.0 M (log Kow = 2.2536 + 0.60037(log μ), r^2 = 0.959, n = 8). The slope relating log Kow to log μ is 0.6.

$$(slope\ term) = \left(1 - \frac{1}{10^{(pH-pKa)}+1}\right) \cdot (0.6) \quad (5)$$

Substituting equations (3) and (5) into equation (4) yields a model to predict log Kow values for PCP at any pH and μ.

$$\log K_{ow(pH/\mu)} = \log K_{ow(pH/0.1M)} + \left(1 - \frac{1}{10^{(pH-pKa)}+1}\right) \cdot (0.6) \cdot (log\mu + 1) \quad (6)$$

The expanded model was evaluated with experimental data collect at μ = 0.1 M and verified at μ = 1 M (Table 3). Equation (6) can be used to estimate the log Kow for PCP at any pH and μ.

Table 3. Evaluation (μ = 0.1 M) and verification (μ = 1.0 M) of the expanded empirical model for PCP.

pH	Log Kow (μ=1.0 M) measured(predicted)	Log Kow (μ=0.1 M) measured(predicted)	Log Kow (μ=0.001 M) measured(predicted)
2.1	4.8 (4.74)	4.74 (4.74)	- (4.74)
4.1	4.8 (4.82)	4.70 (4.72)	- (4.52)
5.7	4.4 (4.58)	4.08 (4.04)	- (2.98)
6.2	3.8 (3.87)	3.25 (3.29)	- (2.14)
6.9	3.0 (2.92)	2.30 (2.32)	- (1.13)
7.9	- (2.50)	- (1.90)	- (0.70)
11.6	2.1 (2.44)	1.79 (1.84)	- (0.64)

for the nonionic form of an acidic compound may not adequately reflect the actual bioaccumulation of a weak acid like PCP. The degree at which a weak acid ionizes depends on its pKa and the pH of the water, where the neutral species predominate below the pKa and the anion predominates above the pKa. This

transition from a neutral compound to an ionized compound will change its lipophilicity and thus its bioaccumulation in biota. The log Kow of the anion of an acidic compound is typically about 3.5 units lower than the neutral compound log Kow (Trapp and Horobin, 2005), but this difference in lipophilicity will vary from compound to compound.

Conclusion

Based on the foregoing, US EPA should have used a log Kow of no more than 3.69, which is the maximum log Kow for PCP at environmentally relevant pH , instead of the log Kow of 5.12 that U.S. EPA used as the denominator in the equation for the Food Chain Multiplication (FCM) factors for each of the three tropic values. Indeed, the log Kow value of 3.69 was determined at an ionic strength of 0.1 M. If the Kow was determined at a more realistic ionic strength, say 0.001 M, then the log Kow would even be lower. We urge the Idaho DEQ to rerun the modeling used to derive the BAFs for PCP with the correct log Kow as Idaho cannot simply adopt U.S. EPA's calculations in its rulemaking without independently assuring the correctness of those calculations.

Respectfully submitted,

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References

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