

AR226-0366

Attached are comments on the 3M Technical Report "Analytical Methodology and Support. Arthur Mendel, Project 9970612643 Fate of Fluorochemicals, Report No. 8, Jan. 17, 1979" made by Professor Stephen A. Boyd, Michigan State University, dated May 19, 1993.

006506

Review of Technical Report Summary Analytical Methodology and Support

Discussion and Results

The octanol-water partition coefficient of FM 3422 was reported as 6.6×10^6 . There is a strong correlation between the octanol water partition coefficient and the solubility in water for organic solutes given by the equation (Chiou et al., 1982, Environ. Sci. Technol. 16:4-10).

$$\log K_{ow} = 0.862 \log S_w + 0.710$$

This relationship would predict a supercooled liquid solubility of ca. 47 ppb FM 3422 based on the K_{ow} value of 6.6×10^6 . For the K_{ow} and S_w values to be compatible require that either FM 3422 is a liquid at room temperature or have a low melting point ($< 100^\circ\text{C}$). If the m.p. is $> 100^\circ\text{C}$ then the actual solubility should be lower ($\sim 10\times$) than the predicted supercooled liquid solubility, i.e., about 5 ppb instead of 50 ppb. If the m.p. of MF 3422 is > 100 to 150°C then either the measured K_{ow} or S is probably wrong. The relationship referred to in the reports is by the same group (Chiou et al.) and I think this is a useful exercise. The line plotted in Fig. 2 looks a little different than the equation above. The main cautionary note is that these relationships predict the supercooled liquid solubility of solids. If the solid has a high m.p. (> 100 to 150°C) the actual water solubility may be substantially ($\sim 10\times$) lower. When working with these equations, you need to plot the supercooled liquid solubility not the measured aqueous solubility of the solid. At any rate, it is a good estimate to give you an idea of where the experimental value should fall. It also emphasizes the importance and utility of obtaining accurate S_w and K_{ow} values.

Similar estimates of bioconcentration factors (BCF) can be obtained from empirical relationships between BCF and either K_{ow} or S_w , with each species (e.g., trout, guppie) yielding its own relationship. A unified relationship can be obtained by normalizing the BCF of a species by its lipid content, analogous to normalizing the soil sorption coefficient, K , to the soil organic carbon content to give K_{oc} . The normalized factor, BCF_1 , is linear with S_w and K_{ow} on a log scale for different species of aquatic organisms (e.g., zooplankton, guppies, rainbow trout, catfish). The equation is:

$$\log BCF_1 = 0.899 \log K_{ow} + 0.623$$

(from Chiou, 1985, Environ. Sci. Technol. 19:57-62). This equation has the advantage of predicting BCF values for different species, as long as you know their lipid content.

As mentioned earlier, the soil TLC plates are of limited value. They didn't distinguish the mobilities of FC 95 and FC 143 versus FM 3422 despite the fact that the former two compounds have much lower soil sorption coefficients than the latter. Hence, the assay seems insensitive.

Experimental

The water solubility here is reported as 5 ppm or 100 times the 0.05 ppm value discussed above. This has to be determined accurately. Micelle formation may occur and result in this high apparent solubility; the compound likely has surfactant qualities judging from its structure. You should know if it forms micelles. This is easily done by measuring the critical micelle concentration (CMC). There are a variety of methods for this determination. Sorption of this compound by soil may be quite different above and below the CMC.

Water solubility determinations. The difference of 43 times in the water solubilities of FM 3925 and FM 3422 seems rather large considering the high degree of structural similarity.

Recommendation

1. Obtain an accurate water solubility for FM 3422 and 3925*.
2. Obtain an accurate octanol-water partition coefficient for FM 3422 and 3925*.
3. Determine if FM 3422 and 3925 form micelles, i.e., measure the critical micelle concentrations.

*A key reference describing methodology for determining water solubility and octanol-water partition coefficient is:

C.T. Chiou and D. W. Schmedding. 1980. Measurement and interpretation of octanol-water partition coefficient and water solubility of organic chemicals. Association of Official Analytical Chemists. Washington, D.C.