Comment on "Policies for chemical hazard and risk priority setting: Can persistence, bioaccumulation, toxicity, and quantity information be combined?"

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In their article, Arnot and Mackay [1] use 200 chemicals from the Canadian Domestic Substances List (DSL) to illustrate a model that integrates persistence, bioaccumulation, toxicity, and quantity information for a specific substance to assess chemical exposure, hazard, and risk. The authors state that "[t]he DSL chemicals used in this study are not expected to appreciably ionize at environmental pH." The following compounds in the Supporting Information list used by Arnot and Mackay [1] have experimental or estimated pK_a values suggesting they would - in constrast to the claims of ref. [1] - be "appreciably ionize[d] at environmental pH" (operationally defined as between pH 5.5 [rainwater] and 8.1 [marine systems]): phenobarbital, 7.4 [2]; tetrabromobisphenol A, 7.5 and 8.5 [3]; pentachlorophenol, 4.74 [4]; 3-hydroxy-2-naphthalenecarboxylic acid, 2.8 [5]; 2-aminophenol, 4.78 [6]; 3-(3,4-dihydroxyphenyl)-2-propenoic acid, 4.62 [7]; (3-α,5)-3-hydroxy-cholan-24-oicacid, 4.75 [8]; 3,5-dichloro-N-(3,4-dichlorophenyl)-2-hydroxybenzamide, 6.78 [8]; 5-chloro-2-(2,4-dichlorophenoxy)phenol, 8.14 [9]; 4,4'-methylenebis[N-(1-methylpropyl)benzenamine, 5.13 and 5.93 [8]; 4,4'-[1,4-phenylenebis(azo)]bisphenol, 7.94 and 8.56 [8]; 1-[(2-chlorophenyl)diphenylmethyl]-1H-imidazole, 6.12 [10]; and 3,3,5,5-tetramethyl-[1,1-biphenyl]-4,4-diamine, 4.81 [8].

The ionization of these compounds means that the use of log K_{ow} (which is pH independent and applies only to a neutral species) for risk assessment needs to be replaced by the use of log D_{ow} (which is pH dependent and incorporates partitioning of the neutral and all ionized species at a particular pH). Similarly, any use of air-water partitioning in the risk assessment for such compounds must also explicitly incorporate ionization (see, e.g., ref. [11–14]). In addition, the authors include compounds which are expected to hydrolyze in aquatic systems (e.g., acyl halides, epoxides, various esters). In particular, the following acyl halides are included in the list by Arnot and Mackay [1], along with the estimated half-life in water provided by these authors: 2,4-dichlorobenzoyl chloride, 2,070 hours; benzoyl chloride, 361 hours; 2,5-dichlorobenzoyl chloride, 2,070 hours; and 3,4-dichlorobenzoyl chloride, 2,070 hours. The hydrolytic half-life of benzoyl chloride is well-established as taking on the order of 16 seconds in aqueous solution [15, 16]. Any substituted derivatives would be expected to have similar half-lives.

In addition, there is a mixture of two compounds as a single entry in the list (i.e., "acetic acid, trichloro-, compd. with N'-(4-chlorophenyl)-N,N-dimethylurea" [CAS 140410]). How does one evaluate the environment fate of such a mixture? The different compounds would dissociate from each other in atmospheric, aquatic, and biological systems, and have their own fates separate from each other. How can such a mixture have a single K_{ow} value? or half-life in a particular matrix? There are a significant number of such mixtures in the Canadian DSL, which makes the uncritical use of this resource for environmental modeling and risk assessments problematic.

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