CHEMICAL DATA BASE FOR HWIR99

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1.0 Introduction

The HWIR assessment tracks individual chemicals from specific waste streams disposed of in a waste management unit (e.g., landfill, wastepile, surface impoundment, land application unit, or aerated tank) into the surrounding multimedia environment at a series of locations around the country. A set of chemical-specific data are required for the environmental simulation models that are used to calculate chemical fate and characterize the resulting exposures and risks. To generate all relevant chemical-specific thermodynamic and kinetic data for the HWIR assessment, the use of measured, calculated and estimated data were necessary. The absence or scarcity of measured thermodynamic data that is reliable necessitated the use of data that had been generated by computational methods. The SPARC (System Performs Automated Reasoning in Chemistry) model, which is a computational method based on fundamental chemical structure theory, was the primary tool for calculating the thermodynamic constants.

The process of assembling kinetic constants for degradation pathways (i.e., hydrolysis, anaerobic biodegradation and aerobic biodegradation) focused on finding, evaluating, and summarizing measured data. Measured hydrolysis rate constants were found for most of the compounds of interest. When hydrolysis data were not available, a team of expert scientists provided rate constants based on the team’s experience with similar compounds, their knowledge of the theory of these processes, and their understanding of structure-activity relationships. Due to complex nature of biodegradation processes, only measured kinetic constants for a select group of high-volume chemicals were entered into the HWIR chemical data base.

A two-phase approach was used in developing the needed metal partition coefficients. In the preferred method of obtaining the coefficients, a literature survey was performed to determine the range and statistical distribution of values that have been observed in field scenarios. This included the collection of published partition coefficients for any of the metals in any of the environmental media of interest, or the estimation of partition coefficients from reported metal concentration data when feasible. The data retrieved in the literature search were recorded in a spreadsheet along with associated geochemical parameters (such as pH, sorbent content, etc.) when these were reported. It was anticipated that the literature search would not supply partition coefficients for all of the metals in all of the environmental media of interest. In the second-phase effort, statistical methods, geochemical speciation modeling, and expert judgement were used to provide reasonable estimates of partition coefficients not available from the literature.

1.1 *Summary of SPARC*

An in-depth description of SPARC procedures is beyond the scope of the discussion of this database project for the Offfice of Solid Waste (OSW) (see SPARC references 1-5). Reactivity assessment and computational algorithms are patterned after those presented by Dewar and Dougherty (6) but similar descriptions have been developed by many others. The basic philosophy is not to compute any chemical property from "first principles". Rather, it is to utilize directly the extensive knowledge base of organic chemistry. Organic chemists have established the types of structural groups or atomic arrays that impart certain types of reactivity and have described, in "mechanistic" terms, the effects on reactivity of other structural constituents appended to the site of reaction. To encode this knowledge base, a classification scheme was developed that defines the role of structural constituents in effecting or modifying reactivity. Furthermore, models have been developed that quantify the various "mechanistic" descriptions commonly utilized in structure-reactivity analysis, such as induction, resonance, and field effects. SPARC execution involves the classification of molecular structures (relative to a particular reactivity of interest) and the selection and execution of appropriate "mechanistic" models to quantify reactivity.

For example, for ionization pKa,

$$pK_a = (pK_a)_c + \delta_p (pK_a)_c$$

where $(pK_a)_c$ describes the ionization behavior of the reaction center, and $\delta_p(pK_a)_c$ is the change in ionization behavior brought about by the appended ‘perturber’ structure. SPARC computes reactivity perturbations, $\delta_p(pK_a)_c$, that are then used to "correct" the ionization behavior of the reaction center for the compound in question in terms of potential perturbation mechanisms.

$$\delta_p (pK_a)_c = \delta_{ele}\, pK_a + \delta_{res}\, pK_a + \delta_{sol}\, pK_a + \ldots$$

where $\delta_{ele}pK_a$ $\delta_{res}pK_a$, and ${}_{\delta sol}pK_a$ describe electrostatic, resonance and differential solvation effects respectively.

2.0 *SPARC Physical Models*

For all physical processes (e.g., vapor pressure, activity coefficient, partition coefficient, etc.), SPARC uses one master equation to calculate a characteristic process parameters:

$$\Delta G_{process} = \Delta G_{interaction} + \Delta G_{monomer}$$

where ΔG(monomer) describes entropy changes associated with mixing, volume changes, or changes in internal (vibrational, rotational) energies going from the initial state to the final state. ΔG(monomer) depends only on the phase change involved and in the present application is presumed to depend only on solute/solvent volumes in each phase. ΔG(interaction) describes the change in the intermolecular interactions in the initial state and final state. For example, for Henry's constant the interaction term describes the difference in the intermolecular interactions in the gas phase versus those in the liquid phase. The interactions in the liquid phase are modeled explicitly, interactions in the gas phase are ignored, and molecular interactions in the crystalline phase are extrapolated from the subcooled liquid state using the melting point.

The intermolecular interactions in the liquid phase are expressed as a summation over all the intramolecular interaction forces between the molecules:

$$\Delta G_{interaction} = \Delta G_{dispersion} + \Delta G_{induction} + \Delta G_{dipole} + \Delta G_{H-bonding}$$

each of these interactions is expressed in terms of a limited set of molecular-level descriptors (density-based volume, molecular polarizability, molecular dipole, and H-bonding parameters) which in turn are calculated from molecular structure.

SPARC presently predicts, for a large number of nonpolymeric organic molecules, ionization pKa's and numerous physical properties such as distribution coefficients between immiscible solvents, solubilities, vapor pressure, density, boiling point etc. The ultimate goal for SPARC is to model the chemical and physical behavior of molecules to predict chemical reactivity parameters and physical properties for the universe of organic molecules strictly from molecular structure.

2.1 *OSW Algorithms*

The algorithms presented below were used as models for fitting SPARC generated data for each of the properties included in this data base over the temperature range of 0°C to 60°C, in increments of 5°C. The coefficients given in the sample data base are those derived from this process.

From the above discussion it is apparent that the SPARC model does not use these algorithms to estimate chemical properties. The SPARC model consists of a set of core models describing intra/inter molecular interactions that are linked by the appropriate thermodynamic relationships to provide estimates of reactivity parameters under the desired conditions (temperature, pH, etc.). Temperature dependence is intrinsic to each core interaction model as opposed to algorithmically described at the property level.

However, using these algorithms to generate coefficients in the data base is the most practical method to incorporate SPARC generated data in light of the fact that OSW's models cannot link directly into the SPARC models.

2.2 *General Model*

For consistency and technical balance, the temperature dependence of all physical/chemical process parameters was represented as log-linear functions of 1/T (i.e., linear functions on a free energy basis).

For all properties (except gas diffusion and liquid density), the following temperature dependence model will be employed.

$$\log P_p^i = A_p^i + \frac{B_p^i}{T}$$

where

A_p^i, B_p^i are fitted coefficients for property "p" and chemical "i".

As an example, for vapor pressure

$$\log VP^i = A_{vp}^i + \frac{B_{vp}^i}{T}$$

or

$$VP^i = 10^{(A_{vp}^i + \frac{B_{vp}^i}{T})}$$

2.3 *Ionization*

As discussed above, ionization constants for HWIR chemicals are given by

$$pKa^i \equiv A_{Ka}^i + \frac{B_{Ka}^i}{T}$$

When multiple ionizations are involved, separate coefficients will be fitted for each ionization site. For example, the ionization constant for a chemical's first ionization site is denoted by

$$pKa(1)^i = A(1)_{Ka}^i + \frac{B(1)_{Ka}^i}{T}$$ for the first ionization.

SPECIAL NOTE

It should be noted that when using input from this data base for models that already have speciation embedded in the code, the data base coefficients for the neutral form should be used.

For example, if the model requiring Henry’s Law Constant coefficients for acrylic acid already has speciation effects embedded in the code, the equation "x", instead of equations "y" and "b", should be used with the coefficients given in the data base. Otherwise, the equations "y" and "b" should be used.

For properties where temperature and pH dependence are both relevant, the following equations will be applied. (The superscript molecule designation is dropped with the understanding that the equations will be fitted for each chemical.)

For organic acids, the fraction of the acid in the neutral form is the following

$$f_n = \frac{1}{1 + \frac{K_a}{H^+}} = \frac{1}{1 + 10^{(pH - pKa)}}$$

with

$$pKa = A_{Ka} + \frac{B_{Ka}}{T} \quad \text{which leads to} \quad f_n = \frac{1}{1 + 10^{[(pH - (A_{Ka} + \frac{B_{Ka}}{T})]}} .$$

For acids with two acid ionization sites (Ka(1), Ka(2)), the fraction of the acid in neutral form is

$$f_n = \frac{1}{1 + \frac{Ka(1)}{H^+} + \frac{Ka(1)Ka(2)}{(H^+)^2}} = \frac{1}{1 + 10^{[pH - pKa(1)]} + 10^{[2pH - pKa(1) - pKa(2)]}}$$

or

$$f_n = \frac{1}{1+10^{[pH-(A_{Ka(1)}+\frac{B_{Ka(1)}}{T}]}+10^{[2pH-(A_{Ka(1)}+A_{Ka(2)}+\frac{B_{Ka(1)}+B_{Ka(2)}}{T})]}}$$

For bases, the fraction of the base in the neutral form is the following

$$f_n = \frac{1}{1+\frac{H^+}{Ka}} = \frac{1}{1+10^{(pKa-pH)}} = \frac{1}{1+10^{(A_{Ka}+\frac{B_{Ka}}{T}-pH)}} .$$

For bases with two basic sites, the fraction of the base in the neutral form is

$$f_n = \frac{1}{1+\frac{H^+}{Ka(1)}+\frac{(H^+)^2}{Ka(1)Ka(2)}} = \frac{1}{1+10^{[pKa(1)-pH]}+10^{[pKa(1)+pKa(2)-2pH]}}$$

or

$$f_n = \frac{1}{1+10^{(A_{Ka(1)}+\frac{B_{Ka(1)}}{T}-pH)}+10^{(A_{Ka(1)}+A_{Ka(2)}+\frac{B_{Ka(1)}+B_{Ka(2)}}{T}-2pH)}} .$$

2.4 *Henry's Law Constant*

For Henry's Constant of a molecule with a single ionization site:

$H = f_n H_n + f_i H_i \approx f_n H_n$ where we assume $H_i \rightarrow 0$

where subscripts n and i denote neutral and ionic forms respectively. Multiple ionizations will be designated i1, i2, i3 ... etc.

The temperature dependence of the neutral form for Henry's Law Constant is given by

$$\log H_n = A_H + \frac{B_H}{T}$$

and as previously stated $H = f_n H_n + f_i H_i \approx f_n H_n$,

$$\log H = \log f_n + \log H_n$$

or

$$\log H = -\log\{1 + 10^{[pH - (A_{Ka} + \frac{B_{Ka}}{T})]}\} + A_H + \frac{B_H}{T}$$

2.5 *Solubility and Kow*

For solubility and octanol water distribution coefficients, the temperature dependence for non-ionizable compounds is given by:

$$\log S = A_S + \frac{B_S}{T} \quad \text{and}$$

$$\log K_{OW} = A_{Kow} + \frac{B_{Kow}}{T}$$

For chemicals that ionize,

$$S = f_n S_n + f_i S_i \quad \text{and}$$

$$K_{OW} = f_n (K_{OW})_n + f_i (K_{OW})_i$$

SPARC does not calculate ionic species solubility, so we will apply a multiplier to the neutral form.

$$S = [f_n + 10^2 (1 - f_n)] S_n = [10^2 - 99 f_n] S_n$$

where the same multiplier (10^2) is assumed for all ionic species.

The temperature and pH dependence are given by:

$$\log S = \log[10^2 - 99 f_n] + A_S + \frac{B_S}{T}$$

If the calculated solubility exceeds 10^5 mg/L, the compound can be assumed miscible.

For Kow (although we can generate estimates of Kow for ions) we have opted for a simpler model—that being the assumption that ions do not partition into octanol.

Therefore,

$$K_{OW} = f_n K_{OW}$$

and

$$\log K_{OW}(n) = A_{Kow} + \frac{B_{Kow}}{T}$$

$$\log K_{OW} = \log f_n + \log K_{OW}(n) = \log f_n + A_{Kow} + \frac{B_{Kow}}{T}$$

where f_n's are described previously.

2.6 *Molar Volume, Gas Diffusion and Density*

For molar volume and gas diffusion coefficient coefficient, we will fit the following equation(s):

$$Volume(V) = A_V + B_V T$$

$$Diffusion(D_f)_{air} = A_{Df}(T)^{B_{Df}}$$

For density, the following equation is used:

$$Densiy(D_n) = \frac{MW}{A_V + B_V T}$$

2.7 *Sorption*

For sorption, the only predictive algorithms are for neutral species. Although more mechanistic sorption models might be in order (especially for charged species), this representation is consistent with the approach used for other properties. Also, the solids characterization employed in this methodology is insufficient to 'drive' a site-specific sorption model(s).

The algorithms used relate the carbon-normalized sorption (K_{oc}) to the octanol water coefficient.

$$\log K_{oc} = \log(K_{ow})_n - 0.32$$

For ions, we will apply multipliers (M_i) to the neutral sorption.

$$K_{oc} = f_n(K_{oc})_n + f_i(K_{oc})_i$$

$$\log(K_{oc})_i = \log(K_{oc})_n + \log M_i$$

where for anions $M_{i1} \equiv M_{a1} \equiv 10^{-2}$

for dianions $M_{i2} \equiv M_{a2} \equiv 10^{-4}$

for monocation $M_{i1} \equiv M_{c1} \equiv 10$

for dication $M_{i2} \equiv M_{c2} \equiv 10^{2}$

The temperature dependence of sorption is assumed to be that of Kow.

$$\log(K_{oc})_n = A_{Kow} + \frac{B_{Kow}}{T} - 0.32$$

As given elsewhere the fraction of the acid in the neutral form, f_n, is given by

$$f_n = \frac{1}{1+10^{(pH-pKa)}} = \frac{1}{1+10^{[pH-(A_{Ka}+\frac{B_{Ka}}{T})]}}$$

$$f_i = f_a = 1 - f_n \,.$$

If two acid sites are involved

$$f_n = \frac{1}{1+\frac{Ka(1)}{H^+}+\frac{Ka(1)Ka(2)}{(H^+)^2}} = \frac{1}{1+10^{[pH-pKa(1)]}+10^{[2pH-pKa(1)-pKa(2)]}}$$

or

$$f_n = \frac{1}{1+10^{[pH-(A_{Ka(1)}+\frac{B_{Ka(1)}}{T})]}+10^{[2pH-(A_{Ka(1)}+A_{Ka(2)}+\frac{B_{Ka(1)}+B_{Ka(2)}}{T})]}}$$

$$f_{i1} = f_{a1} = 10^{[pH-(A_{Ka1}+\frac{B_{Ka1}}{T})]}\, f_n$$ for the monoanion.

$$f_{i2} = f_{a2} = 10^{[2pH-(A_{Ka1}+A_{Ka2}+\frac{B_{Ka1}+B_{Ka2}}{T})]}\, f_n$$ for the dianion.

If one basic site is involved

$$f_n = \frac{1}{1+10^{(pKa-pH)}} = \frac{1}{1+10^{(A_{Ka}+\frac{B_{Ka}}{T}-pH)}}$$

and

$$f_i = f_c = 1 - f_n \,.$$

If two basic sites are potentially involved

$$f_n = \frac{1}{1 + 10^{(A_{Ka(1)} + \frac{B_{Ka(1)}}{T} - pH)} + 10^{(A_{Ka(1)} + A_{Ka(2)} + \frac{B_{Ka(1)} + B_{Ka(2)}}{T} - 2\,pH)}}$$

$$f_{i1} = f_{c1} = 10^{(A_{Ka1} + \frac{B_{Ka1}}{T} - pH)} f_n$$ for the monocation and

$$f_{i2} = f_{c2} = 10^{(A_{Ka1} + A_{Ka2} + \frac{B_{Ka1} + B_{Ka2}}{T} - 2\,pH)} f_n$$ for the dication.

2.8 *Water Diffusivity*

For water diffusivity, the expression for molar volume $(V_T = A_V + B_V T)$ is substituted for V in the following equation (7):

$$D_{f(H_2O)} = \frac{1.4 \times 10^{-4}}{\eta_W^{\ 1.1} V^{0.6}}$$

Also, the viscosity of water, from the CRC Handbook (8) , is fitted to the algorithm, $\eta = A_\eta T^{B\eta}$, and substituted into this equation for η.

The resulting algorithm for water diffusivity is

$$Diffusion\left(D_{f(H_2O)}\right) = \frac{1.12 \times 10^{-22}}{T^{-7.33}\left(A_V + B_V T\right)^{0.6}}$$

3.0 Transformation Processes

The transformation pathways being considered for the HWIR assessment include hydrolysis and anaerobic and aerobic biodegradation. The process of assembling rate constants for these transformation processes focused on finding, evaluating, and summarizing measured data. When hydrolysis data were not available, a team of expert scientists provided rate constants based on the team’s experience with similar compounds, their knowledge of the theory of these processes, and their understanding of structure-activity relationships. Due to complex nature of biodegradation processes, only measured kinetic constants for a select group of high-volume chemicals were entered into the HWIR chemical data base.

3.1 *Hydrolysis*

A team of EPA scientists were responsible for compiling hydrolysis rates and determining probable pathways for hydrolysis reactions (9). The methods used to arrive at the reaction products were based primarily on the team's experience with similar compounds, their knowledge of the theory of these processes, and their understanding of structure-activity relationships. Literature searches were conducted afterwards to find needed fate data for the intermediate products of hydrolysis. If the literature failed to provide the required data, they were determined in the laboratory for some compounds.

The overall hydrolysis rate constant is a summation of the the respective rate constants for acid, neutral and base hydrolysis. The following formula is used:

$$k_{hydrolysis} = k_a[H^+] + k_n + k_b\left(\frac{k_w}{[H^+]}\right)$$

Substitution of 10^{-pH} for $[H^+]$ and $10^{\frac{-6013.79}{T}-23.6521\log T+64.7013+pH}$ for k_w (10) and then multiplication of the entire expression by $e^{\frac{E_a}{R}\left(\frac{T_2-T_1}{T_2T_1}\right)}$ to include temperature dependence leads to the overall equation below. E_a represents the activation energy and R represents the universal gas constant (1.987 cal/mol K). The activation energy used in these calculations is assumed to be constant at 20,000 calories/mole.

$$k_{hydrolysis} = \left[e^{\frac{20000}{1.987}\left(\frac{T_2-T_1}{T_2T_1}\right)}\right]\left[\left(k_a 10^{-pH}\right) + k_n + k_b\left(10^{\frac{-6013.79}{T_2}-23.6521\log T_2+64.7013+pH}\right)\right].$$

The temperatures, T_1 and T_2, are the standard temperature, 298.15 K, and the temperature at which the hydrolysis constant is desired.

3.2 *Aerobic Biodegradation*

As mentioned previously, due to complex nature of biodegradation processes only measured kinetic constants for a select group of high-volume chemicals were entered into the HWIR chemical data base. The Syracuse Research Corporation (SRC) reviewed the available aerobic biodegradation literature 23 high-volume HWIR chemicals (11).

The literature compilation began with an electronic search of two files in SRC's EFDB, DATALOG and BIOLOG, as sources of extensive biodegradation information. Currently, there are over 315,000 catalogued records for 15,965 compounds in DATALOG and nearly 62,000 records for 7,820 compounds in BIOLOG. BIOLOG search terms were used to identify aerobic studies with a mixed population of microbes from soil, sediment, or water. DATALOG was searched for useful field, ecosystem, and biodegradation studies. Relevant papers were retrieved and summarized in the database. In addition to the literature searches, the reference section of every retrieved paper was scanned in order to identify additional relevant articles. To be included in this database, the study was required: 1) to use soil, aquifer material, groundwater, aerobic sediment, or surface water and 2) to be incubated under aerobic conditions. Studies where the environmental material was seeded with microorganisms from other sources *(e.g.* sewage, anaerobic sediment, and enrichment culture experiments) were not included.

A database was constructed in PARADOX with fields for information about the site including location and type of site (*e.g.* spill site, industrial location, pristine site, landfill), the sampling protocol and method of analysis, the type of study (*e.g.* field, laboratory microcosm, *in situ* microcosm), whether the compound was present alone or found in the presence of others, pH, temperature, dissolved oxygen concentrations, redox conditions, initial and final concentrations of the compound, a published or calculated rate constant, length of the study, lag period, control results, identification of reaction products, general comments (to accommodate other important information) and an abbreviated reference from which the information was retrieved. Separation of the data into mineralization and primary degradation studies was initially completed and each category was considered separately. A range was given to represent the dispersion of the data within the group as well as a median value, representing the central tendency of the data. Only the range for primary degradation rates were entered into the HWIR99 chemical data base.

3.3 *Anaerobic Biodegradation*

A detailed discussion of the procedures used to acquire anaerobic biodegradation rate constants appears in a report by EPA's Office of Solid Waste (12). A brief summary of the approach used will be provided here. As with the rate constants for aerobic biodegradation, only measured kinetic constants for a select group of high-volume chemicals were entered into the HWIR chemical data base. This process began with an EPA sponsored workshop in Atlanta, Georgia (1997) on anaerobic degradation. Based on discussions at this industry with representatives from academia, industry and the EPA, the Agency developed criteria for the evaluation of the field as well as laboratory studies. At the workshop, industry representatives provided a report summarizing field and laboratory studies on anaerobic biodegradation. The report titled "Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies" was prepared for the American Petroleum Institute (API) by the Syracuse Research Center, 1997 (13). Because the criteria used by Syracuse Research Center (Appendix C) to review research papers was less stringent than the criteria decided upon at the workshop, EPA conducted a second review of the API-submitted Syracuse Research Center Report and summarized the results in the OSW report (12).

The studies submitted by Syracuse Research Center were divided into field and laboratory studies and the results from these studies are summarized separately. Results of a study were rejected if the study did not satisfy the Agency criteria. Each category (field or laboratory) is further subdivided based on the temperature, pH and the redox regime. The subsurface reducing environment was assumed to be grouped into two broad categories: methanogenic; and sulfate reducing. Studies which identified iron reducing conditions were grouped under sulfate reducing. The pH regimes were grouped as: acidic (<6), neutral (6-8), and alkaline (>8). Two distinct temperature ranges were considered (<15 ^oC and >15 ^oC). If multiple studies were conducted at a site, a simple average was computed for the biodegradation rate and the average was used. The average was computed so that one site may not unduly bias the distribution of rate constants. The individual rates are also reported in parentheses following the average.

4.0 Partition Coefficients for Metals

4.1 *Literature Survey for Metal Partition Coefficients*

A literature survey was conducted to obtain partition coefficients to describe the partitioning of metals between soil and soil-water, between suspended particulate matter (SPM) and surface water, between sediment and sediment-porewater, and between DOC and the dissolved inorganic phase in natural waters (14). In addition, partition coefficients were sought for equilibrium partitioning of metals between waste matrix material and the associated aqueous phase in land application units, waste piles, landfills, treatment lagoons, and aerated tanks. The literature survey encompassed periodical scientific and engineering materials and some non-periodicals including books and technical reports published by the U.S. EPA and other government agencies. Electronic searches of twenty databases were included as part of the literature survey.

4.2 *Analysis of Retrieved Data and Development of Partition Coefficients*

The data gathered from published sources were insufficient to establish a reasonable range for the partition coefficient for all metals in all media-types. A considerable effort was directed at augmenting the values obtained from the literature so as to provide a reasonable range and central tendency for each metal in each media-type. Statistical analysis of retrieved data, geochemical modeling, and expert judgement were all used in developing the partition coefficients. The nature of the available data for natural media systems and waste systems was different to the extent that it was concluded to consider these data sets separately.

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