



## Project Summary

# Estimation Methods for Process Constants and Properties Used in Fate Assessments

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Physical property data, rate constants, and equilibrium constants are required for assessments of the fate of chemicals in the environment. Structure-activity relationships (SARs), property correlations, and reactivity correlations are sources of such data that are increasingly recognized as rapid, practical, and inexpensive methods with which to estimate values of some constants or properties. Although it is unlikely that major environmental decisions will be made based solely on such information, these estimated data are often useful within the context of deciding whether a process may be important for a particular chemical, whether better data are required for an assessment, or as a check on a reported value. In some cases, estimated data are useful in concluding that a chemical will or will not persist in a specific environmental situation by simple analogy to experience with other chemicals having similar properties or reactivities.

This report reviews a broad range of qualitative and quantitative relationships between structure and properties or reactivities as well as correlations among different properties and reactivities. Also included are the specific theoretical and empirical equations used in fate assessments that use data produced by these estimation methods. The limitations of these estimation methods and testing procedures are discussed.

*This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is*

*fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Structure-activity relationships (SARs) are defined as methods by which data or information on the reactivity or other properties of a chemical can be inferred or calculated from a knowledge of the structure of its molecule alone. Some SARs have been expressed in a quantitative form as in the Hammett equation for estimating rate or equilibrium constants:

$$\log \frac{k_x}{k_H} = \sigma \rho \quad (1)$$

where  $k_x$  and  $k_H$  are the respective constants for chemical structures with a substituent X and a reference substituent (usually hydrogen),  $\rho$  is a constant for the reactivity of the chemical, and  $\sigma$  is a constant for the effect of the substituent X on the reaction. Alternatively, SARs may be expressed as additivity relationships.

$$\log k = \sum n_i f_i \quad (2)$$

$$\log k = \sum n_i \alpha_i \beta_i k_o \quad (3)$$

where  $k$  is a property or constant,  $n$  is the number of times the  $i$ -th fragment appears in a molecule, and  $f_i$  is a value for the contribution of the fragment to the property or constant of interest (Equation 2). For

a rate or equilibrium constant, the additivity relationships (Equation 3) can include factors  $\alpha, \beta$ , for the effect of substituents on  $k_o$ , which is a rate constant for a reference (or standard) group bearing no substituents.

Correlations between properties or between reactivities (PRCs) are relations by which one property or reactivity is estimated from another but without a specific concern for molecular structure. One example of a PRC is the correlation of octanol/water partition coefficient,  $K_{ow}$ , with the sediment partition coefficient normalized for fraction of organic carbon in the sediment,  $K_{oc}$ . The form of this equation is shown below.

$$\log K_{oc} = (a) \log K_{ow} + b \quad (4)$$

Although PRCs and other similar correlation equations used in fate assessments do not require specific knowledge of a molecular structure or the use of structural information in the calculations, in many cases the equations do implicitly assume some molecular behavior (e.g., no hydrogen bonding effects, unit activity coefficients). Therefore, understanding the correct use and the limitations of these methods may require some evaluation of molecular structure.

## Scope of Report

The first section of the full report discusses general aspects of the sources, applications and limitations of estimation methods for fate assessments. Subsequent sections describe the methods currently available for estimating property data, rate constants, and equilibrium constants for use in environmental assessments. The survey for SARs, PRCs, and other estimation methods were limited to the properties or constants that may be used in aquatic fate models, such as the Exposure Analysis Modeling System (EXAMS). These are listed in Table 1.

For each property or constant, a brief statement is provided on how the property or constant is used in fate models or otherwise in SARs or PRCs to estimate data for use in fate models. The specific methods available for estimating the particular constant or property are then discussed.

For each constant or property, the practicality and limitations of each method are evaluated for estimating data to be used in fate assessment models. Recommendations for future efforts in developing or expanding the method also are made. Because the data base used to

**Table 1.** Properties and Constants Used in Fate Assessment

Property or Constant	Abbreviation
Molecular Weight	MW
Octanol/Water Partition Coefficient	$K_{ow}$
Sediment Partition Coefficient	$K_p$
Sediment Partition Coefficient, normalized for fraction organic carbon	$K_{oc}$
Melting Point	MP
Solubility in Water	$S_w$
Boiling Point	BP
Heat of Vaporization	$\Delta H_{vap}$
Vapor Pressure	$P_v$
Henry's Constant	$H_c$
Diffusion Coefficients in Liquid Phase and Gas Phase	$D_o, D_g$
Reaeration Rate Ratio	$k_{vc}/k_{vo}$
Volatilization Rate Constant	$k_{vc}$
Dissociation Constant	$K_A, K_B$
First-order Hydrolysis Rate Constant	$k_h$
Acid-Promoted Hydrolysis Rate Constant	$k_A$
Base-Promoted Hydrolysis Rate Constant	$k_B$
Neutral Hydrolysis Rate Constant	$k_N$
Direct Photolysis Rate Constant	$k_p$
Reaction Quantum Yield	$\Phi$
Light Absorption Coefficients	$\epsilon, \lambda$
Oxidation Rate Constants	$k_{ox}$
Second-order Biodegradation Rate Constant	$k_b$

establish the method is often important in understanding the scope and limitations of an estimation method, some comment on the quality and size of the data base is provided when relevant.

In a few cases, the review found that more than one SAR or PRC was available for a particular property or constant, and a critical evaluation of the methods was conducted or recommended. In cases where quantitative SARs are not yet available, possible formats for listing information as SAR data bases or as qualitative SARs are suggested. These formats are designed to be easily included in a computerized SAR system that can be used by a reasonably knowledgeable environmental scientist or engineer. The SARs, PRCs, and estimation methods are discussed in the context of a tiered assessment methodology in recognition of the fact that it is often practical and cost-effective to first identify the most important transformation and transport processes a chemical may undergo, then use more accurate and precise methods to estimate data for the important processes.

## Conclusion

SARs and PRCs are cost-effective and rapid methods for estimating data for use

in some fate assessments. Methods are currently applicable to many chemicals for estimating sediment sorption partition coefficients and rate constants for volatilization, hydrolysis, and oxidation. Direct photolysis and biotransformation are complex processes for which no general and accurate estimation methods are available, but some rules for evaluating the possible importance of these processes are available. Some SARs that are limited to prediction of maximum or minimum rate constants are useful in screening-level assessments for decision of whether to include a process in subsequent and more detailed assessments.

Proper selection and application of SARs for any given assessment situation requires varying degrees of expertise that depend on the structure of the particular chemical of interest, knowledge of the mechanism of the process, the extent of the data base used to develop the SAR, the complexity of the structural analysis required to relate structure to the property or constant, and the needed reliability of the estimated parameters for the problem. All SAR methods are empirical correlations of molecular structure parameters versus reaction or other property constants. They are based on molecular fragment additivity approaches that use

empirical parameters to represent specific structural influences (e.g., steric polar or resonance effects). PRCs also are simple methods for estimating properties or constants and require expertise similar to that necessary for the application of SARs. Although PRCs can, in principle, be replaced by SARs (i.e., calculation of properties or constants directly from structure), many PRCs are simple and accurate methods that make some SARs unnecessary. Computerization of these methods promises to provide a consistent and reliable source of data for future assessments.

The full report also addresses the utility of SARs as screening tools for EPA's fate and hazard assessments of new and old chemicals. Two formats are used to show the existing gaps in SARs and also where SARs can be used with a high degree of confidence in their reliability and accuracy. Both formats are necessary because no one format easily lends itself to illustrating both strengths and deficiencies in the SARs now available and whether more development is needed to improve or extend them.

Table 2 summarizes properties and rate constants for which estimation methods are now available, indicating the state of development, limitations and need for new ones. For each transformation process (hydrolysis, oxidation in air, oxidation in water, photolysis and biotransformation) major classes of organic functional groups that react by that process are identified and the overall utility of applicable SARs is evaluated.

Neither direct photolysis nor biotransformation is sufficiently well understood, in general, to provide quantitative SARs. Useful generalizations are possible in many cases, even though estimation of process rate constants for specific chemical structures may be quite inaccurate and imprecise.

**Table 2.** Status and Needs of SARs

<i>Chemical Property</i>	<i>Status</i>	<i>Needs</i>
<i>P</i>	<i>Estimations poor</i>	<i>Evaluation of available data for new or improved methods.</i>
<i>BP</i>		
<i>H<sub>vap</sub></i>	<i>P vs. T correlations difficult for P &lt; 1 torr</i>	<i>Develop P vs. T for class specific correlations.</i>
<i>MP</i>	<i>Easily measured</i>	--
<i>MW</i>	<i>Easily calculated</i>	--
<i>Solution Property</i>		
<i>K<sub>ow</sub></i>	<i>Several correlations available</i>	<i>Thorough analysis of accuracy of estimating K<sub>ow</sub></i>
<i>S<sub>w</sub></i>	<i>Requires good K<sub>ow</sub> data</i>	<i>Expand data base for K<sub>ow</sub>/S<sub>w</sub></i>
<i>K<sub>p</sub></i>	<i>Estimation methods good where van der Waals forces dominate</i>	<i>More data using standardized sediments. More information and data on sorption due to ion-exchange, and complexation processes.</i>
<i>K<sub>oc</sub></i>		
<i>H<sub>c</sub></i>	<i>Estimation good for low solubility chemicals</i>	<i>Requires P<sub>v</sub> and S<sub>w</sub> data.</i>
<i>D<sub>v</sub>D<sub>o</sub></i>	<i>Good estimation methods available</i>	<i>No work needed.</i>
<i>k<sub>vc</sub></i>	<i>Estimations good for high volatility chemicals</i>	<i>More work required on low to intermediate volatility chemicals.</i>
<i>Transformation Constant</i>		
<i>k<sub>h</sub></i>	<i>Requires knowledge of k<sub>A</sub>, k<sub>B</sub> and k<sub>N</sub></i>	--
<i>k<sub>A</sub></i>	<i>Good to poor, depending on class of chemicals</i>	<i>Fill data gaps to extend SAR; k<sub>A</sub> for some classes not known.</i>
<i>k<sub>B</sub></i>	<i>Excellent to poor depending on class of chemicals</i>	<i>Fill data gaps to extend SARs.</i>
<i>k<sub>N</sub></i>	<i>Poor, unless hydrolysis pH independent</i>	<i>Reliable data in water solvent and mechanism/process studies.</i>
<i>k<sub>pe</sub></i>	<i>Requires knowledge of Φ and ε<sub>λ</sub></i>	--
<i>Φ</i>	<i>Poor; limiting values by assuming Φ = 1</i>	<i>Reliable data in water solvent; mechanism studies also necessary.</i>
<i>ε<sub>λ</sub></i>	<i>Poor; easily measured in most cases</i>	<i>Reliable data in water solvent.</i>
<i>k<sub>ox</sub></i>	<i>Excellent to fair, limiting values estimateable for most organic chemicals</i>	<i>Some selected data gaps need measurements.</i>
<i>k<sub>BIO</sub></i>	<i>Poor</i>	<i>Better fundamental understanding of process; reliable data base organized according to reaction class.</i>