

## Quantitative prediction of K values

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## Introduction

In the previous chapters it has been demonstrated how important it is to have reliable equilibrium partition constants in order to accurately assess the environmental fate of organic pollutants. Because the measurement of such partition constants is often tedious and time-consuming, a number of estimation methods have been developed. These methods may not only be used if no experimental data are available but also to check the plausibility of experimental data. Note that, just as in the previous chapters, the following methods only apply to the partitioning of neutral molecules, not to ions.

From a good model we would expect that 90% of all predicted  $K_{i,12}$ -values should deviate less than a factor 5 (= 0.7 log units)

from the correct values. The models that are used for predicting partition constants differ in the required input information as well as in the underlying concept. Here is an overview of these approaches that are discussed in greater detail on the next pages:

**Fragment models:**

- require only the molecular structure as input
- are completely empirical; depend on the quality of their calibration and (because good experimental calibration data are limited) have quite a limited application domain

**Single-parameter Linear Free Energy Relationships (sp-LFERs):**

- require a physico-chemical parameter (e.g.  $\log K_{ow}$ ) of the compound as input
- typically are completely empirical. They are limited to non-polar compounds because the complex intermolecular interactions of polar molecules cannot be described with a single parameter.

**Poly-parameter Linear Free Energy Relationships (pp-LFERs):**

- require several physico-chemical parameters (corresponding to the various types of intermolecular interactions) of the compound as input.
- Semi-empirical: good mechanistic basis (based on the cavity model introduced in the previous chapter) but with empirically (experimentally) determined parameters.

All above mentioned models have in common that they have to be calibrated somehow to the environmental system for which they are going to be used (e.g. air/water, soil organic matter/water, lipid/water). There are also models that do not require such a system specific calibration. Instead, in these models the system phases have to be identified by their molecular structure. This is not a simple thing to do for complex environmental phases and therefore these models have found little use so far in environmental chemistry. In [Predictive models based on molecular structure](#) we discuss two such models and how they can be used in environmental chemistry.

