

PESTICIDE SOIL SORPTION PARAMETERS: THEORY, MEASUREMENT, USES, LIMITATIONS AND RELIABILITY

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BACKGROUND

The pesticide soil sorption coefficient K_d and the soil organic carbon sorption coefficient K_{oc} are basic parameters used by pesticide scientists and regulatory agencies worldwide in describing the environmental fate and behavior of pesticides. They are a measure of the strength of sorption of a pesticide to soil and other geosorbent surfaces and thus a measure of mobility in the soil.

In a report to be published this Fall we examine the theory, measurement, uses, limitations and reliability of these parameters and provide guidelines for the use of these parameters in describing the behavior and fate of pesticides in the environment.

THE EXPERIMENT

For direct measurement of K_d , a mass of soil m_s (g) is mixed with a volume V (ml) of water (or some medium such as aqueous 0.1M CaCl₂ in order to minimize soil mineral balance disruption). A mass m_p (μg) of pesticide is added to the slurry to give an initial concentration $C_i = m_p/V$ of pesticide in the liquid phase. The slurry is then mixed; the pesticide soil/water distribution approaches a steady state within a few hours. The liquid phase is then analyzed for the "equilibrium" pesticide concentration C_e . The soil sorption constant K_d is then calculated assuming all pesticide removed from the solution is sorbed by the soil, this mass, historically symbolized by x , is calculated as $x = VC_i - C_e$. Then x/m_s is the "concentration" of pesticide in the solid phase (μg/g) and K_d is defined by

$$K_d = \frac{x/m_s}{C_e} \quad (1)$$

Many thousands of measurements of K_d have been made in the last four decades. If a pesticide's K_d is measured in a variety of soils there is generally a high correlation between the organic matter content of the soils and K_d . This has led to a much-used assumption: that it is soil organic matter, acting as a nonpolar phase or surface, that is the main sorbent in soils, attracting pesticides because they are typically nonpolar organic molecules. The soil organic carbon sorption coefficient of a pesticide is calculated by dividing a measured K_d in a specific soil by the Organic carbon fraction F_{oc} of the soil:

$$K_{oc} = \frac{K_d}{F_{oc}} \quad (2)$$

Equation 1, with its apparent "equilibrium constant" K_d implies that pesticides undergo a dynamic sorption equilibrium between the sorption and solid phases of soil, i.e., that "ideal conditions of instantaneous equilibrium, isotherm linearity and desorption reversibility" hold. Equation 2 further suggests that it is soil organic matter that is the sorbing material in the solid phase.

But soil/water/pesticide systems exhibit much more complex behavior than this. There are at least seven complications that may occur. These complications result both from experimental artifacts and theoretical simplifications.

1. Soil Organic Matter is not always the sole sorbent.

For pesticides of very low polarity, organic matter will be the important sorbent simply because of hydrophobic interactions. But other surfaces in soils can become important, particularly in soils where the organic matter fraction is low. In some cases, removal of organic matter appears to free clay mineral sorption sites. With more polar, less hydrophobic solutes, clay sorption, ion-exchange, ligand exchange, sorption mechanisms can occur.

2. Equilibrium is typically only apparent, and involves a complex system of processes with fast and slow kinetics.

- There are at least three time scales describing sorption-desorption kinetics.
- Minutes: first, there is a rapid, reversible diffusion and adhesion to "accessible" sites of soil surfaces near the soil/water interface.
 - Hours to days: second, a slower exchange of pesticide between water and/or the labile sites and more slowly exchanging soil sites occurs. This exchange appears to be fully reversible.
 - Weeks to years: a very slow reaction, which is generally referred to now as "aging". Irreversibly removes pesticide from solution. Aging exposes inert pesticide molecules, that may be freed by subsequent processes.

3. The isotherm may be nonlinear.

The most commonly observed deviation from Equation 1 is a gradual decrease in K_d with pesticide concentration, giving a nonlinear isotherm with a negative curvature. This is usually fitted to a straight line via least-squares regression using a log-log transformation of the data; the result is referred to as the "Freundlich isotherm". Such a log-log transformation will fit almost any adsorbent experiment data in soils. Nonlinearity is observed especially with pesticides which are not extremely hydrophobic and therefore not limited by solubility to extremely low concentrations.

4. Equilibrium may not be fully reversible or single-valued.

There are many reports of an increase in apparent K_d when a slurry sorption equilibration is followed by replacement of the aqueous phase and desorption equilibration. Although the term "hysteresis" has been commonly used to describe this effect, it has become clear in the last decade that the term is probably being misused. Instead, a variety of processes and effects take place when a batch "equilibration" experiment is performed, and subsequent desorption experiments change conditions.

5. Soil organic matter is complex and controversial

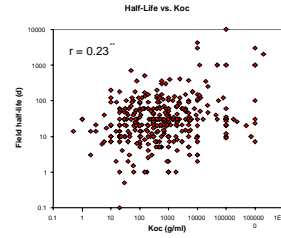
The sorptive properties of soil organic matter have been the subject of hundreds of detailed studies. As a sorbent it has been described as a fibrous solid, an amorphous polymeric phase into which solutes partition, and a porous glassy polymer. Recent studies indicate that it may be all of the above, depending on the solute. "Soil organic matter" is not a single material but a mixture of solid and semisolid materials with a range of properties depending on the history of the sample and the age of the organic matter. Thus, arguments that sorption is an "absorption" or "adsorption" process are probably both valid depending on the conditions of the experiment.

6. Weakly ionisable pesticides may exhibit sorption that is highly sensitive to soil pH

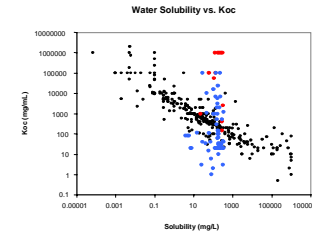
About one in three pesticides is either acidic or basic. Pesticides with ionic equilibrium constants near the range of soil pH will have an apparent K_d that is quite sensitive to the pH of the sorbing soil, since the sorption of the pesticide will be a combination of the sorption of ionized and unionized species. Soil surface ionic charge also changes with pH, amplifying the effect. Anionic species (from acids) have quite low K_d because they are repelled by the negative charge on soil surfaces, while cationic species (from bases) are quite strongly adsorbed for the same reason, and may show more correlation with clay content than organic matter content. Examples include the sharp increases observed in the K_d of some triazines in acidic soils and the increased mobility of carboxylic acids and sulfonylurea herbicides at higher soil pH. Clearly, in such cases a K_d measured at one pH will transfer poorly to another soil with a significantly different pH.

7. Degradation of the pesticide can occur within the time frame of the sorption experiment

A typical soil column study or batch adsorption-desorption study may take 6-48 hours or more, and many pesticides can undergo significant chemical or microbial degradation in soils in that time. Sterilizing the soil appears to be a poor solution as the process, whether by autoclaving, cobalt-60 irradiation, oven drying, or propylene oxide treatment changes soil primary characteristics and thus affects the adsorption. The practical solution is to do the sorption in as short a period as possible and monitor the approach to equilibrium. Many slurry experiments are essentially at steady state within 2 hours.



Pesticide soil sorption intensity and soil persistence are significantly correlated, but the relationship is of little use for predictive purposes for a given K_{oc} : persistence ranges over two orders of magnitude, indicating the important role of chemical-specific biological and chemical degradation processes.



About one-third of pesticides are acidic or basic and, depending on the pH of the soil and the strength of the pesticides dissociation constant, these compounds may be present mainly as anions and cations in the soil. These pesticides do not fit the excellent regression observed for nonionic pesticides between water solubilities and soil sorption coefficients.

"RULES OF THUMB" FOR SOIL SORPTION PARAMETERS: PRECISION FOR A SINGLE PESTICIDE COMPOUND (CV's in %, Factors in X)

SOIL SORPTION CONSTANT K_d

Measurement in a single, well-mixed soil sample: Extreme values may be difficult but typically similar to analytical and mechanical error, ca. 5%

Measurement in a series of soil samples from the same, homogeneous field: depends on variability of sorptive component from point to point in field; typically 50%.

Measurement as a function of depth in a field soil: in agricultural soils, organic matter and sorptive mineral fractions can change 100X from surface to below plow layer, and K_d will follow.

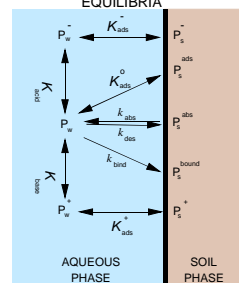
Measurement in different soils: K_d can vary to the degree that sorptive fractions vary between soils; 1000X is to be expected.

SOIL ORGANIC MATTER SORPTION CONSTANT K_{oc}

Range of values from a single, multi-soil study: 30% CV is common and is apparently a measure of the variance in soil OM sorptivity.

Range of values reported from different studies: this range averages close to 10X, indicating that methodology differences contribute significantly to K_{oc} variability.

SOIL SORPTION KINETICS AND EQUILIBRIA



Schematic diagram of the sorption reactions (small K) and instantaneous sorption equilibria (capital K) which may occur with a pesticide in soil water, as neutral basic or acidic molecule. Slow sorption reactions may also occur with cationic or anionic species.