

# A DIMENSIONAL EQUATION FROM ENVIRONMENTAL ENGINEERING

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Generally, we prefer to work with equations that are formulated to be independent of any particular system of units. This is not always convenient to do, and we use many equations that are valid only for a particular system of units. The undergraduate encounters these throughout the chemical engineering curriculum. The appearance of “g<sub>c</sub>” in many equations in texts of American origin prompts the reader to the fact that the units are English of the American variety. Students meet examples of dimensional equations into which values of variables must be entered with particular units; examples of these are empirical correlations for heat and mass transfer coefficients given in the text of McCabe, et al.<sup>[1]</sup>

The need to find empirical correlations has probably been the prime source of dimensional equations. In environmental engineering and science, many empirical correlations involve a relationship between the quantity of interest and the octanol-water partition coefficient,  $K_{ow}$ . This coefficient was originally used by medicinal chemists<sup>[2,3]</sup> interested in finding correlations for equilibrium and transport properties of chemicals within living systems. Many useful correlations involving the octanol-water partition coefficient<sup>[4,5]</sup> exist; these include measures of toxicity, measures of accumulation of chemicals by organisms as well as molecular properties such as water solubility, Henry’s law constants, molar volumes, and measures of a chemical’s surface area.

We wish to discuss the correlation that is widely used for doing an order-of-magnitude estimation of the distribution of hydrophobic chemicals in aquatic systems. It is

$$K_{oc} \cong \alpha \times K_{ow} \quad (1)$$

Here,  $K_{oc}$  is the sediment, or soil, sorption coefficient and  $\alpha$  is a constant, whose values are typically 1.0<sup>[6]</sup> and 0.6.<sup>[7]</sup> A

more general form that is often used is

$$\log K_{oc} = a \cdot \log K_{ow} + b \quad (2)$$

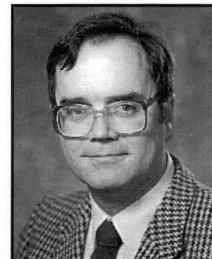
The definitions of the coefficients are

$$K_{oc} = \frac{C_s}{F_{oc} C_{aq}} \quad (3)$$

$$K_{ow} = \frac{C_{oct}}{C_{aq}} \quad (4)$$

Here,  $C_s$  is the mass of chemical per unit mass of dry sediment or soil,  $F_{oc}$  is the fraction of organic carbon in the dry sediment or soil,  $C_{aq}$  is the mass of chemical per unit volume of aqueous phase, and  $C_{oct}$  is the mass of chemical per unit volume of octanol. The common use of the organic-carbon normalized distribution coefficient,  $K_{oc}$ , for nonionic organic chemicals arose out of the work of Karickhoff and coworkers;<sup>[7]</sup> they measured distribution coefficients, using substrates containing various fractions of organic carbon, and demonstrated that the normalized form is essentially independent of the substrate type. Similar observations, involving an organic matter basis (to be discussed later), had been made earlier.<sup>[8-10]</sup> Recent texts<sup>[5,11]</sup> contain more de-

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tailed descriptions.

Equations (1) and (2) are usually used in a tacitly dimensional way with the chosen units being SI units; generally, values of  $\alpha$  are given without units,  $K_{ow}$  is unitless, and  $K_{oc}$  has units of L/kg or mL/g. Our purpose here is to ask, "What is a dimensionally consistent form of these equations?" We wish to show there is pedagogical value in answering this. In our view, the dimensional inconsistency arises from the fact that the concentration bases are different. The concentration of the chemical in sediment or soil,  $C_s$ , is defined as the mass of chemical per *unit mass of dry sediment or soil* and the concentration of the chemical in octanol is defined as the mass chemical per *unit volume of octanol*. So, to obtain a dimensionally consistent equation we should ensure that we have the same composition basis. To do this, we imagine octanol as a sample of soil or sediment.

By definition

$$C_{oct} = \frac{m}{V_{oct}} \quad (5)$$

where  $m$  is the mass of chemical in the volume of octanol  $V_{oct}$ . Using the density of octanol,  $\rho_{oct}$ , and the mass of octanol,  $M_{oct}$ , we transform this equation to

$$C_{oct} = \frac{m}{M_{oct}} \rho_{oct} = C_s \rho_{oct} \quad (6)$$

We recognize the term  $m/M_{oct}$ , the mass of chemical per unit mass of octanol, is equivalent to  $C_s$ . Keeping in mind the form of Eq. (3), we write

$$C_{oct} = C_s \rho_{oct} = \left( \frac{C_s}{F_{oc}} \right) (F_{oc} \rho_{oct}) \quad (7)$$

where  $F_{oc}$  is the *fraction of organic carbon in octanol*. Dividing through by the aqueous concentration of the chemical, we obtain the equation

$$K_{oc} = \frac{K_{ow}}{F_{oc} \rho_{oct}} \quad (8)$$

and this is dimensionally consistent. Recognizing that all the carbon in octanol is organic, we calculate the fraction of organic carbon in octanol from the relative atomic and molecular masses;  $F_{oc} = 0.738$ . The density of octanol<sup>[12]</sup> at 20°C is 0.827 g/mL. So, at 20°C,

$$K_{oc} = 1.638 K_{ow} = K_{oc}^{oct} \quad \text{or} \quad \log K_{oc}^{oct} = \log K_{ow} + 0.214 \quad (9)$$

This transformation gives the octanol-water partition coefficient on the same composition basis as the sediment, or soil, sorption coefficient. It is still the octanol-water partition coefficient, but expressed on a different basis. To emphasize this, we now designate it as  $K_{oc}^{oct}$ . This is a very unusual way of expressing compositions; the transformations between

concentrations, in terms of molarity or molality, and mole fractions are much more familiar to us.

So, given a value of the octanol-water partition coefficient on its normal basis, we can calculate it on an organic carbon basis. The question now is, "To what extent does the octanol-water partition coefficient on the organic carbon basis correspond to the measured sediment, or soil, sorption coefficient?" If the organic carbon in the sediment behaves identically to octanol, then we expect the relationship in Eq. (9) to hold. What is observed? From experimental data, many workers have developed dimensional relationships with the general form of Eq. (2), in which values of  $a$  and  $b$  are determined by linear regression. To make the essential point here, we consider only the relationship developed in a recent comprehensive review<sup>[13]</sup> in which Baker and coworkers developed selection criteria and critically reviewed the available measurements. For  $1.7 < \log K_{ow} < 7.0$ , using data for 72 chemicals, they found

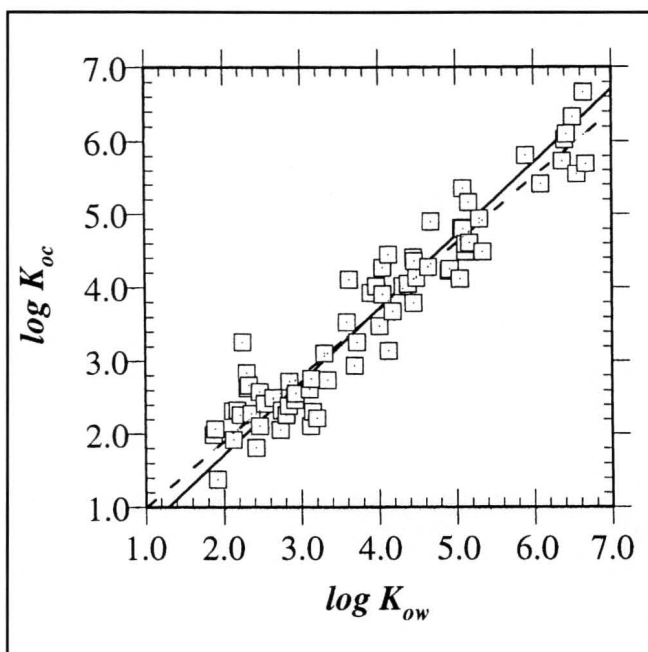
$$a = 0.903 \pm 0.034 \quad b = 0.094 \pm 0.142 \quad r^2 = 0.91$$

We wish to compare Eq. (9) with this result.

The dimensionally consistent relationship that we derived, Eq. (9), however, requires  $a=1$ . Using the data in the review,<sup>[13]</sup> we applied a regression model<sup>[14]</sup> in which we forced  $a$  to be unity. We obtain

$$\log K_{oc} = \log K_{ow} - (0.29 \pm 0.05) \quad r^2 = 0.90 \quad (10)$$

In Figure 1, we have plotted the data, the regression line (Eq.



**Figure 1.** The units of  $K_{oc}$  are L/kg. Data were taken from Ref. 13. The dashed line corresponds to the regression line, Eq. (2), with  $a=0.903$  and  $b=0.094$ . The continuous line corresponds to Eq. (10) in the text.

2 with the values of  $a$  and  $b$  given above), and the line corresponding to Eq. (10). From Eqs. (9) and (11), we find that

$$\frac{K_{oc}(\text{observed, Eq. 10})}{K_{oc}^{\text{oct}}(\text{octanol-like behavior, Eq. 9})} = 0.31 \quad (11)$$

In other words, experimental values of  $K_{oc}$  are about one-third of the values expected if the sediment or soil organic carbon were to have the same partitioning properties as octanol.

The conclusion hinges on an appreciation of how to express compositions in various ways; the way here for soil or sediments is peculiar to environmental work and is a useful exercise for students to work out for themselves. Another closely related example is the earlier use<sup>[8-10]</sup> of the soil sorption coefficient on an organic *matter* basis. This is defined as

$$K_{om} = \frac{C_s}{F_{om} C_{aq}} \quad (12)$$

Here,  $F_{om}$  is the fraction of organic matter. We may derive an expression for the octanol-water partition coefficient on an organic-matter basis,  $K_{om}^{\text{oct}}$ , following the same steps as before. The result is

$$K_{om}^{\text{oct}} = \frac{K_{ow}}{F_{om} \rho_{\text{oct}}} \quad (13)$$

Octanol is all organic “matter,” so  $F_{om} = 1$ , and we obtain

$$K_{om}^{\text{oct}} = 1.209 K_{ow} \quad \text{or} \quad \log K_{om}^{\text{oct}} = \log K_{ow} + 0.082 \quad (14)$$

This may be compared to the approximate experimental relationship found between the soil sorption coefficient on an organic-matter basis and the octanol water partition coefficient,<sup>[4]</sup>  $K_{om} = 0.4 K_{ow}$ . Here again, we may conclude that the experimental values of  $K_{om}$  are about one-third of the values expected if the sediment or soil organic matter were to have the same partitioning properties as octanol. In contrast to octanol, the fraction of organic matter in soils is about twice the fraction of organic carbon.<sup>[5,10,11]</sup> The measurement of the fraction of organic carbon is now easier, and so the use of the organic-carbon basis is now more prevalent.

We think it is important for the student to recognize when an equation is dimensional, and it is often not immediately obvious. The answer to the question, “Why is the sediment, or soil, partition coefficient less than the octanol-water partition coefficient?” is a useful entry point into a discussion of the structure of sediment, or soil, particles (a heterogeneous solid system) and the nature of adsorption. This is in contrast to distribution of a chemical between two essential homogeneous liquid phases, as represented by the octanol-water partition coefficient.

### Problems

1. The composition of a phase is usually described by the mole fractions of the various components. Why is it impractical to describe the composition of a soil or sediment in terms of mole fractions?
2. Equation (10) is a dimensional equation in which the units are SI. What is the equivalent equation in English units?
3. Ten milligrams of naphthalene is added to a container that contains 10 g of sediment (dry wt), 50 mL of water, and 5 mL of octanol. The system is allowed to reach equilibrium. What are masses of naphthalene in the sediment, water, and octanol at equilibrium? The sediment contains 5% organic carbon and the octanol-water partition coefficient for naphthalene is about 2000.

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