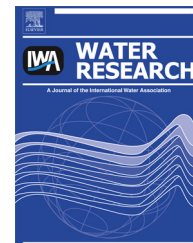




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# An alternative approach for the use of water solubility of nonionic pesticides in the modeling of the soil sorption coefficients

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## ABSTRACT

The collection of data to study the damage caused by pesticides to the environment and its ecosystems is slowly acquired and costly. Large incentives have been established to encourage research projects aimed at building mathematical models for predicting physical, chemical or biological properties of environmental interest. The organic carbon normalized soil sorption coefficient ( $K_{oc}$ ) is an important physicochemical property used in environmental risk assessments for compounds released into the environment. Many models for predicting  $\log K_{oc}$  that have used the parameters  $\log P$  or  $\log S$  as descriptors have been published in recent decades. The strong correlation between these properties ( $\log P$  and  $\log S$ ) prevents them from being used together in multiple linear regressions. Because the sorption of a chemical compound in soil depends on both its water solubility and its water/organic matter partitioning, we assume that models capable of combining these two properties can generate more realistic results. Therefore, the objective of this study was to propose an alternative approach for modeling  $\log K_{oc}$ , using a simple descriptor of solubility, here designated as the logarithm of solubility corrected by octanol/water partitioning ( $\log S_p$ ). Thus, different models were built with this descriptor and with the conventional descriptors  $\log P$  and  $\log S$ , alone or associated with other explanatory variables representing easy-to-interpret physicochemical properties. The obtained models were validated according to current recommendations in the literature, and they were compared with other previously published models. The results showed that the use of  $\log S_p$  instead of conventional descriptors led to simple models with greater statistical quality and predictive power than other more complex models found in the literature. Therefore,  $\log S_p$  can be a good alternative to consider for the modeling of  $\log K_{oc}$  and other properties that relate to both solubility and water/organic matter partitioning.

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Nomenclature			
ARE	Average relative error	$Q^2_{\text{LOO}}$	Coefficient of determination of the leave-one-out validation
CCC	Concordance correlation coefficient	$Q_o$	Solute quantity in the organic phase (mol)
F	F statistic	QSPR	Quantitative Structure–Property Relationships
k	Slope of the regression line without intercept	$Q_w$	Solute quantity in the aqueous phase (mol)
$K_{oc}$	Organic carbon normalized soil sorption coefficient	$R^2$	Coefficient of determination
LNO	Leave-N-out validation	$R^2_o$	Coefficient of determination of the regression line without intercept
LOO	Leave-one-out validation	$r^2_m$	Modified coefficient of determination of external validation
MAXDP	Maximum positive difference between the intrinsic states of the atoms of a molecule	$R^2_{\text{PRED}}$	Coefficient of determination of the external validation
MLR	Multiple linear regression	RSS	Residual sum of squares
Mv	Mean van der Waals volume of the atoms of a molecule	S	Solubility in water ( $\text{mol.L}^{-1}$ )
P	Octanol/water partitioning coefficient	SEC	Standard error of calibration
PCR	Principal component regression	SECV	Standard error of the cross-validation
PLS	Partial least squares regression	SEP	Standard error of the prediction
$\text{PRESS}_{cv}$	Residual error sum of squares of the cross-validation	$S_o$	Solubility in the organic phase ( $\text{mol.L}^{-1}$ )
$\text{PRESS}_{ev}$	Residual error sum of squares of the external validation	$S_p$	Solubility in water corrected by the octanol/water partition ( $\text{mol.L}^{-1}$ )
Q	Total solute quantity (mol)	$S_w$	Solubility in the aqueous phase ( $\text{mol.L}^{-1}$ )
$Q^2_{\text{LNO}}$	Coefficient of determination of the leave-N-out validation	V	Volume (L)
		VAR	Variation (topological descriptor)
		$V_o$	Volume of organic phase (L)
		$V_w$	Volume of aqueous phase (L)

## 1. Introduction

Pesticides or agrochemicals are substances that are widely used in agriculture to increase productivity, improve crop quality and reduce labor and energy costs. However, only a small portion of the pesticides applied to crops reaches its intended target; the remainder tends to transfer into different environmental compartments and can thus contaminate surface water and groundwater (Arias-Estévez et al., 2008).

In recent years, some segments of society have expressed concern over the final destination of these substances and their potential environmental and health risks (Mackay and Webster, 2003). Therefore, studying the physical, chemical and biological properties of these chemicals is essential for planning recovery efforts in contaminated areas and for preserving sites that are not yet contaminated.

The organic carbon normalized soil sorption coefficient ( $K_{oc}$ ) is an important physicochemical property that can be used to determine the final destination of chemicals released to the environment (Doucette, 2003; Huuskonen, 2003). This coefficient is expressed as the ratio between the concentration of the chemical component that is sorbed by the soil ( $\text{mg.kg}^{-1}$ ) and the concentration of the surrounding aqueous phase ( $\text{mg.L}^{-1}$ ), divided by the content of organic carbon (g organic carbon/g dry soil). The smaller is the value of  $K_{oc}$  for a given compound, the greater is its mobility in the soil and the greater is its potential for groundwater contamination (Dearden, 2002; Arias-Estévez et al., 2008).

The  $K_{oc}$  coefficient of a chemical compound can be determined experimentally by the batch equilibrium method (ASTM, 2001) or by the soil column method (Lee et al., 1991).

The extent of the sorption of a chemical compound is influenced by its molecular structure, but it also depends on factors related to the intrinsic characteristics of the soil, such as particle size, porosity, chemical composition, pH and organic matter content (Dearden, 2002). The organic carbon content is a key factor that affects the sorption of hydrophobic compounds. Therefore, the hydrophobicity of these compounds is the driving force during soil sorption (Wen et al., 2012). Hydrophobic interactions are the primary mechanisms underlying the sorption of nonionic compounds, but for compounds with higher polarities, hydrophilic interactions are more relevant. Therefore, the interactions of clay and silica with polar functional groups become important for polar compounds. A more itemized description of the interactions involved in the sorption of organic compounds in soil can be found in the works of von Oepen et al. (1991) and Allen-King et al. (2002).

The need for an updated and reliable database of  $K_{oc}$  values has motivated the proposals and publications of a considerable number of models for the prediction of this parameter (Gramatica et al., 2000). Several studies on quantitative structure–property relationships (QSPR) based on the molecular structures of chemical compounds have become available during the last few decades. Therefore, various descriptors have been used for the modeling of  $K_{oc}$ , such as physicochemical properties, chromatographic parameters, steric factors, linear solvation energy relationships (LSER), topological and quantum parameters (Gawlik et al., 1997; Doucette, 2003; Huuskonen, 2003; Nguyen et al., 2005; Gramatica et al., 2007; Razaque and Grathwohl, 2008; Goudarzi et al., 2009; Wen et al., 2012). However, the vast

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