WATER RESEARCH 53 (2014) 191–199

Available online at www.sciencedirect.com

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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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ARTICLE INFO

Article history:
Received 31 August 2013
Received in revised form
6 January 2014
Accepted 11 January 2014
Available online 23 January 2014

Keywords:
Environmental risk
Hydrophobic parameter
Partition coefficient
Soil contamination
QSPR

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 logK_{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 logK_{oc}, using a simple descriptor of solubility, here designated as the logarithm of solubility corrected by octanol/water partitioning (logS_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 logS_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, logS_P can be a good alternative to consider for the modeling of logK_{oc} and other properties that relate to both solubility and water/organic matter partitioning.

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http://dx.doi.org/10.1016/j.watres.2014.01.023

Nomenclature

ARE	Average relative error
CCC	Concordance correlation coefficient
F	F statistic
k	Slope of the regression line without intercept
K_{oc}	Organic carbon normalized soil sorption coefficient
LNO	Leave-N-out validation
LOO	Leave-one-out validation
MAXDP	Maximum positive difference between the intrinsic states of the atoms of a molecule
MLR	Multiple linear regression
Mv	Mean van der Waals volume of the atoms of a molecule
P	Octanol/water partitioning coefficient
PCR	Principal component regression
PLS	Partial least squares regression
$PRESS_{cv}$	Residual error sum of squares of the cross-validation
$PRESS_{ev}$	Residual error sum of squares of the external validation
Q	Total solute quantity (mol)
Q^2_{LNO}	Coefficient of determination of the leave-N-out validation
Q^2_{LOO}	Coefficient of determination of the leave-one-out validation
Q_O	Solute quantity in the organic phase (mol)
QSPR	Quantitative Structure–Property Relationships
Q_W	Solute quantity in the aqueous phase (mol)
R^2	Coefficient of determination
R^2_0	Coefficient of determination of the regression line without intercept
r^2_m	Modified coefficient of determination of external validation
R^2_{PRED}	Coefficient of determination of the external validation
RSS	Residual sum of squares
S	Solubility in water ($mol.L^{-1}$)
SEC	Standard error of calibration
SECV	Standard error of the cross-validation
SEP	Standard error of the prediction
S_O	Solubility in the organic phase ($mol.L^{-1}$)
S_P	Solubility in water corrected by the octanol/water partition ($mol.L^{-1}$)
S_W	Solubility in the aqueous phase ($mol.L^{-1}$)
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 ($mg.kg^{-1}$) and the concentration of the surrounding aqueous phase ($mg.L^{-1}$), 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; Razzaque and Grathwohl, 2008; Goudarzi et al., 2009; Wen et al., 2012). However, the vast

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