Bull Environ Contam Toxicol (2007) 78:295–298
DOI 10.1007/s00128-007-9167-x

Near Infrared Reflectance Spectroscopy as a Tool to Predict Pesticide Sorption in Soil

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Received: 6 April 2007 / Accepted: 1 June 2007 /

Abstract We used near infrared reflectance spectroscopy (NIR) combined with chemometric methods to predict the sorption of lindane and linuron to 27 agricultural soils from Sweden. The NIR predictions were calibrated by principal component analysis (PCA) of the NIR spectra and sorption data obtained using the batch equilibrium technique. Partial least square regression PLSR of the NIR data could predict 85% of the soil sorption (K_d) for lindane and 84% for linuron, respectively. The results indicate that NIR can be used as a rapid and simple method to predict pesticide sorption to and leaching from soils.

Keywords Chemometrics · Partial least squares regression · Principal component analysis · Soil binding · Leaching · Linuron · Lindane

Accurate determination of the binding to soil is necessary to understand the behavior and environmental fate of organic pollutants, such as pesticides. The sorption coefficient (K_d), i.e., the partitioning of the pollutant between the soil particles and the soil solution, is used to characterize the binding. Most commonly K_d for pesticides has been determined using the batch equilibrium technique (OECD 2000). But other methods such as estimation based on chemical and physical parameters (Gawlik et al. 1997), supercritical fluid extraction (SFE) (Berglöf et al. 2000a, b; Koskinen and Rochette 1996; Rochette and Koskinen 1996, 1998), and pressurized solvent extraction (PSE) (Berglöf et al. 2000b) have been used to characterize the sorption.

Near infrared reflectance spectroscopy, NIR, is a useful tool to determine various properties of solid, bulk materials such as soils. There is much evidence that an NIR spectrum contains information about key parameters for pesticide sorption, e.g., the amount and quality of soil organic matter, clay fractions, cation exchange capacity, and base saturation (Al-Abbas et al. 1972; Chang et al. 2001; Couillard et al. 1997; Morra et al. 1991). In addition, Bengtsson et al. (1996) used NIR to predict the leaching of pesticides from soil. Consequently, if a sufficient number of reference spectra are collected of soils for which the K_d of a pesticide is known, it should be possible to use multivariate statistical procedures, such as principal component analysis (PCA) and partial least squares regression (PLSR) (Joliffe 1996; Martens and Næss 1989), to estimate the K_d of the pesticide in soils for which no direct determination of K_d has been performed.

In this study we evaluated NIR as a tool to predict the sorption of lindane (γ-hexachlorocyclohexane) and linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] to soil. The goal was to develop a method that will produce sorption estimations that are sufficiently accurate to predict the behavior of pesticides in soils with a minimum of chemical and physical analysis.

Materials and Methods

The method includes: (1) obtaining NIR spectra of a large number of soils, (2) selection of soils suitable for detailed

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sorption studies, (3) performance of batch equilibrium experiments to characterize the K_d in the selected soils, (4) calibration of NIR and batch equilibrium data, and (5) test of unknown soil samples.

Water (HPLC-grade) was from Merck-Eurolabs (Spånga, Sweden), while ^{14}C labeled lindane was obtained from International Isotope (Munich, Germany), and ^{14}C labeled linuron was obtained from Izotop (Budapest, Hungary).

The soil samples were scanned from 1,100 to 2,498 nm with a resolution of 2 nm on a NIR 4600 scanning monochromator (NIR Systems, Silver Spring, MD) equipped with an autosampler. The reflectance data were collected on a computer system with NIRS 3 software (Infrasoft International, Silver Spring, MD, USA).

The chemical and physical properties of 76 agricultural soils from different parts of Sweden were determined with standard methods at the Department of Soil Science, Swedish University of Agricultural Sciences, and their NIR spectra obtained. Using principal component analysis (PCA) 27 soils were selected for which the K_d-values were determined by the batch sorption–desorption technique. The soils were selected to represent as much as possible of the variation in the NIR data. The soils were air dried and passed through a 2-mm sieve prior to use.

The sorption coefficients, K_d ($[C_s/C_w]$), were determined calculating the distribution of the chemical between soil $[C_s]$, and water $[C_w]$ by measuring the remaining concentration in the water after batch sorption–desorption experiments (OECD 2000). Soil (5 g, air dried at room temperature) was weighed into 25-mL glass centrifuge tubes and aqueous solution of calcium chloride (2.5 mL, 0.01 mol/L) containing ^{14}C-labeled lindane or linuron added. Initial ^{14}C-lindane and ^{14}C-linuron solution concentrations were 0.10, and 2.5 µg/mL, respectively. The soil slurries were sealed with Teflon-lined caps and shaken for 24 h, and then centrifuged at 1,000 rpm for 30 min. The radioactivity in a subsample (1 mL) of the supernatant was determined by liquid scintillation counting (Perkin Elmer Wallac, Turku, Finland) using OptiSafe Hisafe 2 scintillation cocktail (10 mL, Perkin Elmer Wallac) in 20-mL scintillation vials (Polyvials; Zinsser Analytic; Frankfurt, Germany). Internal standards (activity: 105 100 DPM/capsule; Wallac standard kit for aqueous solutions) were used to correct for sample quenching and to calculate disintegration per minute.

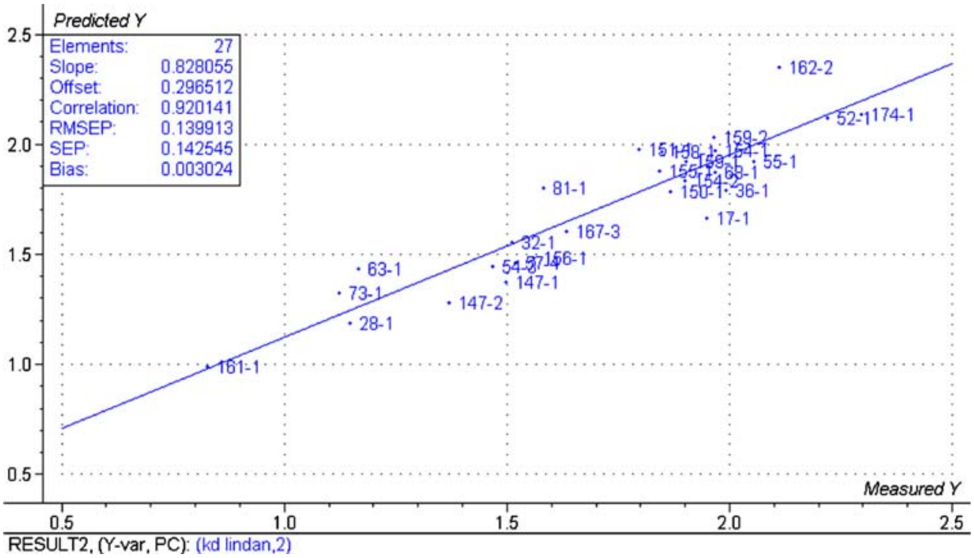
The sorption coefficients determined by the two methods were compared by cross correlation in a PLSR model. Each individual soil sample was treated as unknown and the K_d as predicted from the NIR data was compared to that obtained by the batch sorption–desorption technique.

Table 1 Total variation in chemical and physical parameters of (a) the calibration set of all 76 soils tested, and (b) a test set of the 27 soils samples selected for maximum variability in the NIR-spectra using PCA

Parameter	Calibration soils (n = 76)		Test soils (n = 27)	
	Min	Max	Min	Max
Clay (%)	3	47	3	42
Silt (%)	7	50	7	49
Sand (%)	10	84	16	80
Organic matter (%)	1.7	21.4	1.7	21.4
Total nitrogen (%)	0.04	0.6	0.09	0.6
pH	4.9	7.8	4.9	7.6
Phosphorous (mg/kg)	18	338	18	308
Potassium (mg/kg)	10	335	35	265
Magnesium (mg/kg)	9	479	9	257

The test set was used for cross validation of the predictions obtained from the NIR-spectroscopy

Fig. 1 Sorption coefficient (K_d) values of lindane extracted from soils, measured K_d values from batch sorption–desorption equilibrium experiments plotted against predicted K_d values from NIR with cross validation in a partial least square regression (PLSR) model



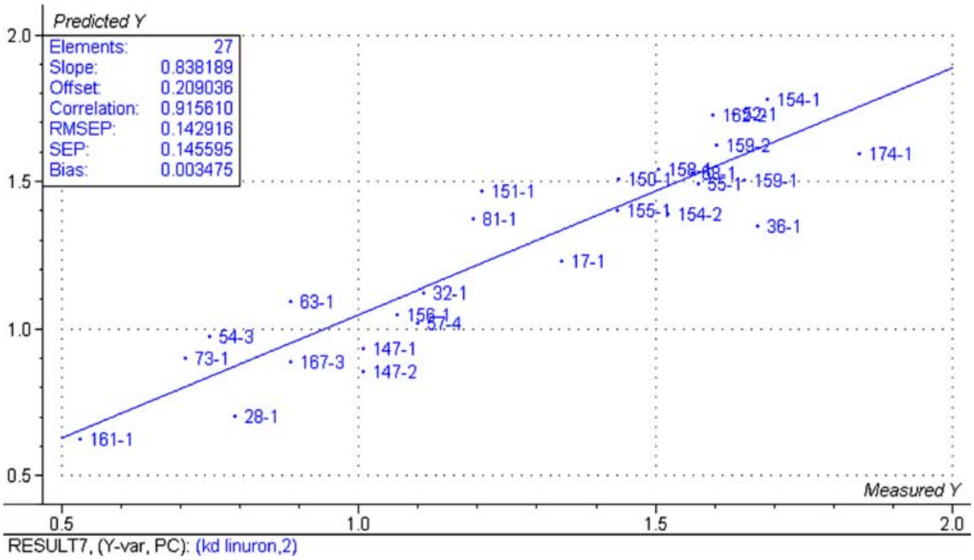


Fig. 2 Sorption coefficient (K_d) values of linuron extracted from soils, measured K_d values from batch sorption–desorption equilibrium experiments plotted against predicted K_d values from NIR with cross validation in a partial least square regression (PLSR) model

Results and Discussion

The minimum–maximum intervals of the chemical and physical properties of the 27 soils that were selected for the final experiment compare well with the minimum–maximum intervals of the properties of the 76 original soil samples. Almost the entire variation span of the determined chemical and physical parameters was covered by the selected samples (Table 1). With two significant principal components in the PLSR model, about 85% of the variation in K_d for lindane were explained with a root mean square error of prediction (RMSEP) of 0.14 (Fig. 1). Similarly, about 84% of the variation in K_d for linuron was explained with an RMSEP of 0.14 (Fig. 2). The results clearly indicate that NIR can be used as a fast alternative for the prediction of lindane and linuron sorption to soil.

The sorption of a contaminant to soil directly affects the risk for movement in the soil with subsequent possible contamination of groundwater and drinking water resources. The most relevant data on the risks are obtained by lysimeter studies (Bergström 1990). However, lysimeter studies are time consuming and require large investments in field equipment, why, for practical reasons, only few soil/contaminant combinations can be studied. It is, therefore, necessary to develop other simpler methods. Mostly the batch slurry method is used, but this is often questionable as the soil/water ratio used in the method never can be reached in a natural soil. In field moist soils, the sorption characteristics of the soil may change with changed water content (Gawlike et al. 1997; Grover and Hance 1970). Therefore, other techniques are sought for to estimate the sorption characteristics. Although we here for simplicity have used the batch sorption–desorption technique there is no reason why other methods to determine K_d could not be used to calibrate the PLSR model.

Sorption of many pesticides is highly correlated to soil properties, such as soil organic matter and clay content (Cheng 1990). In this study, batch sorption–desorption K_d values increased with increased soil organic matter, and ranged from 7 to 198 mL/g for lindane and from 3 to 70 mL/g for linuron. Relatively linear relationships between K_d and soil organic content (OC) ($R^2 = 0.816$) and ($R^2 = 0.746$) were obtained for lindane and linuron, respectively. For lindane the K_{oc} (sorption coefficient normalized for the soil organic carbon, i.e., K_d/%OC) for the soils ranged from 400 to 2,000 mL/g (average 925 mL/g), while K_{oc} for linuron were in the interval 200–800 mL/g (average 325 mL/g). These results are comparable to lindane and linuron K_{oc} values of 1,100 and 400 mL/g, reported in the literature (Hornsby et al. 1996). No correlation was found between sorption and clay content.

Prediction of sorption and leachability of various organic compounds are important in many situations. In this study we have used this method to predict the sorption of two pesticides to agricultural soils, but it is also important to predict the fate of pollutants when deciding on the location of, e.g., refuse dumps or industries. Simple methods, such as determination of organic matter and clay content of the soil, have been used as rapid means to estimate the sorption capacity of soil. Comparing the K_d values predicted from NIR data, with the correlation between organic matter and sorption, shows that NIR spectra contains more information, resulting in a better estimation of the K_d values for lindane and linuron in agricultural soils.

A current limitation of the method discussed here is that sorption can be predicted only for soils with similar characteristics as the soils used to build the calibration model and for similar compounds. However, once a calibration model has been obtained it is a rapid and simple process to generate the NIR data for the soils to be tested. To develop it into a more general method it is necessary to include soils from other climate regimes and to study other pesticides and organic pollutants.

Acknowledgments This study was funded by the Foundation for Strategic Environmental Research, MISTRA.

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