

# Predicting the Leachability of Pesticides from Soils Using Near-Infrared Reflectance

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The purpose of this study was to investigate if near-infrared reflectance (near-IR) spectroscopy and chemometric methods can be used as a rapid and simple procedure to predict the leachability of pesticides from soil samples. The intention was to replace the often tedious determination of a number of chemical and physical parameters used to characterize soils. For selection of calibration samples, near-IR spectra were obtained for 76 different agricultural soil samples. Principal component analysis of the spectra was used to select a subset of 20 samples which were fortified with six pesticides. Extraction was performed with supercritical fluid extraction (SFE) or solid phase microextraction (SPME). Partial least-squares regression of the near-IR data could predict 76% and 77% of the matrix–analyte interactions found by the SFE and SPME methods, respectively. The results clearly indicate that near-IR can be used to characterize soils for the prediction of the leachability of pesticides.

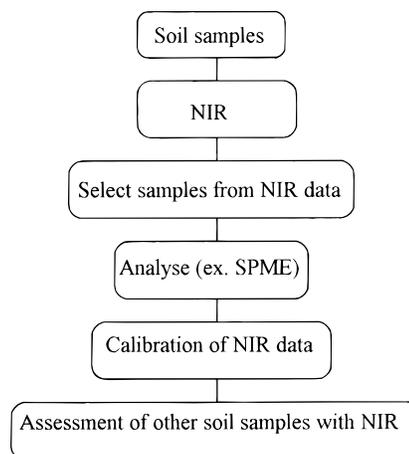
**Keywords:** *Predicting leachability; soil; pesticides; supercritical fluids; solid phase microextraction; near-infrared reflectance spectroscopy; multivariate analysis*

## INTRODUCTION

Knowledge of factors that govern pesticide adsorption to soil particles and adequate methods for characterization of soil are necessary for the assessment of pesticide leachability. Physical, chemical, and biological properties of the soil system highly affect the interactions of pesticides to soil matrices. The analytes may be associated with a variety of inorganic and organic active sites, each with different binding strengths (Koskinen and Harper, 1990).

The conventional methods for characterization of soils are time-consuming and expensive because of the large numbers of variables that have to be analyzed. Limitation of the number of analyses and more rapid and simple methods to evaluate the data are therefore necessary.

With near-infrared reflectance (near-IR) spectroscopy, a vast array of analytical information is obtained with a minimum of sample pretreatment. There is much evidence that a near-IR spectrum contains information about the amount and quality of soil organic matter and the contents and composition of fine mineral fractions (Al-Abbas et al., 1972; Morra et al., 1991). Near-IR spectroscopy is performed with routine instruments with high repeatability and sample capacity (150 samples/day). However, each individual near-IR spectrum is hard to interpret. The spectroscopic data have to be converted into numerical variables, after which multivariate statistical projection methods such as principal component analysis (PCA) and/or partial least-



**Figure 1.** Outline of the analytical procedure.

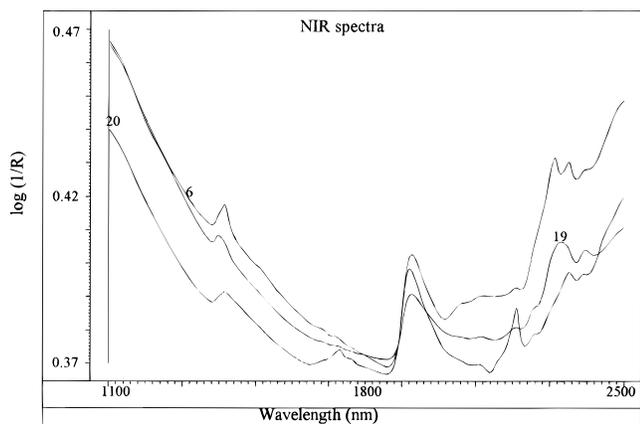
squares regression (PLSR) are used to extract qualitative and quantitative information (Martens and Næs, 1989).

The aim of the present investigation was (I) to study near-IR as an alternative method to chemical and physical analysis for characterization of soil samples and (II) to develop a fast method procedure for the assessment of leachability of pesticides from different soils. To obtain a measure of the leachability of various pesticides, two extraction techniques were used: supercritical fluid extraction (SFE) and solid phase microextraction (SPME).

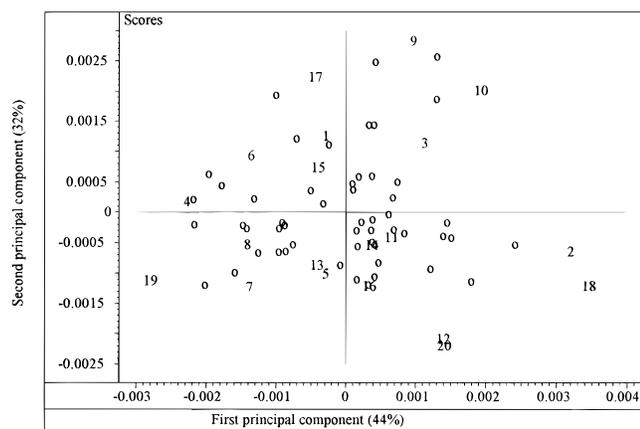
## EXPERIMENTAL PROCEDURES

**General Outline of the Method.** The procedure is outlined in Figure 1. Step by step this includes (1) near-IR spectroscopy of all soil samples, (2) selection of samples

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**Figure 2.** Example of spectroscopic data from soil samples scanned, at every second nanometer, between 1100 and 2498 nm with the near-IR instrument.



**Figure 3.** Score plot of the first and second principal components from near-IR analysis of 76 soil samples (1–20, samples selected for further analysis; samples not selected are labeled with o).

suitable for leachability studies, (3) spiking of soil samples with pesticides and extraction to characterize the strength of binding between pesticide and soil matrix, (4) calibration of near-IR and SPME or SFE, and (5) testing of unknown soil samples.

**Soil Samples.** Samples of 76 agricultural soil samples of various physical and chemical properties were collected from different parts of Sweden. The soils were dried at 35 °C and passed through a 2 mm sieve.

**Near-IR.** The sifted samples were scanned from 1100 to 2498 nm at every second nanometer (Figure 2, 700 data points) on a NIRS 4600 scanning monochromator (NIR Systems, Silver Spring, MD) equipped with an autosampler. The reflectance data were collected on a PC-based computer system with NIRS 3 software (Infrasoft International, Silver Spring, MD).

**Sample Selection.** The sample selection procedure was performed by PCA (Figure 3) and the predicting models with PLSR (Martens and Næs, 1989) using the software package UNSCRAMBLER (Camo A/S, Trondheim, Norway).

All PLSR models were validated by both cross-validation and the root mean square error of prediction (RMSEP) to find the number of significant PLSR factors. Before further work, multiplicative signal corrections (MSC) and first derivatives on all spectra were used to conceal the optical interferences (Geladi et al., 1985; Martens and Næs, 1989).

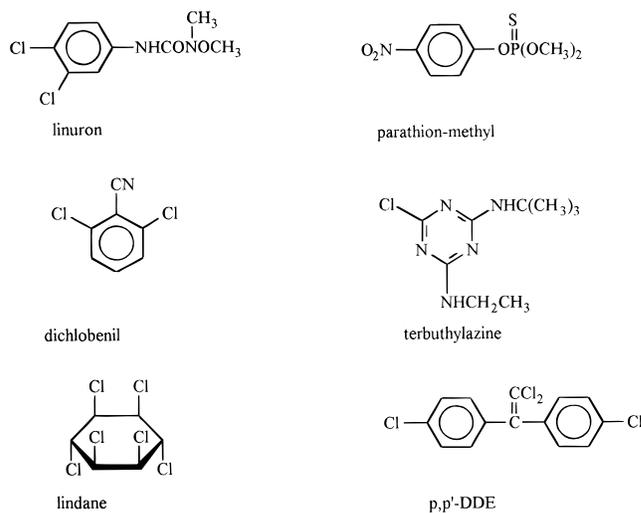
A subset of 20 samples from the original 76 was visually selected by using the score plot of the first two principal components from the near-IR data matrix (76 × 700) (Nordkvist et al., 1994; Stenberg et al., 1995).

**Solvents and Chemicals.** All chemicals and solvents were of analytical grade. All pesticides had 98–100% purity (Dr. Ehrenstorfer, GmbH). A standard solution containing linuron,

**Table 1. Concentrations and Properties of Pesticides Spiked to Soil Samples (Different Spikings Were Used for the SFE and SPME Experiments)**

compd	concn ( $\mu\text{g g}^{-1}$ )		water solubility <sup>a</sup> (mg L <sup>-1</sup> )	log $K_{ow}$ <sup>a</sup>	$K_{oc}$ <sup>a</sup> (mL g <sup>-1</sup> )
	SFE	SPME			
linuron	2.47	1.24	75	4.4	400
parathion-methyl	0.88	0.44	60	3.0	5100
dichlobenil	0.16	0.08	21	3.6	400
terbutylazine	1.03	0.52	10	3.0	200
lindane	0.10	0.05	7	3.8	1100
<i>p,p'</i> -DDE	0.10	0.05	0.1	5.7	5000

<sup>a</sup> Hornsby et al. (1996).



**Figure 4.** Pesticides fortified to the soil samples.

parathion-methyl, dichlobenil, terbutylazine, lindane, *p,p'*-DDE, and parathion (as internal standard) was prepared in acetone, and the soil samples were fortified with 0.05–2.47  $\mu\text{g g}^{-1}$  of each pesticide (Table 1; Figure 4). Calibration standards for gas chromatography (GC) were also prepared from these standard solutions.

**Chromatography.** Extracts were analyzed on a Hewlett-Packard (Wilmington, DE) HP 5890 gas chromatograph equipped with either an HP 7672A autosampler (SFE extracts) or a Varian 8200 autosampler (Varian Associates, Inc., Walnut Creek, CA) with an SPME device. The GC was equipped with two <sup>63</sup>Ni electron capture detectors (ECD) and two columns (CP-Sil 19CB and CP-Sil 5 CB, 20 m × 0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness; Chrompack, Middelburg, The Netherlands) attached to the same injector. Alternatively the extracts were analyzed on a Varian 3400 gas chromatograph with a Varian 8200 autosampler (with or without SPME device) equipped with two nitrogen–phosphorus detectors (NPD) and the same type of columns as above.

**Chromatographic Conditions:** splitless injection (60 s); injection volume, 2  $\mu\text{L}$ ; nitrogen as carrier and makeup gas to ECD and helium to NPD; injector temperature, 250 °C; detector temperature, 300 °C.

**Temperature Program:** 1 min at 90 °C, then 30 °C min<sup>-1</sup> to 180 °C followed by 4 °C min<sup>-1</sup> to 260 °C, hold for 12 min. Equilibration time after cooling to the next run was 2 min. Total run time between injections was about 40 min. A GynkoSoft chromatography data system (Gynkotek, GmbH) was used to collect and process the data.

**Binding/Leachability Studies. Method 1. Supercritical Fluid Extraction.** All extractions were performed with an ISCO (Lincoln, NE) SFE System 2200, equipped with an SFX 2-10 dual-chamber extraction module, two Model 260D syringe pumps, and a pump controller. A stainless steel tube was used as restrictor, producing a flow of 1 mL min<sup>-1</sup> of the supercritical fluid (SF) at 80 °C and 350 atm (flow measured at the pump). Carbon dioxide (99.998%, AGA Speciality Gases, Stockholm, Sweden) was used as the extraction medium.

**Table 2. Total Variation in Content of Various Soil Parameters after Chemical and Physical Analysis of (I) All 76 Soil Samples and (II) the 20 Samples Selected for Maximum Variability from Their Near-IR Spectra**

	I. chemical/physical analysis		II. near-IR and PCA	
	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
P (mg/100 g)	1.8	33.8	1.8	23.8
K (mg/100 g)	1.0	33.5	3.5	20.0
Mg (mg/100 g)	0.9	47.9	0.9	25.7

**Spiking Procedure.** The standard solution (1 mL) containing six different pesticides was added to each soil sample (5.0 g). Final levels of pesticides in the soil samples are given in Table 1. The mixture was stirred for several hours and evaporated to dryness at room temperature prior to extraction with SFE.

**Extraction Procedure.** One gram of the sample was mixed with copper granules to avoid restrictor plugging caused by high content of elemental sulfur in the sample (Reindl and Höfler, 1994). The mixture was then sandwiched between plugs of sand to reduce the void volume, and methanol (25  $\mu$ L) was added as a modifier before the extraction. Soil samples were extracted at 70 °C and 100 atm. The restrictor was heated to 80 °C. Five minutes of static extraction was followed by extraction in the dynamic mode (10 mL of CO<sub>2</sub>) with flow rates of 0.2–0.4 mL min<sup>-1</sup>. Analytes were collected in a 10 mL screw-cap vial, containing cyclohexane (2 mL) fortified with parathion as an internal standard. Small additions of cyclohexane were made during the extraction to maintain the solvent volume at 2 mL. The vial was placed in a water bath at room temperature during extraction to avoid ice formation.

**Method 2. Solid Phase Microextraction. Spiking Procedure.** Soil samples (10.0 g) were premixed with water (25 mL) prior to addition of the standard solution (50  $\mu$ L) in acetone. Water was added so as to hydrate active sites in the soil matrix, thus allowing the analytes to distribute evenly over the soil and to interact with active sites. The mixture was stirred for 0.5 h and left at room temperature overnight.

**Extraction Procedure.** Soil samples were centrifuged (2000g, 5 min), and the amount of pesticides remaining in the water phase was determined with SPME. The SPME device (Supelco, Bellefonte, PA), consisting of a syringe with a fused silica fiber glued to the plunger and coated with poly(dimethylsiloxane) (100  $\mu$ m), was installed in a Varian 8200 autosampler.

The fiber (1 cm) was immersed directly into the water sample containing the pesticides. After adsorption (45 min), analytes were desorbed (5 min) thermally in the injector of the gas chromatograph.

To check the recovery of the individual analytes in the SPME method, tap water, without addition of soil, was spiked at five different levels with the standard solution.

To get an independent measure of the recovery, the soil pellet from the centrifugation was extracted with SFE on a subset of samples. Conditions were chosen to give total recovery of the analytes (70 °C and 400 atm): 5 min of static extraction was followed by dynamic extraction (10 mL of CO<sub>2</sub>, 0.5–0.7 mL min<sup>-1</sup>, flow measured at the pump). The sample was prepared and analytes were collected as described earlier in method 1, with the exception that methanol (200  $\mu$ L) was added as a modifier prior to extraction.

**Physical and Chemical Analysis.** After physical and chemical analysis, the influence of different chemical constituents on the adsorption of pesticides to the soil was investigated using target rotated loadings (Kvalheim et al., 1989) from the PLSR model (software package SIRIUS, Pattern Recognition System A/S, Bergen, Norway). All analyses were performed at the National Laboratory for Agricultural Chemistry on air-dried soil, according to the directions for soil analysis in Sweden (KLK, 1965), in which the following parameters are determined: clay, silt, sand, organic matter, total nitrogen, pH, phosphorus, potassium, and magnesium.

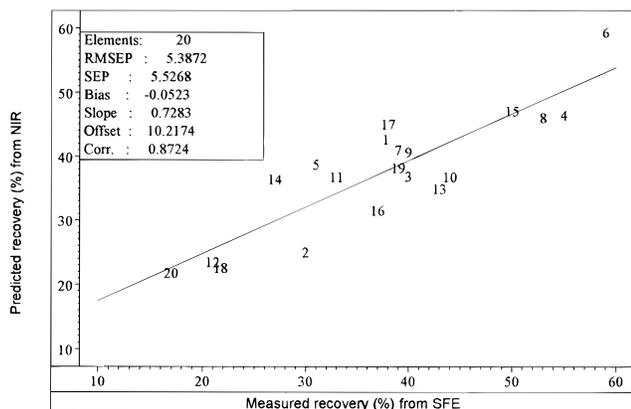
## RESULTS

**Sample Selection.** The minimum–maximum interval of the main components in the 76 soil samples analyzed with chemical and physical methods was compared with the minimum–maximum interval from the 20 soil samples selected with near-IR and PCA. The selected samples included almost the entire span of variation for most of the determined parameters (Table 2).

**SFE.** Recoveries for each pesticide ranged from 0% to 95%, depending upon the soil matrix and analyte (Table 3). Higher recoveries were obtained for dichlobenil and lindane than for the rest of the analytes. Both dichlobenil and lindane are nonpolar and relatively volatile. Less volatile nonpolar compounds (*p,p'*-DDE, parathion-methyl, and terbutylazine) were extracted at medium recoveries, while the more water soluble linuron was extracted at lower recoveries. The sum of recoveries of the six pesticides fortified to each soil sample was used in a PLSR model with cross-validation to predict the recovery from near-IR data. With three significant principal components in the model, about

**Table 3. Mean Recovery Data for Pesticides from Soil Samples after SFE at Moderate Conditions (n = 3) [in Order of Increasing Content of Organic Matter (OM)]**

sample	linuron	parathion-methyl	dichlobenil	terbutylazine	lindane	<i>p,p'</i> -DDE	sample mean recovery (%)	OM (%)	N (%)
17	11	27	79	20	55	35	38	1.7	0.10
6	11	56	86	49	76	73	59	2	0.09
4	9	49	95	35	79	60	55	2	0.13
1	12	38	61	29	47	38	38	2.9	0.12
9	7	28	70	19	62	54	40	3.2	0.16
3	10	36	75	22	54	43	40	3.4	0.15
15	12	49	85	38	64	53	50	4	0.14
19	10	31	91	14	47	38	39	4	0.17
10	5	31	84	18	68	60	44	4.4	0.23
7	13	37	74	26	46	40	39	5.5	0.30
11	7	33	64	22	38	36	33	5.6	0.22
18	0	16	58	11	25	22	22	6.3	0.22
13	11	35	72	29	55	55	43	6.4	0.26
14	3	25	57	17	32	28	27	9.4	0.43
8	16	58	84	43	58	57	53	9.9	0.15
5	4	28	67	18	32	34	31	11.5	0.28
16	12	36	63	25	43	45	37	12.2	0.20
2	4	29	72	15	36	25	30	12.9	0.59
12	2	20	46	14	23	21	21	13.5	0.41
20	0	14	55	6	14	13	17	21.4	0.60

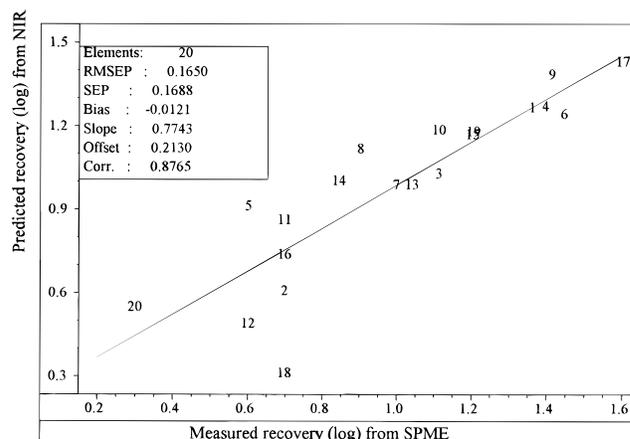


**Figure 5.** Recovery of pesticides extracted from soils, measured recovery (percent) from SFE plotted against predicted recovery values from near-IR with cross-validation in a PLSR model.

76% of the variation in total recovery of pesticides was explained with an RMSEP of 5.4 (Figure 5). The PLSR model was not improved by combining both near-IR and physical and chemical data. The SFE was done under conditions suboptimal for total extraction to allow the soil analyte interactions to influence the recoveries. Extraction under more severe conditions (70 °C, 160 atm, 200  $\mu$ L of methanol) gave quantitative recoveries (80–120%), for all six pesticides, excluding losses due to the spiking procedure (evaporation step). This indicates that the recoveries of the added pesticides are indeed influenced by the soil-analyte interactions. Therefore, nonquantitative extraction methods can be used to access the relative strength of these interactions.

**Method 2 (SPME).** All of the analytes were detectable and showed good linearity when extracted from fortified tap water ( $R^2 = 0.99$ –1.0).

Recoveries for each pesticide ranged from 0% to 72%, depending upon the soil matrix and analyte (Table 4). The highest recovery was obtained for terbuthylazine owing to the low  $K_{oc}$  value. Compounds with higher  $K_{oc}$  values gave lower recoveries (Table 1). The sum of recoveries for pesticides extracted from the water phase was calculated and used in a PLSR model with cross-validation, to predict the recovery from the near-IR data set. Logarithmic transformation was used on the recovery data from SPME to linearize data and stabilize the variance. With one significant principal component



**Figure 6.** Recovery of pesticides extracted from soils, measured recovery (percent) from SPME plotted against predicted recovery values from near-IR with cross-validation in a PLSR model.

in the model, about 77% of the variation in total recovery of pesticides was explained (Figure 6). With a PLSR model based on physical and chemical data, 73% of the variation in total recovery was explained with two significant principal components. If the model was based on both near-IR data and physical and chemical data, 80% of the variation in total recovery could be explained with three significant principal components. With this local PLSR model, the influence of various parameters on the recovery was studied. Target rotated loadings from the model show that organic matter and total content of nitrogen had a high negative influence on the recovery.

## DISCUSSION

Cross-validation of PLSR models is often done by predicting  $y$  for each object by a separate model based on the other objects (Wold, 1978). RMSEP is shown as

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^n (y_{i,\text{pred}} - y_{i,\text{obs}})^2}{n}}$$

where  $y_{\text{pred}}$  and  $y_{\text{obs}}$  are the predicted and observed values, respectively, and  $n$  is the number of observa-

**Table 4.** Mean Recovery Data for Pesticides from Supernatant Samples after SPME ( $n = 2$ ) [in Order of Increasing Content of Organic Matter (OM)]

sample	linuron	parathion-methyl	dichlobenil	terbuthylazine	lindane	sample mean recovery (%)	OM (%)	N (%)
17	38	21	40	72	28	40	1.7	0.10
6	26	26	29	44	17	28	2.0	0.09
4	18	14	22	52	18	25	2.0	0.13
1	15	9	42	31	19	23	2.9	0.12
9	25	7	27	54	18	26	3.2	0.16
3	9	8	19	21	6	13	3.4	0.15
15	13	11	22	26	8	16	4.0	0.14
19	14	13	25	22	6	16	4.0	0.17
10	11	7	18	25	6	13	4.4	0.23
7	6	5	19	13	5	10	5.5	0.3
11	3	2	11	6	3	5	5.6	0.22
18	3	2	12	7	2	5	6.3	0.22
13	9	7	17	20	3	11	6.4	0.26
14	4	3	16	9	3	7	9.4	0.43
8	8	4	11	16	3	8	9.9	0.15
5	2	2	9	5	2	4	11.5	0.28
16	3	3	8	8	2	5	12.2	0.20
2	3	3	13	5	2	5	12.9	0.59
12	4	2	9	5	2	4	13.5	0.41
20	0	2	5	3	1	2	21.4	0.60

tions. A model is finally built on the number of PLSR factors giving the first local minimum in prediction error. With this calibration model, prediction of recoveries from the other 56 soil samples in the score plot (Figure 3) or from near-IR spectra of other soil samples (within the same multivariate space in the score plot as the calibration set) is possible (Nordkvist and Larsson, 1994) (Figures 5 and 6). To achieve a general predictive method, the sum of recoveries was used instead of the individual pesticide recoveries.

**Method 1.** Supercritical fluid extraction (SFE), now accepted as an alternative to more conventional extraction procedures (Hawthorne, 1990; Bøwadts and Hawthorne, 1995), was used as one extraction technique. Several investigations regarding the use of SFE for the analysis of pesticides such as organophosphorus and organochlorine pesticides (Lopez-Avila et al., 1990; Snyder et al., 1993), triazine herbicides (Robertson and Lester, 1994; Steinheimer et al., 1994), and phenylurea herbicides (Robertson and Lester, 1994) in soil and sediment samples have been published.

The purpose of this investigation was not to optimize SFE conditions for maximum extraction yields but rather to study the influence of matrix-analyte interactions on the recovery. Moderate extraction conditions were therefore selected to obtain nonquantitative recoveries, influenced by the adsorption of analytes to the matrix. At the moderate extraction conditions used there is a maximum in the selectivity, with recoveries spread over the full range from quantitative to insignificant (0–95%).

All pesticides in this study are nonpolar and therefore easily soluble in nonpolar extraction media, such as supercritical carbon dioxide. This indicates that factors other than solubility control the extraction process, such as interactions between the analytes and the soil matrix and/or transport of the analytes from the solid to the solvent phase (diffusion) (McNally, 1995).

The model constructed with the near-IR procedure proposed here predicts that a high content of organic matter will increase the retention of nonpolar agrochemicals. This is in accord with the general understanding that organic matter plays an important role in the adsorption of pesticides, as described in reviews by Stevansson (1972) and Cheng (1990). A study by Steinheimer et al. (1994) shows a high negative correlation between carbon content of the soil and recoveries for triazines using SFE as extraction method. Hawthorne et al. (1992) found the extractability of the analytes to be matrix dependent, requiring extended SFE conditions for samples with high organic carbon content.

**Method 2.** The SPME, developed by Pawliszyn and co-workers (Boyd-Boland et al., 1994; Zhang et al., 1994), was used as a nonquantitative extraction method to investigate soil-pesticide interaction. SPME is used for organic compounds such as pesticides in aqueous samples (Arthur et al., 1992a,b) and has been applied to many of the volatile analytes included in U.S. Environmental Protection Agency Method 624 (U.S. EPA, 1983). Also, headspace SPME-GC on volatile contaminants in aqueous solutions and in foods has been reported (Page and Lacroix, 1993). The adsorption of the analytes from the water phase onto the coating of the fiber is a function of the partitioning coefficient,  $K$ , of the individual analyte. Recoveries from the 20 selected samples were evaluated together with spectroscopic data from near-IR and/or physical and chemical data, using PLSR.

The soil samples had been mixed with water prior to addition of standard to hydrate polar groups in the soil,

thus allowing the analytes to interact with the active sites in the matrix. After centrifugation, the amount of pesticides remaining in the water phase was analyzed with SPME. However, it was not possible to detect *p,p'*-DDE, the most nonpolar analyte in the study, with SPME. Therefore, a subset of soil phase samples from the SPME experiment (the pellet after centrifugation) was also extracted with SFE and *p,p'*-DDE was detected at recoveries close to 80%. This indicates that the reason *p,p'*-DDE was not detected with SPME was its strong adsorption to the soil. Carter and Suffet (1982) found that a significant fraction of DDT in water samples may be bound to dissolved humic matter. Wershaw et al. (1986) suggested that the retention of nonpolar substances such as DDT can be explained by interactions with the hydrophobic interior of the humic substances. There are also indications that humic acids, fulvic acids, and humin are active fractions for adsorption of many pesticides as demonstrated for lindane and DDT by Chiou et al. (1986) and for terbutylazine by Dousset et al. (1994).

Parathion-methyl yielded low recoveries from some soils (water phase). This may partly be explained by enzymatic activity of the soil. The ester linkage of the phosphate moiety may be hydrolyzed by soil phosphatases. Extracellular soil phosphatases are adsorbed to the soil colloids, and their catalytic capacity can be preserved for a long time even in air-dried soils. Furthermore, a high carbon content in the soil generally increases the pool of extracellular phosphatases (Eivazi and Tabatabai, 1977).

For the biochemical decomposition of other pesticides used in this study, induced production of enzymes is necessary. Biochemical decomposition of those pesticides during the relatively short time between spiking and extraction is therefore not expected. Reddy and Gambrell (1987) and Sanches-Martin and Sanches-Camazo (1991) demonstrated positive correlation between adsorption of parathion-methyl and soil organic matter content. Singh et al. (1990) found a positive correlation between adsorption of linuron and soil organic matter content. Our results indicate that the availability of active sites (for example, associated with carbon) in the different matrices depends on the spiking and extraction procedure. The addition of water to the dry soil in method 2 possibly opens up the lattice and increases the ability of interactions between pesticides and matrices. The recoveries obtained with the SFE and SPME methods correlate to some degree with the soil organic matter (Tables 3 and 4). Qualitative data of the organic matter in soil are therefore necessary for prediction of the leachability of pesticides, and the use of near-IR is a simple and fast method to achieve this information.

**Conclusions.** The results in this study indicate that (I) near-IR can replace chemical and physical analysis for characterization of soil samples, given that a calibration matrix is first constructed correlating near-IR data with conventional methods, (II) the use of PCA on near-IR data offers a rapid method for selection of samples that optimally describe the maximum variation from one population, and (III) the near-IR and SPME procedures described in method 2 offer a fast way to generally assess the leachability of pesticides in a large number of different soils (Figure 1).

To further elaborate on the predictive strength of the models, it would be valuable to use authentic samples for the calibration, as the binding cannot be expected to be identical in authentic and spiked samples. If field measurements of the leachability of various pesticides in different soils can be included in the model, it might

also be possible to get a semiquantitative assessment of how individual pesticides will behave in the field situation.

#### ABBREVIATIONS USED

AL, ammonium lactate; ECD, electron capture detector; GC, gas chromatography; LLE, liquid-liquid extraction; MSC, multiplicative signal corrections; near-IR, near-infrared reflectance spectroscopy; NMR, nuclear magnetic resonance; NPD, nitrogen-phosphorus detector; PCA, principal component analysis; PLSR, partial least-squares regression; RMSEP, root mean square error of prediction; SFE, supercritical fluid extraction; SPME, solid phase microextraction.

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