

Prediction of Atrazine Sorption Coefficients in Soils Using Mid-Infrared Spectroscopy and Partial Least-Squares Analysis

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This study explored the potential of mid-infrared spectroscopy (MIR) with partial least-squares (PLS) analysis to predict sorption coefficients (K_d) of pesticides in soil. The MIR technique has the advantage of being sensitive to both the content and the chemistry of soil organic matter and mineralogy, the important factors in the sorption of nonionic pesticides. MIR spectra and batch K_d values of atrazine were determined on a set of 31 soil samples as reference data for PLS calibration. The samples, with high variability in soil organic carbon content (SOC), were chosen from 10 southern Australian soil profiles (A1, A2, B, and C in one case). PLS calibrations, developed for the prediction of K_d from the MIR spectra and reference K_d data, were compared with predictions from K_{oc} -based indirect estimation using SOC content. The reference K_d data for the 31 samples ranged from 0.31 to 5.48 L/kg, whereas K_{oc} ranged from 30 to 680 L/kg. Both coefficients generally increased with total SOC content but showed a relatively poor coefficient of determination ($R^2 = 0.53$; $P > 0.0001$) and a high standard error of prediction (SEP = 1.22) for the prediction of K_d from K_{oc} . This poor prediction suggested that total SOC content alone could explain only half of the variation in K_d . In contrast, the regression plot of PLS predicted versus measured K_d resulted in an improved correlation, with $R^2 = 0.72$ ($P > 0.0001$) and standard error of cross-validation (SECV) = 0.63 for three PLS factors. With the advantages of MIR-PLS in mind, (i) more accurate prediction of K_d , (ii) an ability to reflect the nature and content of SOC as well as mineralogy, and (iii) high repeatability and throughput, it is proposed that MIR-PLS has the potential for an improved and rapid assessment of pesticide sorption in soils.

KEYWORDS: Soil organic carbon; partial least-squares; PLS; pesticide risk assessment; infrared spectroscopy; atrazine

INTRODUCTION

The current standard technique of estimating the sorption coefficient of an organic compound in soil using the K_{oc} approach (1–3) is often inadequate (4–6), as it is based on soil organic carbon content (SOC) alone. It does not take into account the chemical nature of the soil organic matter (SOM) or other contributing factors to sorption of pesticides. K_{oc} as an extrapolation parameter is commonly used, not because it is accurate but simply because of the lack of a suitable alternative. Numerous studies have reported large variations in K_{oc} values for a specific pesticide in soils from the same or different regions (7). Some 35 years ago, Hamaker and Thompson (5) compiled large data sets and cautioned against treating K_{oc} or K_{om} as a

constant due to their large variation among soils. This large variation has been attributed to the differences in the affinities of pesticide molecule for SOC in various soils (8–11), the contribution of minerals to sorption (12), and organo–mineral interactions in soils that could block sorption sites (13). These effects may be quantified separately by laboratory analyses but these can be time-consuming and expensive. Alternatively, near-infrared (NIR) and mid-infrared (MIR) spectroscopy can provide soil compositional information regarding the nature and content of both organic and mineral matter and, thus, offer an attractive alternative method to overcome problems inherent in the K_{oc} method.

Infrared spectroscopy is now increasingly being used as a rapid method for soil analysis in place of the more traditional laboratory methods. Bengtsson et al. (14) found that NIR spectroscopy could be used to estimate >80% of the sorption of lindane and linuron in a set of 27 soils. NIR spectral peaks, however, are often difficult to interpret due to extensive peak

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Table 1. Taxonomical (USDA Soil Taxonomy 1994^a) Classification and Selected Physicochemical Properties of the 31 Soils Used in the Study

| soil | profile | classification | depth (cm) | SOC (g/kg) | pH (1:5 0.01 M CaCl ₂) | sand (g/kg) | silt (g/kg) | clay (g/kg) | clay minerals ^b | K _d (L/kg) | K _{oc} (L/kg) |
|------|----------|---|------------|------------|------------------------------------|-------------|-------------|-------------|-----------------------------|-----------------------|------------------------|
| 1 | 1413A1 | Aquic Natrixeralfs, very-fine, mixed, mesic | 0–10 | 13.3 | 5.10 | 910 | 60 | 30 | K < I < Q < RIM | 1.16 | 87 |
| 2 | 1413A2 | | 10–50 | 3.5 | 5.15 | 920 | 45 | 35 | | 0.31 | 89 |
| 3 | 1413B | | 50–105 | 3.0 | 4.80 | 210 | 40 | 750 | | 0.35 | 117 |
| 4 | 1416A1 | Aquic Natrixeralfs, very-fine, mixed, mesic | 0–15 | 22.8 | 4.40 | 700 | 190 | 110 | K < V < Q < RIM | 1.81 | 79 |
| 5 | 1416A2 | | 15–50 | 5.0 | 5.87 | 515 | 95 | 390 | | 0.34 | 68 |
| 6 | 1416B | | 50–100 | 2.0 | 7.80 | 500 | 50 | 450 | | 0.41 | 205 |
| 7 | 1418A1 | Albic Natraqualfs, fine-loamy, mixed, mesic | 0–10 | 26.0 | 5.10 | 860 | 100 | 40 | K < I < Q < V | 2.59 | 100 |
| 8 | 1418A2 | | 10–30 | 1.0 | 5.30 | 850 | 100 | 50 | | 0.54 | 540 |
| 9 | 1419A1 | Albic Natraqualfs, fine-loamy, mixed, mesic | 0–10 | 15.0 | 5.10 | 890 | 70 | 40 | K < I < Q < V | 3.39 | 226 |
| 10 | 1419A2 | | 10–30 | 1.0 | 5.40 | 850 | 80 | 60 | | 0.56 | 560 |
| 11 | 1419B | | 30–70 | 3.75 | 5.10 | 500 | 10 | 470 | | 0.65 | 173 |
| 12 | 1419C | | 70–170 | 1.0 | 6.80 | 610 | 70 | 320 | | 0.64 | 640 |
| 13 | 1422A1 | Aquic Natrixeralfs, very-fine, mixed, mesic | 0–10 | 38.3 | 4.80 | 790 | 90 | 110 | K < RIM = V < I < Q | 2.48 | 65 |
| 14 | 1422A2 | | 10–30 | 9.0 | 4.70 | 760 | 70 | 170 | | 0.98 | 109 |
| 15 | 1422B | | 30–75 | 4.2 | 5.28 | 275 | 55 | 670 | | 0.40 | 95 |
| 16 | 1428-1A1 | Typic Albaqualfs, fine, mixed, mesic | 0–10 | 75.2 | 4.60 | 870 | 80 | 50 | K < I < Q | 4.52 | 60 |
| 17 | 1428-1A2 | | 10–20 | 8.0 | 4.40 | 900 | 60 | 50 | | 4.58 | 573 |
| 18 | 1428-1B | | 20–60 | 5.5 | 4.25 | 520 | 100 | 380 | | 1.48 | 269 |
| 19 | 1428-2A1 | Typic Albaqualfs, fine, mixed, mesic | 0–10 | 47.0 | 4.60 | 880 | 80 | 50 | K < I < Q | 4.52 | 96 |
| 20 | 1428-2B | | 20–40 | 1.0 | 4.40 | 540 | 95 | 360 | | 0.68 | 680 |
| 21 | 1432A1 | Typic Glossaqualfs, fine, mixed, mesic | 0–10 | 30.7 | 4.40 | 800 | 130 | 70 | K < V = I < RIM > Q | 0.93 | 30 |
| 22 | 1432A2 | | 10–30 | 3.0 | 4.90 | 840 | 120 | 40 | | 0.38 | 127 |
| 23 | 1432B | | 30–100 | 1.0 | 5.46 | 490 | 110 | 400 | | 0.54 | 540 |
| 24 | 1433A2 | Plinthic Haploxeralfs, fine, mixed, mesic | 10–30 | 20.0 | 4.40 | 650 | 160 | 190 | K < I = RIM = V = Q (minor) | 2.45 | 123 |
| 25 | 1433B | | 30–100 | 4.6 | 4.81 | 520 | 240 | 340 | | 1.08 | 235 |
| 26 | 1437A1 | Typic Natrixeralfs, fine, mixed, mesic | 0–15 | 16.2 | 4.30 | 920 | 40 | 40 | K = RIM > I < Q | 2.45 | 151 |
| 27 | 1437A2 | | 15–65 | 1.2 | 4.97 | 900 | 36 | 54 | | 0.52 | 433 |
| 28 | 1437B | | 65–100 | 2.0 | 6.31 | 620 | 30 | 350 | | 0.45 | 225 |
| 29 | 1440A1 | Arenic Albaqualfs, fine, mixed, mesic | 0–10 | 38.9 | 4.20 | 920 | 50 | 30 | V = RIM > K < I < Q | 1.46 | 38 |
| 30 | 1440A2 | | 10–50 | 2.0 | 4.60 | 915 | 55 | 30 | | 0.34 | 170 |
| 31 | 1440B | | 50–100 | 4.0 | 5.20 | 620 | 40 | 320 | | 0.53 | 133 |

^a Soil Survey Staff. *Keys to Soil Taxonomy*, 5th ed.; SMSS Technical Monograph 19; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1994; 422 pp.

^b K, kaolinite; I, illite; Q, quartz; V, vermiculite; RIM, randomly interstratified minerals (only measured for surface horizons).

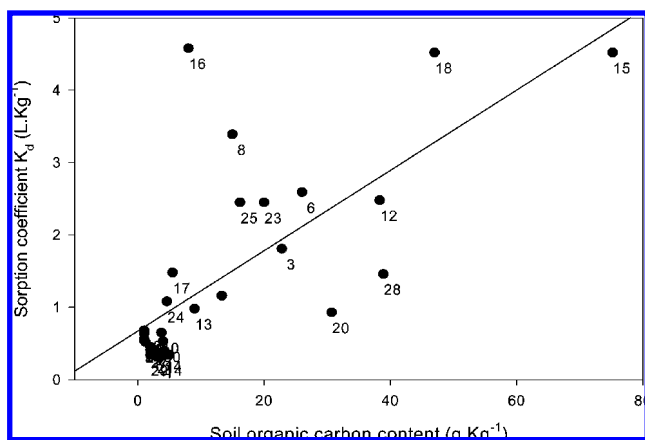


Figure 1. Relationship between atrazine sorption distribution coefficients (K_d) and the content of soil organic carbon (SOC) in 31 soils. A low coefficient of determination ($R^2 = 0.53$) and a high relative standard error ($SE = 1.22$) were noted for the best fit line.

overlap of the overtone and combination vibrations and can be insensitive to some common soil components such as quartz. Mid-infrared (MIR) spectroscopy has also been used for many years for qualitative soil analysis (15). The MIR frequencies in soils are characterized by relatively intense fundamental vibrations of organic functional groups involving $-CH$, $-OH$, $-NH$, $-CO$, $-CN$, and $-CC$ bonds within alkyl, hydroxyl, amide, carboxyl, and aromatic groups in the soil organic matter (16) and also by $-Fe-O$, $Si-O$, and $Al-OH$ groups characteristic of the mineral components (15, 17, 18). Each molecular group gives a multiplicity of fundamental vibrations as well as some

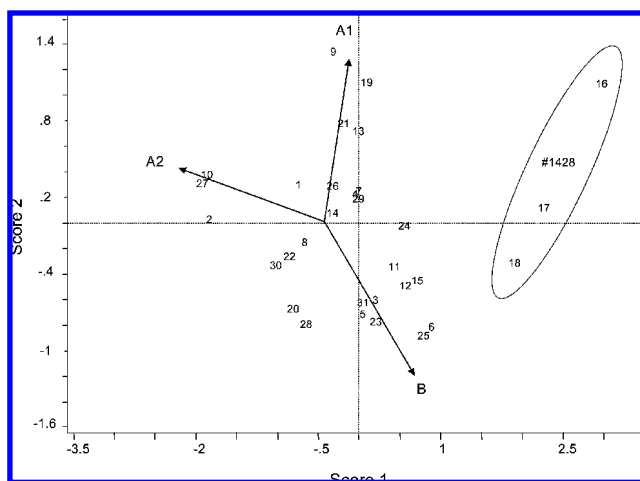


Figure 2. Partial least-squares score plot for sorption coefficients in 31 soils. Three soils from profile 1428 stands out as a different cluster among the 31 soils used here. Vectors show the tendency of different soil horizon groupings.

overtones and combinations, the specific frequencies being dependent on interactions between molecules and on the molecular environment. The complexity of the spectral signatures in the MIR and the overlap of the organic peaks with those of the mineral constituents in the soil have, however, been seen as an impediment to the use of MIR for SOM studies. Further research, however, has indicated that by using the diffuse reflectance infrared Fourier transform (DRIFT) technique to derive soil spectra (with minimum sample preparation) coupled

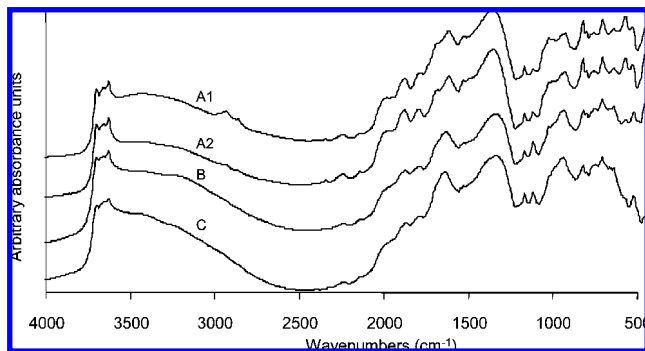


Figure 3. Mid-infrared spectra of different horizons of the soil profiles studied. Spectra are shown averaged from the (a) A1, (b) A2, and (c) B horizons and (d) the single C horizon.

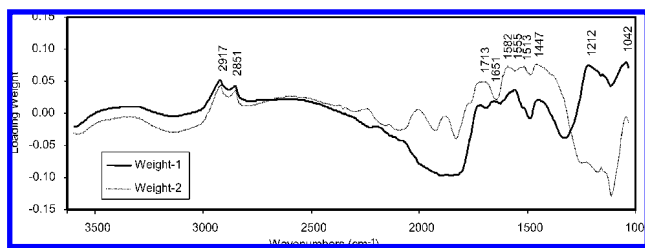


Figure 4. PLS loading weights 1 and 2 for sorption coefficients (K_d) of atrazine.

with chemometrics application, a quantitative soil analysis can be made (19).

During the past decade or so, partial least-squares (PLS) regression has been used to reduce the complexity of the infrared spectra into much simpler orthogonal factor descriptors for predictive model development. PLS regression is a bilinear modeling method in which spectral and soil property reference data are combined into a small number of “latent” variables (PLS loadings) and scaling terms (PLS scores). The procedure for PLS analysis adopted here is similar to that was described by Haaland and Thomas (20) and later reported for soil analysis by MIR spectroscopy (21) and PLS analysis (MIR-PLS). Both NIR and MIR spectroscopy with PLS analyses have been applied effectively in estimating soil properties, for example, in determining total SOC content and SOC fractions (21–23), but the potential of MIR spectroscopy with PLS regression (MIR-PLS) for the assessment of pesticide sorption into soils is yet to be fully explored.

In this study we explored the potential application of MIR-PLS analysis as an efficient predictive tool for atrazine sorption using measured reference sorption data and MIR-DRIFT spectra on a set of surface and subsurface samples sourced from *Pinus radiata* plantation soils in southern Australia. These soils had similar mineralogical composition, essentially sand and kaolinite/smectite clays, with widely varying SOC contents. PLS calibrations were developed for the prediction of K_d from MIR spectra and reference K_d values in comparison to predictions from a K_{oc} model derived from total SOC content.

MATERIAL AND METHODS

Soils and Atrazine Herbicide. Soil samples were collected from 10 different soil profiles from *P. radiata* (D. Don) plantations in the Warren reservoir catchment (113 km² in Adelaide hills, South Australia). Soil samples were collected in triplicate for sorption and degradation studies in the laboratory from the A1, A2, and B horizons in the 10 profiles: A1 for the surface sandy organic-rich layer, A2 for the subsurface layer, and B for the clay-rich layer for 9 profiles, with an additional C layer for one sample containing weathered parent rock

material for the 10th profile. Thus, in total, 31 different soil samples were collected in triplicate for this study. The soils were predominantly acidic sands with kaolinite, illite, and randomly interstratified mineral (RIM) clay mineralogy (Table 1). After collection, the soil replicates were bulked for each horizon and thoroughly mixed by hand. The samples from each horizon were oven-dried at 40 °C for 4 days for use in the sorption study, followed by grinding, homogenization, and “dry” sieving through a 2 mm metal sieve. A description of their soil properties and taxonomical classification is presented in Table 1.

The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamine-*s*-triazine) was used as a test compound in this study for a number of reasons: (i) it is a widely used compound commonly detected in surface and ground waters; (ii) it is relatively stable and easy to analyze; (iii) a lot of literature data on its sorption properties is available for comparison; and (iv) its sorption has been reported to be affected by both the amount and the chemistry of SOC (24). According to Tomlin (25), atrazine has a molecular weight of 215.7, vapor pressure of 3.85×10^{-2} mPa (25 °C), solubility in water of 33 mg L⁻¹ (20 °C), and $\log K_{ow} = 2.5$ (25 °C) and is weakly basic with a pK_a value of 1.7 (21 °C).

Atrazine Sorption. Atrazine sorption was determined by spiking an aliquot of 5 g of soil with 5–20 μ g of atrazine in 10 mL of solution containing 0.01 M CaCl₂ and equilibrating the slurry overnight (16 h) in an end-over-end shaker using Teflon-capped centrifuge tubes. Equilibrations at all concentrations were run in triplicate. The shaking time was chosen following a sorption kinetics experiment using 1.0 mg/L of atrazine and equilibrating it at the same soil/solution ratio for 0.25, 1, 3, 8, 16, and 24 h shaking times. Following equilibration, the supernatant solution was decanted and passed through a 0.45 μ m nylon membrane syringe filter into a vial. The analysis for atrazine was undertaken on an Agilent 1100 series high-performance liquid chromatograph (HPLC) fitted with a diode array detector and an SGE C₁₈ RS column (250 \times 4.6 mm, 5 μ m). The mobile phase used was 60:40 methanol/water (HPLC grade methanol and Milli-Q water), an injection volume of 20 μ L, and a detection wavelength of 220 nm with a detection limit of 0.1 mg/L. Total carbon concentration was determined by dry combustion using a Leco CR-12 Carbon Analyzer (LECO Corp. St. Joseph, MI). Values of K_d were determined from the data by fitting to a linear form of isotherm, whereas K_{oc} was determined from K_d divided by the mass fraction of SOC. In some cases when nonlinearity was significant, the lowest concentration was used to calculate the K_d as the effect of nonlinearity increases with solution concentration. Results of atrazine sorption K_d , K_{oc} , and SOC for the soil samples are presented in Table 1.

Mid-Infrared Spectroscopy. Portions of soil sample (100 mg), from the composited and ground soil samples for each horizon used for sorption study, were analyzed as neat powders using the MIR-DRIFT technique. Spectra were scanned in a rapid scanning Fourier transform spectrometer (Bio-Rad 175C), with 60 co-added scans collected over 60 s for each sample. The instrument was equipped with an extended range KBr beam splitter and DTGS detector, with a spectral range of 8300–470 cm⁻¹ at 8 cm⁻¹ resolution. Spectral frequencies were referenced against an internal He–Ne laser to give a precision and accuracy of 0.01 cm⁻¹. The DRIFT accessory (DRS-3SO, Harrick) used an off-axis geometry and was set up for maximum energy without removal of stray specular radiation. Only the MIR portion of the spectra between 4000 and 500 cm⁻¹ was used for the chemometrics analysis. An initial KBr blank spectrum was run to test the spectrometer performance and as a reference for calculating the sample spectra in absorbance units. Sample absorbance spectra were directly scanned into Grams/AI SPC format (Thermo Electron Corp.).

Partial Least-Squares Analysis. Spectra were imported into the PLSplus/IQ software together with the corresponding analytical data (K_d , SOC, and K_{oc}). The spectra were mean-centered and preprocessed with automatic baseline correction and the optimum spectral ranges selected for training the PLS models. PLS calibration models to predict atrazine K_d were developed using PLSplus/IQ (Thermo-Electron Corp.) software. PLS model training was carried out by “leave-one-out” cross-validation, where each sample is removed in turn from the set and its value predicted from models based on the remaining samples. Training continued for the preset number of PLS terms (factors) until the

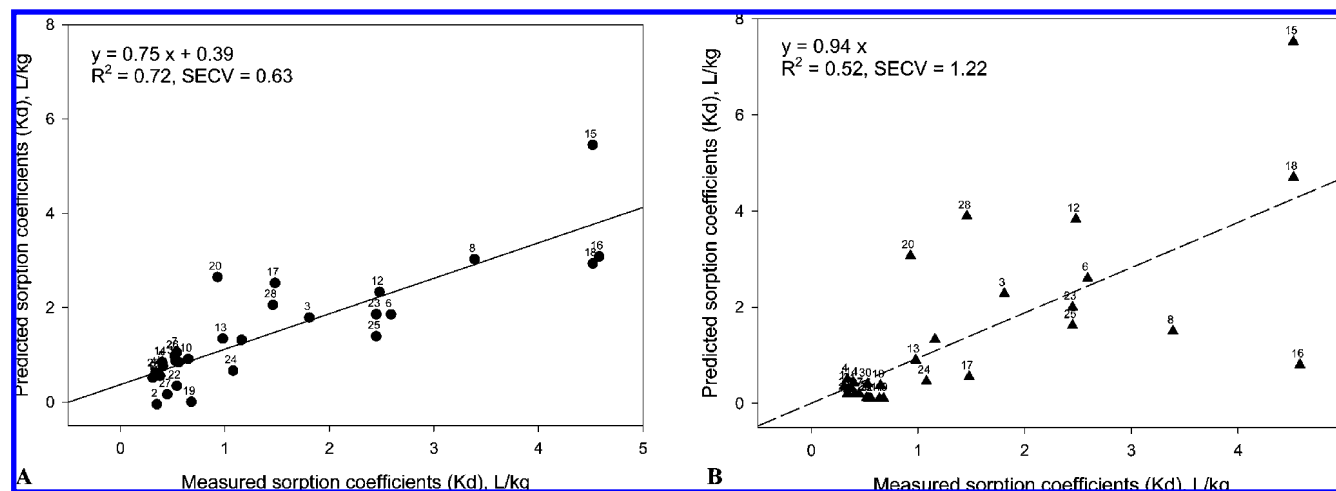


Figure 5. MIR-PLS prediction regression of sorption coefficients (K_d) for 31 soils (A) and K_{oc} predicted sorption coefficients (B). The MIR-PLS used three factors (organic matter, mineralogy, and quartz particle size), which significantly improved $R^2 = 0.72$ compared to a $R^2 = 0.52$ when only organic matter factor was taken into account.

minimum prediction residual error sum of squares (PRESS) was reached. The number of factors required to reach this minimum was taken as the optimum dimensionality of the model. The first few loading weights account for most of the variation in the MIR-PLS model and express the component spectra most related to the analyte of interest. As well as PLS loadings, the first few PLS loading weights, somewhat similar to “pure component” spectra of the analyte, and the scores for the first two PLS components were used to describe the variation between samples in the model. Moreover, principal component analysis (PCA) was performed to show the clustering or distribution of sample spectra in a two-dimensional score versus score plot.

The resulting prediction model generally requires validation using a set of independent unknown samples. However, a separate validation set was not available, and the size and nonuniformity of the calibration set did not allow us to perform a thorough independent validation process by dividing the calibration set into random sets of calibration and validation samples. In this study, therefore, we could develop the prediction model only through cross-validation, which involves a self-validation process. Further improvement and validation of the model have been left for follow-up studies, but, in the present study the predictive ability of the calibration models was assessed by calculating the coefficient of determination (R^2) and the standard error of cross-validation (SECV) calculated as

$$SECV = \sqrt{\frac{\sum d_i^2}{n}}$$

where $d_i = r_i - p_i$ is the difference between reference and model predicted data for sample i and n is the number of samples in the calibration set (26).

RESULTS AND DISCUSSION

The sorption data were fitted to a linear sorption isotherm to obtain sorption coefficients (K_d), which in most cases described the data well ($R^2 > 0.94$). In six samples the nonlinearity was obvious, and in these cases the lowest concentration was used to calculate the K_d . Laboratory-measured K_d values (reference) were in the range from 0.31 to 5.48 L/kg for the 31 soils (Table 1). The K_d values generally increased with total SOC content (Figure 1), but with a low coefficient of determination ($R^2 = 0.527$; $P < 0.0001$) with standard error of estimation = 1.22. This regression showed that carbon content alone could explain only half the variance in K_d . The distribution of K_{oc} data for this data set (Table 1) showed a wide range from 30 to 680, a 23-fold variation among soils from a single land use, and supported the poor regression between K_d and low SOC values.

Atrazine is a very widely studied compound with a widely used average value of K_{oc} , according to a large published database, of 100 L/kg (27). The K_d values for these soils were estimated using this K_{oc} value from the literature. Values for K_{oc} from only about one-third of our soil samples were somewhat closer (within 20%) to this average value, and the majority of samples showed a large difference. Several previous studies also reported such a wide variation in the K_{oc} values of atrazine (e.g., see refs 24 and 28).

The MIR spectra of the soils showed large variations in spectral patterns, as expected from the large variation in carbon content, soil compositions, and other properties. PLS regression analysis for K_d prediction resulted in good separation of the PLS scores for the B horizon spectra from those of the A1 and A2 horizons. Clustering between the two groups is depicted in the score versus score plot in Figure 2. Some separation of the scores for A1 and A2 samples, and particularly for all horizons belonging to sample 1428, occurred along the score 1 axis. Spectra of the soils averaged from the A1, A2, and B horizons and the single C horizon are presented in Figure 3. The spectra suggest that high organic matter in the A1 horizon was characterized by peaks at 2930–2850 cm^{-1} due to aliphatic $-\text{CH}_2$ stretching vibrations. These organic peaks were barely observed in the A2 horizon and were absent in the B and C horizons in accord with the known reference values of SOC concentration and clay contents. Peaks in Figure 3 were clearly evident for quartz and also for kaolinite, illite, and smectite probably occurring in RIM structures (17). Quartz (as sand) usually dominates Australian soils, resulting in many strong MIR diffuse reflectance peaks in the 2000–1800 cm^{-1} region, and are often overlapped with other clay mineral and soil organic matter peaks in the spectral region from 1400 to 500 cm^{-1} (29). It appeared that the quartz peaks, strongest in the A1 horizon, were reduced in intensity for the A2, B, and C horizons, being replaced by strong water peaks near 3400 and 1630 cm^{-1} due to water within illite/smectite in RIM clay interlayer structures. Strong and sharp kaolinite peaks near 3695–3620 cm^{-1} were also reduced in the C horizon.

The first two PLS loading weights are illustrated in Figure 4. These represent the spectra of soil components that correlated most strongly with K_d , with additional soil components contributing in the subsequent loading weights. As depicted in Figure 4, the first PLS loading weight was characterized by organic matter, with peaks in loading weight 1 observed at

2917–2851 cm^{-1} (alkyl $-\text{CH}_2$), 1730 cm^{-1} (carboxylic acid $-\text{COOH}$), and 1651 and 1555 cm^{-1} (amide $-\text{CO}-\text{NH}$). Loading weight 2 was correlated with both SOC (positive) and quartz (negative). The third loading weight (not shown) featured a negative peak due to clay at 1030 cm^{-1} and to clay–water near 1630 cm^{-1} .

Figure 5 shows the cross-validation regression plot of PLS predicted versus reference values of K_d , with an $R^2 = 0.72$ and $\text{SECV} = 0.63$. A single PLS factor, characterized mostly by peaks in the first loading weight due to organic matter, gave an $R^2 = 0.22$. Including a second factor, characterized by organic matter plus mineral (quartz), gave an improved R^2 of 0.67. Adding the third factor, mostly peaks due to clay and some quartz band distortion due to variations in quartz particle size, improved the regression further, giving an $R^2 = 0.72$. The MIR-PLS prediction not only achieved a better R^2 than that observed for the K_{oc} model, but its SECV was also lower (**Figure 5**), despite the compositional heterogeneity between the surface and subsoils (**Figure 2**). It is likely that separation of the data set surface and subsoils could further improve the prediction by producing a more robust PLS model based on more relevant sample compositional characteristics, although in this instance there are insufficient numbers of samples to form further data sets. These observations are supported by results from previous studies involving NIR spectroscopy in predicting the leachability and sorption of pesticides (14, 30).

The correlation between MIR spectra and K_d can be improved in a number of ways. First, the current PLS model is significantly better than the K_d versus SOC correlation despite the fact that surface and subsurface soils formed different clusters in the PCAs. Improved predictions may be possible using soils more closely matched according to the MIR spectra and hence only either A, B, or C horizons. Second, in the present study the intention was to seek a “proof of concept” and to simply explore if MIR can potentially be used to predict the K_d of pesticides. Only a simple PLS model was used to predict K_d from MIR. The data suggest that a nonlinear regression method, rather than the usual linear PLS algorithm, could potentially further improve the prediction.

The MIR-PLS method has been shown in this study to provide an estimate of pesticide sorption more accurate than that achieved by the current method of assessment via K_{oc} . Furthermore, the MIR-PLS method has the advantage of providing a more direct estimation involving fewer steps than the indirect estimate via K_{oc} and thus reducing errors in the measurement of SOC and K_d , resulting in a cost-effective and repeatable technique for fast throughput of samples.

Considering the high repeatability of MIR-PLS, its integrative ability to characterize both the concentration and nature of organic and mineral materials in soil (all of which are potential important for pesticide sorption measurement), and a reasonable correlation between pesticide sorption and IR spectral properties, there is a good case for using MIR-PLS as an assessment tool for pesticide sorption. This is particularly so in the cases when sorption coefficients are needed for a first-tier assessment or for relative risk assessment between different compounds or soils. Given that the MIR-PLS method is increasingly being used to characterize soils, especially for SOC concentration (needed for the K_{oc} model anyway), it is appropriate that the large amount of compositional information that the MIR spectra technique is capable of simultaneously extracting with no extra cost is utilized for K_d determinations. As a next step, calibration models should be developed from a large number of widely variable soils, possibly employing improved regression algo-

gorithms and validated with an independent set of data. In the first instance, the technique should be tested on a range of compounds and applied to a larger number of surface soils.

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