Infrared Spectroscopy and Advanced Spectral Data Analyses to Better Describe Sorption of Pesticides in Soils

MOHSEN FOROUZANGOHAR

In the fulfilments of the degree of
DOCTOR OF PHILOSOPHY

A thesis by prior publications submitted to
Discipline of Soil and Land Systems
School of Earth and Environmental Sciences
The University of Adelaide

August 2009

In God, the Greatest

Dedication

for my dear parents, Fakhree and Reza

Contents

Acknowledgments

I first wish to thank my principal supervisor Rai Kookana who is one of the most positive people I have ever met, always welcoming me, even when I had developed ideas for exotic experiments! Thank you Rai for the enduring support you have given me throughout my candidature. I would also like to thank my co-supervisors Ronal Smernik and David Chittleborough. The help and the time that Ron gave me in implementing my NMR experiments, analysing my data and editing my publications and thesis is greatly appreciated. I also truly acknowledge the help and support I have received from David. Outside the formal supervisory panel, I would like to thank Daniel Cozzolino and Sean Forrester who helped me with infrared and chemometrics techniques.

This research project would not have been possible without the technical support of many colleagues at the University of Adelaide and CSIRO, namely David Maschmedt, Colin Rivers, Danni Oliver, Michael Karkkainen, Janine McGowan, Lester Smith, Gillian Cozens and Natasha Waller. I am grateful to all of them for their time and patience.

I must not and cannot forget the significance of the friendships I have made during my candidature here in Adelaide. I do not want to miss anyone by naming people individually. I have never overlooked the value of a friendly chat, motivating me through the rest of the day. In Soil and Land Systems, I never felt alone or helpless.

Finally and most sincerely, I wish to deeply thank my precious family and friends who through their thought, support and love gave me the strength and courage to continue.

Abstract

The fate and behaviour of hydrophobic organic compounds (e.g. pesticides) in soils are largely controlled by sorption processes. Recent findings suggest that the chemical properties of soil organic carbon (OC) significantly control the extent of sorption of such compounds in soil systems. However, currently there is no practical tool to integrate the effects of OC chemistry into sorption predictions. Therefore, the K_{OC} model, which relies on the soil OC content (f_{OC}), is used for predicting soil sorption coefficients (K_d) of pesticides. The K_{OC} model can be expressed as $K_d = K_{OC} \times f_{OC}$, where K_{OC} is the OC-normalized sorption coefficient for the compound. Hence, there is a need for a prediction tool that can effectively capture the role of both the chemical structural variation of OC as well as f_{OC} in the prediction approach. Infrared (IR) spectroscopy offers a potential alternative to the K_{OC} approach because IR spectra contain information on the amount and nature of both organic and mineral soil components.

The potential of mid-infrared (MIR) spectroscopy for predicting K_d values of a moderately hydrophobic pesticide, diuron, was investigated. A calibration set of 101 surface soils from South Australia was characterized for reference sorption data (K_d and K_{OC}) and f_{OC} as well as IR spectra. Partial least squares (PLS) regression was employed to harness the apparent complexity of IR spectra by reducing the dimensionality of the data. The MIR-PLS model was developed and validated by dividing the initial data set into corresponding calibration and validation sets. The developed model showed promising performance in predicting K_d values for diuron and proved to be a more efficacious than the K_{OC} model. The significant statistical superiority of the MIR-PLS model over the K_{OC} model was caused by some calcareous soils which were outliers for the K_{OC} model. Apart

from these samples, the performance of the two compared models was essentially similar. The existence of carbonate peaks in the MIR-PLS loadings of the MIR based model suggested that carbonate minerals may interfere or affect the sorption. This requires further investigation.

Some other concurrent studies suggested excellent quality of prediction of soil properties by NIR spectroscopy when applied to homogenous samples. Next, therefore, the performance of visible near-infrared (VNIR) and MIR spectroscopy was thoroughly compared for predicting both f_{OC} and diuron K_d values in soils. Some eleven calcareous soils were added to the initial calibration set for an attempt to further investigate the effect of carbonate minerals on sorption. MIR spectroscopy was clearly a more accurate predictor of f_{OC} and K_d in soils than VNIR spectroscopy. Close inspection of spectra showed that MIR spectra contain more relevant and straightforward information regarding the chemistry of OC and minerals than VNIR and thus useful in modelling sorption and OC content. Moreover, MIR spectroscopy provided a better (though still not great) estimation of sorption in calcareous soils than either VNIR spectroscopy or the K_{OC} model. Separate research is recommended to fully explore the unusual sorption behaviour of diuron in calcareous soils.

In the last experiment, two dimensional (2D) nuclear magnetic resonance/infrared heterospectral correlation analyses revealed that MIR spectra contain specific and clear signals related to most of the major NMR-derived carbon types whereas NIR spectra contain only a few broad and overlapped peaks weakly associated with aliphatic carbons. 2D heterospectral correlation analysis facilitated accurate band assignments in the MIR and NIR spectra to the NMR-derived carbon types in isolated SOM.

In conclusion, the greatest advantage of the MIR-PLS model is the direct estimation of K_d based on integrated properties of organic and mineral components. In addition, MIR spectroscopy is being used increasingly in predicting various soil properties including f_{OC}, and therefore, its simultaneous use for K_d estimation is a resource-effective and attractive practice. Moreover, it has the advantage of being fast and inexpensive with a high repeatability, and unlike the K_{OC} approach, MIR-PLS shows a better potential for extrapolating applications in data-poor regions. Where available, MIR spectroscopy is highly recommended over NIR spectroscopy. 2D correlation spectroscopy showed promising potential for providing rich insight and clarification into the thorough study of soil IR spectra.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Mohsen Forouzangohar and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis (as named in List of Publications) resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue, the Australian Digital Theses Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

Mohsen Forouzangohar _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ **Date** _ _ _ _ _ _ _ _ _ _ _

List of Publications

Forouzangohar, M.; Kookana, R. S.; Forrester, S. T.; Smernik, R. J.; Chittleborough, D. J. Midinfrared spectroscopy and chemometrics to predict sorption distribution coefficient of diuron in soils. *Environmental Science & Technology*. 2008. 42, 3283-3288.

Forouzangohar, M.; Cozzolino, D.; Kookana, R. S.; Smernik, R. J.; Forrester, S. T.; Chittleborough, D. J. Direct comparison between visible near- and mid-infrared spectroscopy for describing diuron sorption in soils. *Environmental Science & Technology. 2009.* 43, 4049-4055.

Forouzangohar, M.; Cozzolino, D.; Smernik, R. J.; Kookana, R. S.; Forrester, S. T.; Chittleborough, D. J. Two-dimensional nuclear magnetic resonance/infrared heterospectral correlation analysis of carbon types in soil organic matter. *Environmental Science & Technology.* Submitted.

Forouzangohar, M.; Kookana, R. S.; Forrester, S. T.; Smernik, R. J.; Chittleborough, D. J. Midinfrared spectroscopy and partial least squares regression for a better prediction of diuron sorption in soils. Soils 2008 Conference. Massey University, Palmerston North, New Zealand 1-5 December 2008.

1 Review of Literature

1.1. INTRODUCTION: SORPTION OF PESTICIDES TO SOILS

Pesticides are widely used in modern agriculture and their significant positive effects on agricultural production are now well accepted. The current trend towards conservation tillage systems has also led to a greater reliance on pesticide use in agricultural systems. It is believed that when pesticides are applied under appropriate soil and environmental conditions and according to the recommended amounts and methods, they can control target pests with little adverse effect on adjacent ecosystems (1). However, due either to not following the prescribed methods of application or to the inherent effects of their usage, trace amounts of pesticides have been detected in soil, water and the atmosphere, where they have not been applied. For example, the herbicide atrazine was found for the first time in some groundwater samples in the United States in mid-seventies (2). Because of their toxic nature, the presence of pesticides in the environment produces a natural concern about their impacts on public health and environmental quality. The negative effects of some pesticides have been observed on non-target living organisms (3, 4). Given the known benefits of using pesticides, it seems essential to know exactly what happens to a pesticide when it enters the environment under specific conditions.

The key processes governing the fate of pesticides in the environment include sorption, transformation and transport processes (1). Of these, sorption plays a significant role, especially because it considerably affects the other processes (5). For example, pesticide transport to the atmosphere, groundwater and surface water is strongly controlled by sorption (6). The problem is, however, the underlying physical and chemical phenomena responsible for sorption are as yet not fully understood. For example, there are no direct observations regarding the exact molecular-scale locations where the pesticide molecules associate with sorbents (7). Therefore, researchers draw inferences about sorption mechanisms based on macroscopic observations. Accordingly the first hypothesis which mechanistically described sorption of pesticides in soils was partitioning (dissolution) of hydrophobic organic contaminant molecules into natural organic matter in the environment (8, 9). Subsequently, nonlinearity was observed in the sorption of pesticides to soils, an incompatible result with a simple partitioning mechanism. This observation led researchers to believe that adsorption onto geosorbents occurred via another mechanism (10, 11). Although mechanistic hypotheses for sorption can be postulated based on macroscopic observations, the complexity of sorption phenomena (e.g. diffusion of pesticide molecules into and out of different matrices, hysteretic sorption and aging effects) complicates interpretations. Therefore, analytical characterisation of sorption at microscale dimensions is necessary to develop more precise mechanistic models for sorption of pesticides to various geosorbents. (7).

Similar to other processes, sorption exhibits variability based on soil and environmental factors, including the type and content of mineral and organic materials, soil pH, soil temperature and moisture (5, 6), as well as molecular properties of the pesticide such as its hydrophobicity, charge characteristics and ionisability (12). Soil organic matter (SOM) is recognised as the most important variable for controlling sorption behaviour of non-ionic pesticides in soils, simply because the solvent in the soil system is water and the hydrophobic nature and high binding affinities of these compounds to organic matter are the driving force (13). It used to be assumed that the effect of organic matter on sorption is predictable just based on its content in soil (14). Under this assumption, the *soil organic carbon sorption coefficient* (K_{OC}) of a pesticide may be calculated using the following equation: $K_d = K_{OC} \times f_{OC}$, where, f_{OC} is the organic carbon fraction of the soil and K_d is the *soil sorption coefficient* of a pesticide in a specific soil. Once the K_{OC} of a pesticide is calculated from a set of K_d and f_{OC} measurements for a given pesticide in a soil, the sorption (K_d) of that pesticide in any soil can be estimated knowing its f_{OC} and assuming that a K_{OC} measured in one soil applies to any other (13).

The K_{OC} values of pesticides are widely used in pesticide fate stimulation models as a primary parameter and typically are employed along with the f_{OC} of a specific body of soil or sediment, to calculate K_d (13). Because K_{OC} has been considered the primary parameter for environmental fate modelling of pesticides, different methods have been developed for its determination. Some of these techniques involve direct measurement of the K_d and consequent calculation of K_{OC} using the equation above, whereas others are indirect methods for estimating K_{OC} without any need to measure K_d first. While the direct techniques require modern experimental facilities and are mostly time consuming and expensive, the indirect methods rely on molecular characteristics of pesticides, which seem to be more economical and useful, particularly in data-deficient areas.

Although it is appealing to regard K_{OC} as a constant parameter, there is now strong evidence against the assumption of its constancy (5, 13). Ahmad *et al.* (12) investigated the sorption of two non-ionic pesticides, carbaryl and phosalone, in 48 soils from Australia, Pakistan and the United Kingdom. They observed a variation in K_{OC} values of both pesticides in soils with a decreasing order as follows: Pakistani > Australian > British. Since they did not find any significant correlations between K_d and the f_{OC} values of the soils, they concluded that this factor, alone, was insufficient to predict sorption behaviour, even for non-ionic pesticides. The results of their research along with several others cited by Wauchope *et al.* (13) confirm that the assumption of constancy of K_{OC} for a pesticide in different soils is not true and that f_{OC} is not the only variable controlling sorption of non-ionic pesticides. Therefore, the practice of using the simple equation, $K_d = K_{OC} \times f_{OC}$, and extrapolating data to predict sorption under local conditions is not reliable. In another study, Liyanage *et al.* (15) studied the sorption behaviour of carbofuran and diuron in 43 tropical soils from Sri Lanka, and compared sorption data for these soils with published data, mostly from European and North American soils. They noticed that, while the range of the K_{OC} values from Sri Lankan soils were within the wide range of such values reported in the literature, values for both pesticides were noticeably higher in soils from dry areas than those from moist areas. By referring to findings of some previous research (e.g. 16, 17), they proposed that the differences in the nature of SOM are probably responsible for the wide range of the K_{OC} values in soils.

1.2. EFFECTS OF THE NATURE OF SOIL ORGANIC MATTER ON SORPTION OF HYDROPHOBIC PESTICIDES

There are numerous published studies which deal with the effects of chemical structure of SOM on sorption of hydrophobic pesticides (e.g. 7, 13, 18). In the following section the chemistry of SOM will be reviewed briefly, followed by a survey of the literature on how SOM chemistry can affect the sorption behaviour of such pesticide molecules in soils and sediments.

1.2.1. AN OVERVIEW OF THE CHEMICAL STRUCTURE OF SOIL ORGANIC MATTER

Soil organic matter (SOM) consists of three classes of organic materials, namely biomass or living organisms (plants, animals and microorganisms); organic residues or undecayed and partially decomposed dead bodies of such organisms; and most importantly “humus”. Humus, which accounts for 60 to 80 percent of the SOM, is actually a mixture of highly decomposed and chemically variable organic compounds (19, 20). Humus is composed of two groups of materials: nonhumic substances and humic substances (21). Nonhumic substances consist of chemically recognizable classes of organic compounds which are not specific to the soil environment. These organic compound classes include simple and complex carbohydrates (polysaccharides) including cellulose and lignin, amino acids and proteins including some enzymes and hormones, lipids including waxes and steroids, nucleic acids and a variety of organic acids. Humic substances, on the other hand, are made up of a chemically heterogeneous mixture of organic compounds which cannot be ascribed to particular families of organic compounds, and are exclusive to nonliving terrestrial and aquatic environments (20).

Humic substances form the major fraction of SOM by a contribution of up to 80 per cent. (20). Owing to the chemically heterogeneous nature of humic substances, it is impossible to define their exact molecular structure. Different models, however, have been proposed to describe a typical molecular structure for humic substances. Most recently, Sutton & Sposito (22) described humic substances as a collection of very different types of organic components with relatively low molecular masses which are dynamically associated via hydrophobic interactions and hydrogen bonds. Unlike nonhumic substances, the humic fraction is relatively resistant to further microbial decomposition because of the highly recalcitrant nature of its components and also its close association with mineral surfaces, which in turn may isolate it from soil microorganisms (19, 20). In fact, clay minerals help stablise SOM, and up to 90% of SOM content may be present as SOM-clay complexes (23). Although the new molecular structural view considers relatively small, independent moieties in humic substances, it also determines the ability of forming micelles for these diverse low-molecular-mass molecules in aqueous solutions e.g. soil solution (22).

Despite the lack of a consistent molecular structure model for humic substances, these materials have been characterized intensively by state-of-the-art spectroscopic techniques (e.g. nuclear magnetic resonance and infrared spectroscopy) for different functional groups and structural entities. These studies enable differentiation of SOM in terms of chemical nature, and are of particular importance because the different chemical properties of SOM govern its behaviour in soil processes such as the sorption of hydrophobic pesticide molecules.

One type of spectral analysis of particular importance is carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy which has greatly enhanced our understanding of carbon chemical types (i.e. functional groups and structural entities) in SOM. In this context, the ^{13}C NMR spectra of SOM are generally divided into four major chemical-shift regions, namely alkyl carbon (0-45 ppm), O-alkyl carbon (45-110 ppm), aromatic carbon (110-160 ppm) and carboxyl carbon (160-210 ppm) (24). Different soil samples have various amounts of these four carbon fractions which results in a wide variety of soils in terms of chemistry of organic carbon from highly aliphatic to highly aromatic. Although NMR spectra are often divided into four main regions, much more information about the chemistry of organic carbon is found in NMR data (25). In fact, particular spectral signatures within each region are associated with particular structural entities and functional groups. Figure 1.1 shows an example of a ^{13}C NMR spectrum of SOM. Seven main spectral peaks are found at chemical shifts around 33, 57 74, 105, 130, 155 and 174 ppm. The alkyl region (0-45ppm) is dominated by a sharp peak around 33 ppm due to methylene groups in long-chain aliphatic compounds from various origins particularly lipids (24). The spectral region between 33 and 55 ppm contains resonances due to amino acids and proteins (24). In the O-alkyl (alkoxy) region (45-110 ppm), the signal around 57 ppm is assigned to methoxy and ethoxy groups found in carbohydrates, alcohols, esters and ethers (20, 26). The signals around 74 ppm (together with the shoulders around 65 ppm and 80-90 ppm) and 105 ppm are generally assigned to polysaccharides and acetal/ketal compounds, respectively (20, 24, 26). In the aromatic (aryl) carbon region (110-165 ppm), the peak around 130 ppm is due to unsubstituted and alkyl- and olefin-substituted aromatic carbons (20, 26). In the chemical shift between 140 and 160 ppm (around 155 ppm), aromatic COR or CNR groups, phenol, aromatic ether and aromatic amines are identified (20, 24). The sharp signal around 174 ppm in the carboxyl region (165-220 ppm) is mainly caused by carboxyl groups in aromatic and/or aliphatic structures (20, 24).

NOTE:
This figure is included on page 8 of the print copy of
the thesis held in the University of Adelaide Library.

Figure 1.1. A typical carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum of soil organic matter (SOM). The four general regions and chemical shift assignments of major peaks are identified [Adapted from Skjemstad *et al.* (27)].

1.2.2. HOW THE CHEMICAL STRUCTURE OF SOIL ORGANIC MATTER AFFECTS SORPTION

It is believed that about half of the variability in K_{OC} values comes from variability in the nature of organic matter, and the rest is due to other factors such as experimental error (13). Therefore, the study of the chemical nature of SOM is essential to gain an insight into its role in the sorption behaviour of pesticides, particularly non-ionic types. Grathwohl (28) investigated the sorption process of some chlorinated aliphatic hydrocarbons and reported that the degree of oxidation of organic matter, as measured by the hydrogen/oxygen ratio, affects its adsorptivity for these compounds. In another study, the polarity of organic matter was determined for 19 soil and 9 freshwater sediment samples using solid-state ^{13}C NMR spectroscopy and was compared with K_{OC} values for carbon tetrachloride (29). The results of the research showed a distinct separation between soil and sediment samples based on polar organic carbon fraction, which could be responsible for observed differences in the sorption affinities. It was suggested that the polarity of organic matter shows an inverse relationship with K_{OC} values.

In a comparison between the K_{OC} values of two non-ionic pesticides (carbaryl and phosalone) in soils from different regions of Australia and Pakistan, and carbon chemistry of the SOM, Ahmad *et al.* (16) found a significant relationship between the aromaticity of SOM and the K_{OC} values. They proposed that the aromatic fraction of the SOM could be an appropriate variable for better predicting pesticide sorption. Moreover, Ahmad (unpublished data) found that two other molecular components of SOM, lignin and charcoal, had also a good correlation with K_{OC} values of carbaryl and phoslone. The influence of the aromatic fraction of soil organic carbon on sorption of hydrophobic organic compounds was supported by another study on the chemical composition of 18 different geosorbents using solid-state ^{13}C NMR spectroscopy (30). Ahangar *et al.* (31) reported a distinct separation in the magnitude beween K_{OC} values of two consecutive surface and subsurface horizons in which the surface layer had higher K_{OC} values. A ^{13}C NMR analysis revealed a clear difference between the two horizons with respect to the proportion of aromatic fraction. There was a positive correlation between aromatic fraction of SOM and K_{OC}. Furthermore, Ahangar *et al.* (32) studied the effects of the lipid fraction in SOM on sorption of hydrophobic pesticides, and concluded that lipids probably block sorption sites on SOM and/or compete with pesticide molecules. Moreover, concurrent NMR analysis of samples before and after lipid extraction showed that lipid extraction only resulted in loss of alkyl carbon. Therefore, the fact that lipids reduce the sorption affinity of SOM for hydrophobic molecules is consistent with their previous finding (31) regarding the observed negative correlation between aliphatic carbon fraction in SOM and sorption.

These studies clearly show that structural differences in the chemical composition of SOM must be taken into account when sorption behaviour of hydrophobic pesticides is being modelled. As Ahmad *et al.* (16) pointed out, relying on an average K_{OC} value of a pesticide is not sufficient to assess the ability of a soil to sorb pesticides even those with a hydrophobic nature. Therefore, the variation in organic carbon chemistry must be included in sorption models quantitatively to enhance their veracity. One strategy is extra analysis (e.g. NMR spectral analysis) which is costly and time-consuming. IR spectroscopy could offer an appealing alternative because IR spectra are made up of information on the amount and chemistry of organic carbon as well as mineral soil components (33).

1.3. INFRARED SPECTROSCOPY TO STUDY THE CHEMICAL STRUCTURE OF SOIL ORGANIC MATTER

Researchers studying the relationships between the chemical nature of SOM and the sorption of hydrophobic pesticides in soils did not propose any practical tool to account for structural variations in sorption estimations. Using NMR spectroscopy is not only very expensive and time-consuming but also involves working with strong toxic chemicals. In the search for a feasible tool, however, IR spectroscopy looks promising because it is a high-throughput, cost-effective, easy-to-use technique with a broad applicability in agricultural and environmental fields. It has already been used successfully for predicting SOM content (34-36) and characterizing its chemical structure (37-39) and has a rather high sensitivity to both organic and inorganic components in soils and sediments (33). The structural atoms and groups bonded within the molecules experience a wide variety of vibrational motions, and absorb infrared radiation that corresponds in energy to those vibrations (40). In the near infrared region (NIR), electromagnetic radiation in the range of 12500 to 4000 cm-1 (800-2500 nm) is applied, and compared to mid infrared (MIR), is dominated by weaker and broader overlapping signals that arise from combinations and overtones associated with C-H, O-H, and N-H bands (41). NIR bands are actually overtones and combinations of fundamental bands which occur in the MIR region and in particular around 3500-1600 cm^{-1} (42). MIR spectroscopy uses radiation in the range from 4000 to 400 cm^{-1} (2500-25000 nm), and is characterized by intense spectral peaks caused by the strong absorption in this region (43). In the MIR region spectral intensities (bands) result from absorption of radiation by fundamental stretching and bending (deformation) vibrational modes of covalent bonds (44).

1.3.1. NEAR INFRARED SPECTRA OF SOIL

Since NIR spectra contain broad and overlapped peaks not resulting from fundamental vibrations but from combinations and overtones, they are not as informative as those in the fingerprint region (see below) in the MIR range, and therefore, direct qualitative analysis of NIR spectra is not seen useful in assessing the chemical nature of SOM (42). Instead, NIR spectroscopy has proven very useful in quantitative measurements of materials such as water, alcohol, amines and all types of organic materials including SOM (e.g. 45-48) which are essentially made up of C-H, O-H and N-H groups (33, 41, 42). An example of an NIR spectrum of an organic matter-rich soil is shown in Figure 1.2. The NIR signals around 1400 and 1900 nm are related to hydroxyl groups, mostly from free water, but also from hydroxyl groups in SOM. Therefore, these peaks possibly are not directly proportional to SOM content or chemistry. Broad spectral signals around 2200 nm towards the high-wavelength end of the spectrum, however, are assigned to organic carbon, in general (43, 49). No separation of aliphatic and aromatic structure has been established in this NIR region for SOM. Accordingly, perhaps we should not expect NIR spectroscopy to discriminate between aliphatic and aromatic fractions of SOM. Terhoeven-Urselmans *et al.* (39), however, found that NIR spectroscopy is capable of predicting NMR-derived carbon types, quantitatively. They did not propose any assignments for various carbon types in the NIR region. This author believes that their finding is yet to be validated by some qualitative analysis of NIR spectra probably in comparison with NMR spectra of SOM.

NOTE:
This figure is included on page 12 of the print copy of
the thesis held in the University of Adelaide Library.

Figure 1.2. An example of a near infrared (NIR) spectrum of an organic matter-rich soil [Reproduced from McCarty *et al.* (43)].

1.3.2. MID-INFRARED SPECTRA OF SOIL ORGANIC MATTER

MIR spectra of SOM contain spectral absorption bands originated from fundamental vibrations of either functional groups (e.g. $C\equiv O$, $C\equiv C$, $C\equiv N$, methyl, methylene, etc.) or skeletal groups forming the molecular backbone or skeleton of the molecule (e.g. aliphatic structure as in alkanes or aromatic structure as in benzenes) (42). The absorption bands with two different origins, in fact, develop two sub-regions in the MIR range, namely the *characteristic group frequency* and *fingerprint* regions. In the characteristic group frequency region (4000-1250 cm^{-1}) each absorption band corresponds to a particular vibration of a specific bond that occurs always at a given frequency (38). Therefore, the absorption bands in this region are relatively unaffected by the general molecular structure of the compound. In the fingerprint region (1250-400 cm^{-1}), the absorption bands are strongly affected by the general molecular structure of the compound (38), and therefore, could be useful in identifying the structural entities in the materials under study (e.g. aliphatic or aromatic moities). Initially, MIR spectroscopy was used mainly for qualitative characterization of SOM because it was thought to require sample dilution with KBr to prevent spectral distortions and nonlinearities due to the strength of absorption bands in the MIR region (43, 50). Further studies demonstrated the usefulness of MIR spectra with minimum sample pre-treatment for quantitative soil analysis in which *diffuse reflectance infrared Fourier-transform* (DRIFT) technique is used in conjunction with multivariate data analyses (49, 51, 52).

Among spectroscopic techniques, MIR spectroscopy has played an important role (after NMR spectroscopy) in qualitative characterization of SOM and humic substances (38). As shown in Table 1, various components in SOM give characteristic bands in the MIR region and indicate the potential of MIR spectroscopy for quantitative analysis of SOM in terms of content and chemistry. The IR spectra are quite complex (Figure 1.3). Spectral intensity values over the entire frequency range produce a great deal of information which all together could be used to determine (estimate) a single analyte of interest. To overcome and reduce the apparent complexity of spectra, researchers have used methods of multivariate analysis. These advanced statistical and mathematical techniques have enabled estimation of many properties in complex materials like soil, simultaneously, using a calibration set of IR spectra. In this context, predictive calibration models are developed between the entire spectra and the properties of interest.

NOTE:
This figure is included on page 14 of the print copy of
the thesis held in the University of Adelaide Library.

Figure 1.3. An example of mid-infrared (MIR) spectrum derived from the particulate fraction of soil organic matter (SOM) [Reproduced from Wershaw *et al.* (53)].

Table 1.1. Absorption bands attributed to soil organic matter (SOM) in the mid-infrared (MIR) spectral range [Reproduced from Madari *et al.* (50)].

Absorption band (cm^{-1})	Assignments
3380	O-H stretching of phenolic OH
3400-3300	O-H stretching (H bonded OH groups), N-H stretching
3030	Aromatic C-H stretching
2940-2900	Aliphatic C-H stretching
2600	O-H stretching of H-bonded -COOH
1725-1720	C=O stretching of –COOH and ketones
1660-1630	C=O stretching of amide groups (amide I band), quinine C=O and/or C=O of H-bonded conjugated ketones
1620-1600	Aromatic C=C stretching and/or asymmetric –COO stretching
1590-1517	COO- symmetric stretching, N-H deformation + C=N stretching (amide II band)
1525	Aromatic C=C stretching
1460-1450	Aliphatic C-H
1400-1390	O-H deformation and C-O stretching of phenolic OH, C-H deformation of CH_2 and CH_3 groups, COO- asymmetric stretching
1350	Symmetric COO- stretching and/or –CH bending of aliphatics
1270	C-OH stretching of phenolic OH
1280-1200	C-O stretching and OH deformation of COOH, C-O stretching of aryl ethers
1225	C-O stretching and O-H deformation of COOH
1170-950	C-O stretching of polysaccharides or polysaccharide-like substances
1170	C-OH stretching of aliphatic OH
1170	Polysaccharides
1070	C-C stretching of aliphatic groups
1050	Polysaccharides
830	Aromatic CH out of plane bending
775	Aromatic CH out of plane bending

1.4. APPLICATIONS OF CHEMOMETRICS IN UTILISING INFRARED SPECTRAL DATA FOR QUANTITATIVE SOIL ANALYSIS

Chemometrics in general and the methods of multivariate calibration in particular are now playing an essential role in analytical chemistry (54). They are quite effective tools to harness the apparent complexity of analytical data derived from sophisticated systems (e.g. soil spectra). To fully describe methods of multivariate analysis, a strong background in matrix algebra is required. This is beyond the scope of this text. The aim will be, however, to review the purpose, power and some applications of the most popular multivariate methods in soil-related research. More details regarding different methods of multivariate analysis and mathematical calculations involved can be found in some text books and review articles (54-56).

1.4.1. PRINCIPAL COMPONENT ANALYSIS

In spectroscopy, each single measurement (spectrum) of a sample is usually comprised of thousands of intensity values over the frequency range under study. The aim of many multivariate data analysis techniques is to reduce the amount of data so that the underlying correlations between variables become apparent (57). Principal component analysis (PCA) is one of the main data reduction techniques in multivariate analysis. When dealing with data of high dimension, which cannot be examined by graphical representation, PCA serves as a tool to identify patterns in data and to highlight their similarities and differences. As a result, the number of dimensions in data can be reduced by eliminating the redundant information in data without much loss of essential information (57, 58). It must be noted that PCA is a useful technique only if there is an underlying correlation between the data. In this context, *principal components* (PCs) or *latent variables* (PC_1, PC_2, …, PC_n) are identified as linear combinations of the original variables (X_1, X_2, …, X_n) describing each sample:

$$PC_1 = a_{11}X_1 + a_{12}X_2 + \ldots a_{1n}X_n$$

$$PC_2 = a_{21}X_1 + a_{22}X_2 + \ldots a_{2n}X_n$$

$$PC_n = a_{n1}X_n + a_{n2}X_2 + \ldots a_{nn}X_n$$

The coefficients (a_{11}-a_{nn}) are calculated in a way that there will be no correlation between latent variables. The maximum number of PCs that can be generated is equal to the number of original variables. The first PC usually explains the largest amount of variation in the data and PC_2 explains the second largest variation and so on. In practice the number of useful PCs is much smaller than the number of original variables, because one can decide to ignore the PCs with lesser significance. Of course it will result in losing some information, but the lost information could be just noise. This particular property of PCA led Jung (59) to propose PCA as a tool to denoise spectra. For this purpose, when PCs of a set of spectra are known, the spectra are reconstructed using the selected significant PCs. The reconstructed spectra will have few dimensions (equal to the number of selected PCs) compared to the original data and do not include unimportant and non-significant spectral variations that could serve only as noise.

1.4.2. PARTIAL LEAST SQUARES REGRESSION

The concept of multivariate calibrations (regressions) forms when the variables in a data set can be divided into groups of *response* variables and *predictor* variables. In spectroscopy, predictor variables are the spectral data and the response variables are the concentrations of the analytes of interest (e.g. soil properties). The methods of linear regression can be used to calculate a regression equation for which predictor variables (e.g. absorbance at each spectral frequency) are related to a response variable. The resultant calibration equation in general is

$$Y_p = a_1X_1 + a_2X_2 + ... + a_nX_n + b$$

where Y_p is the predicted value for the response variable, a_1 to a_n are the PLS regression coefficients for predictor variables X_1 to X_n, and b is the equation intercept. If there are multiple response variables, separate regression equations may be developed corresponding to each of the response variables, using the same data set of predictor variables. When the regression equation is developed based on a data set for a response variable, a meaningful prediction of the response variable for any unknown sample can be generated provided that the unknown sample belongs to the same population as the data set.

Partial least squares (PLS) regression is one of the multivariate linear regression techniques in which linear combinations of latent predictor variables (PCs) are related to a response variable to develop the PLS regression equation:

$$Y_p = a_1PC_1 + a_2PC_2 + ... + a_nPC_n + b$$

In PLS, the latent predictor variables which correlate more with the response variable are given more weight. This results in a more effective prediction of the response variable.

This is the main difference between PLS regression and PCA-based regression called principal component regression (PCR). In other words, PCR consists of a PCA step followed by a multivariate linear regression. In PLS regression, however, the PCs are identified in a way that they are highly correlated with the response variable as well as explaining the variation in predictor variables (57). More details regarding PLS regression are available in some related books and articles (54, 55, 60, 61).

1.4.3. APPLICATIONS IN SOIL RESEARCH

PCR in combination with NIR spectroscopy has been successfully applied to predict various soil properties (e.g. total C, total N, CEC) (62). Some research has shown similar performance of spectral calibrations built by PCR and PLS regression (63, 64). As mentioned above, however, it is expected that PLS regression results in a more reliable prediction when compared to PCR (65, 66). Haaland & Thomas (67) presented the use of PLS regression coupled with infrared spectral analysis and demonstrated how chemically interpretable qualitative information can be extracted from a PLS algorithm in addition to quantitative analysis. Therefore, PLS regression has received more attention than PCR in soil studies where properties of interest are to be predicted using spectroscopic techniques and the qualitative information is used to obtain a deeper insight into soil mechanisms.

Early applications of MIR combined with PLS regression (MIR-PLS) includes a couple of studies (35, 68) in which the content of soil major oxides, pH, sum of cations Ca, Mg, K, Na, total N, clay content, and organic carbon content were estimated. Later on, the increasing need for monitoring carbon dynamics and sequestration in terrestrial ecosystems demanded the development of new, rapid and cost-effective tools to estimate carbon content in soils using NIR- and MIR-PLS approaches (43, 49, 69). Cozzolino & Moron (34) and Zimmermann *et al.* (36) showed that MIR and NIR spectroscopy not only can estimate organic carbon content in total but also in different particle-size fractions. The power of infrared techniques in the study of SOM has been explored further in attempts to predict the chemistry of organic carbon. In this context, both NIR (39) and MIR (40, 70) spectroscopic probes have been demonstrated to be useful in developing calibration models between NMR-derived carbon types and IR spectra. This power has been attributed to the fact that functional groups and structural entities in SOM give rise to specific spectral bands in various regions of infrared spectra. More recently, Bornemann *et al.* (71) tested MIR spectra for describing black carbon in soil and found that due to the existence of specific spectral signatures related to such material, MIR spectroscopy could be used for effective estimations of black carbon in soils.

While virtually any soil characteristics and components that result in some IR spectral bands could be estimated by these spectroscopic methods in combination with multivariate calibration analysis, the qualitative information available in the spectra is not as straightforwardly identified. Most of the assignments of the infrared bands related to organic carbon have been derived from working on pure organic compounds. In soil, however, organic matter is rarely presented in isolation and is associated with minerals which results in overlapping and shifting of the organic carbon bands with those of mineral components. In addition, there are still some bands in the IR range that are referred to as “unknown”. Our limited ability to thoroughly interpret IR spectra reduces and even questions the usefulness of such spectral data in deriving qualitative information. Therefore, the information available in IR spectra, particularly related to various organic carbon types, is yet to be identified and validated by some reference information. One approach to solve this problem is *generalized two-dimensional (2D) correlation spectroscopy* which facilitates direct correlation of bands in IR spectra with those of another spectroscopic probe for which assignments are well-established (e.g. ^{13}C NMR spectra). In the next section, 2D correlation spectroscopy is introduced and its potential use in soil spectroscopy is explored.

1.5. GENERALIZED TWO-DIMENSIONAL CORRELATION SPECTROSCOPY: PROSPECTIVE APPLICATIONS IN SOIL RESEARCH

Two-dimensional (2D) correlation spectroscopy, as opposed to 1D spectroscopy, is a technique in which spectral intensity is plotted against two orthogonal axes of independent spectral variables (v_1, v_2) which form a 2D spectral plane (72). As a result, the spectral intensity will be the intensity of correlation between two spectral variables at each coordinate on the spectral plane (Figure 1.4). The method of generalized 2D correlation spectroscopy was first proposed by Noda in 1986 (73) for use in the field of infrared spectroscopy. It has the potential for application in a much broader range of electromagnetic radiation from X-ray to magnetic resonance (74). It is an extension of 2D NMR spectroscopy, which was developed some 35 years ago. The advantage of 2D correlation spectroscopy is in spreading the spectral peaks over the second dimension, which makes the visualisation of the overlapped peaks in a complex spectrum much easier (75). This method is widely used in the study of various systems including protein and other biological macromolecules, synthetic and natural polymers, liquid crystalline systems, Langmuir-Brogett films, pharmaceuticals, food, physiological fluids, paper products, solvents such as water and alcohols, colloids and solutions, minerals and catalysts, xerogels, carbon nanotubes, nanoparticles and superconducting materials (76-78).

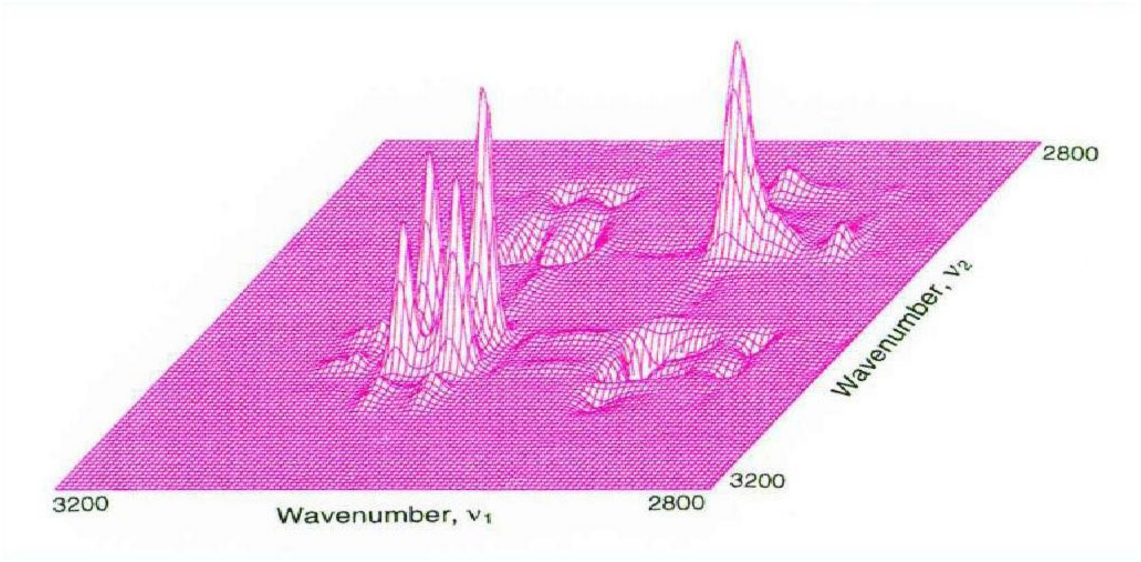


Figure 1.4. An example of a fishnet representation of a 2D-IR correlation spectrum [Adapted from Noda *et al.* (72)].

Generalized 2D correlation spectroscopy is based on external perturbation (t). In this context, the system under study is affected by a sequence of perturbations, $T_{min} \leq t \leq T_{max}$ (e.g. electrical, thermal, magnetic, chemical, mechanical and acoustic excitations) and is concurrently scanned by the spectroscopic probe of choice (e.g. NIR, MIR, NMR spectroscopy). The response of the system to the externally applied perturbation, as spectral intensity $y(\nu, t)$, is reflected on the series of collected spectra known as dynamic spectra $\tilde{y}(\nu,t)$. In essence, any spectroscopic experiment in which an external perturbation is utilised to generate dynamic spectra could be subjected to 2D correlation spectroscopy (72). The correlation analysis of the two independent spectral variables (ν_1, ν_2) in each possible pair of wavelengths results in a correlation Z value (R^2). Therefore, each point in the 2D correlation spectrum is described by three values made up of two coordinates related to the spectral plane and a Z value which can be visualized for the all possible coordinates as a 3D surface, as demonstrated in Figure 1.4. More details regarding the theory of generalized 2D correlation spectroscopy can be found in Noda & Ozaki (75).

A very interesting application of generalized 2D correlation spectroscopy occurs where two totally different spectroscopic probes (e.g. IR versus NMR) are used to form two sets of independent spectral variables v_1 and v_2. This type of spectroscopy is called *2D heterospectral correlation analysis*. Here again a system should be under the same perturbation while being analysed by the spectroscopic techniques and, depending on the types of collected spectra, the applied perturbation and the system itself, various information can be derived. This technique is extremely useful in proposing band assignments for a less-understood set of spectra (e.g. IR spectra) when applied using a spectroscopic technique for which the band assignments are well established (e.g. NMR spectra). Although, to the author's knowledge, soil science literature is devoid of generalized 2D correlation spectral analysis, the technique does have considerable potential to further science and technology in soil systems, for instance, by providing reliable tools to study and understand reaction dynamics, chemical processes occurring at colloid surfaces, thermally induced reactions, bonding mechanisms of organic compounds and chemical separations (44, 74, 78).

1.6. KNOWLEDGE GAP

As discussed so far in this review of literature, the scientific knowledge on the sorption of hydrophobic pesticides in the environment is relatively advanced. At this stage, the preferred approach for deriving structural information on the chemistry of SOM is NMR spectroscopy. The ^{13}C NMR data has shown promising correlations with the sorption affinities of SOM in soils (i.e. K_{OC} values). The application of NMR spectroscopy is, however, very expensive and time-consuming in terms of sample pre-treatment. Moreover, environmental modellers need to access a method which practically integrates the observed relationship between K_{OC} and organic carbon chemistry into the models of K_d prediction. It seems one thing to pursue in the next stage is to develop an alternative, practical tool which could utilise the information on the chemistry of SOM for sorption estimations while being cost-effective, high-throughput and easy-to-use. An attractive, potential alternative is IR spectroscopy because soil IR spectra contain a great deal of information associated with the content and nature of both organic and inorganic fractions of soils. IR spectra are complex and difficult to interpret, and obtaining quantitative and qualitative information from them is very difficult. In this study, I aimed to investigate if multivariate calibration techniques would be able to harness the apparent complexity of soil IR spectra for the sorption estimation of pesticides. I also investigated that how useful and relevant the quality and quantity of information in soil IR spectra are when compared to those of NMR spectra.

1.7. SPECIFIC OBJECTIVES OF THE STUDY

The major aim of this study was to utilise IR spectroscopy to describe and estimate the sorption of hydrophobic pesticides in soils. Specific objectives of the project were to:

- develop a predictive tool for estimating sorption coefficients (K_d) of diuron in soil using MIR spectroscopy in combination with partial least squares (PLS) regression (MIR-PLS model).

- compare the performance of the MIR-PLS model against the K_{OC} model, the latter of which is currently widely used in environmental modelling.
- develop an NIR-PLS calibration model and compare its performance in describing and predicting sorption of diuron in soils with that of the MIR-PLS model.
- find regions in the NIR and MIR spectra of SOM that correlate with and describe different NMR-derived carbon types using the 2D heterospectral correlation analysis, thereby enhancing our understanding on the content and quality of information in the IR spectra of SOM.

1.8. STRUCTURE OF THESIS

The starting point of this study was to investigate the applicability of MIR spectroscopy in combination with multivariate calibrations for sorption estimation of hydrophobic pesticides in soils. For this purpose, diuron was chosen as a test compound. Supporting Information 6.1. contains detailed information on the properties of diuron and the reason why it was used in this study. To select the soil samples, an Australian soil archive (79) developed by Department of Water, Land and Biodiversity Conservation was used to select a set of 101 surface soil samples from South Australia. Detailed information on the localities and the general properties of the selected soils is available in Supporting Information 6.2. The next chapter (Chapter 2) covers the first stage in this study, in which MIR spectroscopy was successfully utilised for diuron sorption prediction in soil. The sorption properties (K_d and K_{OC}) and the organic carbon content (f_{OC}) of the soils were measured by reference laboratory methods (see Supporting Information 6.3. for diuron K_d and K_{OC}, and f_{OC} values in soils). In addition, the developed MIR spectroscopy-based model was thoroughly compared with the K_{OC} model.

A question then arose regarding the possible competitive performance of NIR compared to MIR spectroscopy. In particular, it is because NIR spectroscopy had been recently shown to be very useful in estimating various NMR-derived carbon types (39) and the sorption of lindane and linuron pesticides in soils (80). In Chapter 3, NIR and MIR spectroscopy were compared in describing and predicting diuron sorption in soils. In Chapter 2, few calcareous soils showed extremely different sorption behaviour compared to the rest of the soils. This issue was investigated further in Chapter 3.

Although I investigated the possibility of building calibration models based on IR spectroscopic techniques for predicting diuron sorption in soils, a question remained how effectively IR techniques are at actually capturing and describing organic carbon types in SOM. The fact that a variation in the chemical structure affects the affinity of SOM for sorbing pesticides was first suggested by ^{13}C NMR studies. Therefore, it is important to work out how the information regarding organic carbon types in IR spectra is correlated with those of NMR spectra. This question was answered in Chapter 4 using the 2D heterospectral correlation analysis. Lastly, there is a summary and conclusion in Chapter 5 where implications of this study’s findings for the related scientific and practical fields are addressed. In addition, some recommendations for further investigations are made.

1.9. REFERENCES

(1) Cheng, H. H. Pesticides in the soil environment-An overview. In *Pesticides in the soil environment: Processes, Impacts, and Modelling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, 1990.

(2) Junk, G. A.; Spalding, R. F.; Richard, J. J. Areal, vertical, and temporal differences in groundwater chemistry. 2. Organic constituents. *J. Environ. Qual.* **1980**, 9, 479-483.

(3) Gammon, D. W.; Aldous, C. N.; Carr Jr, W. C.; Sanborn, J. R.; Pfeifer, K. F. A risk assessment of atrazine use in California: human health and ecological aspects. *Pest. Manag. Sci.* **2005**, 61, 331-355.

(4) Rohr, J. R.; Crumrine, P. W. Effects of an herbicide and an insecticide on pond community structure and processes. Ecological Applications. *Ecol. Appl.* **2005**, 15, 1135-1147.

(5) Kookana, R. S.; Ahmad, R. Emerging need for better extrapolation of pesticide fate data from temperate to tropical regions. In *Perspectives of agricultural research and development*; Ramasamy, C., Ramanathan, S., Dhakshinamoorthy, M.; Tamil Nadu Agricultural University: Coimbatore, 2005.

(6) Koskinen, W. C.; Harper, S. S. The retention process: Mechanisms. In *Pesticides in the soil environment: Processes, Impacts, and Modelling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, 1990.

(7) Luthy, R. G.; Aiken, G. R.; Brussaeu, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J. J.; Westall, J. C. Sequestration of hydrophobic organic contaminants by geosorbent. *Environ. Sci. Technol.* **1997**, 31, 3341-3347.

(8) Chiou, C. T. Roles of organic matter, minerals, and moisture in sorption of nonionic compounds and pesticides by soil. In *Humic substances in soil and crop sciences;* MacCarthy, P., Clapp, C. E., Malcom, R. L., Bloom, P. R., Eds.; American Society of Agronomy, Soil Science Society of America: Madison, 1990.

(9) Chiou, C. T.; Peters, L. J.; Freed, V. H. A physical concept of soil-water equilibria for nonionic organic compounds. *Science*. **1979**, 206, 831-832.

(10) Mingelgrin, U.; Gerstl, Z. Reevaluation of partioning as a mechanism of nonionic chemicals adsorption in soils. *J. Environ. Qual.* **1983**, 12, 1-11.

(11) Xing, B.; Pignatello, J. J. Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **1997**, 31, 792-799.

(12) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Bromilow, R. H. Differences in sorption behaviour of carbaryl and phosalone in soils from Australia, Pakistan and the United Kingdom. *Aust. J. Soil Res.* **2001**, 39, 893-908.

(13) Wauchope, R. D.; Yeh, S.; Linders, J. B. H. J.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katamaya, A.; Kordel, W.; Gerstl, Z.; Lane, M.; Unsworth, J.B. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest. Manag. Sci.* **2002**, 58, 419-445.

(14) Green, R. E.; Karickhoff, S. W. Sorption estimates for modelling. In *Pesticides in the soil environment: Processes, Impacts, and Modelling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, 1990.

(15) Liyanage, J. A.; Watawala, R. C.; Aravinna, A. G. P.; Smith, L.; Kookana, R. S. Sorption of carbofuran and diuron pesticides in 43 tropical soils of Sri Lanka. *J. Agr. Food Chem.* **2006**, 35, 878-884.

(16) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Skjemstad, J. O. The nature of soil organic matter affects sorption of pesticides. 1. Relationship with carbon chemistry as determined by 13C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* **2001**, 35, 878-884.

(17) Golding, C. J.; Smernik, R. J.; Birch, G. F. Investigation of the role of structural domains identified in sedimentary organic matter in the sorption of hydrophobic organic compounds. *Environ. Sci. Technol.* **2005**, 39, 3925-3932.

(18) Cornelissen, G.; Gustafsson, O.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; Van Noort, P. C. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005**, 39, 6881-6895.

(19) Dubbin, W., *Soils*; The Natural History Museum: London, 2001.

(20) Senesi, N.; Loffredo, E. The chemistry of soil organic matter. In *Soil physical chemistry*; Sparks, D. L., Ed.; CRC Press: Boca Raton, 1999.

(21) Stevenson, F. J. *Humus chemistry. genesis, composition, reactions*; Wiley: New York, 1994.

(22) Sutton, R.; Sposito, G. Molecular structure in soil humic substances: the new view. *Environ. Sci. Technol.* **2005**, 39, 9009-9015.

(23) Sparks, D. L. *Environmental soil chemistry*; Academic Press: Boston, 2003.

(24) Kogel-Knabner, I. 13C and 15N NMR spectroscopy as a tool in soil organic matter studies. *Geoderma*. **1997**, 80, 243-270.

(25) Preston, C. M. Applications of NMR to soil organic matter analysis: history and prospects. *Soil Sci.* **1996**, 161, 144-166.

(26) Wershaw, R. L. Application of nuclear magnetic resonance spectroscopy for determining functionality in humic substances. In *Humic substances in soil, sediment, and water : geochemistry, isolation, and characterization*; Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley & Sons: New York, 1985.

(27) Skjemstad, J. O.; Janik, L. J.; Taylor, J. A. Non-living soil organic matter: what do we know about it? *Aust. J. Exp. Agr.* **1998**, 38, 667-680.

(28) Grathwohl, P. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on Koc. *Environ. Sci. Technol.* **1990**, 24, 1687-1693.

(29) Kile, D. E.; Wershaw, R. L.; Chiou, C. T. Correlation of soil and sediment organic matter polarity to aqueous sorption of non-ionic compounds. *Environ. Sci. Technol.* **1999**, 33, 2053-2056.

(30) Abelmann, K.; Kleineidam, S.; Knicker, H.; Grathwohl, P.; Kogel-Knabner, I. Sorption of HOC in soils with carbonaceous contamination: Influence of organic matter composition. *J. Plant Nutr. Soil Sc.* **2005**, 168, 1-14.

(31) Ahangar, A. G.; Smernik, R. J.; Kookana, R. S.; Chittleborough, D. J. Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. *Chemosphere*. **2008**, 70, 1153-1160.

(32) Ahangar, A. G.; Smernik, R. J.; Kookana, R. S.; Chittleborough, D. J. The effect of lipids on the sorption of diuron and phenanthrene in soils. *Chemosphere*. **2009**, 74, 1062-1068.

(33) Janik, L. J.; Merry, R. H.; Skjemstad, J. O. Can mid infrared diffuse reflectance analysis replace soil extraction? *Aust. J. Exp. Agr.* **1998**, 38, 681-696.

(34) Cozzolino, D.; Morón, A. Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil organic carbon fractions. *Soil Till. Res.* **2006**, 85, 78-85.

(35) Janik, L. J.; Skjemstad, J. O. Characterization and analysis of soils using mid-infrared partial least squares. II. Correlations with some laboratory data. *Aust. J. Soil Res.* **1995**, 33, 637-650.

(36) Zimmermann, M.; Leifeld, J.; Fuhrer, J. Quantifying soil organic carbon fractions by infrared-spectroscopy. *Soil Biol. Biochem.* **2007**, 39, 224-231.

(37) Inbar, Y.; Chen, Y.; Hadar, Y. Solid-state carbon-13 nuclear magnetic resonance and infrared spectroscopy of composted organic matter. *Soil Sci. Soc. Am. J.* **1989**, 53, 1695-1701.

(38) MacCarthy, P.; Rice, J. A. Spectroscopic methods (other than NMR) for determining functionality in humic substances. In *Humic substances in soil, sediment, and water. Geochemistry, isolation, and characterization*; Aiken, G. R., McKnight, D. G., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley & Sons: New York, 1985.

(39) Terhoeven-Urselmans, T.; Michel, K.; Helfrich, M.; Flessa, H.; Ludwig, B. Near-infrared spectroscopy can predict the composition of organic matter in soil and litter. *J. Plant Nutr. Soil Sc.* **2006**, 169, 168-174.

(40) Johnston, C. T.; Davies, W. M.; Erickson, C.; Delfino, J. J.; Cooper, W. T. Characterization of humic substances using Fourier transform infrared spectroscopy. In *Humic substances in the global environment and implications on human health*; Senesi, N., Miano, T. M., Eds.; Elsevier Science: Amsterdam, 1994.

(41) Small, G. W. Chemometrics and near-infrared spectroscopy: Avoiding the pitfalls. *Trends Anal. Chem.* **2006**, 25, 1057-1066.

(42) Socrates, G. *Infrared and raman characteristic group frequencies*; John Wiley & Sons: Chichester, 2001.

(43) McCarty, G. W.; Reeves III, J. B.; Reeves, V. B.; Follett, R. F.; Kimble, J. M. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. *Soil Sci. Soc. Am. J.* **2002**, 66, 640-646.

(44) Johnston, C. T.; Aochi, Y. O. Fourier transform infrared and Raman spectroscopy. In *Methods of soil analysis: Part 3, chemical methods*; Sparks, D. L., Ed.; SSSA: Madison, 1996.

(45) Batten, G. D. Plant analysis using near infrared reflectance spectroscopy: the potential and the limitations. *Aust. J. Exp. Agr.* **1998**, 38, 697–706.

(46) Brown, D. J.; Shepherd, K. D.; Walsh, M. G.; Mays, M. D.; Reinsch, T. G. Global soil characterization with VNIR diffuse reflectance spectroscopy. **2006**, 132, 273-290.

(47) Brunet, D.; Barthes, B. G.; Chotte, J. L.; Feller, C. Determination of carbon and nitrogen contents in Alfisols, Oxisols and Ultisols from Africa and Brazil using NIRS analysis: Effects of sample grinding and set heterogeneity. *Geoderma*. **2007**, 139, 106-117.

(48) Cohen, M. J.; Prenger, J. P.; DeBusk, W. F. Visible-near infrared reflectance spectroscopy for rapid, nondestructive assessment of wetland soil quality. *J. Environ. Qual.* **2005**, 34, 1422-1434.

(49) Reeves III, J. B.; Follett, R. F.; McCarty, G. W.; Kimble, J. M. Can near or mid-infrared diffuse reflectance spectroscopy be used to determine soil carbon pools? *Commun. Soil Sci. Plan.* **2006**, 37, 2307-2325.

(50) Madari, B. E.; Reeves III, J. B.; Machado, P. L. O. A.; Guimarães, C. M.; Torres, E.; McCarty, G. W. Mid- and near-infrared spectroscopic assessment of soil compositional parameters and structural indices in two Ferralsols. *Geoderma*. **2006**, 136, 245-259.

(51) McCarty, G. W.; Reeves III, J. B. Comparison of near infrared and mid infrared diffuse reflectance spectroscopy for field-scale measurement of soil fertility parameters. *Soil Sci.* **2006**, 171, 94-102.

(52) Reeves III, J. B.; van Kessel, J. A. S. Spectroscopic analysis of dried manures. Near- versus mid-infrared diffuse reflectance spectroscopy for the analysis of dried dairy manures. *J. Near Infrared Spec.* **2002**, 10, 93-101.

(53) Wershaw, R. L.; Leenheer, J. A.; Cox, L. *Characterization of dissolved and particulate natural organic matter (NOM) in Neversink Reservoir, New York*; U.S. Geological Survey Scientific Investigations Report 2005-5108, 19p, 2005.

(54) Naes, T.; Isaksson, T.; Fearn, T.; Davies, T. *A user-friendly guide to multivariate calibration and classification*; NIR Publications: Chichester, 2002.

(55) Esbensen, K. H. *Multivariate data analysis in practice*; Prentice Hall: 1998.

(56) Forina, M.; Lanteri, S.; Casale, M. Multivariate calibration. *J. Chromatogr. A*. **2007**, 1158, 61-93.

(57) Miller, J. N.; Miller, J. C. *Statistics and chemometrics for analytical chemistry*; Pearson Prentice Hall: Harlow, 2005.

(58) Jolliffe, I. T. *Principal component analysis*; Springer-Verlag: New York, 1986.

(59) Jung, Y. M. Principal component analysis based two-dimensional (PCA-2D) correlation spectroscopy: PCA denoising for 2D correlation spectroscopy. *B. Kor. Chem. Soc.* **2003**, 24, 1345-1350.

(60) Geladi, P.; Kowalski, B. R. Partial least-squares regression: a tutorial. *Anal. Chim. Acta*. **1986**, 185, 1-17.

(61) Haenlein, M.; Kaplan, A. M. A beginner's guide to partial least squares analysis. *Und. Stat.* **2004**, 3, 283-297.

(62) Chang, C. W.; Laird, D. A.; Mausbach, M. J.; Hurburgh, J., C.R. Near-infrared reflectance spectroscopy-Principal components regression Analyses of soil properties. *Soil Sci. Soc. Am. J.* **2001**, 65, 480-490.

(63) Li, B.; Kasemsumran, S.; Hu, Y.; Liang, Y.; Ozaki, Y. Comparison of performance of partial least squares regression, secured principal component egression, and modified secured principal component regression for determination of human serum albumin, γ-globulin and glucose in buffer solutions and in vivo blood glucose quantification by near-infrared spectroscopy. *Anal. Bioanal. Chem.* **2007**, 387, 603-611.

(64) Molfetta, F. A.; Bruni, A. T.; Rosselli, F. P.; da Silva, A. B. F. A partial least squares and principal component regression study of quinone compounds with rypanocidal activity. *Struct. Chem.* **2007**, 18, 49-57.

(65) Setiowaty, G.; Che Man, Y. B. Multivariate determination of cloud point in palm oil using partial least squares and principal component regression based on FTIR Spectroscopy. *J. Am. Oil Chem. Soc.* **2004**, 81, 7-11.

(66) Vigneau, E.; Bertrand, D.; Qannari, M. Application of latent root regression for calibration in near-infrared spectroscopy. Comparison with principal component regression and partial least squares. *Chemometr. Intell. Lab.* **1996**, 35, 231-238.

(67) Haaland, D. M.; Thomas, E. V. Partial least-squares methods for spectral analyses. 2. Relation to other quantitative calibration methods and the extraction of qualitative information. *Anal. Chem.* **1988**, 60, 1193-1202.

(68) Janik, L. J.; Skjemstad, J. O.; Raven, M. D. Characterization and analysis of soils using mid-infrared partial least-squares .1. Correlations with XRF-determined major-element composition. *Aust. J. Soil Res.* **1995**, 33, 621 - 636.

(69) Madari, B. E.; Reeves III, J. B.; Coelho, M. R.; Machado, P. L. O. A.; De-Polli, H.; Coelho, R. M.; Benites, V. M.; Souza, L. F.; McCarty, G. W. Mid- and near-infrared spectroscopic determination of carbon in a diverse set of soils from the Brazilian national soil collection. *Spectrosc. Lett.* **2005**, 38, 721-740.

(70) Leifeld, J. Application of diffuse reflectance FT-IR spectroscopy and partial least-squares regression to predict NMR properties of soil organic matter. *Eur. J. Soil Sci.* **2006**, 57, 846-857.

(71) Bornemann, L.; Welp, G.; Brodowski, S.; Rodionov, A.; Amelung, W. Rapid assessment of black carbon in soil organic matter using mid-infrared spectroscopy. *Org. Geochem.* **2008**, 39, 1537-1544.

(72) Noda, I.; Dowrey, A. E.; Marcott, C.; Story, G. M.; Ozaki, Y. Generalized two-dimentional correlation spectroscopy. *Appl. Spectrosc.* **2000**, 54, 236A-248A.

(73) Noda, I. 2-Dimensional infrared (2D IR) spectroscopy - theory and applications. *Appl. Spectrosc.* **1990**, 44, 550-561.

(74) Geng, M. L.; Noda, I.; Ozaki, Y. Preface for 2DCOS-3 conference. *J. Mol. Struct.* **2006**, 799, 1.

(75) Noda, I.; Ozaki, Y. *Two-dimensional correlation spectroscopy, applications in vibrational and optical spectroscopy*; John Wiley & Sons: Chichester, 2004.

(76) Jung, Y. M.; Noda, I. New approaches to generalized two-dimensional correlation spectroscopy and its Applications. *Appl. Spectrosc. Rev.* **2006**, 41, 515-547.

(77) Noda, I. Progress in two-dimensional (2D) correlation spectroscopy. *J. Mol. Struct.* **2006**, 799, 2-15.

(78) Noda, I. Advances in two-dimensional correlation spectroscopy. *Vib. Spectrosc.* **2004**, 36, 143-165.

(79) Soil and Land Information Group. *Regional Land Resource Information on CD-ROM for Agricultural Regions of South Australia*; Department of Water, Land and Biodiversity Conservation: South Australia, 2005.

(80) Bengtsson, S.; Berglof, T.; Kylin, H. Near infrared reflectance spectroscopy as a tool to predict pesticide sorption in soil. *B. Environ. Contam. Tox.* **2007**, 78, 295-298.

2 Midinfrared Spectroscopy and Chemometrics to Predict Diuron Sorption Coefficients in Soils

MOHSEN FOROUZANGOHAR, [†]
RAI S. KOOKANA, [‡]
SEAN T. FORRESTER, [‡]
RONALD J. SMERNIK, [†]
DAVID J. CHITTLEBOROUGH [†]

[†] School of Earth and Environmental Sciences, University of Adelaide, PMB 1, Glen Osmond 5064, Australia.

[‡] Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water, PMB 2, Glen Osmond 5064, Australia.

Environmental Science & Technology 2008; 42 (9), 3283-3288

The Supporting Information of this paper is contained in Chapter 6, sections 6.1, 6.2, 6.3 and 6.4.

STATEMENT OF AUTHORSHIP

MIDINFRARED SPECTROSCOPY AND CHEMOMETRICS TO PREDICT DIURON SORPTION COEFFICIENTS IN SOILS

Environmental Science & Technology 2008; 42 (9), 3283-3288

FOROUZANGOHAR, M. (Candidate)

Performed analysis on all samples, data analysis and critical interpretation, wrote manuscript.

I hereby certify that the statement of contribution is accurate.

Signed Date

KOOKANA, R. S.

Supervised development of work and data interpretation, reviewed and edited manuscript and acted as corresponding author.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

FORRESTER, S. T.

Helped in MIR analysis, multivariate analysis of spectra and data interpretation, reviewed and edited manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

SMERNIK, R. J.

Supervised data analysis and interpretation, provided critical evaluation and revision of manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

CHITTLEBOROUGH, D. J.

Supervised manuscript evaluation, reviewed and edited manuscript.

I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.

Signed Date

Forouzangohar, M., Forrester, S.T., Smernik, R.J. & Chittleborough, D.J. (2008) Midinfrared spectroscopy and chemometrics to predict diuron sorption coefficients in soils
Environmental Science and Technology, v. 42(9), pp. 3283-3288

3 Direct Comparison between Visible Near- and Mid-Infrared Spectroscopyfor Describing Diuron Sorption in Soils

MOHSEN FOROUZANGOHAR, †
DANIEL COZZOLINO ‡
RAI S. KOOKANA, §
RONALD J. SMERNIK, †
SEAN T. FORRESTER, §
DAVID J. CHITTLEBOROUGH †

† School of Earth and Environmental Sciences, University of Adelaide, PMB 1, Glen Osmond 5064, Australia.

‡ The Australian Wine Research Institute (AWRI), Waite Road, Glen Osmond 5064, Australia.

§ Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water, PMB 2, Glen Osmond 5064, Australia.

Environmental Science & Technology 2009; 43 (11), 4049-4055

The Supporting Information of this paper is contained in Chapter 6, sections 6.1, 6.2, 6.3, 6.5 and 6.6.

STATEMENT OF AUTHORSHIP

DIRECT COMPARISION BETWEEN VISIBLE NEAR- AND MID-INFRARED SPECTROSCOPY FOR DESCRIBING DIURON SORPTION IN SOILS

Environmental Science & Technology 2009; 43 (11), 4049-4055

FOROUZANGOHAR, M. (Candidate)

Performed analysis on all samples, data analysis and critical interpretation, wrote manuscript and acted as corresponding author.
I hereby certify that the statement of contribution is accurate.
Signed Date

COZZOLINO, D.

Contributed in planning article, helped in NIR analysis, data analysis and interpretation; reviewed and edited manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

KOOKANA, R. S.

Supervised development of work and data interpretation, provided critical evaluation and revision of manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

SMERNIK, R. J.

Supervised data analysis and interpretation, provided critical evaluation and revision of manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

FORRESTER, S. T.

Helped in MIR analysis, provided critical review of manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

CHITTLEBOROUGH, D. J.

Supervised manuscript evaluation, reviewed and edited manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

Forouzangohar, M., Cozzolino, D., Kookana, R.S., Smernik, R.J., Forrester, S.T. & Chittleborough, D.J. (2009) Direct comparison between visible near-and mid-infrared spectroscopy for describing diuron sorption coefficients in soils.
Environmental Science and Technology, v. 43(11), pp. 4049-4055

4 Two-Dimensional Nuclear Magnetic Resonance / Infrared Heterospectral Correlation Analysis of Carbon Types in Soil Organic Matter

MOHSEN FOROUZANGOHAR †

DANIEL COZZOLINO ‡

RONALD J. SMERNIK †

RAI S. KOOKANA §

SEAN T. FORRESTER §

DAVID J. CHITTLEBOROUGH †

† School of Earth and Environmental Sciences, University of Adelaide, PMB 1, Glen Osmond 5064, Australia.

‡ The Australian Wine Research Institute (AWRI), Waite Road, Glen Osmond 5064, Australia.

§ Commonwealth Scientific and Industrial Research Organisation (CSIRO) Land and Water, PMB 2, Glen Osmond 5064, Australia.

Environmental Science & Technology 2009, Submitted Paper

STATEMENT OF AUTHORSHIP

TWO-DIMENSIONAL NUCLEAR MAGNETIC RESONANCE/INFRARED HETEROSPECTRAL CORRELATION ANALYSIS OF CARBON TYPES IN SOIL ORGANIC MATTER

Environmental Science & Technology 2009; Submitted Paper

FOROUZANGOHAR, M. (Candidate)

Performed infrared analysis on samples, data analysis and critical interpretation, wrote manuscript.
I hereby certify that the statement of contribution is accurate.
Signed Date

COZZOLINO, D.

Contributed in planning article, helped in NIR analysis and data analysis and interpretation, reviewed and edited manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

SMERNIK, R. J.

Performed NMR analysis, supervised data analysis and interpretation, provided critical evaluation and revision of manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

KOOKANA, R. S.

Supervised development of work, reviewed and edited manuscript, acted as corresponding author.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

FORRESTER, S. T.

Helped in MIR analysis and reviewed manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

CHITTLEBOROUGH, D. J.

Supervised manuscript evaluation, reviewed and edited manuscript.
I hereby certify that the statement of contribution is accurate and I give permission for the inclusion of the paper in the thesis.
Signed Date

Two-Dimensional Nuclear Magnetic Resonance/Infrared Heterospectral Correlation Analysis of Carbon Types in Soil Organic Matter

Mohsen Forouzangohar, Daniel Cozzolino, Ronald J. Smernik, Rai S. Kookana, Sean T. Forrester, and David J. Chittleborough

Forouzangohar, M., Cozzolino, D., Smernik, R.J., Kookana, R.S., Forrester, S.T. & Chittleborough, D.J. (2009) Two-dimensional nuclear magnetic resonance/infrared heterospectral correlation analysis of carbon types in soil organic matter. *Environmental Science and Technology, Submitted Paper (2009)*

5 Summary and Conclusion

Among all the processes governing the fate and behaviour of pesticides in soil (sorption, transformation and transport processes), sorption is considered to be key because it strongly affects the other processes (1). Sorption of hydrophobic pesticides is highly dependent on the amount of organic carbon in the soil (i.e. the organic carbon fraction, f_{OC}). This is because hydrophobic interactions between the hydrophobic pesticides and organic matter are the driving force for sorption of these compounds in the soil system where the solvent is water (2). Formerly, the content of organic carbon in soil has been largely regarded as the only factor that controls the sorption behaviour of such pesticide molecules in soil. In this context, K_{OC} is defined as the *organic carbon-normalized sorption coefficient* of a pesticide which acts as an intervening parameter for simple estimation of the soil sorption coefficient (K_d), where $K_d = K_{OC} \times f_{OC}$ (2). Once the K_{OC} of a pesticide is determined by a sorption (K_d) measurement (e.g. using batch equilibrium) using the above equation, it can be used to predict the K_d values of that pesticide in any other soil. In essence, the K_{OC} approach assumes that the affinity of soil organic matter (SOM) for a given organic compound is the same in all other soils (1, 2).

Recent studies using carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy (e.g. 3-6) have shown that variations in the chemical structure affect the affinity of SOM in sorbing organic pollutants and should be taken account of in the modelling of sorption, in addition to the content of SOM. Although the relationship between the carbon chemistry of SOM and the sorption of hydrophobic pesticides has been demonstrated using ^{13}C NMR, no practical method has, so far, been developed to take it into account when estimating sorption coefficients (K_d). In spite of the improved knowledge in this field, the K_{OC} modelling approach remains the only practical predictive method of K_d values. Obviously, this is an oversimplification caused by the lack of a better prediction approach, and can only be resolved by the development of a novel predictive tool. A potential approach to tackle the problem is using infrared (IR) spectroscopy.

IR spectroscopy is an easy-to-use, inexpensive and rapid analysis technique with broad applicability in agricultural and environmental studies (7). It has already been used successfully for estimating the organic carbon content (f_{OC}) in the whole soil (e.g. 8-10) and also in its different particle-size fractions (e.g. 11-13). The chemical structure of organic carbon has also been studied by IR techniques (e.g. 14-18). Consequently, IR spectroscopy was shown to be effective in predicting different NMR-derived carbon types in SOM (19, 20). Moreover, IR spectroscopy has been demonstrated to be capable of determining the content and properties of clay minerals in soils (e.g. 21-23). Since the integrated effects of these properties control the sorption of organic compounds, such as pesticides, to soils, theoretically the sorption itself could also be estimated by IR spectroscopic probes.

In this study, visible near-infrared (VNIR) and mid-infrared (MIR) spectroscopy were utilised for estimating the soil sorption coefficients (K_d) of a hydrophobic pesticide (diuron) based on the integrated information on the content and chemistry of organic and inorganic soil constituents available in IR spectra. The usefulness of the information contained in NIR and MIR spectra was compared in terms of describing the sorption of diuron in soils. In addition, IR spectra were directly compared with ^{13}C NMR spectra to investigate the capability of NIR and MIR spectra for describing various NMR-derived carbon types.

5.1. IMPLICATIONS OF THE RESEARCH FINDINGS

MIR spectra coupled with PLS regression was utilised successfully to develop a novel MIR-PLS calibration tool for predicting the sorption of diuron in soils. Inspection of the PLS loadings revealed that the developed model integrates information about both mineral and organic materials in soils in order to predict the diuron sorption in an unknown sample. The performance of the MIR-PLS technique is much better than that of the K_{OC} model because it provides a more realistic prediction for the outliers to the K_{OC} model. In particular, a few extreme outliers to the K_{OC} model were predicted well by the MIR-PLS model which improved the statistical indices of the performance assessment, namely correlation index (R^2), standard error (SE), and residual prediction deviation (RPD) (see Chapters 2 and 3 for definition of these indices). Apart from the outliers, the accuracy of the predictions provided by the K_{OC} and MIR-PLS models were quite similar. If the MIR spectroscopy is capable of capturing the chemistry of organic carbon as the NMR spectroscopy does, it is not clear why the MIR-PLS model did not improve the prediction of diuron K_d values for the majority of the soils in this study (except for calcareous soils). To answer this question, one needs to know exactly how effective MIR spectroscopy is in identifying carbon types in the chemical structure of SOM. This was investigated in Chapter 4, and will be discussed later on in this section. First, the advantages of the MIR-PLS technique over the K_{OC} model are addressed.

The existence of outlier detection tools in the MIR-PLS approach results in “eyes-open” predictions as opposed to “blind” predictions by the K_{OC} model. Therefore, when an unknown sample is introduced to the MIR-PLS model for prediction, it can easily be determined whether it belongs to the same population of samples on which the MIR-PLS model was developed. If not, a reliable prediction is not expected by the model. In the K_{OC} model, however, an unknown sample cannot be inspected in terms of being a possible outlier on the model. This may mislead the user into accepting an inappropriate prediction as a valid one. Another advantage of using the MIR-PLS approach for property estimations is that several properties of interest could be quantitatively predicted simultaneously (24). Based on these results, it is clear that while the IR spectroscopy is being used to predict various soil characteristics, including the content of soil organic carbon, it is also attractive to use it for predicting pesticide sorption. It provides more reliable predictions, especially for soils in which minerals become somehow involved in sorption (e.g. calcareous soils).

Our results revealed that calcareous soils showed a different sorption behaviour for diuron which was poorly explained by the K_{OC} model. In fact, calcareous soils comprised most of the outliers on the K_{OC} model. The carbonate peaks appeared strongly in the loadings of the MIR-PLS model. This led us to believe that carbonate minerals affect the sorption processes by some mechanisms which are not yet known. While MIR spectroscopy improved the prediction of diuron sorption for calcareous soils, VNIR spectroscopy did not show such effect and carbonate signals did not appear in its PLS loadings. VNIR spectroscopy performed poorly not only for calcareous soils but also for the rest of calibration set as compared to MIR spectroscopy. For the quantitative estimation of f_{OC} and diuron sorption (K_d), MIR spectroscopy clearly outperformed VNIR spectroscopy and provided much more useful qualitative information, as well. The better performance of MIR spectroscopy observed for estimation of soil f_{OC} was in agreement with many previously publications (e.g. 9, 25, 26). In a homogeneous calibration set of soils, however, NIR-PLS model has been shown to perform slightly better than MIR-PLS model (8). The poorer performance of NIR spectroscopy has often been attributed to the effect of particle size variation between samples, but the samples in this study were ground and homogenized in with respect to particle size, and yet MIR spectroscopy resulted in a much higher prediction accuracy. This result was attributed to the higher quality of information available in the MIR spectra in comparison with the VNIR spectra.

A practical consideration in using the IR-PLS modelling approach is that one cannot use IR calibration models to predict unknown samples from completely different soil sets. These techniques are normally used when a large number of samples is available for analysis, especially for several properties. In this case, a calibration set which is representative of the complete soil set is selected, and a calibration model is developed. Then the rest of the samples are characterized as unknown samples. Therefore, these unknown samples are all from the same area as the calibration samples and have similar spectra. Considering the current state of the IR calibration techniques, it is not recommended in normal circumstances to use such calibration models for predicting parameters of unknown samples from other separated areas.

Another objective of this study was to determine the relative abilities of NIR and MIR spectra in identifying carbon types in SOM as compared to NMR spectroscopy. Direct correlation of ^{13}C NMR spectra with NIR and MIR spectra, separately, through 2D heterospectral correlation analysis (Chapter 4) supported our results in Chapter 3 showing a higher quality of information available in MIR spectra for identification of the chemistry of carbon in SOM. Moreover, new band assignments for organic carbon were established, and the employed technique showed a promising performance for further applications in research concerning SOM spectral analysis. The extent of IR spectral information on the chemical structure of organic and inorganic components of soils is not yet fully explored (e.g. there are disagreements in assigning some IR bands to particular structural and functional groups of organic carbon) (16). Therefore, generalized 2D correlation spectroscopy could become an invaluable tool to closely investigate and provide an insight into the scientific field of IR spectroscopy of SOM and other soil constituents.

5.2. SUGGESTIONS FOR FURTHER STUDIES

The results of this study may lead into and trigger new scientific gaps and investigations that could be dealt with by further research:

- The scale of the area on which the soil samples were taken was limited to a part of South Australia (Supporting Information 6.2), and in particular surface soils, which led to the development of a relatively homogeneous calibration set. The resultant calibration model, therefore, is only suitable for application in the same region and for analysing unknown soil samples which belong to the same population. There are attempts to develop IR spectral libraries for characterization of various soil properties with a global perspective (27, 28). In this regard, one possibility is to try to develop more extensive calibration set for which the resultant calibration model would be applicable to a greater range of soil types from various agro-geo-climatic regions. This would lead towards the development of a global model.

- The mechanisms which control the sorption of diuron in calcareous soils seem to be different from non-calcareous soils. The better prediction of sorption in such soils through the MIR-PLS model compared to the K_{OC} model, and the existence of carbonate peaks in the MIR-PLS loadings of the calibration model provide an evidence for this hypothesis. It is not known how the carbonate minerals cause this phenomenon, and whether it is a physical or a chemical effect.

- In this study, VNIR and MIR ranges of electromagnetic radiation were used, separately, for the quantitative estimation of sorption K_d values. It would be worthwhile, however, to examine how the combined spectral regions (VNIR-MIR) perform in terms of accuracy of the developed calibration model. It has been shown that a combined application of the visible and IR regions for quantitative assessment of some soil properties has resulted in improved the prediction of some properties (24, 29).

- In the 2D NMR/IR heterospectral correlation analysis, the spectroscopic probes were applied to HF-treated soils because these materials are suitable for ^{13}C NMR analysis. Therefore, the spectra used for that experiment were not derived from intact soils in which minerals and organic materials are both present and produce spectral signatures in the IR spectra. Since the results, eventually, need to be related to real situations where soil IR spectra are investigated and used, 2D correlation spectroscopy could be attempted in order to directly correlate MIR spectra of HF-treated soils with those of untreated soils. It may also be possible to examine a 2D correlation spectroscopy between the ^{13}C NMR spectra of HF-treated soils and intact soil MIR spectra. In this way, one may identify how effectively the chemistry of SOM can be captured in the MIR spectra of whole soil.

- It is believed that the use of particular wavelengths (IR bands), which directly relate to a specific property, improves the performance of the developed calibration model (30). Choosing the right IR bands, however, is not free of the risk of losing some useful information unless there is a deep understanding about the IR band assignments. Since the 2D NMR/IR heterospectral correlation analysis reveals the bands associated directly with the chemistry and content of organic carbon, IR calibration models could be developed using relevant selected bands. This may increase the accuracy of the IR prediction tools in quantitative assessments of f_{OC}, organic carbon chemistry, and sorption K_d values for hydrophobic pesticides.

5.3. REFERENCES

(1) Koskinen, W. C.; Harper, S. S. The retention process: Mechanisms. In *Pesticides in the soil environment: Processes, Impacts, and Modelling*; Cheng, H. H., Ed.; Soil Science Society of America: Madison, 1990.

(2) Wauchope, R. D.; Yeh, S.; Linders, J. B. H. J.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katamaya, A.; Kordel, W.; Gerstl, Z.; Lane, M.; Unsworth, J.B. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest. Manag. Sci.* **2002**, 58, 419-445.

(3) Abelmann, K.; Kleineidam, S.; Knicker, H.; Grathwohl, P.; Kogel-Knabner, I. Sorption of HOC in soils with carbonaceous contamination: Influence of organic matter composition. *J. Plant Nutr. Soil Sc.* **2005**, 168, 1-14.

(4) Ahangar, A. G.; Smernik, R. J.; Kookana, R. S.; Chittleborough, D. J. Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. *Chemosphere*. **2008**, 70, 1153-1160.

(5) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Skjemstad, J. O. The nature of soil organic matter affects sorption of pesticides. 1. Relationship with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* **2001**, 35, 878-884.

(6) Kile, D. E.; Wershaw, R. L.; Chiou, C. T. Correlation of soil and sediment organic matter polarity to aqueous sorption of non-ionic compounds. *Environ. Sci. Technol.* **1999**, 33, 2053-2056.

(7) McKelvy, M. L.; Britt, T. R.; Davis, B. L.; Gillie, J. K.; Lentz, L. A.; Leugers, A.; Nyquist, R. A.; Putzig, C. L. Infrared spectroscopy. *Anal. Chem.* **1996**, 68, 93R-160R.

(8) Madari, B. E.; Reeves III, J. B.; Coelho, M. R.; Machado, P. L. O. A.; De-Polli, H.; Coelho, R. M.; Benites, V. M.; Souza, L. F.; McCarty, G. W. Mid- and near-infrared spectroscopic determination of carbon in a diverse set of soils from the Brazilian national soil collection. *Spectrosc. Lett.* **2005**, 38, 721-740.

(9) McCarty, G. W.; Reeves III, J. B.; Reeves, V. B.; Follett, R. F.; Kimble, J. M. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. *Soil Sci. Soc. Am. J.* **2002**, 66, 640-646.

(10) Van Waes, C.; Mestdagh, I.; Lootens, P.; Carlier, L. Possibilities of near infrared reflectance spectroscopy for the prediction of organic carbon concentrations in grassland. *J. Agr. Sci.* **2005**, 143, 487-492.

(11) Cozzolino, D.; Morón, A. Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil organic carbon fractions. *Soil Till. Res.* **2006**, 85, 78-85.

(12) Janik, L. J.; Skjemstad, J. O.; Shepherd, K. D.; Spouncer, L. R. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Aust. J. Soil Res.* **2007**, 45, 73-81.

(13) Zimmermann, M.; Leifeld, J.; Fuhrer, J. Quantifying soil organic carbon fractions by infrared-spectroscopy. *Soil Biol. Biochem.* **2007**, 39, 224-231.

(14) Johnston, C. T.; Davies, W. M.; Erickson, C.; Delfino, J. J.; Cooper, W. T. Characterization of humic substances using Fourier transform infrared spectroscopy. In *Humic substances in the global environment and implications on human health*; Senesi, N., Miano, T. M., Eds.; Elsevier Science: Amsterdam, 1994.

(15) Lammers, K.; Arbuckle-Keil, G.; Dighton, J. FT-IR study of the changes in carbohydrate chemistry of three New Jersey pine barrens leaf litters during simulated control burning. *Soil Biol. Biochem.* **2009**, 41, 340-347.

(16) MacCarthy, P.; Rice, J. A. Spectroscopic methods (other than NMR) for determining functionality in humic substances. In *Humic substances in soil, sediment, and water. Geochemistry, isolation, and characterization*; Aiken, G. R., McKnight, D. G., Wershaw, R. L., MacCarthy, P., Eds.; John Wiley & Sons: 1985.

(17) MacCarthy, P.; Mark Jr, H. B.; Griffiths, P. R. Direct measurement of the infrared spectra of humic substances in water by fourier transform infrared spectrsoscopy. *J. Agr. Food Chem.* **1975**, 23, 600-602.

(18) Wagner, G. H.; Stevenson, F. J. Structural arrangement of functional groups in soil humic acid as revealed by infrared analyses. *Soil Sci. Soc. Am. Pro.* **1965**, 29, 43-48.

(19) Leifeld, J. Application of diffuse reflectance FT-IR spectroscopy and partial least-squares regression to predict NMR properties of soil organic matter. *Eur. J. Soil Sci.* **2006**, 57, 846-857.

(20) Terhoeven-Urselmans, T.; Michel, K.; Helfrich, M.; Flessa, H.; Ludwig, B. Near-infrared spectroscopy can predict the composition of organic matter in soil and litter. *J. Plant Nutr. Soil Sc.* **2006**, 169, 168-174.

(21) Madejova, J. FTIR techniques in clay mineral studies. *Vib. Spectrosc.* **2003**, 31, 1-10.

(22) Sorensen, L. K.; Dalsgaard, S. Determination of clay and other soil properties by near infrared spectroscopy. *Soil Sci. Soc. Am. J.* **2005**, 69, 159-167.

(23) Waiser, T. H.; Morgan, C. L. S.; Brown, D. J.; Hallmark, C. T. In situ characterization of soil clay content with visible near-infrared diffuse reflectance spectroscopy. *Soil Sci. Soc. Am. J.* **2007**, 71, 389-396.

(24) Viscarra Rossel, R. A.; Walvoort, D. J. J.; McBratney, A. B.; Janik, L. J.; Skjemstad, J. O. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. *Geoderma*. **2006**, 131, 59-75.

(25) Reeves III, J. B.; Follett, R. F.; McCarty, G. W.; Kimble, J. M. Can near or mid-infrared diffuse reflectance spectroscopy be used to determine soil carbon pools? *Commun. Soil Sci. Plan.* **2006**, 37, 2307-2325.

(26) Siebielec, G.; McCarty, G. W.; Stuczynski, T. I.; Reeves III, J. B. Near- and Mid-infrared diffuse reflectance spectroscopy for measuring soil metal content. *J. Environ. Qual.* **2004**, 33, 2056-2069.

(27) Brown, D. J.; Shepherd, K. D.; Walsh, M. G.; Mays, M. D.; Reinsch, T. G. Global soil characterization with VNIR diffuse reflectance spectroscopy. **2006**, 132, 273-290.

(28) Shepherd, K. D.; Walsh, M. G. Development of reflectance spectral libraries for characterization of soil properties. *Soil Sci. Soc. Am. J.* **2002**, 66, 988-998.

(29) Pirie, A.; Singh, B.; Islam, K. Ultra-violet, visible, near-infrared, and mid-infrared diffuse reflectance spectroscopic techniques to predict several soil properties. *Aust. J. Soil Res.* **2005**, 43, 713-721.

(30) Minasny, B.; McBratney, A. B. Regression rules as a tool for predicting soil properties from infrared reflectance spectroscopy. *Chemometr. Intell. Lab.* **2008**, 94, 72-79.

6 Supporting Information

6.1. TEST COMPOUND: DIURON

A hydrophobic pesticide diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] was chosen as a test compound in this study. Diuron is an herbicide which has been registered in Australia for more than 20 years now. There have always been concerns about the potential adverse effects of diuron on environmental health and quality especially because it has the ability to contaminate waterways as a result of runoff from lands where it has been applied (1). It is a substituted phenylurea-based herbicide that acts through the inhibition of photosynthesis with a wide range of agricultural and non-agricultural applications (1). Diuron has a relatively high *octanol-water partition coefficient* (K_{OW} = 710) and a moderate to low aqueous solubility (36.4 mg/L at 25 °C). Moreover, diuron is chemically stable and resistant to hydrolysis within the normal pH range found in the environment (pH 4 to 9) and is moderately sorbed into SOM ($K_{OC} \approx 400\text{-}500$) (2, 3). Such molecular properties makes diuron a relatively persistent xenobioitic in the soil environment (half life of 90–180 d) (2). The above properties plus being free from confounding factors such as speciation and pH effects, potential degradation during experiments and ease and sensitivity of its residue analysis, make diuron a suitable test compound for this study. The availability of substantial sorption data (K_{OC}) in the literature, reports of surface water contamination and its current environmental relevance further justified choice of diuron as test compound.

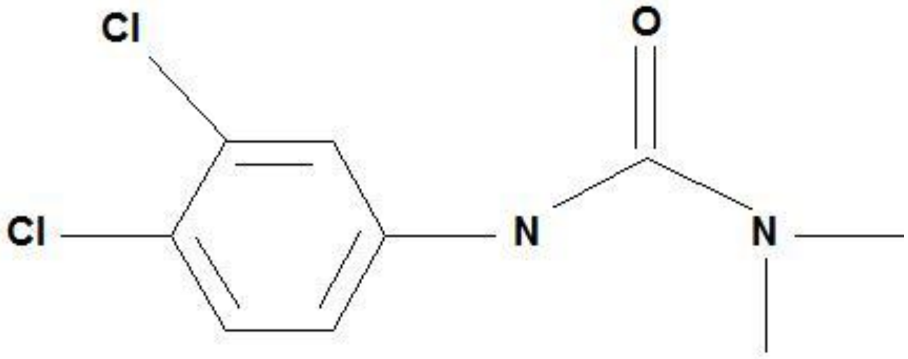


Figure 6.1. Carbon skeleton diagram showing the molecular structure of diuron.

6.2. SELECTED SOILS

A set of 112 surface soils from south-eastern South Australia was chosen from an existing soils database (4). Detailed information on the organic carbon content and sorption properties of these soils can be found in section 6.3. Figure 6 gives an overview on the localities of the selected soil samples. The soils cover a wide range of annual rainfall, vegetation and land use, but represent similar parent material and soil genesis. Parent materials are either highly siliceous or argillaceous sedimentary rocks and metasediments, or Tertiary and Quaternary sediments derived from these rocks. Quaternary aeolian carbonate deposition has resulted in the development of calcareous soils, some of which have horizons high in carbonate in their surface horizons. A subset of the soils have moderate to high salinity, an outcome of clearing that has caused the rise of a saline ground water table.

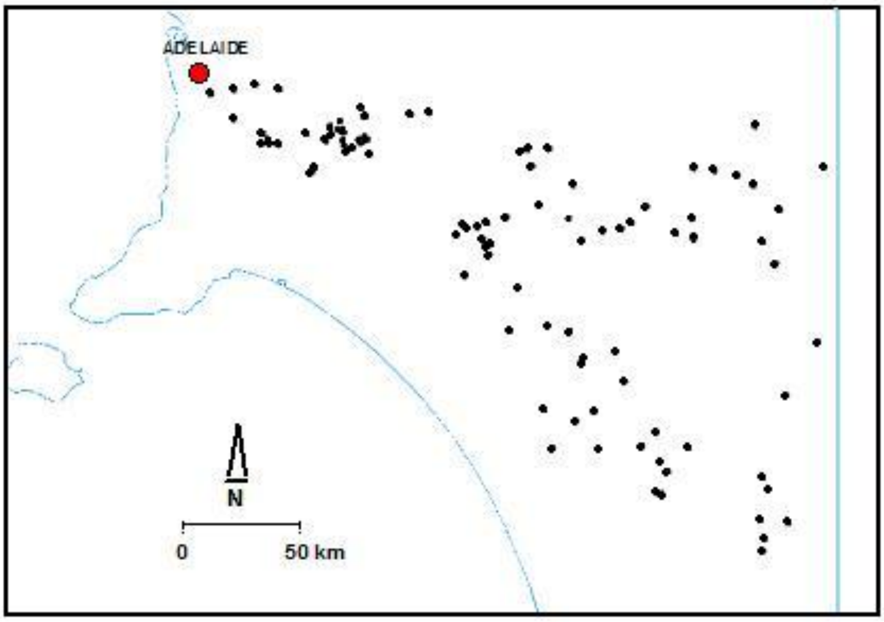


Figure 6.2. Map showing the soil profile locations in South Australia (n = 112).

6.3. SORPTION PROPERTIES AND ORGANIC CARBON CONTENT OF SOILS

Soil ID	f_{OC} **(%)**	**K_d (L/Kg)**	**Soil ID**	f_{OC} **(%)**	**K_d (L/Kg)**
01	2.72	23.01	**27**	1.13	4.15
02	8.30	29.65	**28**	0.93	2.93
03	2.64	19.16	**29**	0.62	2.64
04	1.68	7.05	**30**	2.24	8.13
06	1.84	7.29	**31**	0.93	3.60
07	4.35	32.43	**32**	1.03	3.40
08	3.77	12.80	**33**	1.28	2.96
09	8.95	37.36	**34**	1.59	5.15
10	3.38	15.80	**35**	0.98	2.79
11	2.16	8.12	**36**	0.48	1.12
12	2.60	8.29	**37**	1.35	2.65
13	0.22	0.20	**38**	1.43	5.44
14	1.11	2.95	**39**	1.33	4.21
15	1.92	5.46	**40**	0.78	3.35
16	2.51	11.33	**41**	0.65	1.85
17	1.18	2.86	**42**	0.77	1.41
18	1.31	3.55	**43**	1.42	5.40
19	1.07	3.14	**44**	0.85	1.54
20	0.81	1.40	**46**	1.22	3.51
21	0.71	1.63	**47**	1.16	5.23
22	0.53	1.22	**48**	1.15	3.69
23	2.23	5.38	**49**	1.56	7.83
24	0.41	0.86	**50**	1.66	6.35
25	1.12	3.95	**51**	0.58	2.93
26	1.89	5.34	**52**	0.26	0.52

6.3. Continued.

Soil ID	**f_{OC} (%)**	**K_d (L/Kg)**	**Soil ID**	**f_{OC} (%)**	**K_d (L/Kg)**
53	0.95	5.02	**78**	1.49	4.34
54	1.22	5.44	**80**	2.21	5.14
55	1.25	5.29	**81**	0.06	0.01
56	0.88	5.78	**82**	1.54	41.97
57	0.79	2.52	**83**	1.37	4.62
58	0.94	2.45	**84**	1.19	8.38
59	0.40	0.58	**85**	1.02	2.41
60	0.87	2.79	**86**	1.86	6.81
61	1.01	2.15	**87**	1.69	3.85
62	0.68	2.86	**88**	0.44	0.91
63	0.48	1.66	**89**	1.62	5.64
64	0.54	1.42	**90**	1.87	4.77
65	1.99	5.71	**91**	0.38	1.68
66	1.39	4.77	**92**	0.46	1.16
67	1.68	5.63	**93**	0.97	3.70
68	3.03	15.36	**94**	0.65	1.86
69	1.98	10.19	**95**	2.54	8.40
70	2.10	10.17	**96**	2.84	15.80
71	1.85	10.58	**97**	0.94	2.40
72	1.61	4.68	**98**	1.65	3.75
73	2.75	9.60	**99**	1.28	3.78
74	1.49	4.24	**100**	3.67	15.56
75	0.84	1.20	**101**	0.63	1.06
76	1.35	4.26	**102**	1.64	3.98
77	0.88	2.10	**104**	1.80	6.53

6.3. Continued.

Soil ID	**f_{OC} (%)**	**K_d (L/Kg)**	**Soil ID**	**f_{OC} (%)**	**K_d (L/Kg)**
107	3.08	66.84	**113**	3.14	91.34
108	3.59	30.05	**114**	1.64	4.14
109	6.05	40.03	**115**	1.29	4.80
110	6.54	36.22	**116**	1.90	10.79
111	2.24	2.61	**117**	1.46	3.19
112	2.67	7.85	**118**	3.54	12.13

6.4. DETAILS OF THE CORRECTIONS MADE FOR MOISTURE CONTENT, SORPTION BY TEST VESSELS AND FILTERS

6.4.1. CORRECTIONS FOR THE ACTUAL MASS TAKEN FROM SOILS CONSIDERING THE AIR-DRIED WATER CONTENT

Although 5 g of each soil sample was taken for each replication, the actual mass of soil was slightly less due to water content of the samples in air-dried condition. Therefore, the air-dried water content for all the soil samples was measured and actual mass of soil was used in calculating K_d values.

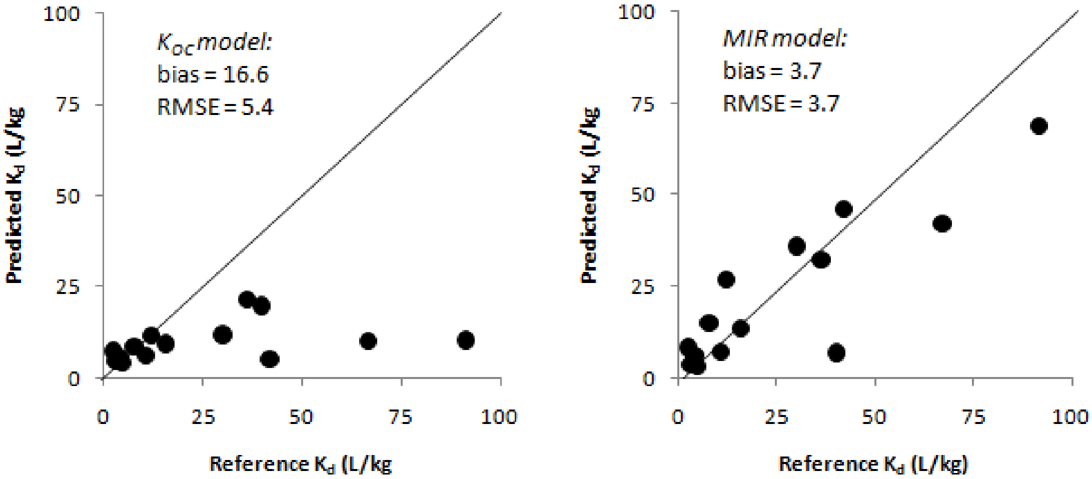
6.4.2. SORPTION TO TEST VESSELS

Control samples (which contained no soil) were used to minimize the effect of adsorption of the test compound to the surface of vessels on the determination of K_d. Control samples were run with each batch of samples, and the concentration remaining in those at the end of the experiment was considered as the initial concentration, i.e. it was assumed that the same amount of diuron was sorbed to the surface of the vessels in each treatment as was the case for the control samples. Preliminary experiments showed an average sorption of 2.7% from 10 ml solution with an initial diuron concentration of 1 ppm after 24 hours shaking.

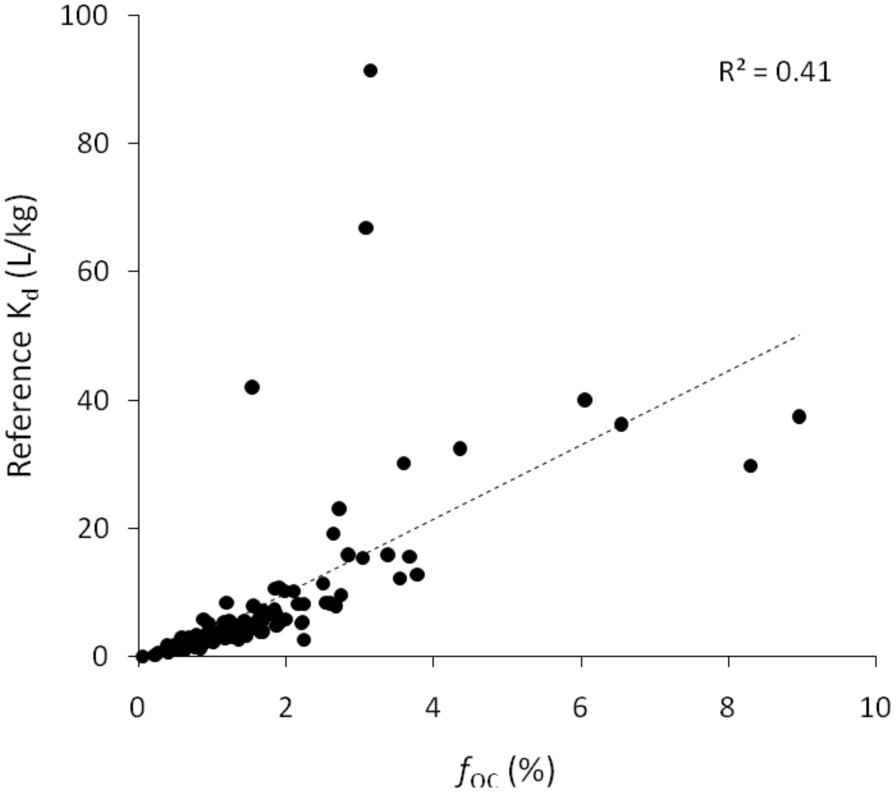
6.4.3. SORPTION TO FILTERS

Diuron sorption to filters was measured in preliminary experiments at three different concentrations. Diuron sorption percentages from 0.25, 0.45, 0.95 μg/mL were 9.5%, 8.2%, and 5.0%, respectively, from 2 mL of the syringed solution. An average value of 7.6% was used to correct for this effect in calculating equilibrium concentrations.

6.5. REGRESSION PLOTS FOR PREDICTION OF DIURON SORPTION (K_d) IN 14 CALCAREOUS SOILS BY MIR-PLS MODEL VERSUS K_{OC} MODEL



6.6. PLOT OF CORRELATION BETWEEN f_{OC} AND REFERENCE K_d VALUES (n=112)



6.7. SOME PROPERTIES OF SOILS (OTHER THAN f_{OC} AND DIURON K_d)

Soil ID	Site No[†]	Profile description[‡]	pH[§]	Sand[§] (%)	Silt[§] (%)	Clay[§] (%)	CO_3[§] (%)
1	CH117	Deep gradational clay loam	6.3	---	---	---	0
2	CH047	Deep gradational clay loam	4.9	---	---	---	0
3	CH097	Acidic gradational loam over rock	6.4	---	---	---	0
4	CH041	Acidic clay loam over red clay on rock	5.0	---	---	---	0
6	CH139	Gradational sandy loam over sandstone	6.1	---	---	---	0
7	CH111	Acidic loam over red clay on rock	5.8	---	---	---	0
8	CH001	Sandy loam over brown clay	5.4	76	11	13	---
9	CH112	Acidic ironstone sandy loam	5.7	---	---	---	0
10	CH113	Sandy loam over poorly structured brown clay	5.3	---	---	---	0
11	CH062	Acidic sandy loam over red clay on rock	5.4	---	---	---	0
12	CH136	Shallow sandy loam on rock	7.6	---	---	---	0
13	MO043	Deep sandy loam	8.0	93	0	6	0
14	MO045	Sandy loam over red clay	6.5	81	4	18	0
15	MO036	Deep sand	7.4	96	2	2	0.9
16	MO003	Loam over dark clay on calcified rock	7.2	60	15	25	0
17	MO026	Sandy loam over red clay on calcified rock	7.5	85	3	12	0
18	MO025	loamy sand over red clay on calcified rock	7.7	82	10	8	0
19	MO021	sandy loam over poorly structured red clay	7.0	80	6	14	14
20	MO039	loamy sand over poorly structured red clay	8.6	83	10	7	1
21	MO020	Shallow sandy loam over rock	7.3	91	2	7	0
22	MO040	Thick sand over red sandy clay loam	6.9	90	8	2	0
23	MO033	Shallow calcareous loam	---	80	6	14	---
24	MO027	Gradational red clay	8.3	62	4	34	0.4

[†] Site No. as stated in South Australian Soils Database (4).
[‡] Description as given in South Australian Soils Database (4).
[§] Information from surface horizon.

6.7. Continued.

Soil ID	Site No[†]	Profile description[‡]	pH[§]	Sand[§] (%)	Silt[§] (%)	Clay[§] (%)	CO_3[§] (%)
25	MO034	Gradational calcareous clay loam	8.4	72	4	24	0.2
26	MO035	Grey cracking clay	8.7	68	4	28	8.2
27	MO002	Deep bleached sand	7.8	94	3	3	0.1
28	MO017	Sandy loam over red sandy clay on rock	7.2	89	1	11	0
29	MO011	Bleached sand over sandy clay loam	7.0	96	1	3	0
30	MO015	Shallow sandy loam over calcrete	8.3	85	4	11	2
31	MO005	Loamy sand over dispersive red clay on rock	7.0	95	3	2	0
32	MO008	Loamy sand over hard clay on rock	8.1	90	3	7	0.2
33	MO009	Shallow sandy loam over rock	8.4	80	4	16	0.7
34	MO038	Shallow gradational sandy loam over rock	8.0	80	10	10	0
35	MO037	Sand over red sandy clay loam	8.2	90	5	5	0.2
36	MO051	Deep sandy loam	8.6	88	3	9	0
37	MM027	Calcareous sandy loam	8.6	---	---	---	8
38	MM020	Shallow calcareous sandy loam on calcrete	8.5	---	---	---	3
39	MM011	Shallow calcareous sandy loam on calcrete	7.8	---	---	---	2
40	MM013	Gradational red sandy loam	6.4	---	---	---	0
41	MM014	Deep bleached siliceous sand	6.9	---	---	---	1
42	MM048	Loamy sand over red sandy clay	7.5	---	---	---	0
43	MM018	Shallow calcareous sandy loam on calcrete	8.0	---	---	---	1
44	MM064	Shallow calcareous sandy loam on calcrete	8.9	---	---	---	1
46	MM067	Shallow calcareous sandy loam on calcrete	8.7	---	---	---	1
47	MM147	Gradational sandy loam	7.2	---	---	---	0
48	MM146	Shallow calcareous sandy loam on calcrete	8.3	---	---	---	0.9
49	MM152	Loamy sand over poorly structured clay	7.9	---	---	---	0.1
50	MM134	Sandy clay loam over dispersive red clay	7.5	---	---	---	0

6.7. Continued.

Soil ID	Site No[†]	Profile description[‡]	pH[§]	Sand[§] (%)	Silt[§] (%)	Clay[§] (%)	CO_3[§] (%)
51	MM131	Sand over poorly structured brown clay	7.4	---	---	---	0
52	MM042	Bleached sand over sandy clay loam	6.3	---	---	---	0
53	MM041	Sandy loam over poorly structured brown clay	5.8	---	---	---	0.7
54	MM031	Sandy clay loam over dispersive red clay	7.2	---	---	---	0.3
55	MM039	Sand over poorly structured brown clay	6.0	---	---	---	0.5
56	MM037	sandy loam over poorly structured red clay	6.7	---	---	---	0
57	MM122	Sandy loam over dispersive sandy clay loam	7.6	---	---	---	0.1
58	MM035	Sand over dispersive red clay	6.2	---	---	---	0
59	MM034	Deep bleached siliceous sand	6.1	---	---	---	0
60	MM130	Loamy sand over sandy clay loam	8.5	---	---	---	0.7
61	MM131	Calcareous sandy loam over clayey substrate	8.6	---	---	---	4.2
62	MM049	Loamy sand over dispersive brown sandy clay	6.7	---	---	---	---
63	MM063	Thick sand over sandy clay	6.6	---	---	---	1
64	MM057	Thick sand over sandy clay	6.8	---	---	---	1
65	MM056	Grey cracking clay	8.2	---	---	---	3
66	SE005	Sand over dispersive brown clay	6.6	---	---	---	0
67	SE079	Thick bleached sand over brown clay	8.2	---	---	---	0.5
68	SE078	Sandy loam over grey brown clay	6.8	---	---	---	0
69	SE002	Ironstone sandy loam over red alkaline clay	7.7	---	---	---	0.6
70	SE015	Sandy loam over poorly structured brown clay	6.3	---	---	---	0
71	SE004	Loam over poorly structured brown clay	6	---	---	---	0
72	SE045	Sand over sodic brown clay	7.2	---	---	---	0

6.7. Continued.

Soil ID	Site No[†]	Profile description[‡]	pH[§]	Sand[§] (%)	Silt[§] (%)	Clay[§] (%)	CO_3[§] (%)
73	SE044	Sand over sodic brown clay	7.6	---	---	---	0
74	SE046	Shallow calcareous loam over calcrete	8.3	---	---	---	3.4
75	SE047	Shallow sand over clay on calcrete	8.4	---	---	---	0
76	SE043	Sand over friable sandy clay loam	6.4	---	---	---	0
77	SE007	Bleached siliceous sand	6.1	---	---	---	0
78	SE072	Bleached sand over calcrete	6.7	---	---	---	0
80	SE073	Sand over sandy clay loam on calcrete	8.2	---	---	---	3
81	MM107	Shallow sand over sandy clay on calcrete	6.8	---	----	---	1
82	SE074	Deep saline sand	9.2	---	---	---	23
83	MM105	Shallow sand over sandy clay on calcrete	7.3	---	---	---	1
84	MM068	Wet saline soil	9.1	---	---	---	3
85	MM010	Bleached sand over sandy clay loam	6.7	---	---	---	0.1
86	MM102	Calcareous clay	8.2	---	---	---	3
87	MM097	Sandy loam over sandy clay on calcrete	7.6	---	---	---	2
88	MM096	Bleached siliceous sand	6.8	---	---	---	1
89	MM080	Sandy clay loam over dispersive brown clay	8.2	---	---	---	2
90	MM079	Shallow calcareous sandy clay loam	8.4	---	---	---	5
91	MM082	Bleached siliceous sand	7.1	---	---	---	1
92	MM075	Bleached siliceous sand	6.3	---	---	---	1
93	MM084	Thick bleached sand over sandy clay loam	6.7	---	---	---	1
94	MM073	Deep sand	6.9	---	---	---	1
95	MM116	Shallow saline clay loam over calcrete	8.4	---	---	---	3
96	MM119	Saline calcareous sandy clay loam	9.3	---	---	---	12
97	MM118	Shallow sand over sandy clay on calcrete	6.5	---	---	---	0
98	MM109	Gypseous calcareous loam	7.8	---	---	---	1

6.7. Continued.

Soil ID	Site No[†]	Profile description[‡]	pH[§]	Sand[§] (%)	Silt[§] (%)	Clay[§] (%)	CO_3[§] (%)
99	MM113	Shallow gradational sandy loam over calcrete	7.8	---	---	---	1
100	MM111	Wet saline clay loam	7.4	---	---	---	1
101	MM108	Saline calcareous sandy loam	8.4	---	---	---	1
102	MM071	Shallow calcareous sandy loam over calcrete	7.6	---	---	---	1
104	MM070	Shallow sandy loam over calcrete	6.8	---	---	---	1
107	MM069	Shallow highly calcareous sandy loam	8.4	---	---	---	25
108	SE068	Wet calcareous clay	8.7	---	---	---	24
109	SE084	Calcareous black cracking clay	8.1	---	---	---	40
110	SE054	Calcareous clay on marl	7.9	---	---	---	15.6
111	CH086	Highly calcareous loamy sand	8.4	---	---	---	31
112	EC097	Highly calcareous sandy loam	8.3	---	---	---	62
113	SE034	Wet saline soil	9.0	---	---	---	44.7
114	EF021	Shallow highly calcareous sandy loam	8.3	---	---	---	32
115	EF017	Highly calcareous saline sandy loam	8.9	---	---	---	31.5
116	EF018	Highly calcareous sandy loam	8.2	---	---	---	45
117	EC089	Highly calcareous sandy loam	8.4	---	---	---	40.3
118	EL035	Highly calcareous sandy loam	8.2	---	---	---	63

[†] Site No. as stated in South Australian Soils Database (4).
[‡] Description as given in South Australian Soils Database (4).
[§] Information from surface horizon.

6.8. REFERENCES

(1) Australian Pesticides & Veterinary Medicines Authority. *The reconsideration of the approvals of the active constituent diuron, registrations of products containing diuron and their associated labels*; APVMA: Canberra, Australia, 2005.

(2) Gooddy, D. C.; Chilton, P. J.; Harrison, I. A field study to assess the degradation and transport of diuron and its metabolites in a calcareous soil. *Science of the Total Envireonment*. **2002**, 297, 67-83.

(3) Tomlin, C. D. S. *The pesticide manual*; British Crop Protection Council: Surry, UK, 1997.

(4) Soil and Land Information Group. *Regional Land Resource Information on CD-ROM for Agricultural Regions of South Australia*; Department of Water, Land and Biodiversity Conservation: South Australia, 2005.