

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

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In God, the Greatest

Dedication

for my dear parents, Fakhree and Reza

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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

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List of Publications

Forouzanoghar, 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.

Forouzanoghar, 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.

Forouzanoghar, 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.

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