Bull. Environ. Contam. Toxicol. (2000) 64:518-525
© 2000 Springer-Verlag New York Inc.
DOI: 10.1007/s001280000034

Bulletin of Environmental Contamination and Toxicology

Spectroscopic Study of the Sorption of Isoxaflutole and Its Diketonitrile Metabolite in Dissimilar Soils

S. Mitra,* P. C. Bhowmik

Department of Plant and Soil Sciences, Stockbridge Hall, University of Massachusetts, Amherst, MA 01003, USA

Received: 1 October 1999/Accepted: 26 January 2000

Isoxaflutole, [4-(2-methanesulphonyl-4-trifluoromethylbenzoyl)-5-cyclopropyl isoxazole], is a new preemergence herbicide which belongs to the isoxazole class of herbicides (Cain et al. 1993). Isoxaflutole is chemically benzoyl isoxazole and it rapidly converts to a diketonitrile (DKN) metabolite, [2-cyano-3-cyclopropyl-1 -(2-methylsulphonyl-4-trifluoromethylphenyl) propan-1, 3-dione] by opening the isoxazole ring (Pallett et al. 1997). The conversion to DKN takes place in both plants and soil. In soil, isoxaflutole undergoes rapid conversion to diketonitrile and it is partially sensitive to light. In soil, the half-life of isoxaflutole is 20 hrs under light and 23 hrs under dark, respectively. Under aqueous photolysis conditions the half-life of isoxaflutole is 40 hrs. (Mitra et al. 1999).

Isoxaflutole has been reported to provide excellent selective control of both grass and broadleaf weeds in corn (Bhowmik et al. 1996; Luscombe et al. 1995). Being a pre-emergence herbicide, isoxaflutole acts through the soil and therefore sorption process plays an important role in understanding its fate and behavior in soil. Soils are heterogeneous systems and they have a tremendous capacity to sorb chemicals particularly the applied herbicides. The removal of herbicides from solution by soprtion is a major factor controlling herbicide activity, mobility, persistence, and environmental fate (Wauchope and Koskinen, 1983; Weber and Peter, 1982).

Fourier Transform Infrared (FTIR) spectroscopy is a well established tool for investigating the chemical composition of chemicals. Martin-Neto et al. (1994) used FTIR to obtain information about the molecular mechanisms of interaction of atrazine, (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) and humic acids extracted from tropical soils. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) is a modified form of FTIR and it has been used by White and Nair (1989) to study the dehydroxylation of amorphous silica. Friesen and Michaelian (199 1) have used diffuse reflectance FTIR to study the CH stretching region in infrared spectra of coal.

Present address: Eco Soil Systems, Inc, 10740 Thornmint Road, San Diego, CA 92127, USA
Correspondence to: S. Mitra

The technique and theory of DRIFT are well documented and reviewed (Fuller and Griffiths 1978; Painter et al. 1985). The DRIFT spectra can be recorded as reflectance or absorbance units and peak assignments in Drift are same as in transmission IR spectroscopy (Fuller and Grifffths 1978). The DRIFT system has been applied extensively to research on various materials, including coal.

According to Painter et al. (1985), this technique offers several advantages over transmission IR spectroscopy: (i). A simpler sample-preparation procedure is required for DRIFT measurements than for FTIR; (ii) insensitivity to water associated with the sample or with KBr used in sample preparation leads to an enhanced resolution; (iii) resolution of the spectra is further increased as a result of a reduction in the sensitivity towards light scattering; and (iv) DRIFT provides a more reliable method for quantitative estimations of functional groups.

The purpose of this work was to study the applicability of DRIFT in studying the characteristic bands of the molecular structures of isoxaflutole and DKN and investigate the presence of intermolecular hydrogen bonding with the soil particles.

MATERIALS AND METHODS

Experiments were performed on a MIDAC (Series M 2010) Diffuse reflectance Fourier transformed infrared (DRIFT) spectrophotometer (MIDAC Corporation, Irvine, CA 92714). The technical grade isoxaflutole (98.0% pure) and DKN (99.0% pure) were obtained from Rhône-Poulenc Secteur Ag. Co. (14-20 Rue Pierre Baizet B.P. 9163, 69263 Lyon Cedex 09, France). Soils from Moorhead, MN; East Monroe, CO; Ellendale, MN; South Deerfield, MA and Chelsea, MI were used for the experiments with isoxaflutole (Figure 1), while a soil from Amherst, MA was used instead of the Ellendale, MN soil for experiments with DKN (Figure 2). The soil from Amherst, MA was used, since the organic matter content of the soil was higher. DKN has a higher aqueous solubility and to detect appreciable amounts of DKN sorbed on a soil we had to use a soil with higher organic matter content. The soils were collected from the Ap horizon (0-l5 cm) having a wide variation in their soil texture, pH, organic matter, adsorbed cation (Ca^{2+}) and cation exchange capacity (CEC).

All the samples were mixed with 30-mg KBr pellets and were ground properly (Inbar et al. 1990). The aqueous solubility of isoxaflutole is 6.2 µg ml^{-1}, while DKN has a solubility of 326 µg ml^{-1}. Thus 2 µg ml^{-1} of isoxaflutole and 100 µg ml^{-1} of DKN per g of soil were used for the experiments. Isoxaflutole and DKN solutions were prepared in methylene chloride and were mixed with the soil samples. The soil mixtures were air-dried and were placed in a dessicator. For all experiments, 2-3 mg of the samples were added to 100 mg KBr. Using this proportion of the samples to KBr, we found that spectra with better resolution were obtained as compared to samples with the proportion of 1 mg of sample to

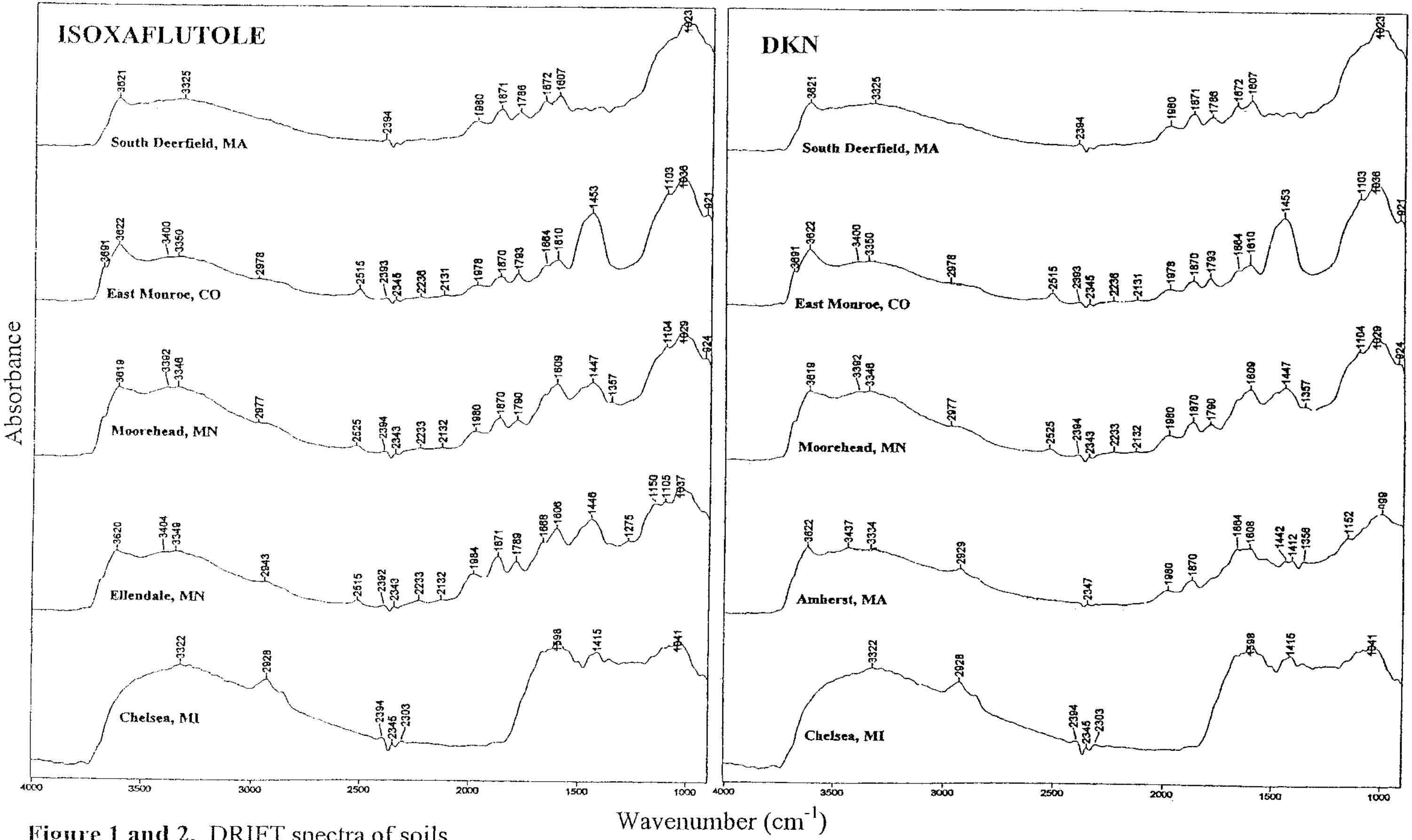

Figure 1 and 2. DRIFT spectra of soils.

100 mg KBr. Similarly, Martin-Neto et al. (1994) reported that 2-3 mg of humic acid or humic acid atrazine complex and 100 mg KBr gave them good resolution.

RESULTS AND DISCUSSION

The spectra of isoxaflutole and DKN had prominent and well resolved bands indicative of aliphatic C-H, carboxyl, nitrile, sulphonyl functional groups, aromatic C = C, and C-O stretch. Isoxaflutole was characterized by a prominent carbonyl stretching frequency, C = O (1670 cm^{-1}), aromatic C-H stretch (3027 cm^{-1}), and asymmetric C-H stretch of $-CH_2$ (3100 and 2925 cm^{-1}) (cyclo propyl group) (Laird et al. 1994) (Figure 3). The SO_2- group is represented by a peak at 1324 cm^{-1} wavenumber while the aromatic ring is denoted by the absorbance peak at 1572 cm^{-1} (Pavia et al. 1979).

With the conversion of isoxaflutole to DKN the functional groups get rearranged. As a result the DKN molecule has two keto groups (C = O) and a nitrile group (CN), while, rest of the functional groups remain intact. The DKN molecule was characterized by a prominent nitrile absorbance band (2217 cm-‘) and a high intensity of carbonyl stretching frequency (1569 - 1502 cm^{-1}) (Figure 4). An asymmetric S = O stretch (1317 cm^{-1}) and a symmetric S = O stretch (1151 cm^{-1}) of equal intensity was recorded. The absorbance peaks in the 908 -to- 965 cm^{-1} range corresponded to out of plane stretches of the aromatic groups. Symmetric C-H stretch of $-CH_2$- group was depicted by the peak at 2816 cm^{-1}, while, the peak at 1416 indicated aromatic C = C stretch (Figure 4).

Generally a typical keto group (C = O) is represented by an absorbance peak at 1720 cm^{-1} wavenumber (Laird et al. 1994) but the two keto groups in the DKN molecule had twin peaks of high intensity at 1548 and 1569 cm^{-1}. The two keto groups might exhibit tautomerism and a ketoenol group may be formed. The reason for this shift can be accounted by intramolecular hydrogen bonding between the two keto groups. Hence, the shift of the C =0 group peaks to a lower wavenumber can be explained by isomerism and the presence of other functional groups.

On careful observation it was found that the intensity of the absorbance bands for the Si-O-Si functionalities (1023 -to- 1041 cm^{-1}) (Fuller and Smyrl 1990) decreased with an increase in the organic matter content of the soils (Figures 1 and 2). The absorbance bands for these moieties clearly indicate a decrease in mineral content of the soils. White and Nair (1989) have studied silica dehydroxylation with DRIFT spectroscopy and they found Si-O-Si stretching absorbance bands from 970 to 1200 cm^{-1} wavenumbers.

Further analysis of the DRIFT spectra revealed that intermolecular hydrogen bonding was observed when isoxaflutole and DKN were added to soils. In classical hydrogen bonding the close proximity of electron-rich species

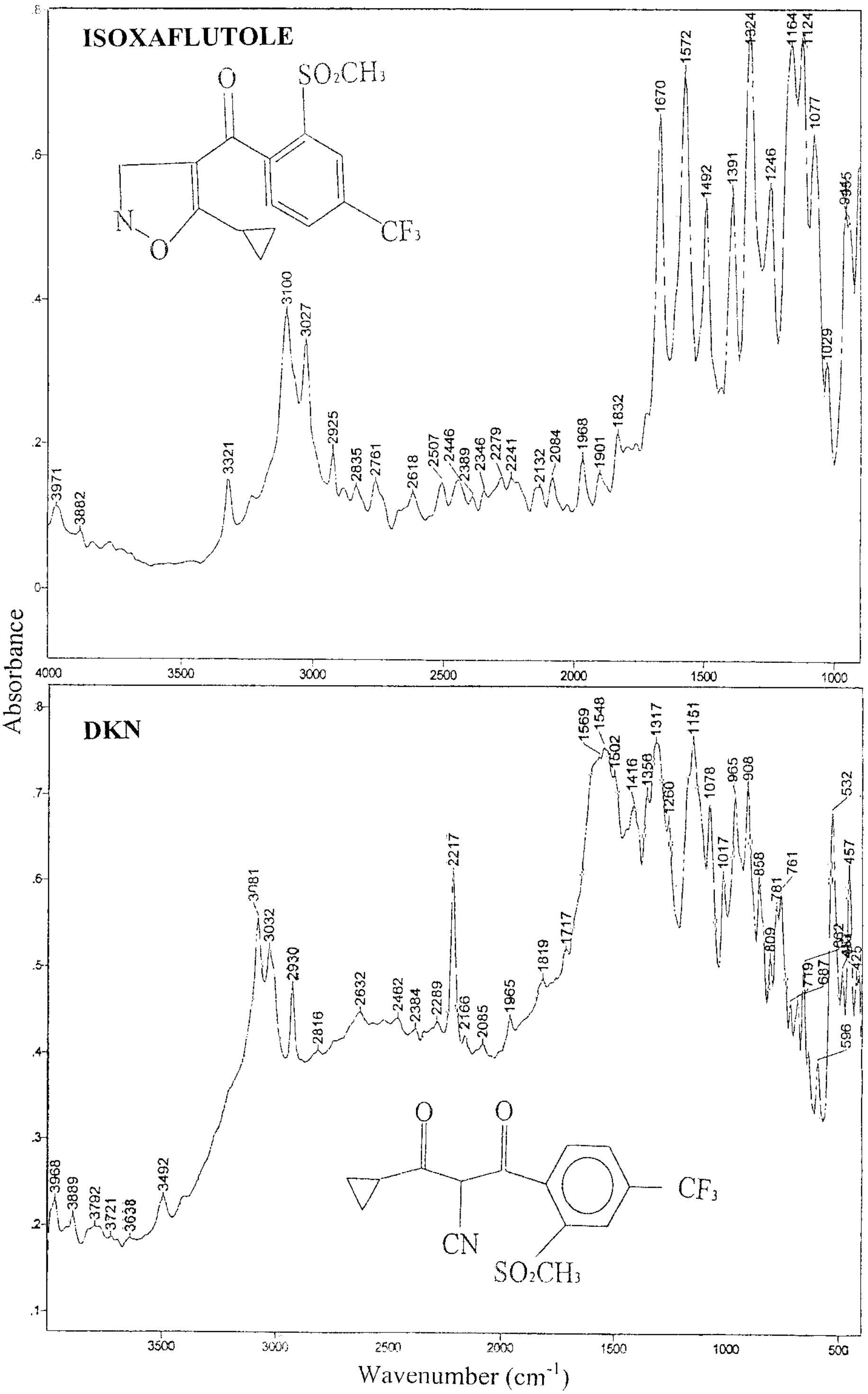

Figure 3 and 4. DRIFT spectrum of isoxaflutole and DKN.

(primarily other O-H groups, carbonyl groups, and carboxylic groups) attracts the hydrogen of the donor O-H with a concomitant shift of its vibrational frequency to lower wavenumbers (Fuller and Smyrl 1990). When hydrogen bond formation occurs rather drastic changes are observed in the vibrational spectrum which include, for an O-H- - - - - O bond, the following happen (Fuller and Smyrl 1990).

(i) The O-H stretching frequency decreases

(ii) The O-H bending frequency increases

The O-H stretching frequency of carbonyls is observed around 3200 - 3500 cm^{-1} wavenumbers (Pavia et al. 1979). The isoxaflutole spectra had an absorbance band of 3321 cm^{-1} (O-H stretching frequency) which decreased to 3027, 3028, 3027, 3026, and 3287 when isoxaflutole was added to South Deerfield, East Monroe, Moorhead, Ellendale, and Chelsea soils, respectively (Figure 5). While, in the DKN spectra a small peak was observed at 3492 cm^{-1} which decreased to 3388, 3400, 3396, 3355, and 3329 cm^{-1} when added to South Deerfield, East Monroe, Moorhead, Amherst, and Chelsea soils (Figure 6).

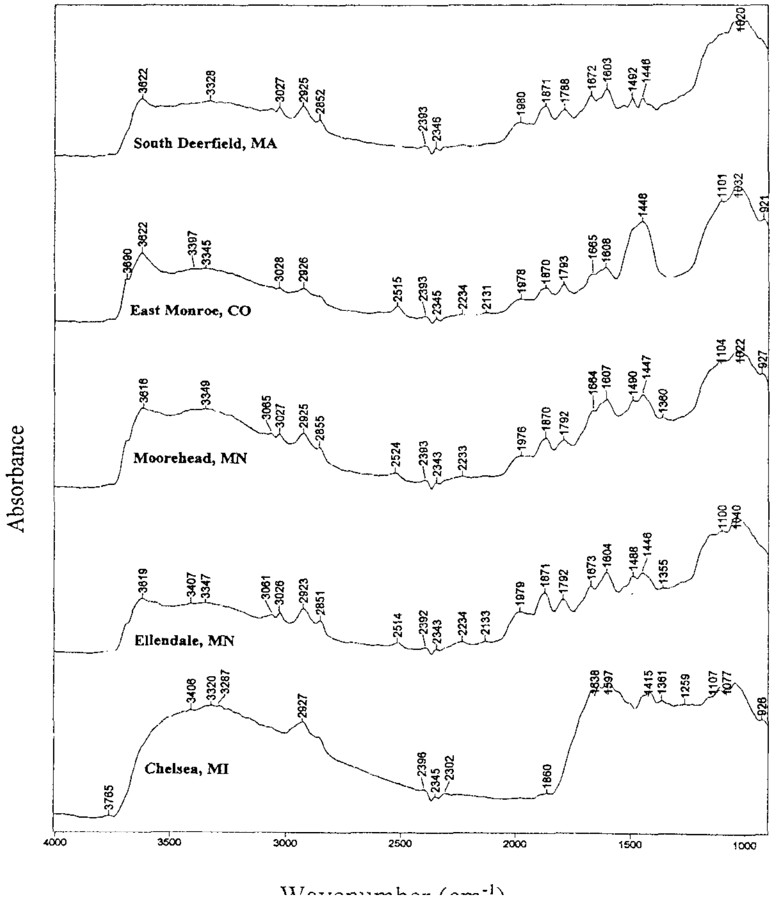

Figure 5. DRIFT spectra of soils after addition of isoxatlutole

The O-H bending mode is represented by 1343 - 1387 cm^{-1} wavenumbers (Fuller and Smyrl 1990). An increase in the wavenumber of the O-H bending frequency in DKN (1356 cm-‘) was observed when it was added to the soils. Similar results of hydrogen bonding have been reported in atrazine sorption (Martin-Neto et al. 1994). Fuller and Smyrl 1990 have reported that hydrogen bonding is a major force, which binds coals together.

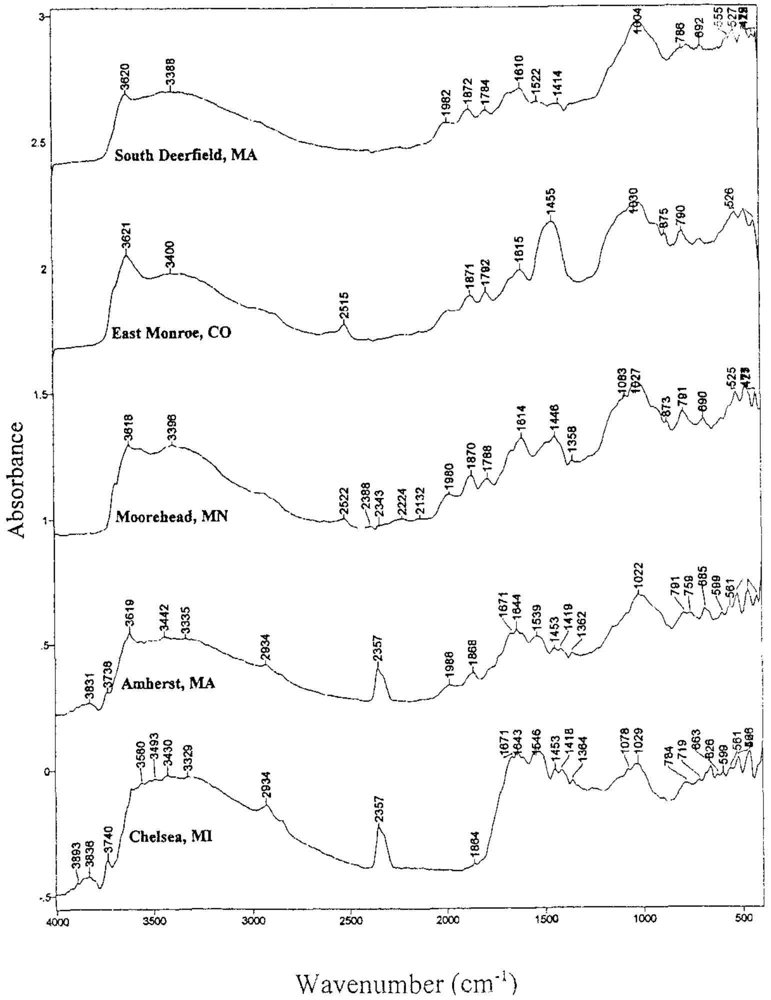

Figure 6. DRIFT spectra of soils after addition of DKN.

REFERENCES

Bhowmik PC, Vrabel TE, Prostak R, Cartier J (1996) Activity of RPA 201772 in controlling weed species in field corn. Second Int Weed Control Congress 2:807-812

Cain PA, Cramp SM, Little GM, Luscombe BM (1993) EP Patent 0527036.

Friesen WI, Michaelian KH (1991) Deconvolution and curve-fitting in the analysis of complex spectra: The CH stretching region in infrared spectra of coal. Appl Spectrosc 45:50-56

Fuller MP, Griffiths PR (1978) Diffuse reflectance measurements by infrared Fourier transform spectrometry. Anal Chem 50: 1906-l919

Fuller Fuller EI Jr, Smyrl, NR (1990) Chemistry and structure of coals: Hydrogen bonding structures evaluated by diffuse reflectance infrared spectroscopy. Appl Spectrosc 44:1451-461

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

Laird DA, Yen PY, Koskinen WC, Steinheimer TR, Dowdy RH (1994) Sorption of atrazine on soil clay components Environ Sci Technol 28:1054-1061

Luscombe BM, Pallett KE, Loubiere P, Millet JC, Melgarejo J, Vrabel TE (1995) RPA 201772: a novel herbicide for broadleaf and grass weed control in maize and sugarcane. Proc Brighton Crop Cont Conf-Weeds 2:35-42

Martin-Neto L, Viera EM, Sposito G (1994) Mechanism of atrazine sorption by humic acid: A spectroscopic study Environ Sci Technol 28: 1867-1873

Mitra S, Bhowmik PC, Xing B (1999) Sorption of isoxflutole by five different soils varying in physical and chemical properties. Pestic Sci 55:935-942

Painter P, Starsinic M, Coleman M (1985) Determination of functional groups in coal by Fourier transform interferometry. In: Ferraro JR, Basile LJ (ed) Fourier Transform Spectroscopy. Application to Chemical Systems, vol 4. Academic Press, Orlando, FL, p 169-241

Pallett KE, Little JP, Veerasekaran P, Viviani F (1997) Inihibition of 4-hydroxyphenyl pyruvate dioxygenase: The mode of action of RPA 201771 (Isoxaflutole). Pestic Sci 50:83-84

Pavia Dl, Lampman GM, Kriz GSJr (1979) Introduction to spectroscopy: A guide for students of organic chemistry. WB Saunders Company, Philadelphia

Wauchope RD, Koskinen WC (1983) Adsorption-desorption equilibria of herbicides in soil: thermodynamic perspective. Weed Sci 31:504-512

Weber JB, Peter CJ (1982) Adsorption bioactivity and evaluation of soil tests for alachlor, acetochlor, and metolachlor. Weed Sci 30: 14-20

White RL, Nair A (1990) Diffuse reflectance infrared spectroscopic characterization of silica dehydroxylation Appl Spectrosc 44:69-75