

The effect of minerals on non-ionic compound sorption by changing the sorption capacity of soil organic matter

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Abstract

For non-ionic compounds, the preliminary role in the sorption process is played by soil organic matter (SOM). However, it is necessary to determine the relative contribution of soil minerals, in particular, soil clay minerals and SOM constituents, to improve prediction of the sorption process. Here, the results show that sorption capacity of SOM can be affected by mineral–SOM interaction. The organic carbon-normalized sorption coefficient (K_{oc}) after hydrofluoric acid (HF) treatment increased an average of 124% and 98% for A11 horizons and 185% and 162% for A12 horizons for diuron and phenanthrene, respectively. We propose that the increased K_{oc} values in the A12 horizons are due to a higher percentage of clay in A12 horizons as well as a loose connection of SOM with clay minerals in A11 horizons. We suggest that the mineral components of soil contribute greatly to sorption of even non-ionic compounds with alteration of the sorption properties of SOM, which need to be considered in determining the fate and availability of non-ionic compounds in the soil environment.

Keywords: sorption, diuron, phenanthrene, clay minerals.

1. Introduction

The fate of organic pollutants, including their dissipation, mobility and degradation, generally takes place in the soil and is largely controlled by their sorption. Research during the last decade has revealed that for non-ionic compounds, the key factor to determine the extent of sorption is the organic carbon content of the soil (Kile *et al.*, 1995; Fall *et al.*, 2003; Ahangar *et al.*, 2008a; Gao *et al.*, 2007). Linear sorption processes and partitioning between the solution and soil organic matter (SOM) are most commonly used for non-ionic compounds, and the C-normalized partition coefficient (K_{oc}) quantifies the sorption interaction (Chiou, 1989). However, in some situations, sorption interaction cannot be explained. The variability of K_{oc} values among soils with different physical and chemical characteristics has shown the sorption of non-ionic compounds to be affected by a variety of soil properties. Therefore, SOM cannot be regarded as a sole sorbent. Previous studies (Schlautman and Morgan, 1993a; Fall *et al.*, 2003; Huang *et al.*, 2003; Celis *et al.*, 2006) have shown that soil characteristics, liquid phase composition, organic matter heterogeneity and the contribution of mineral phases to sorption cause K_{oc} variability. Although there is a general consensus that structural properties of organic matter can greatly influence its affinity for non-ionic compounds, a consensus has not been reached on the manner in which the nature of the organic matter affects sorption properties. Many studies have shown that the aliphatic group of organic matter is responsible for the sorption properties of non-ionic pollutants (Chefetz *et al.*, 2000; Salloum *et al.*, 2002; Chen *et al.*, 2007). Conversely, several others have suggested that the key role is played by aromatic domains (Mao *et al.*, 2002; Abelman *et al.*, 2005; Golding *et al.*, 2005; Lixia *et al.*, 2011).

The extent to which soil minerals can contribute to this variation remains unclear. This specific point

is the focus of this paper. The potential effects of soil minerals can be surmised, although in the classical sense, SOM plays a key role in sorption of non-ionic compounds. It has been demonstrated that even in soils with high carbon content, clay minerals with 2:1 structure can be as important as SOM in sorption of non-ionic compounds. For example, it has been shown that capacities of the reference smectites to phenanthrene sorption are comparable to those of soil clays containing a significant amount of carbon content (Hundal *et al.*, 2001).

An additional potential effect of soil minerals is their indirect influence on the sorption capacity of SOM through the blocking of SOM sorption sites or by conformational changes in the structures of organic compounds (Pusino *et al.*, 1992; Jones and Tiller 1999; Celis *et al.*, 2006). Thus, it has been suggested that, to some extent, soil minerals are responsible for variations in K_{oc} between soils, although the extent to which soil minerals are responsible for these variations is less certain.

This study was conducted to provide further insight into the relative contribution of soil minerals in the sorption of non-ionic compounds. For this purpose, the sorption of phenanthrene and diuron by twelve soil surface horizons, A11 and A12 before and after HF treatment, was investigated to determine possible effects of clay minerals on K_{oc} variation.

2. Materials and methods

2.1. Soil and chemicals

Sorption studies were conducted on Mollic Haploxeralfs soils from a paddock of approximately 2 hectares (Soil Survey Staff, 1999). The A1 horizons were subdivided into A11 and A12 horizons based on the darker colour of the former.

Diuron and phenanthrene (>99% purity) were purchased from Sigma-Aldrich (Sydney, Australia). High-performance liquid chromatography (HPLC)-grade solvents and calcium chloride were obtained from Merck Pty Ltd. (Victoria, Australia). A stock solution of 1000 mg L⁻¹ of diuron and phenanthrene was prepared in methanol.

2.2. NMR analysis

The soils were HF-treated prior to NMR analysis using the procedure of Skjemstad *et al.* (1994). Solid-state ¹³C cross polarization (CP) NMR spectra were acquired with magic angle spinning (MAS) at a ¹³C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000±100 Hz in a Doty Scientific MAS probe. A 1-ms contact time and a 1-s recycle delay were used, and 4000 transients were collected for each spectrum. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero-filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

2.3. Sorption Experiments

Measurements were conducted in the upper two horizons (approximately 0–20 cm) of six soil cores. Sorption experiments were performed in batch incubation experiments according to OECD guidelines (OECD, 2000). To minimize changes in ionic strength and to avoid dispersion, 0.01 M CaCl₂ was used as a background solution, and 200 mg L⁻¹ HgCl₂ was used as a microbial growth inhibitor (Wolf *et al.*, 1989; Trevors, 1996). For single point measurements, solutions

of soil (1 g) and diuron (1.5 mg L⁻¹, 10 mL) and soil (0.5 g) and phenanthrene (0.8 mg L⁻¹, 100 mL) were shaken end-over-end for 24- and 16-hour periods, respectively. At the end of the equilibrium period, suspensions were centrifuged at 3000 g for 20 minutes, and 1 mL aliquots of the supernatant were filtered through 0.45 mm Teflon filters and analysed.

Diuron and phenanthrene concentrations were determined using an Agilent 1100 series HPLC equipped with a diode array detector and C18 column (250 mm × 4.6 mm internal diameter, 5 µm particle size). The mobile phase was 70% acetonitrile and 30% water, and the flow rate was 1 mL min⁻¹. Diuron and phenanthrene were detected at UV wavelengths of 210 nm 254 nm, respectively. Retention times under these conditions were 4.48 and 15.70 minutes for diuron and phenanthrene, respectively. The detection limit was 0.05 mg L⁻¹ for both compounds. Blanks without diuron and phenanthrene and those without soil were analysed, and appropriate corrections were applied. Sorbed concentrations were calculated from the difference between the initial solution and equilibrium solution concentrations.

2.4. Total Carbon Content

Soils were analysed for total C using a LECO elemental analyser after combustion at 1650 °C and subsequent infrared detection of CO₂ (Tabatabai and Bremner, 1970).

2.5 Results and discussion

Partitioning coefficients (K_d and K_{oc}) are presented in Table 1 for six core soil samples containing diuron and phenanthrene, respectively. Following the destruction of the soil mineral phase by HF treatment, K_{oc} values were calculated again under the precise conditions used for parent materials. These values are

presented in Table 1, and specific physical characteristics of the soil samples are presented in Table 2. For both compounds, K_d values decreased with an increase in soil depth. Therefore, in all cases, K_d values in the second horizons were lower than those in the

first. This result was expected and has been well documented (Fall *et al.*, 2003; Wu *et al.*, 2011; Gao *et al.*, 2007) because SOM is the dominant sorbent phase for non-ionic compounds.

Table 1. Sorption coefficients (K_d and K_{oc}) for each soil horizon for diuron and phenanthrene. Standard deviation shown in brackets. Taken from Ahangar *et al.* (2008).

Core number	Horizon	Depth (cm)	K_d (L kg ⁻¹) (diuron)	K_d (L kg ⁻¹) (phenanthrene)	K_{oc} (L kg ⁻¹ soil C) Before HF (diuron)	K_{oc} (L kg ⁻¹ soil C) After HF (diuron)	K_{oc} (L kg ⁻¹ soil C) Before HF (phenanthrene)	K_{oc} (L kg ⁻¹ soil C) After HF (phenanthrene)
22	A11	0-9	21.3	1458	459 (7)	855 (12)	32000 (3000)	35000 (1000)
22	A12	9-17	10.9	510	583(2)	1560 (80)	27000(700)	49000 (2200)
28	A11	0-5	16.8	1044	473 (2)	1100 (17)	30000 (800)	71000 (3500)
28	A12	5-12	10.7	461	679 (25)	2300 (30)	30000 (3000)	78000 (2000)
30	A11	0-8	17.3	1018	477 (12)	900 (40)	28000 (1200)	45000 (1400)
30	A12	8-19	10.6	389	678 (25)	1600 (90)	25000 (800)	60000 (4000)
33	A11	0-5	17.7	784	428 (5)	1300 (80)	19000 (1000)	55000 (4000)
33	A12	5-18	14.8	348	707 (18)	2500 (90)	16000 (800)	42000 (1500)
35	A11	0-9	17.0	861	452 (2)	900 (40)	23000 (1000)	39000 (500)
35	A12	9-17	8.8	287	579 (15)	1600 (50)	19000 (200)	65000 (2300)
40	A11	0-8	15.0	764	405 (2)	850 (25)	20000 (1000)	43000 (3000)
40	A12	8-18	9.0	318	547 (22)	1100 (30)	20000 (900)	55000 (2700)

After HF treatment, K_{oc} increased an average of 124% and 98% for A11 horizons and 185% and 162% for A12 horizons for diuron and phenanthrene, respectively. The increase in the K_{oc} values after HF treatment for both compounds clearly demon-

strates the effect of the mineral phase on the sorption ability of SOM. However, it is difficult to assess the independent contribution of the mineral phase, SOM functionality and molecular structure on the K_{oc} variation.

Table 2. Some physico-chemical characteristics of soil samples.

Core number	Horizon	Depth (cm)	Clay%	Silt%	Sand%	pH	CEC (Cmol kg ⁻¹)	C content (%)
22	A11	0-9	7.5	27.5	65.0	5.15	17.3	4.6
22	A12	9-17	10.0	30.0	60.0	5.76	15.1	1.9
28	A11	0-5	15.0	27.5	58.0	5.70	18.5	3.6
28	A12	5-12	20.0	25.0	55.0	6.01	16.0	1.6

Core number	Horizon	Depth (cm)	Clay%	Silt%	Sand%	pH	CEC (Cmol kg ⁻¹)	C content (%)
30	A11	0-8	12.5	25.0	63.0	5.65	16.2	3.6
30	A12	8-19	15.0	27.5	57.5	5.81	11.3	1.6
33	A11	0-5	12.5	25.0	63.0	5.86	19.5	4.2
33	A12	5-18	15.0	23.0	63.0	6.09	16.9	2.1
35	A11	0-9	12.5	30.0	57.5	5.25	18.3	3.8
35	A12	9-17	15.0	30.0	55.0	5.80	15.9	1.5
40	A11	0-8	15.0	27.5	57.5	5.70	17.5	3.7
40	A12	8-18	15.0	25.0	60.0	5.83	16.0	1.6

Two primary contributions for the mineral phase of soil to sorption can be considered; however, the direct contribution of soil minerals to sorption is not the focus of our study. SOM has been widely believed to be the main sorbent for non-ionic species (Schwarzenbach *et al.*, 1993; Kile *et al.*, 1995; Fall *et al.*, 2003; Ahangar *et al.*, 2008a; Gao *et al.*, 2007). However, for soils with less than 0.1% organic carbon content by mass, the mineral phase should be considered as a significant sorbate (Karickhoff, 1984; Schwarzenbach *et al.*, 1993). Increases in K_{oc} values after HF treatment indicate that sorptive properties of SOM and accessibility can be strongly influenced by SOM–mineral interaction. In addition, soil clay minerals can affect the sorption characteristics of the entire soil unit by reducing the sorption capacity of organic components. We propose that bound organic compounds with minerals, and in particular, hydrophobic domains of SOM are less accessible to diuron and phenanthrene. Our finding is consistent with that of previous research that proposes the extent of organic matter contribution to the sorption process is influenced by association mechanisms between the mineral phase and soil organic constituents. Therefore, in this condition, the organic phase is less accessible to

organic pollutants (Pusino *et al.*, 1992; Jones and Tiller, 1999). Several researchers have observed that sorption of hydrophobic organic chemicals by humic and fulvic acids are reduced in the presence of aluminium and iron oxides. They hypothesized that strong ligands of solid organic matter with mineral surfaces prevent the organic matter from sorbing the organic pollutants (Schlautman and Morgan, 1993b; Laird *et al.*, 1994).

Moreover, we propose that bound organic matter within the mineral phase can cause reduction in the accessibility of the hydrophobic domains of SOM. Similarly, it has been demonstrated that the association of mineral phase and SOM could result in tight aggregation and limitations in organic matter sorption site accessibility for aqueous-phase organic pollutants (Njoroge *et al.*, 1998).

Figure 1 shows the proportion of K_{oc} in A12 horizons to A11 horizons for phenanthrene and diuron. In most cases, increases in the K_{oc} values for A12 horizons are higher than those for A11 horizons for both compounds. We propose that the higher K_{oc} values in the A12 horizons are due to a higher percentage of clay in A12 horizons as well as loose connection of SOM with clay minerals in A11 horizons.

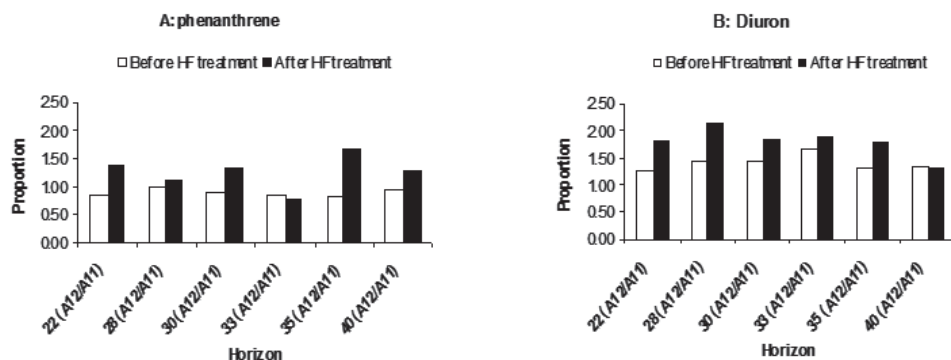


Figure 1. Proportion of A12 Koc to A11 Koc before and after HF treatment for henanthrene (A) and Diuron (B).

Figures 2 and 3 show a connection between K_{oc} alteration before and after HF treatment and particle size. The changes in K_{oc} values can be justified by the percentage of clay minerals: $r^2 = 0.43$, significance level <0.01 and $r^2 = 0.26$, significance level <0.07 , respectively, for phenanthrene and diuron. The weak relationship between K_{oc} alteration and clay minerals indicates that the clay content of soils is an influential factor on K_{oc} variation, in addition to the intimate and complicated association between clay minerals and organic compounds. Therefore,

the effect of organic pollutants on this relationship should be considered.

These findings strongly demonstrate that the extent of soil sorption affinity for the given organic compounds is strongly dependent on the organic matter content. In addition, soil mineral matter exerts influence on alteration of the sorption characteristics of SOM. Although it is not an easy task to evaluate the independent contribution of the mineral phase in the entire sorption process, it is a priority for research in the area of sorption.

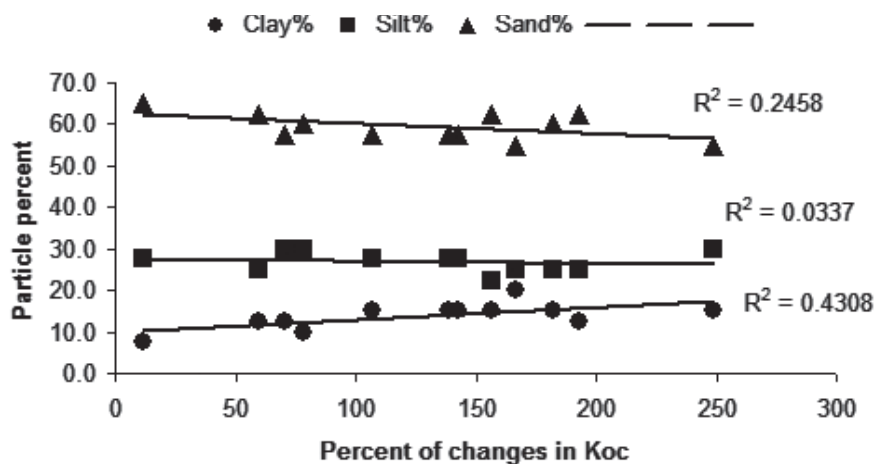


Figure 2. Relationship between percent of sand, silt and clay and changes in K_{oc} before and after HF treatment for phenanthrene.

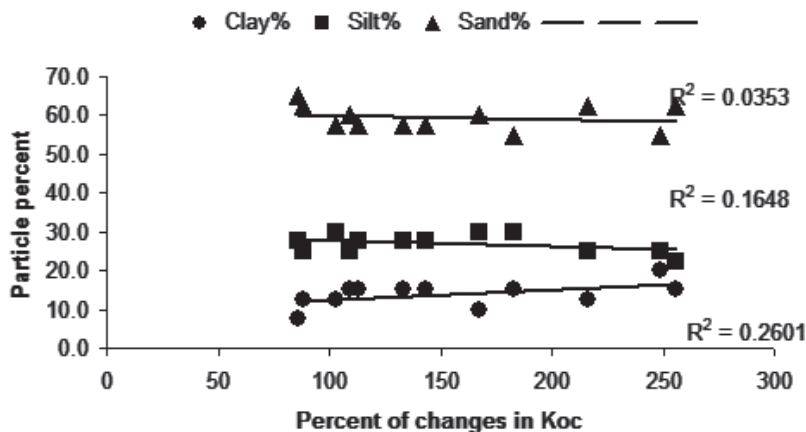


Figure 3. Relationship between percent of sand, silt and clay and changes in Koc before and after HF treatment for diuron.

3. Conclusion

SOM is important in the process of non-ionic compound sorption, although sorption cannot be predictable exclusively from the organic matter content of soils. Improved prediction of sorption of non-ionic compounds in soils requires a better understanding of the relative contribution of mineral and organic soil components to the sorption process. The increased K_{oc} values after HF treatment is higher for the A12 horizons than those for A11 ones. We suggest that alteration of the sorption properties of SOM by the mineral components of soil should be taken into account as the main reason. The findings of this study showed that HF-treatment can increase soil K_{oc} for diuron and phenanthrene, and attributed this to organic matter-mineral interactions that block organic matter sorption sites in the whole soils. Thus it can be suggested that suitable descriptors for the extent of organic matter-mineral interactions would help to improve current K_{oc} -based sorption predictions, which in turn can improve the assessment of risk associated with the presence of non-ionic pollutants in soil.

References

- Abelmann, K., Kleinedam, S., Knicker, H., Grathwohl, P., Kogel-kanber, I. 2005. Sorption of HOC in soils with carbonaceous contamination: Influence of organic-matter composition. *J. Plant Nutr. Soil Sci.* 168, 293-306.
- Ahangar, A.G., Smernik, R.J., Kookana, R.S., Chittlerborough, D.J. 2008. Separating the effects of organic matter-mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. *Chemosphere*. 72, 886-890.
- Celis, R., De Jonge, H., De Jonge, L.W., Real, M., Hermosin, M.C., Cornejo, J. 2006. The role of mineral and organic components in phenanthrene and dibenzofuran sorption by soil. *European journal of soil science*. 57, 308-319.
- Chefetz, B., Deshmukh, A.P., Hatcher, P.G., Guthrie, E.A. 2000. Pyrene sorption by natural organic matter. *Environ. Sci. Technol.* 34, 2925-2930.
- Chen, D., Xing, B., Xie, W. 2007. Sorption of phenanthrene, naphthalene and o-xylene by soil organic matter fraction. *Geoderma*. 139, 329-335.

- Chiou, C.T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. Reactions and movement of organic chemicals in soils. B. L. Sawhney and K. Brown. Madison, WI, Soil Science Society of America. Inc, 1-29.
- Fall, C., Chaouki, J., Chavarie, C., Elena-Ortega, R. 2003. Multivariate study on phenanthrene sorption in soils. *Journal of environmental engineering*. 129, 1030-1040.
- Gao, Y., Xiong, W., Ling, W., Wang, X., Li, Q. 2007. Impact of exotic and inherent dissolved organic matter on sorption of phenanthrene by soils. *Journal of hazardous material*. 140, 138-144.
- Golding, C.J., Smernik, R.J., Birch, G.F. 2005. Investigation of the role of structure domains identified in sedimentary organic matter in the sorption of hydrophobic organic compounds. *Environ . Sci. Technol.* 39, 3925-3932.
- Huang, W., Peng, P., Yu, Z., Fu, J. 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Applied Geochemistry*. 18, 955-972.
- Hundal, L.S., Thompson, M.L., Laird, D.A., Carmo, A.M. 2001. Sorption of phenanthrene by reference smectites. *Environ . Sci. Technol.* 35, 3456-3461.
- Jones, K.D., Tiller, C.L. 1999. Effect of solution chemistry on the extent of binding of phenanthrene by a soil humic acid: A comparison of dissolved and clay bound humic. *Environ . Sci. Technol.* 1999, 580-587.
- Karickhoff, S.W. 1984. Organic pollutant sorption in aqueous system. *J. Hydraul.Eng.* 110, 707-735.
- Kile, D.E., Chiou, C.T., Zhou, H., Li, H., Xu, O. 1995. Partition of nonpolar organic pollutants from water to soil and sediment organic matter. *Environ . Sci. Technol.* 29, 1401-1409.
- Laird, D.A., Yen, P.Y., Koskinen, W.C., Steinheimer, T.R., Dowdy, R.H. 1994. Sorption of atrazine on soil clay components. *Environ . Sci. Technol.* 28, 1054-1061.
- Lixia, J., Mengchang, H., Jinghuan, Z., Xinghui, X. 2011. Norfloxacin sorption to different fractions in sediments from typical water systems in China. *Soil and Sediment Contamination*. 20, 564-580.
- Mao, J.D., Hundal, L.S., Thompson, M.L., Schmidt Rohr, K. 2002. Correlation of poly(methylene)-rich amorphous aliphatic domains in humic substances with sorption of a nonpolar organic contaminant, phenanthrene. *Environ . Sci. Technol.* 36, 929-936.
- Njoroge, K.B.N., Ball, W.P., Cherry, R.S. 1998. Sorption of 1,2,4-trichlorobenzene and tetrachloroethene within an authigenic soil profile: Changes in Koc with soil depth. *Journal of contaminant hydrology*. 29, 347-377.
- OECD, 2000. Adsorption/desorption using a batch equilibrium method, test guideline 106. OECD guidelines for testing chemicals, OECD publications, Paris.
- Pusino, A., Liu, W., Gessa, C. 1992. Influence of organic matter and its clay complexes on metolachlor adsorption on soil. *Pestic. Sci.* 36, 283-286.
- Salloum, M.J., Chefetz, B., Hatcher, P.G. 2002. Phenanthrene sorption by aliphatic-rich natural organic matter. *Environ . Sci. Technol.* 36, 1953-1958.
- Schlautman, M.A., Morgan, J.J. 1993a. Effect of aqueous chemistry on the binding of polycyclic aromatic hydrocarbons by dissolved humic acid. *Environ . Sci. Technol.* 27, 961-969.
- Schlautman, M.A., Morgan, J.J. 1993b. Binding of fluorescent hydrophobic organic probe by dissolved humic substances and organically-coated aluminum oxide surface. *Environ . Sci. Technol.* 27, 2523-2532.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. 1993. Environmental organic chemistry. New York, Wiley-Interscience.

- Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., Newman, R.H. 1994. The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS n.m.r. study. *Aust. J. Soil Res.* 32, 1215-1229.
- Soil Survey Staff. 1999. *Soil Taxonomy*. 2nd ed. United States Department of Agriculture, Natural Resources Conservation Service, Washington DC.
- Tabatabai, M.A., Bremner, J.M. 1970. Use of the Leco automatic 70-second carbon analyzer for total carbon analysis of soils. *Soil Sci.Soc. Am. Proc.* 34,608-610.
- Trevors, J.T. 1996. Sterilization and inhibition of microbial activity in soil. *J.Microbiol.Methods.* 26, 53-59.
- Wolf, D.C., Dao, T.H., Scott, H.D., Lavy, T.L. 1989. Influence of sterilization methods on selected soil microbiological, physical and chemical properties. *J.Environ.Qual.* 18, 39-44.
- Wu, X. M., Li, M., Long, Y.H., Liu, R. X., Yu, Y.L., Fang, H., Li, S. N. 2011. Effects of adsorption on degradation and bioavailability of metolachlor in soil. *Journal of Soil Science and Plant Nutrition.* 11 ,3, 83-97.

