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Effects of maize root exudates and organic acids on the desorption of phenanthrene from soils

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Abstract

The effects of maize root exudates and low-molecular-weight-organic anions (LMWOAs) on the desorption of phenanthrene from eight artificially contaminated soils were evaluated. A significant negative correlation was observed between the amounts of phenanthrene desorbed and the soil organic carbon (SOC) contents ($P < 0.01$), and the influences of soil pH and clay content on phenanthrene desorption were insignificant ($P > 0.1$). Neither maize root exudates nor oxalate and citrate anions influenced desorption of phenanthrene with the addition of NaN_3. A faster phenanthrene desorption occurred without the addition of NaN_3 in the presence of maize root exudates than oxalate or citrate due to the enhanced degradation by root exudates. Without the addition of NaN_3, oxalate or citrate at different concentrations could inhibit phenanthrene desorption to different extents and the inhibiting effect by citrate was more significant than by oxalate. This study leads to the conclusion that maize root exudates can not enhance the desorption under abiotic condition with the addition of NaN_3 and can promote the desorption of phenanthrene in soils without the addition of NaN_3.

Key words: phenanthrene; desorption; low-molecular-weight-organic anions (LMWOAs); root exudates; soils

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Introduction

Root exudation includes the secretion of ions, free oxygen and water, enzymes, mucilage, and a diverse array of carbon-containing primary and secondary metabolites (Bais *et al*., 2006). Up to 40% of the net carbon fixed during photosynthesis can be released into soil (Lynch and Whipps, 1990). Such quantities of organic materials released into soil are likely to produce significant changes in soil properties, particularly for the rhizosphere.

Retention and mobility of organic contaminants in soil are the primary determinants of their environmental fate and behavior, including bioavailability, persistence, and leaching potential. Enhancing desorption would increase bioavailability of the contaminants to plants and soil organisms, and their transportation to ground and surface waters. Due to the important roles of root exudates in mediating the physicochemical and biological properties of soils, a better understanding of the effect of root exudates on sorption and desorption of contaminants is a prerequisite to elucidate the fate of organic contaminants in soils. Previous studies have demonstrated that root exudates increase the desorption of DDT (Luo *et al*., 2006) and DDE (White *et al*., 2003) from soils. However, their effect on the desorption of polycyclic aromatic hydrocarbons (PAHs) from soil has not been reported although PAHs are among the most ubiquitous and toxic hydrophobic organic contaminants (USEPA, 1993; Wilson and Jones, 1993).

In addition, root exudates have been found previously to enhance the degradation of organic compounds by stimulating microbial growth and activity (Hsu and Bartha, 1979; Anderson *et al*., 1993, 1994; Haby and Crowley, 1996; Liste and Alexander, 2000). Early in 1979, Hsu and Bartha found that the mineralization of organophosphate insecticide parathion in soil was stimulated by the addition of bush bean root exudates. Haby and Crowley (1996) reported that the degradation of 3-chlorobenzoate was increased by the addition of a synthetic root exudate solution. Under biotic condition, namely, in the presence of microorganisms, the degradation of organic contaminants will occur and may accelerate the desorption of contaminants from soils.

Low-molecular-weight organic anions (LMWOAs), widely existing in soil, are mainly derived from plant roots, dead plant material, microbial activity and atmospheric inputs (Jones, 1998). They are the primary components of root exudates (Shen *et al*., 1996) and have been implicated in many soil processes including mobilization and uptake of nutrients by plants and microorgasnisms, detoxification of metals by plants, microbial proliferation in the rhizosphere and dissolution of soil minerals (Marschner, 1995).

Therefore, the aim of this study was to investigate the effects of maize root exudates and LMWOAs, oxalate and

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citrate, on the desorption of phenanthrene from soils under abiotic and biotic conditions, respectively, with or without the addition of NaN_3 to inhibit microbial activity. Furthermore, in order to clarify the influence of soil properties on phenanthrene desorption, eight Chinese soils with various physicochemical properties were used in this study.

1 Materials and methods

1.1 Materials

1.1.1 Chemicals and XAD-2 resin

Phenanthrene was purchased from Acros Organics (New Jersey, USA) with a labeled purity of > 99% and used as received. Oxalic acid (pKa_1 = 1.25 and pKa_2 = 4.27) and citric acid (pKa_1 = 3.13, pKa_2 = 4.76, and pKa_3 = 6.40) of reagent grade in sodium salt were from Beijing Chemical Reagent Company, China. Amberlite XAD-2 resin (Supelco, Bellefonte, USA) has a particle size of 20–60 mesh, a surface area of 300 m^2/g and a pore diameter of 90 nm. Before use, the XAD-2 beads were rinsed in succession with methanol, a freshly prepared solution of 0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3 in Milli-Q treated water (10 times for each solution, 10 mL/g XAD). The equilibrated XAD-2 resin was refrigerated as slurry in a glass flask with an excess of 0.01 mol/L $CaCl_2$ solution to prevent dehydration. NaN_3 was added to inhibit microbial activity in the aqueous solution and microbial growth on the XAD-2 resin beads. $CaCl_2$ solution was decanted off to leave the resin as a damp solid before use.

1.1.2 Soils

Eight surface soils (0–20 cm) from different parts of China were used in this study, which were across a range of soil types in China and had various physicochemical properties (Table 1). Soil samples were air-dried, homogenized and ground to pass through a 0.45-mm diameter mesh and maintained at 4°C prior to the chemical analysis and experiments. They were analyzed for pH in soil to water ratio of 1:5 (*W/V*), soil organic carbon (SOC) and dissolved organic carbon (DOC) contents (Nelson and Sommers, 1982) and particle size distribution. The soils were artificially contaminated by spiking with phenanthrene dissolved in acetone and thoroughly mixed to obtain an initial concentration of 10 mg/kg soil. They were stored in an open container under a sterile fume hood for 5 weeks to assure no acetone left and then stored in brown glass containers at 4°C for another 15 weeks. The final phenanthrene concentrations in the spiked soils were then measured.

Soil samples were subjected to Soxhlet extraction. One gram of soil was mixed with 2 g anhydrous Na_2SO_4 in paper extraction thimble, then extracted with 100 mL of dichloromethane/acetone (1:1, *V/V*) for 24 h at a rate of six cycles per hour in a Soxhlet extraction apparatus. The extract was condensed in a rotary evaporator to approximately 10 mL and subsequently concentrated to 1 mL under a stream of nitrogen. The residue was transferred to a column (1 cm internal diameter × 5 cm length) prepared by packing 2 g of silica gel (60–80 mesh), covered by a 2-cm layer of anhydrous Na_2SO_4, and then washed with 15 mL of hexane/dichloromethane (1:1, *V/V*). The eluate was condensed in a rotary evaporator to approximately 5 mL, dried under a stream of nitrogen and dissolved in 1 and 10 mL methanol for analysis by HPLC for the original and spiked soils respectively. The recovery was 93.2%–105.1% (n = 4) for the entire procedure.

1.1.3 Root exudates collection

Root exudates were collected from the culture solution of maize (*Zea mays* L. cv. TY2). The seeds were obtained from Chinese Agricultural University, and surface-sterilized by soaking in a solution of H_2O_2 (3%) for 15 min and then in $Ca(NO_3)_2$ (3.0 mmol/L) for 4 h prior to cultivation. The seedlings were cultivated in culture dishes under growth chamber conditions at a day:night cycle of 16 h:8 h at 25°C:20°C. The plants were allowed to grow for two weeks in nutrient solution (300 mL for 10 seedlings in one dish), which were positioned randomly in the growth chamber and re-randomized once every day. The compositions of the nutrient solution were: KNO_3, $Ca(NO_3)_2$, $MgSO_4$, and $NH_4H_2PO_4$ at 1.5, 1.0, 0.5, and 0.25 mmol/L, respectively; Fe-EDTA, H_3BO_3, $MnSO_4$, $ZnSO_4$, $CuSO_4$, and $(NH_4)_6Mo_7O_{24}$ at 11.9, 11.5, 1.25, 0.2, 0.075, and 0.025 μmol/L. The solution was buffered at pH 5.8 with 2 mmol/L Mes-Tris. Beginning at the 10th day after germination, the culture solution was replaced twice a day with 300 mL distilled and sterilized water in the morning and fresh nutrient solution in the evening. The day-culture solution collected in the evening was filtered through 0.22 μm hydrophilic membranes and used as the source of root exudates. To avoid contamination, the filters had been prewashed with deionized water, methanol and followed by chloroform/methanol/water (1:2:0.8, *V/V/V*), which were then dried at 105°C for 12 h. The filtered root exudates were collected in plastic bottles and stored at –18°C before use. The pH of the root exudates was 6.58 and TOC was 17.8 mg C/L determined by a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann, USA).

1.2 Desorption experiment

Each phenanthrene spiked soil (1 g) was weighed into glass centrifuge tubes with Teflon-lined caps. Maize root exudates or organic anions (citrate and oxalate) at different concentrations (0, 0.0005, 0.001, 0.005, 0.01, 0.05, and 0.10 mol/L) were added in 20 mL of distilled water. NaN_3 solution (200 mg/L) was supplied to inhibit microbial activity. The suspension was adjusted to pH 6.5 with NaOH or HNO_3. The tubes were then sealed and placed on a rotary shaker in the dark at 100 r/min at 20 ± 1°C for 3 d. The samples were centrifuged at 1000 ×g for 30 min and the supernatant from each tube was analyzed for phenanthrene concentration. Triplicates were set up for each soil and treatment. Previous kinetic measurements showed that 48 h was sufficient for phenanthrene to attain the equilibrium desorption from soils.

Assisted desorption was carried out in the presence of XAD-2 which served as an infinite sink for the dissolved

hydrophobic organic compounds. XAD-2 beads (500 mg) were added in each tube. After 3 d desorption, 2.0 g of K_2CO_3 was added to the tube to promote phase separation, the tubes were resealed and vigorously shaken by hand. The XAD-2 beads were then separated from the soils by centrifuging and transferred to a capped vial containing 5 mL of hexane and 0.5 g of anhydrous Na_2SO_4, and the vials were placed on a shaker at 25°C for 24 h. A portion of hexane was then dried under a stream of nitrogen and dissolved in 10 mL of methanol for phenanthrene analysis by HPLC. Recovery of phenanthrene sorbed by XAD-2 was obtained by the beads to quantitatively sorb 20 mL of 500 μg/L phenanthrene followed by desorption. Recoveries ranged from 87.2% to 96.5% (n = 6).

1.3 Kinetic phenanthrene desorption experiment

Kinetic desorption of phenanthrene by maize root exudates, deionized water and 0.001 mol/L/0.01 mol/L citrate or 0.003 mol/L/0.03 mol/L oxalate was carried out according to the procedure described in Section 1.2 with or without the addition of NaN_3 (200 mg/L) to distinguish the influence of microbial activity on desorption. Phenanthrene contents in both solution and soil were measured at various time periods. Phenanthrene concentration in soil was measured after being centrifuged, decanted off the supernatant liquid, freeze-dried and Soxhlet extracted using the method described in Section 1.1.2.

1.4 Phenanthrene analysis

Phenanthrene concentration was determined by an Agilent Technologies 1200 series HPLC (Agilent, USA) using an Eclipse XDB-C_{18} column (5 μm, 4.6 × 150 mm). A mobile phase of methanol/water (90/10, *V/V*) with a flow rate of 1 mL/min, and absorbance wavelength of 254 nm for ultraviolet detector for concentrations ranging from 50 to 1000 μg/L and extinction/emission wavelengths of 280 nm/340 nm for fluorescence detector for concentrations from approximately 0.5 to 100 μg/L were applied.

1.5 Data analysis and statistics

Phenanthrene desorption percentage was calculated by dividing the desorbed phenanthrene content by its initial content in soil. Data were analyzed using the Origin 7.0 software. The *t*-test at the 95% confidence level was used to assess the statistical significance of differences in phenanthrene concentrations. The statistical package used was SPSS (Statistical Package for Social Science) v. 13.0.

2 Results

2.1 Relationship between phenanthrene desorption and soil properties

The original soil phenanthrene concentrations as well as the final concentrations after phenanthrene addition and incubation are listed in Table 1. A significant negative correlation between the amounts of phenanthrene desorbed and soil organic carbon (R = 0.83, P < 0.01) (Fig. 1), indicated that organic carbon in the soils played a predominant role in phenanthrene desorption from soils. Moreover, a negative correlation was also existed between the amounts of phenanthrene desorption and DOC contents (R = 0.786, P < 0.05). The influence of other soil properties was also examined. Soil pH and soil clay content showed negligible effects on phenanthrene desorption from the soils with a correlation coefficient of 0.54 or lower (P > 0.1).

2.2 Effect of maize root exudates on phenanthrene desorption with the addition of NaN_3

As can be seen from Table 2, no significant difference (P > 0.05) was observed between the amounts of phenanthrene desorbed by deionized water and maize root exudates with the total organic carbon content of 17.8 mg C/L. No significant enhanced phenanthrene desorption was

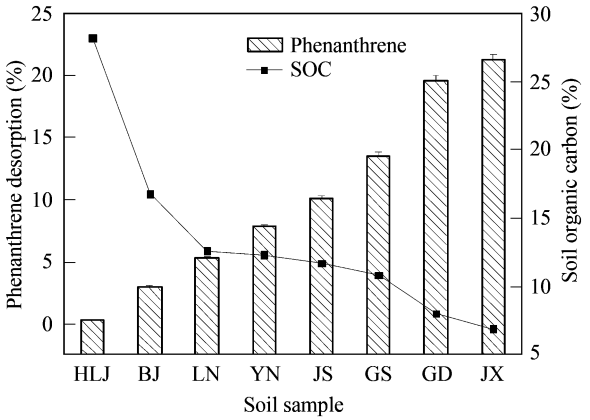

Fig. 1 Relationship between phenanthrene desorption and soil organic carbon content. Error bars represent the standard deviations of triplicate samples. HLJ: Heilongjiang; BJ: Beijing; LN: Liaoning; YN: Yunnan; JS: Jiangsu; GS: Gansu; GD: Guangdong; JX; Jiangxi.

Table 1 Physiochemical properties of the soils

Sampling site	Order	pH	SOC (g/kg)	DOC (mg/kg)	Clay (%)	Silt (%)	Sand[a] (%)	Phe conc. (mg/kg soil)	
								Original	Final[b]
Jiangxi	Ultisol	5.6	6.9	298	42.6	25.5	31.9	0.15	9.05 ± 0.74
Guangdong	Oxisol	5.0	8.0	207	74.8	14.2	11.0	0.07	9.03 ± 0.74
Gansu	Aridisol	8.1	10.8	218	14.7	57.7	27.6	0.19	9.31 ± 0.20
Jiangsu	Alfisol	8.2	11.7	312	21.4	65.5	13.1	0.12	8.53 ± 0.32
Yunnan	Ultisol	7.6	12.3	383	30.9	30.1	39.0	0.05	9.04 ± 0.33
Liaoning	Alfisol	6.0	12.6	361	29.8	40.1	30.1	0.10	8.79 ± 0.19
Beijing	Alfisol	8.0	16.8	548	24.1	43.7	32.2	0.03	8.67 ± 0.67
Heilongjiang	Mollisol	7.7	28.2	852	39.6	56.0	4.4	0.24	9.03 ± 0.15

[a] Soil grain size classification is according to international criterion: clay < 0.002 mm, silt < 0.02 mm, 0.02 mm < sand < 0.2 mm.
[b] Data are expressed as mean ± SE, n = 3.

even observed by maize root exudates at a 5-fold higher concentration (89.0 mg C/L) obtained by freeze-drying (data not shown). In order to observe the influence of root exudates on phenanthrene desorption more obviously, XAD-2 assisted desorption was conducted and the results are listed in Table 3. Because of its strong affinity to aromatic compounds, Amberlite XAD-2 resin served as an infinite sink for the desorbed phenanthrene (Gustafson and Dickhut, 1997; Utvik *et al*., 1999). For XAD-2 assisted desorption, the desorption percentage ranged from 58.25% to 88.07% for deionized water and from 60.90% to 92.25% for exudates, which are much higher than the values without XAD-2 assistance. Statistic analysis showed that there were no significant ($P > 0.05$) differences between the extents of phenanthrene desorption by deionized water and maize root exudates.

Table 2 Desorption percentage of phenanthrene by deionized water and exudates with the addition of NaN_3

Soil origin	Desorption percentage of phenanthrene (%)	
	Deionized water	Exudates
Jiangxi	21.26 ± 0.45	21.57 ± 0.23
Guangdong	20.01 ± 0.43	20.55 ± 0.56
Gansu	12.44 ± 0.62	13.02 ± 0.35
Jiangsu	9.72 ± 0.69	10.18 ± 0.39
Yunnan	6.54 ± 0.24	6.64 ± 0.11
Liaoning	5.30 ± 0.15	5.53 ± 0.41
Beijing	2.47 ± 0.05	2.31 ± 0.16
Heilongjiang	0.89 ± 0.02	0.91 ± 0.03

Data are expressed as mean ± SE, $n = 3$.

Table 3 Desorption percentage of phenanthrene with XAD-2 assistance by deionized water and exudates with the addition of NaN_3

Soil origin	Desorption percentage of phenanthrene (%)	
	Deionized water	Exudates
Jiangxi	66.97 ± 5.14	72.00 ± 2.60
Guangdong	88.07 ± 1.89	92.25 ± 1.42
Gansu	58.25 ± 4.03	68.67 ± 3.34
Jiangsu	72.83 ± 4.79	66.61 ± 3.45
Yunnan	72.63 ± 2.06	72.25 ± 1.14
Liaoning	64.28 ± 2.54	67.85 ± 6.18
Beijing	63.98 ± 1.41	60.90 ± 2.20
Heilongjiang	73.09 ± 1.29	74.61 ± 1.18

Data are expressed as mean ± SE, $n = 3$.

2.3 Effect of LMWOAs on phenanthrene desorption with the addition of NaN_3

LMWOAs as the most primary components of root exudates have been demonstrated to enhance the desorption of some organic contaminants from soils (White *et al*., 2003; Luo *et al*., 2006). Therefore, the desorption of phenanthrene from the soils by citrate and oxalate was conducted and the results are given in Table 4. Citrate and oxalate at all the tested concentrations did not significantly enhance phenanthrene desorption from the soils ($P > 0.05$) with very limited exceptions found in Jiangsu, Yunnan, and Liaoning soils with oxalate at 0.05 mol/L. Oxalate is highly reactive with some soil fractions such as metal oxides and clay minerals (Stumm, 1986; Bhatti *et al*., 1998). The addition of oxalate can result in the change of soil morphology and influence the phenanthrene desorption from soils. Only very limited scatter data were obtained which could be due to the differences in the physico-chemical properties of the soils.

2.4 Kinetic desorption of phenanthrene by root exudates and LMWOAs

With the addition of NaN_3, the percentage of phenanthrene desorbed from the soil was nearly constant at different time for all the extractants as displayed in Fig. 2 by taking Jiangsu soil as an example. Very similar results were obtained for all studied soils. However, a significant decrease in desorption without the addition of NaN_3 was observed for all the extractants except for 0.01 mol/L citrate (Fig. 2). Phenanthrene contents in the soils were measured at different time intervals and added with the phenanthrene contents in solution to check whether there was any phenanthrene loss. The sum of the total phenanthrene was constant and around 100% recovery in the presence of NaN_3 for all extractants, while it decreased

Table 4 Desorption percentage of phenanthrene under different concentrations of citrate and oxalate with the addition of NaN_3

Soil origin	Desorption percentage of phenanthrene (%)					
	0 mol/L	0.001 mol/L	0.005 mol/L	0.01 mol/L	0.05 mol/L	0.1 mol/L
	Citrate					
Jiangxi	21.26 ± 0.45	22.25 ± 0.32	21.24 ± 0.24	22.59 ± 1.13	21.85 ± 0.30	21.03 ± 0.63
Guangdong	20.01 ± 0.43	18.26 ± 0.17	19.11 ± 0.64	18.65 ± 0.45	20.22 ± 0.45	20.63 ± 0.33
Gansu	12.44 ± 0.62	12.57 ± 0.43	12.41 ± 0.20	11.89 ± 0.02	11.94 ± 0.14	12.24 ± 0.35
Jiangsu	9.72 ± 0.69	9.71 ± 0.21	10.26 ± 0.34	10.57 ± 0.02	10.59 ± 0.20	10.55 ± 0.59
Yunnan	6.54 ± 0.24	6.34 ± 0.39	6.88 ± 0.56	6.97 ± 0.41	9.86 ± 0.28	8.01 ± 0.41
Liaoning	5.30 ± 0.15	5.36 ± 0.18	5.40 ± 0.39	5.37 ± 0.09	5.86 ± 0.40	5.71 ± 0.31
Beijing	2.47 ± 0.05	2.41 ± 0.17	2.49 ± 0.13	2.55 ± 0.20	2.47 ± 0.29	2.43 ± 0.20
Heilongjiang	0.89 ± 0.02	0.91 ± 0.07	0.93 ± 0.04	0.91 ± 0.09	0.94 ± 0.03	0.84 ± 0.08
	Oxalate					
Jiangxi	21.26 ± 0.45	22.12 ± 0.28	21.54 ± 0.30	22.25 ± 0.35	22.18 ± 0.30	20.99 ± 0.41
Guangdong	20.01 ± 0.43	20.07 ± 0.28	19.79 ± 0.31	20.00 ± 0.45	20.87 ± 0.22	19.83 ± 0.35
Gansu	12.44 ± 0.62	12.59 ± 0.38	12.62 ± 0.20	12.64 ± 0.13	12.38 ± 0.03	12.30 ± 0.25
Jiangsu	9.72 ± 0.69	10.64 ± 0.19	10.26 ± 0.29	10.23 ± 0.26	12.90 ± 0.19	9.26 ± 0.18
Yunnan	6.54 ± 0.24	6.65 ± 0.15	6.47 ± 0.28	6.53 ± 0.42	8.75 ± 0.25	6.17 ± 0.14
Liaoning	5.30 ± 0.15	5.39 ± 0.17	5.30 ± 0.06	5.31 ± 0.16	8.45 ± 0.11	4.38 ± 0.26
Beijing	2.47 ± 0.05	2.46 ± 0.18	2.54 ± 0.15	2.53 ± 0.18	2.57 ± 0.23	2.46 ± 0.17
Heilongjiang	0.89 ± 0.02	0.91 ± 0.09	0.93 ± 0.06	0.92 ± 0.06	0.99 ± 0.03	0.84 ± 0.02

Data are expressed as mean ± SE, $n = 3$.

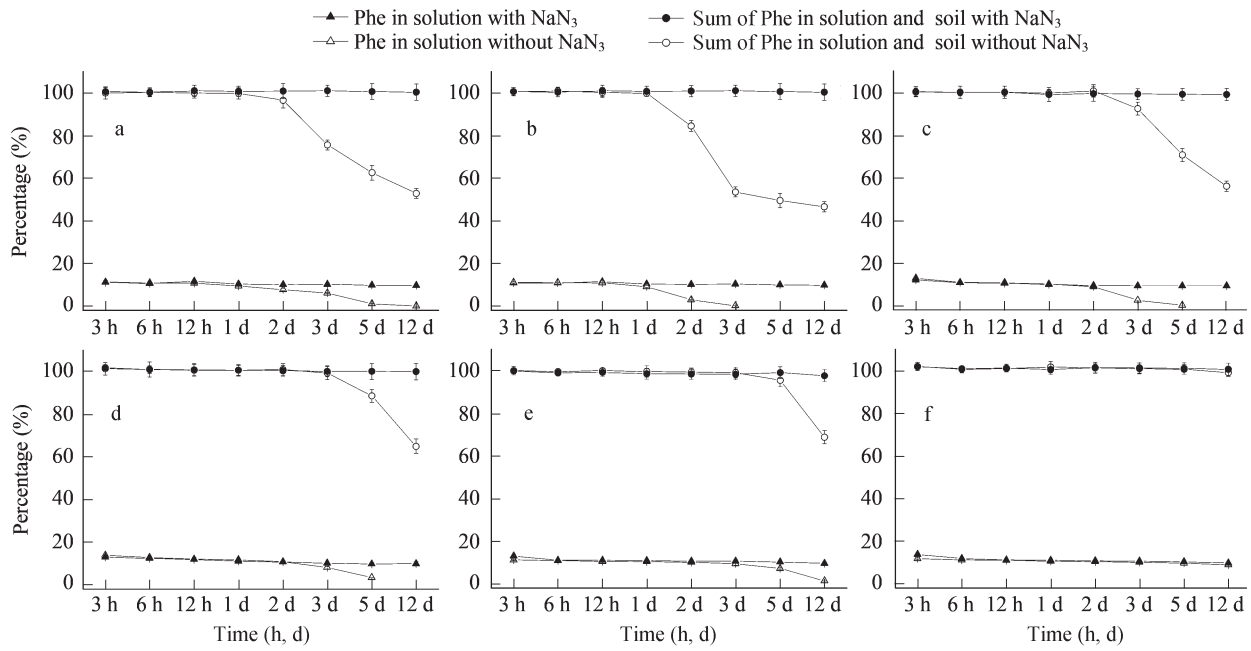

Fig. 2 Phenanthrene content in percentage to the initial soil phenanthrene content in the presence of a (water), b (exudates), c (0.003 mol /L oxalate), d (0.03 mol/L oxalate), e (0.001 mol /L citrate) and f (0.01 mol /L citrate) for Jiangsu soil. Error bars represent the standard deviations of triplicate samples.

significantly over time without the addition of NaN_3 when root exudates or oxalate were used as the extractants (Fig. 2), an obvious evidence of phenanthrene loss from the soil-solution system in addition to phenanthrene desorption.

3 Discussion

Desorption of phenanthrene from the soils was significantly related to SOC contents, which is consistent with the general view that SOC plays a dominant role in the sorption/desorption of hydrophobic organic compounds (HOCs) on/from soils (Pignatello *et al*., 1993; Cornelissen *et al*., 1998; Morillo *et al*., 2004). A negative correlation was obtained between the amounts of phenanthrene desorbed and soil DOC contents ($R = 0.786$, $P < 0.05$). This result seemed to be contrary to the previous work in which DOC in soil was observed to enhance the dissolution of atrazine and prometryn (Seol and Lee, 2000) and DDT and its metabolites (Tao *et al*., 2004) from soil. Further analysis found a positive correlation between SOC and DOC contents ($R = 0.961$, $P < 0.001$). Therefore, the negative relationship between phenanthrene desorption and soil DOC could be attributed to the dynamic equilibrium between SOC and DOC in the soils (Antoniadis and Alloway, 2002).

The results of this study suggest that either maize root exudates or oxalate/citrate do not influence phenanthrene desorption from the soils in the presence of NaN_3. This is different from the previous work in which maize root exudates (42.3 mg C/kg) were observed to enhance the desorption of DDT and DDE from soils (Luo *et al*., 2006). Such difference is perhaps ascribed to the differences of contaminant properties and further researches are necessary to elucidate the mechanism. Without the addition of NaN_3, maize root exudates promoted phenanthrene desorption while oxalate and citrate inhibited phenanthrene desorption, which could contribute to the degradation of phenanthrene when root exudates were used for desorption. Moreover, a faster loss of phenanthrene occurred for maize root exudates than for deionized water, oxalate and citrate, further suggesting phenanthrene degradation happened in the presence of exudates. Phenanthrene degradation can contribute to the effect of phenolic substrates and enzymes released by root exudates. Preliminary results have indicated that enzyme activity is generally higher when root exudates exist (Badalucco and Kuikman, 2001) and phenolic substrates released by plant roots can act as an inducer of PAH metabolism by stimulating PAH dioxygenase activity (Chen and Aitken, 1999; Kamath *et al*., 2004).

It is interesting to note that phenanthrene desorption in the absence of NaN_3 was inhibited by oxalate and citrate, especially by 0.01 mol/L citrate. Although such observation has not been reported, it is in line with the previous statements that LMWOAs represented a readily utilizable C source for microorganisms (van Hees *et al*., 2002) and inhibited the degradation of aromatic compounds (Duetz *et al*., 1994; Mason, 1994; Dal *et al*., 2002). Dal *et al*. (2002) have also reported that the consumption of aromatic compounds can be delayed in the presence of LMWOAs until the labile substrates have been depleted. To further substantiate the above observation, phenanthrene desorption was carried out with the same amount of C supplied by oxalate and citrate or different amount of C by the same organic anion at different concentrations (Fig. 2). Phenanthrene in 1 g soil at the concentration of 10 mg/kg can supply 7.8×10^{-7} mol C source, whereas 20 mL of 0.001 mol/L sodium citrate or 0.003 mol/L sodium oxalate

can supply 1.2×10^{-4} mol C source and 20 mL of 0.01 mol/L sodium citrate or 0.03 mol/L sodium oxalate can supply 1.2×10^{-3} mol C source. We can find that the greater amount of C supplied with citrate or oxalate, the less amount of phenanthrene lost (comparing Fig. 2c to 2d and 2e to 2f). This observation confirmed that soil microorganisms would selectively consume the C source supplied by oxalate or citrate. When the same amount of C supplied by oxalate and citrate, less phenanthrene lost in the presence of citrate than oxalate (comparing Fig. 2c to 2e and 2d to 2f), which implies that different LMWOA anions results in different effects on phenanthrene degradation.

The present work demonstrates that maize root exudates, oxalate and citrate do not influence desorption of phenanthrene from the soils under the abiotic condition with the addition of NaN_3 to inhibit the microbial activity. However, maize root exudates promoted phenanthrene desorption under the biotic condition without the addition of NaN_3. Oxalate and citrate can inhibit phenanthrene desorption under the biotic condition in different degrees. These results are preliminary important for understanding the behavior of PAHs in soils especially in rhizosphere soil due to the importance of root exudation and microbial activities in the rhizosphere.

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