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Electron transfer capacity of soil dissolved organic matter and its potential impact on soil respiration

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Abstract
Purpose Soil dissolved organic matter (DOM) as the labile fraction of soil organic carbon (SOC) is able to facilitate biogeochemical redox reactions effecting soil respiration and carbon sequestration. In this study, we took soil samples from 20 sites differing in land use (forest and agriculture) to investigate the electron transfer capacity of soil DOM and its potential relationship with soil respiration.
Materials and methods DOM was extracted from 20 soil samples representing different land uses: forest (nos. 1–12) and agriculture (nos. 13–20) in Guangdong Province, China. Chronoamperometry was employed to quantify the electron transfer capacity (ETC) of the DOM, including electron acceptor capacity (EAC) and electron donor capacity (EDC), by applying fixed positive or negative potentials to a working electrode in a conventional three-electrode cell. The reversibility of electron accepting from or donating to DOM was measured by applying switchable potentials to the working electrode in the electrochemical system with the multiple-step potential technique. Carbon dioxide produced by soil respiration was measured with a gas chromatograph.
Results and discussion Forest soil DOM samples showed higher ETC and electron reversible rate (ERR) than agricultural soil DOM samples, which may be indicative of higher humification rate and microbial activity in forest soils. The average soil respiration of forest soil (nos. 1–12) and agricultural soil (nos. 13–10) was 26.34 and 18.58 mg C g^{-1} SOC, respectively. Both EDC and EAC of soil DOM had close relationship with soil respiration ($p<0.01$). The results implied that soil respiration might be accelerated by the electroactive moieties contained in soil DOM, which serve as electron shuttles and facilitate electron transfer reactions in soil respiration and SOC mineralization.
Conclusions DOM of forest soils showed higher ETC and ERR than DOM of agricultural soils. As soil represents one of the largest reservoirs of organic carbon, soil respiration affects C cycle and subsequently CO_2 concentration in the atmosphere. As one of the important characteristics of soil DOM related to soil respiration, ETC has a significant impact on greenhouse gas emission and soil carbon sequestration but has not been paid attention to.

Keywords Electron reversible rate · Electron transfer capacity · Soil dissolved organic matter · Soil organic carbon · Soil respiration

1 Introduction

Dissolved organic matter (DOM) as a mixture of various organic molecules with different structures, sizes, and functional properties represents one of the most mobile and reactive organic matter fractions in the ecosystem (Zsolnay 2003). DOM is widely distributed in the natural ecosystem, where it plays an important role in carbon biogeochemistry coupling terrestrial and aquatic carbon pools (Chen et al. 2002). DOM consists of low molecular weight substances, such as organic acids and amino acids, as well as complex molecules of high molecular weight, such as humic substances and enzymes (Yuan et al. 2011).

Recently, DOM as redox-active natural organic compounds has drawn a great deal of interest because of its capability of mediating biogeochemical redox reactions associated with microbially catalyzed metal reduction (Lovley et al. 2000),

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the fate of environmental pollutants (Blodau et al. 2009; Zhang and Weber 2009), and cycling of soil carbon (Heitmann et al. 2007). The redox properties of DOM, including the electron acceptor capacity (EAC) and electron donor capacity (EDC) of DOM and its reversibility in electron transfer, have been widely investigated with electrochemical techniques (Aeschbacher et al. 2010; Bauer et al. 2007; Nurmi and Tratnyek 2002).

The increase of greenhouse gas emission and the resulted global climate change necessitate a comprehensive understanding of carbon cycling. Soil is a major carbon source for CO_2 in the atmosphere because the organic matter stored in the soil represents one of the largest reservoirs of organic carbon on a global scale (Ni et al. 2012; Silveira et al. 2008). Soil organic carbon (SOC) as a mixture of dead plant and animal-derived substances with highly variable physical and chemical properties is controlled by a complex of biogeochemical processes (Roy et al. 2010). Soil DOM is regarded as the labile fraction of SOC which is especially important in that it is readily degradable and is the major energy source for microorganisms (Hu et al. 1997). Soil DOM was found to be able to reflect the effects of land use on SOC and be related to soil respiration and the turnover rate of SOC (Haynes 2000). Soil respiration of SOC as a straightforward indicator can reflect soil stability due to its more direct expression of potential microbial activities. Although it is known that soil DOM can act as a redox buffer or electron shuttle for microbial respiration, thus playing an important role in soil carbon dynamics, no effort has been made to investigate the potential relationship between the electron transfer capacities (ETCs) of soil DOM and soil respiration.

The aim of this work was to probe the ETC, including EAC and EDC, of soil DOM with different land uses. Chronoamperometry (CA) measurements were performed to evaluate the ETC of soil DOM, and multiple-step potential technique was applied to measure the reversibility of electron transfer. Furthermore, ETC as a significant parameter of soil DOM might impact soil respiration, and therefore, the relationship between ETC and soil respiration was explored. It is expected that results from this study can lead to better understanding of impacts of soil DOM ETC on soil biogeochemical redox reactions, greenhouse gas emission, and soil carbon sequestration.

2 Materials and methods

2.1 Soil samples

Soil samples were collected from 20 sampling sites with different land uses: forest (nos. 1–12) and agriculture (nos. 13–20) in Guangdong Province, China. These sites were described, and the soils were characterized in Table 1. Soil parent material of all sites was a granitic rock. All soil samples were taken from the 0–20-cm layer.

After visible roots and plant fragments were removed, soil samples were air-dried, passed through a 2-mm sieve, and stored at room temperature in airtight, polyethylene containers until analyzed. Particle size fraction standard proposed by USDA was used as follows: 53 to 2,000 μm for sand, 2 to 53 μm for silt, and smaller than 2 μm for clay. Soil pH was measured with a water/dry soil ratio of 2.5:1 using a pH meter (Bi et al. 2010). Total organic C (TOC) was determined with the potassium dichromate method (Bi et al. 2010). Total N (N_{tot}) was determined using the semimicro Kjeldahl method. Particle size distribution was analyzed using the hydrometer method (Chen et al. 2010).

2.2 Extraction and analysis of soil DOM

As described by Yuan et al. (2011) and Chen et al. (2004), soil DOM was extracted with distilled water by preparing the soil with a solid/water ratio of 1:5 (*w*/*v*, dry weight basis) and then shaking the samples at 200 rpm in a reciprocal shaker for 16 h at 20 °C. The suspension was subsequently centrifuged at 12,000×*g* for 20 min, and the supernatant was filtered through a 0.45-μm sterile membrane (GN-6 Metrice, Gelman Sciences, Ann Arbor, MI, USA). TOC of the soil DOM was measured using a TOC digital reactor block (DRB200, HACH, USA) equipped with a spectrophotometer (DR2700, HACH, USA). After diluting to 50 mg C L^{-1}, the soil DOM was stored at 4 °C before use.

Electrochemical experiments were performed using the electrochemistry workstation CHI660D (Chenhua Co. Ltd., Shanghai, China) with a conventional three-electrode cell at ambient temperature. A graphite plate with a projected surface area of 17.5 cm^2 was used as the working electrode, and Pt net and Hg/Hg_2Cl_2 electrodes, as the counter and reference electrodes, respectively. Quantitatively, ETC is the mole equivalent of electrons transferred from a donor or to an acceptor per gram carbon of soil DOM and is determined by integrating the peak current of the amperometric response at the graphite working electrode over time. CA measurements were performed to evaluate the EDC and EAC of soil DOM in a nitrogen-saturated phosphate buffer solution (pH=7.0). Soil DOM was transferred to the gastight electrochemical cell, and EDC was measured at a positive potential of +0.5 V (vs. Hg/Hg_2Cl_2), while EAC was measured at a negative potential of −0.6 V (vs. Hg/Hg_2Cl_2) (Yuan et al. 2011). The reversibility of electron accepting from or donating to DOM was measured by applying switchable potentials to the working electrode in the electrochemical system with a multiple-step potential technique. The details were as follows: the diluted soil DOM was transferred to a gastight electrochemical cell and completely reduced at a negative potential of −0.6 V (vs. Hg/Hg_2Cl_2) and then completely

Table 1 Coordinates, land use type, and chemical and physical properties of the soil samples

Soil sample	Coordinates		Land use type	pH	TOC (g kg^{-1})	DOC (mg L^{-1})	N_{tot} (g kg^{-1})	Sand	Silt	Clay
No.	Latitude (N)	Longitude (E)						(%)		
1	23°12′	115°45′	Forest land	4.84	12.88	100	1.09	23.30	55.18	21.52
2	24°56′	112°59′		4.52	46.40	128	3.42	60.43	23.83	15.74
3	23°17′	114°22′		4.32	41.76	145	2.84	52.57	20.75	26.68
4	24°48′	112°52′		4.51	65.20	180	1.57	58.64	34.00	7.36
5	23°18′	114°07′		5.68	12.41	145	1.19	76.81	12.11	11.08
6	24°11′	116°11′		4.02	117.7	336	6.24	24.27	48.05	27.68
7	24°12′	116°22′		4.02	28.65	265	1.52	29.58	34.11	36.31
8	22°28′	111°21′		4.36	30.51	190	3.56	55.02	26.21	18.77
9	22°33′	111°10′		4.59	8.76	55	0.61	40.04	23.11	36.85
10	24°48′	113°20′		6.09	20.53	159	1.77	56.76	13.91	29.33
11	25°15′	114°12′		4.57	22.68	202	1.09	37.30	26.57	36.13
12	23°57′	116°35′		4.82	22.16	64	1.58	53.30	25.40	21.30
13	22°35′	113°17′	Agricultural land	6.44	20.19	59	1.01	32.38	31.29	36.33
14	22°15′	112°52′		6.36	11.48	55	1.12	35.16	41.93	22.91
15	23°11′	111°47′		4.20	10.44	50	0.81	39.65	4.94	55.41
16	22°24′	112°50′		4.93	31.67	122	2.44	40.57	22.28	37.15
17	23°32′	114°03′		5.50	11.43	100	1.12	61.83	17.71	20.46
18	23°16′	113°38′		6.67	21.17	90	1.91	35.88	35.54	28.58
19	23°55′	116°39′		4.17	29.12	125	1.53	33.82	20.78	45.40
20	22°04′	112°26′		5.67	6.43	233	0.64	68.72	17.92	13.36

reoxidized at a positive potential of +0.5 V (vs. Hg/Hg_2Cl_2). The whole process was repeated for at least three times, and the electrochemical workstation recorded the current responses with time. The reversibility of electron transfer, termed as electron reversible rate (ERR), was mathematically expressed as (Yuan et al. 2012) follows:

$$\mathrm{ERR}(\%) = \frac{\mathrm{EAC}_2 + \mathrm{EAC}_3 + \cdots + \mathrm{EAC}_n}{(n-1)\mathrm{EAC}_1} \times 100\%$$

where EAC_1 is the EAC value of the first cycle, and EAC_n is that of the nth cycle (n=3 in this study).

Three-dimensional excitation/emission matrix (3DEEM) fluorescence spectroscopy was used to determine the functional groups of the extracted soil DOM. The 3DEEM spectra of soil DOM were recorded with a fluorescence spectrophotometer (Model F-4600, Hitachi, Japan) equipped with a 150-W xenon arc lamp as the excitation source. A PMT voltage of 700 V and an automatic response time were applied. Spectra were recorded using 5-nm excitation and emission slits. Wavelengths were set from 200 to 600 nm for both excitation and emission. Samples were kept at constant temperature (20±1 °C in water bath) before being placed into the quartz cells. The Sigma Plot software was used to handle the EEM data.

2.3 Soil respiration rate

Soil sample (20 g) was put in a vessel with 100 mL headspace above, and double-distilled water was added to rewet all the soils to a constant percentage of water holding capacity. Incubation was carried out in triplicate for each soil sample at 25±1 °C for 20 days. During incubation, soil moisture was maintained with double-distilled water daily when needed. Gas in the headspace was sampled at days 1–7, 10, 15, and 20. At each sampling day, immediately after the vessel was sealed with a butyl rubber stopper and aluminum crimps, a 200-μL syringe was used to take the 0 h gas sample from the headspace, and 2 h later, another gas sample was taken before the bottle was unsealed. CO_2 concentration in the gas samples was measured with a gas chromatograph (Tianmei GC7500, Shanghai) equipped with a flame ionization detector. Temperatures of the column and the detector were 80 and 360 °C, respectively. High purity nitrogen served as the carrier gas (18 mL min^{-1}). Daily respiration rate was the amount of CO_2 produced normalized to SOC and time (2 h). Soil respiration as the amount of mineralized

carbon during the 20-day incubation was calculated by integrating the respiration rate over time (20 days) using the Origin 8.0.

2.4 Statistical analysis

Data from this study were analyzed with the statistical package SPSS version 16.0 for PC Windows (SPSS, Inc., Chicago, IL). Correlation between ETC and soil respiration was performed using the Pearson correlation procedure. Statistical significance of the correlation was evaluated with ANOVA. Results were reported as mean ± standard deviation unless otherwise noted.

3 Results and discussion

3.1 ETC of soil DOM

In the present study, EDC was in the range of 5.41–15.42 $\mu mol_{e^-} g^{-1}$ C (Fig. 1a), and EAC was in the range of 119.60–543.13 $\mu mol_{e^-} g^{-1}$ C (Fig. 1b). The higher EAC compared to the corresponding EDC for all DOM samples indicates that DOM is highly oxidized. The average EDC and EAC of forest soil (nos. 1–12) DOM were 10.75 and 337.29 $\mu mol_{e^-} g^{-1}$ C, respectively. However, those of agricultural soil (nos. 13–10) DOM were 9.64 and 231.63 $\mu mol_{e^-} g^{-1}$ C, respectively. Averagely, forest soil DOM has a higher ETC than agricultural soil DOM (Fig. 1), which was in accordance with the differences in TOC and DOC (Table 1). The great variability could be due to differences in organic matter quality and also be caused by different land uses, vegetation type, and other factors. To date, considerable evidence has shown that containing electroactive groups such as quinone moieties, DOM contributes to biogeochemical redox processes as an electron mediator (Cory and Mcknight 2005; Heitmann et al. 2007; Nurmi and Tratnyek 2002). It has been pointed out that land use changes can affect soil microbial activity and the chemical nature of SOC through changing the rates of aromatization or humification (Fontaine et al. 2007). A higher ETC may be indicative of higher humification rate and microbial activity in forest soils (Liang et al. 1998). The ability of soil DOM to shuttle electrons from donors to acceptors was mainly due to the electroactive moieties (Scott et al. 1998), which are ubiquitous in living cells, extracellular material, humic substances, and dissolved organic matter (Cory and Mcknight 2005).

DOM can be reversibly oxidized and reduced (Aeschbacher et al. 2010; Yuan et al. 2012), by which electron transfer is sustained, and reversibility through multiple reduction–oxidation cycles is a key requirement for environmentally sustainable ETC (Ratasuk and Nanny 2007). The percentage of electrons still involving in the next redox cycle can be evaluated with ERR. Three representative soil samples (nos. 1, 6, and 12) with low, medium, and high ETC were selected to evaluate the ERR of their DOM. As shown in Fig. 2, all the EACs from the second and third cycles were smaller than those from the first cycle, and ERRs of soil nos. 1, 6, and 12 were 48.15, 60.23, and 67.73%, respectively, which indicated that only part of the electrons was recycled. Numerous studies have suggested that the electroactive quinone moieties are the main redox-active groups in DOM (Nurmi and Tratnyek 2002; Ratasuk and Nanny 2007). Although there may be other non-quinone redox-active moieties in DOM, those groups have been shown to have no reversibility in electron transfer (Uchimiya and Stone 2009).

3.2 Fluorescence spectroscopy of soil DOM

While the role of DOM as electron mediators has been demonstrated, more knowledge on DOM as an electron mediator would result in better understanding of the structural components responsible for its redox behavior. Studies employing electron spin resonance (Scott et al. 1998) and fluorescence spectroscopy (Klapper et al. 2002) have provided evidence for the presence of electroactive moieties in soil DOM, and these moieties are believed to be the main contributor to the ETC of

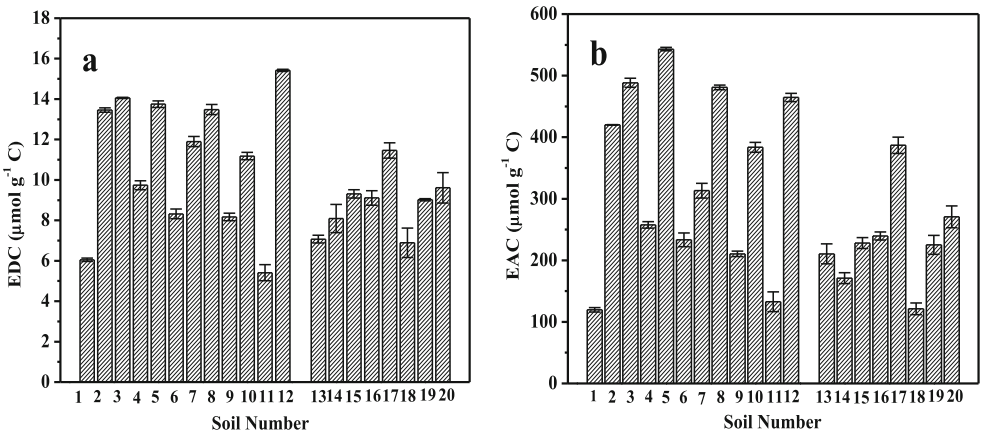

Fig. 1 Electron donor capacity of the soil DOM in aqueous solution at the applied potentials of +0.5 V (vs. Hg/Hg_2Cl_2) (**a**) and electron acceptor capacity of the soil DOM in an aqueous solution at the applied potentials of −0.6 V (vs. Hg/Hg_2Cl_2) (**b**); data in the figure are means (n=3); the *bars* represent standard deviation of the means

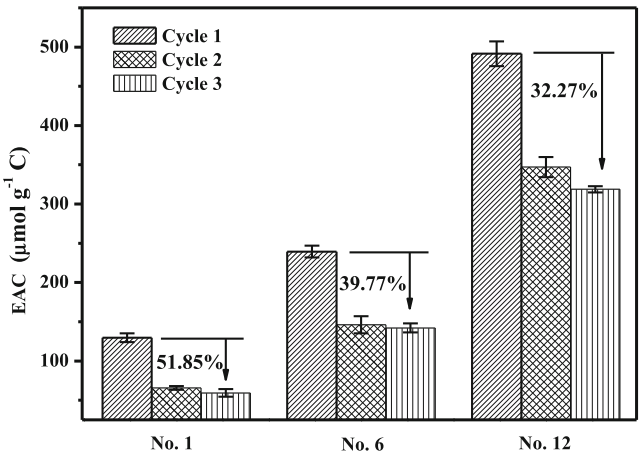

Fig. 2 Electron reversible rate of the soil DOM of the representative soil samples: nos. 1, 6, and 12; data in the figure are means (n=3); the *bars* represent standard deviation of the means

soil DOM. Therefore, different ETCs among the soil samples were probably due to their differences in electroactive group content (Cervantes et al. 2000).

Fluorescence spectroscopy was used to obtain the spectroscopic fingerprints of the three representative soil samples. Spectroscopic fingerprints can give us information on structural differences which can help further explain differences in ETC. Two distinct fluorescence peaks at similar excitation (Ex)/emission (Em), but with different intensities, were observed for the three samples (Fig. 3). As shown, for soil no. 1 with a lower capacity and reversibility of electron transfer as indicated by its ETC, a fluorescence peak appeared at Ex 270 nm/Em 425 nm, and another showed at Ex 330 nm/Em 420 nm with intensity of 1.017 and 1.023, respectively (Fig. 3a). For soil no. 6, peaks appeared at Ex 265 nm/Em 420 nm and Ex 325 nm/Em 415 nm with intensity of 1.469 and 1.432 (Fig. 3b). Higher fluorescence peak intensity (5.601 and 2.993) was observed for soil no. 12 with peaks showing at Ex 240 nm/Em 405 nm and Ex 300 nm/Em 405 nm, respectively (Fig. 3c). After comparing the spectra of DOM with those of model quinines (Cory and Mcknight 2005), it can be told that the majority of fluorophore moieties contained in DOM were quinone-like fluorophores. Stronger peak intensity was obtained for samples with higher ETC, suggesting a potential relationship between the fluorophores in soil DOM and the ETC of soil DOM.

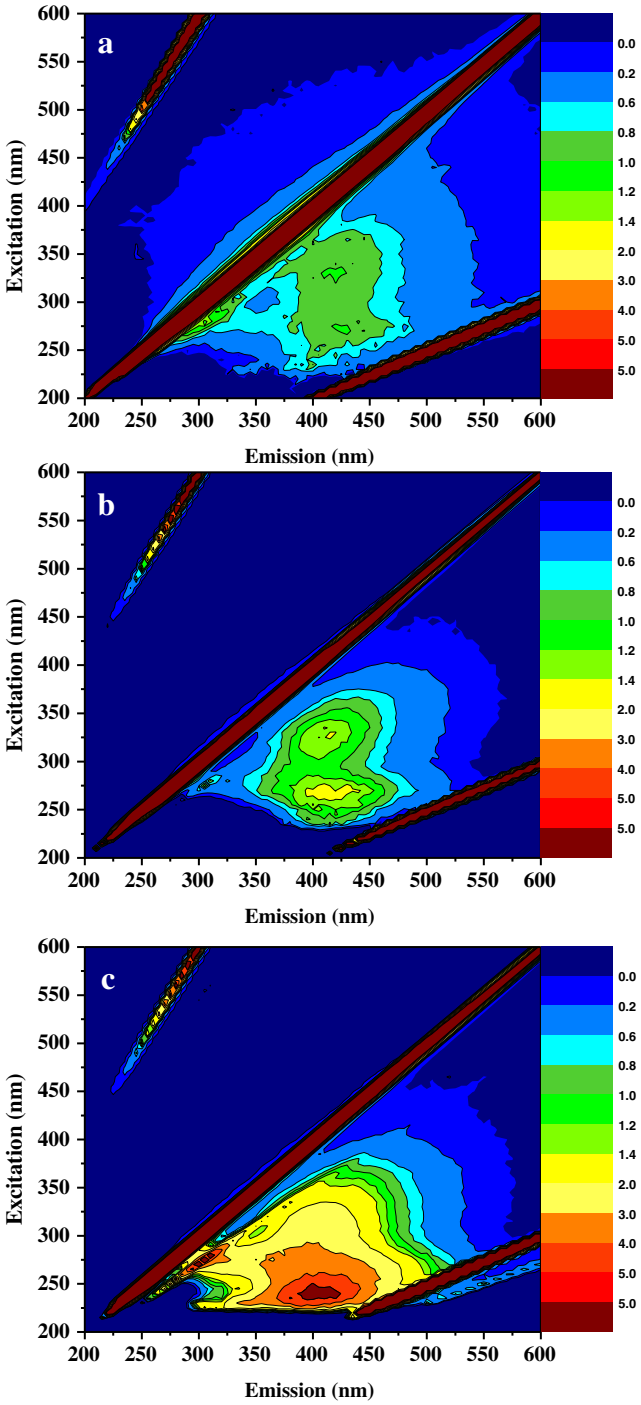

Fig. 3 Three-dimensional excitation/emission matrix plots of the soil DOM of the representative soil samples: nos. 1 (**a**), 6 (**b**), and 12 (**c**)

3.3 Respiration rate of SOC

The respiration rate of all the 20 soil samples changed significantly during the first week and, after that, remained stable (Fig. 4). The inherent SOC was the substance for the microbial metabolism, and microbial activity was higher with richer SOC in the first week and then decreased to a constant level. Soil respiration during the incubation period varied greatly among the soil samples with a range of 13.44–37.79 mg C g^{-1} SOC (Fig. 4e). The average soil respiration of forest soil (nos. 1–12) and agricultural soil (nos. 13–10) was 26.34 and 18.58 mg C g^{-1} SOC, respectively. Moreover, forest soils which on average have a higher DOC also had a

higher respiration rate than agricultural soils (Table 1, Fig. 4e).

SOC can be compartmentalized into different pools, such as the labile pool and the recalcitrant pool based on their reactivity (Rovira and Vallejo 2003). The labile fraction of SOC is largely comprised of chemically labile compounds such as proteins, nucleic acids, and polysaccharides, while the recalcitrant fraction mainly consists of compounds that are resistant to acid hydrolysis, such as aromatic, humified components and long-chain aliphatics (Rovira and Vallejo 2003). When an unmanaged ecosystem like forest is converted to agricultural production, it can initiate a series of changes in the physicochemical characteristics inherent to the soil and may consequently affect its SOC pools (Kimetu et al. 2009). The stability of soil organic carbon with respect to microbial respiration is determined by the inherent recalcitrance of organic compounds, interaction with absorptive substances, and accessibility to microorganisms (Sollins et al. 1996). As microbes prefer labile compounds (organic acids, sugars, amino acids), the

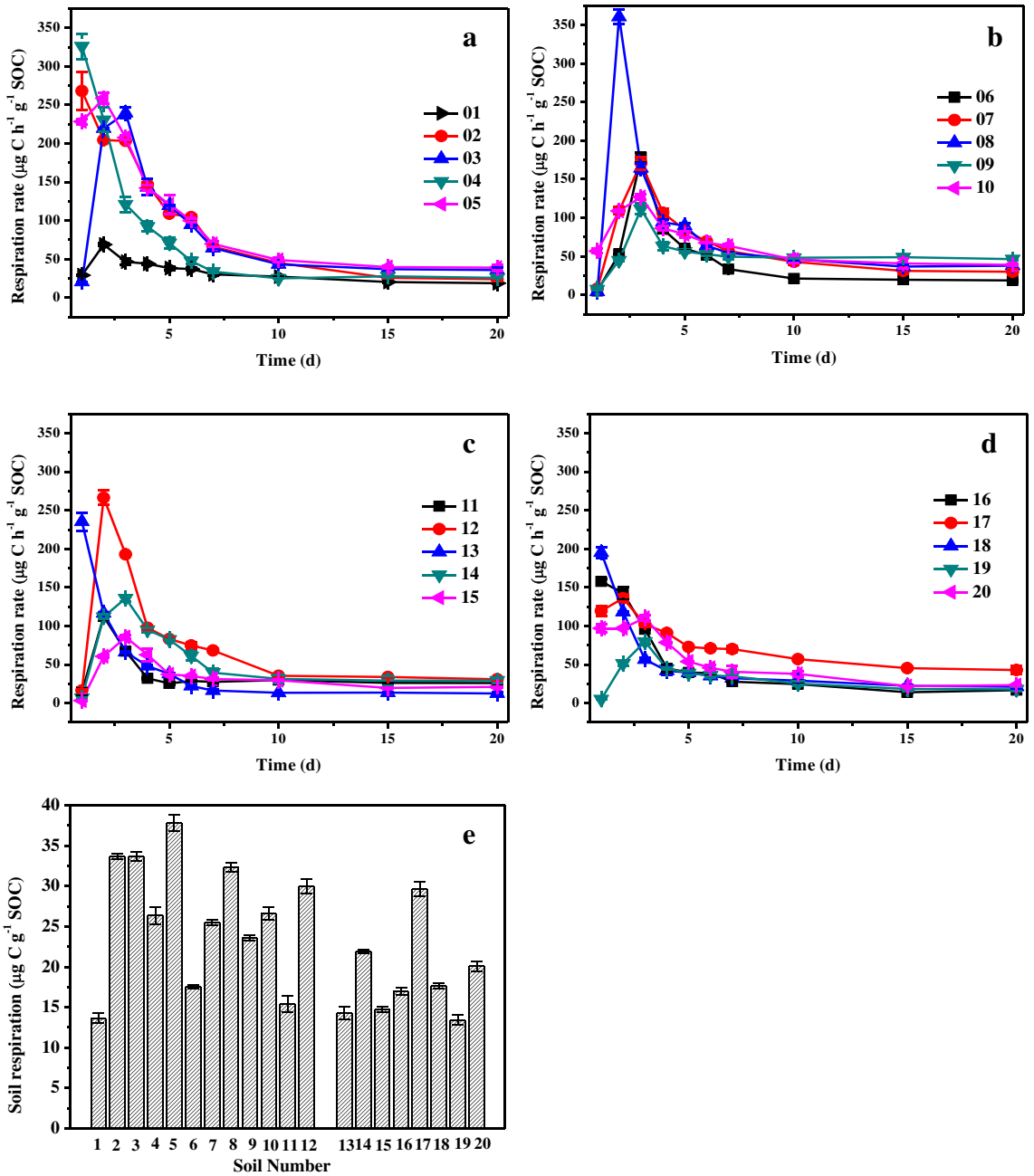

Fig. 4 Respiration rate changes: nos. 1–5 (**a**), 6–10 (**b**), 11–15 (**c**), and 16–20 (**d**) and soil respiration values (**e**) of the soil samples during the incubation period; data in the figure are means (n=3); the *bars* represent standard deviation of the means

labile organic carbon in soil samples was degraded, producing more mineralized carbon. The process, where microbes selectively degrade the less recalcitrant compounds and thus gradually increase the average recalcitrance of SOC, has been referred to as "selective preservation" (Sollins et al. 1996).

3.4 Relationship between ETC and soil respiration

As a labile fraction of SOC, soil DOM has received little attention previously. However, soil DOM can be considered as a fine indicator of soil quality because it influence soil function in specific ways and is much more sensitive to changes in soil management practice. Soil DOM is especially important in that it is readily degradable and is the major energy source for microorganisms (Haynes 2005; Hu et al. 1997). Soil DOM is related to soil mineralization and the turnover rate of SOC and can reflect the effects of land use on SOC (Haynes 2000). Therefore, more information on soil DOM is essential to understand how organic carbon in soil reacts to global change and affects the CO_2 concentration in the atmosphere. However, so far, the electron transfer capability of soil DOM has not been directly correlated with the respiration rate of SOC.

Significant relationships were found between ETC (EDC and EAC) and soil respiration with R^2 of 0.7537 and 0.8437, respectively ($p<0.01$) (Fig. 5). Microbes can reversibly mediate extracellular synthesis reactions by releasing extracellular peroxidases and phenol oxidases that oxidize phenols to quinones (Sollins et al. 1996), which implied that both EDC and EAC of soil DOM were closely related to the activity of microorganism and the respiration of soil organic matter. This point is underscored by the fact that electroactive moieties are a versatile class of biomolecules found in numerous substances such as living cells, extracellular material, and so forth, and they mainly contribute to the reversibly electron transfer in soil DOM. Electron transfer during soil respiration processes might be accelerated by the electroactive moieties contained in soil DOM. In addition, previous studies have focused on the stability of SOC with respect to its easiness in conversion to CO_2 (Sollins et al. 1996). Carbon dioxide is believed to be mainly produced during the aerobic respiration of microorganisms. However, Cervantes et al. (2000) pointed out that quinone respiration as a novel respiration pathway in an anoxic environment contributed greatly to CO_2 production. The fact that exogenous electroactive molecules can participate in electron transfer indicates that they may make a significant contribution to soil respiration, especially in iron(III) oxide-rich soils (Lovley et al. 1999; Newman and Kolter 2000). In anoxic soil environments, conventional electron transfer is affected by limited electron acceptors with a more positive redox potential. As a result, the part of soil DOM that is available for microbe as electron donors remains. Electroactive moieties-containing soil DOM can serve as electron shuttles during the anaerobic microbial oxidation of soil organic matters, resulting in an enhanced anaerobic respiration of SOC (Cervantes et al. 2000; Lovley et al. 1998). Therefore, ETC of soil DOM can greatly improve soil respiration and SOC stability assessing, which is of great significance to soil C sequestration and greenhouse effect mitigation.

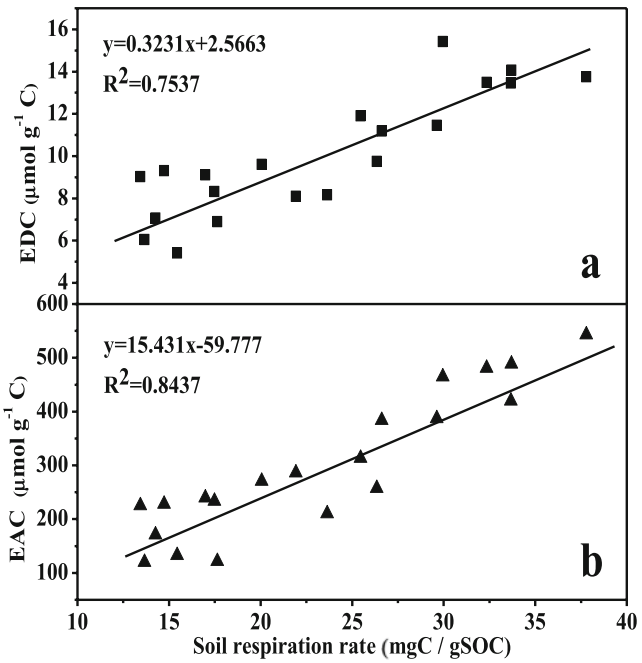

Fig. 5 Correlation between EDC and soil respiration ($p<0.001$) (**a**), and EAC and the soil respiration ($p<0.001$) (**b**)

4 Conclusions

In this study, ETC and ERR of DOM extracted from soil samples were evaluated with electrochemical approaches, and the results showed that the forest soils had a higher ETC. Furthermore, ETC of soil DOM had a close relationship with soil respiration. The results implied that soil respiration rate might be accelerated by the electroactive moieties contained in soil DOM, which serve as electron shuttles and facilitate electron transfer processes in soil respiration. ETC parameters of great importance to characterize soil DOM have helped understand the impacts on biogeochemical redox reactions, which has illuminated a new thought to explore the greenhouse gas emission and soil carbon sequestration, thereby mitigating the greenhouse effect.

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