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Electron donor capacity of reducing dissolved organic matter from crop residue decomposition as probed by chronoamperometry

Ran Bi [a,b], Tian Yuan [b], Qin Lu [b], Yong Yuan [b], Shungui Zhou [b,*]

[a] Guangdong Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 51064, PR China
[b] Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, PR China

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ABSTRACT

Reducing dissolved organic matters (RDOMs) from the anaerobic decomposition of crop residue can greatly affect the physicochemical and biological properties of soils. Electrochemical methods that can effectively protect them from oxidation and rapidly obtain results, such as differential pulse voltammetry (DPV), have been applied to qualitatively analyzing properties of RDOMs. However, the donated amount of electrons from RDOMs as a capacity factor may be more crucial for evaluating their important roles. For the first time, matured chronoamperometry (CA) was applied to quantitatively determining the electron donor capacities of RDOMs in crop residue management. The electron donor capacities of RDOMs from green manure were much higher than those from rice straw, which indicated that the former had greater effect on the redox status and reactions of soil. Chronoamperometry was proposed as a practical and effective method to quantitatively characterize RDOMs from residue decomposition.

1. Introduction

Decomposition of crop residue takes place anaerobically when residues are incorporated into flooded soils during land preparation. Incorporated residues have great impacts on the physicochemical and biological properties of the flooded soils (Devevre and Horwath, 2000; Johnson et al., 2006). For instance, Zhang et al. (1995) revealed that physical properties of soil, such as structure, water content, and temperature were influenced by the incorporation of residues. Lyamuremye and Dick (1996) found that the addition of residues improved soil fertility due to increased organic C, enzyme activities and P availability. Aulakh et al. (2001) pointed out that crop residue as natural resources are a significant replenishment to soil organic matter, increasing microbial activity and sustaining soil productivity.

Reducing dissolved organic matters (RDOMs) derived from decaying organic matters in flooded environments are important due to their biogeochemical properties (Zhou et al., 2001; Li et al., 2008). RDOMs as electron donors are essential in soil redox reactions involving the transformation of numerous substances, especially in soils rich in iron oxides (Yu et al., 1996; Ding, 2010, 2011). RDOMs can directly consume oxygen causing a reducing status of soil, which might encourage the growth of toxin-producing anaerobic microbes (Wobeser, 1997) and inhibit the germination of plant seeds (Zhang et al., 2009). RDOMs can also serve as electron donors during denitrification and dissimilatory nitrate reduction (Lovley et al., 1999), which decreases plant nitrogen uptake and subsequently photosynthesis activity (DeLaunea et al., 1998). Therefore, knowledge of RDOMs derived from anaerobic decomposition is essential for residue management and of great biogeochemistry importance. The significance of RDOMs was not seriously considered until electrochemical methods were applied (Yu and Ji, 1993), whose notable advantage over other methods is that they can characterize RDOMs in a complex system and effectively protect them from oxidation. Electrochemical methods such as DC voltammetry (Yu and Ji, 1993) and differential pulse voltammetry (DPV) (Li et al., 2003) can tell us the number of components in RDOMs but cannot quantify the electron donating capacities (EDC, i.e., the number of mole equivalents of electrons RDOMs can donate). Yet more than often, EDC is more crucial when redox reactions are involved. Chronoamperometry (CA) has been proven to be a useful approach to rapidly and accurately measure EDC.

Herein, this work was aimed to investigate the characteristics of RDOMs produced from the anaerobic decomposition of crop residue using electrochemical methods (i.e., DPV and CA), and to compare the difference in reducibility of RDOMs from various residues. To our best knowledge, this is the first time CA was applied to investigate the redox characteristics of RDOMs from crop residues in an attempt to better crop residue management.

* Corresponding author. Address: Guangdong Institute of Eco-Environmental and Soil Sciences, 808 Tianyuan Road, Guangzhou 510650, PR China. Tel./fax: +86 20 37300951.
E-mail address: sgzhou@soil.gd.cn (S. Zhou).

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2. Materials and methods

2.1. Crop residue and soil preparation

Two commonly used crop residue, green manure (*Vicia sativa*) and rice straw, were chosen for this study. Green manure was collected from a greenhouse of Guangdong Institute of Eco-Environmental and Soil Sciences. Rice straw was gathered after rice harvest from the experimental field of South China Agricultural University, Guangdong Province. The residues were washed with distilled water to remove soil particles, hung for the water to drain, dried at 60 °C overnight and ground into powder. The organic powder was kept at 4 °C until use.

The paddy soil used in this study was collected from the experimental field of South China Agricultural University. The soil is 27% sand, 44% silt, and 29% clay with a pH (H_2O) of 6.1, a total organic C content of 20.53 g kg^{-1} and a total N content of 1.77 g kg^{-1}. The soil was air-dried, sieved through a 2 mm sieve to remove coarse plant debris, transferred into airtight, polyethylene containers, and kept at 25 °C until use (Devevre and Horwath, 2000).

2.2. Anaerobic decomposition of crop residue

Forty grams of powdered residue (green manure or rice straw) was mixed with 800 g of paddy soil in a 2500 mL incubation vessel, and 2000 mL of double-distilled water was added to form a suspension. For the control, the conditions were the same as the treatments except that no residue was added. Prior to incubation, the suspensions were deaerated for 4 h with oxygen-free nitrogen using a vacuum pump and incubated in an anaerobic chamber Bactron-I (Sheldon Manufacturing Inc., Oregon, USA) at 25 °C. pH and Eh of the anaerobic suspensions during incubation were monitored using an oxidation–reduction potential meter (ORP) FJA-5 (Chuandi Co. Ltd., Nanjing, China).

2.3. RDOMs extraction and chemical characterization

Dissolved organic matter is often defined operationally as "the part of organic matter that is able to pass through a filter with a pore size of 0.45 μm" (Zhou et al., 2001). At certain incubation intervals (0, 1st, 3rd, 5th, 7th, 14th, 21st, 28th, 35th and 42nd day), 20 mL solution was taken from each incubation vessel and filtered through a 0.45 μm sterile membrane twice (GN-6 Metrice, Gelman Sciences, Ann Arbor, MI, USA). To prevent possible oxidation of the RDOMs during sampling, all the operations were carried out in the anaerobic chamber. Extracted RDOMs were stored in polyethylene containers sealed with butyl rubber stoppers and aluminum crimps at 4 °C before use. Subsequent measurements were carried out as soon as possible to prevent possible property changes of the RDOMs. Water dissolved organic C (C_w) content was determined with the potassium dichromate method (Bi et al., 2010). Total organic N (N_{org}) content was determined using the semimicro Kieldahl method (Chen et al., 2010). C_w, N_{org} and C_w/N_{org} changes of the RDOMs obtained under the experimental conditions were given in Table 1.

2.4. Volatile organic acids (VOAs) measurement

The extracted RDOMs were further centrifuged at 12 000 × g for 20 min (4 °C) and volatile organic acids in the supernatants were measured using an ICS-90 ion chromatography system with an ICE-AS6 ion exclusion (9 × 250 mm) and an anion micromembrane suppressor (Dionex Corp., USA). Hydrochloric acid (0.4 mM) and 5 mM tetrabutylammonium hydroxide (TBAOH) were used as eluent (flow rate of 1.0 mL min^{-1}) and regenerant (flowing pressure of 5–10 psi), respectively. VOA standard samples were filtered through a 0.45 μm sterile membrane (GN-6 Metrice, Gelman Sciences, Ann Arbor, MI, USA) before use.

2.5. Electrochemical measurements

Electrochemical measurements were performed using an electrochemistry workstation CHI660D (Chenhua Co. Ltd., Shanghai, China) with a conventional three-electrode cell at ambient temperature. Differential pulse voltammetry (DPV) was employed to investigate the redox-active components in RDOMs as previously described by Zhang et al. (2009). A glassy carbon electrode was used as the working electrode, and a Pt net and Hg/Hg_2Cl_2 electrodes as the counter and reference electrodes, respectively. One mL filtrate was transferred to the electrochemical cell, and 9.0 mL of 5.0 mM ammonium acetate was added. The operating conditions to obtain voltammograms included a scanning speed of 10 mV s^{-1}, pulse voltage of 50 mV, and operating voltage range of −0.5 to 1.0 V. Throughout the experiment, the electrochemical cell was purged with pure nitrogen to prevent RDOMs from oxidation. Supplemental DPV experiments were also similarly carried out to investigate the effects of pH (5.0, 6.0, 7.0, 8.0 and 9.0) on peak potentials. The pH was adjusted by the dropwise addition of 0.1 M sodium hydroxide or 0.1 M ammonium acetate to the electrolyte solution. Chronoamperometry (CA) measurements were performed to evaluate the EDC of RDOM in a N_2-saturated phosphate buffer solution (pH = 7.0) at applied potentials under stirring. A graphite plate with a projected surface area of

Table 1
C_w, N_{org} concentration and C_w/N_{org} of the RDOMs extracted.

Treatment	Incubation time (d)	C_w (mg kg^{-1})	N_{org} (mg kg^{-1})	C_w/N_{org}
Control	3	54.52	25.00	2.18
	7	46.88	26.00	1.80
	14	41.76	28.00	1.49
	21	35.77	32.00	1.12
	42	33.64	35.00	0.96
Green manure	3	44.08	82.00	0.54
	7	628.45	82.00	7.66
	14	1412.06	79.00	17.87
	21	722.24	76.00	9.50
	42	545.24	71.00	7.68
Rice straw	3	37.12	70.00	0.53
	7	356.60	72.00	4.95
	14	823.43	76.00	10.83
	21	236.45	66.00	3.58
	42	98.61	54.00	1.83