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Discrepant responses of the electron transfer capacity of soil humic substances to irrigations with wastewaters from different sources

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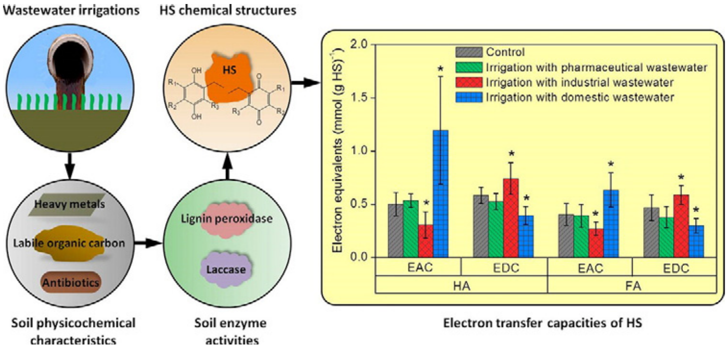
HIGHLIGHTS

- EAC of HS increased and EDC of HS decreased after irrigation with domestic wastewater.
- EAC of HS decreased and EDC of HS increased after irrigation with industrial wastewater.
- EAC and EDC of HS exerted no changes after irrigation with pharmaceutical wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

An increasing area of agricultural land is irrigated with wastewater worldwide due to the scarcity of fresh water resources. Whether wastewater irrigations can affect the electron transfer capacity (ETC) of natural organic matter in soils is unclear. In this study, we assess the responses of the electron-accepting capacity (EAC) and electron-donating capacity (EDC) of soil humic substances (HS) to irrigations with wastewaters from different sources. We show that the EAC of soil HS increases and the EDC of soil HS decreases after irrigation with domestic wastewater. Conversely, the EAC of soil HS decreases and the EDC of soil HS increases after irrigation with industrial wastewater. The EAC and EDC of soil HS exert no changes after irrigation with pharmaceutical wastewater. Irrigations with wastewaters from different sources can cause the distinct directions of changes in the activities of lignin peroxidase and laccase by altering the content of labile organic carbon, heavy metals or antibiotics in soils, thereby changing the chemical structures and finally the ETC of HS along different directions. These results can provide insights into the role of HS in environmentally relevant processes in agricultural soils under the context of wastewater irrigations.

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1. Introduction

Demographic growth, economic development, improvement of living standard, climate change and pollution have caused unsustainable rates of water consumption. Thus, the major issue of water scarcity in dry lands and freshwater regions worldwide has emerged (Bixio et al., 2006; EU, 2007; FAO, 2012). Consequently, the use of alternative water supplies, including recycled wastewater for irrigation purposes, has attracted increasing interest (Becerra-Castro et al., 2015). Wastewater is derived from a number of sources, including domestic sewage, agricultural and industrial effluents, and stormwater (Kunhikrishnan et al., 2012). Although wastewater irrigation exhibits many positive effects, such as reliable water supply to farmers, improved crop yield, and pollution reduction of river and other surface water resources (Niemczynowicz, 1999; Anderson, 2003; Asano and Cotruvo, 2004; Toze, 2006; Kunhikrishnan et al., 2012), it can alter soil factors, such as the physicochemical and microbiological characteristics and the chemical and biological contaminants in soil (Becerra-Castro et al., 2015), thereby causing soil salinity, land degradation, loss of biodiversity, and risk to human and environmental health (Hanjra et al., 2012).

Humic substances (HS) are traditionally defined as the recalcitrant decomposition product formed through the partial decay of plant materials and microbial precursors (Stevenson, 1994). HS are a major fraction of natural organic matter in soils, sediments, and aquatic systems (Aiken et al., 1985; Stevenson, 1994). Under anoxic conditions, HS can be reduced by different microorganisms, such as iron-reducing (Lovley et al., 1996), sulfate-reducing (Cervantes et al., 2002), and fermenting bacteria (Benz et al., 1998). Reduced HS can subsequently donate electrons to other electron acceptors with large positive redox potentials, such as poorly accessible iron oxides and hydroxides (Lovley et al., 1996; Bauer and Kappler, 2009) and various organic and inorganic pollutants, including chlorinated compounds (Kappler and Haderlein, 2003), nitrobenzenes (Van der Zee and Cervantes, 2009), U(VI) (Gu and Chen, 2003), and Cr(VI) (Wittbrodt and Palmer, 1997). Thus, the so-called electron transfer properties of HS can exert a significant impact on the environmentally relevant processes of redox-active substances in natural ecosystems.

Considerable evidence supports the viewpoint that the electron transfer capacity (ETC) of HS is attributed to their intrinsic chemical structures, such as quinone–hydroquinone moieties and other redox-active functional groups and metals (Scott et al., 1998; Struyk and Sposito, 2001; Chen et al., 2003; Einsiedl et al., 2008; Aeschbacher et al., 2011). The distributions and abundances of these redox-active functional constituents in HS are generally dependent on the microbial enzyme-catalyzed degradation and transformation of HS in soils (Stevenson, 1994; Kleber and Johnson, 2010). Soil factors are important in governing soil microbial growth and activity (Cheeke et al., 2013). Therefore, these factors can further exert substantial effects on the degradation and transformation, and ultimately the ETC of soil HS.

Although the wastewater irrigation and the ETC of soil HS are simultaneously associated with soil factors, whether irrigations of wastewater from different sources exert discrepant impacts on the ETC of HS in soils is presently unknown. Understanding the mechanisms of the effect of irrigations with wastewaters from different sources on the ETC of soil HS is critical to managing soil environment efficiently under the context of wastewater irrigation.

We simultaneously sampled the agricultural soils irrigated with groundwater and pharmaceutical, industrial, and domestic wastewaters in an agroecosystem. The ETCs, including electron-accepting capacity (EAC) and electron-donating capacity (EDC), of humic acid (HA) and fulvic acid (FA) extracted from these soils were quantified using an electrochemical approach to evaluate the responses of ETCs of soil HA and FA to wastewater irrigations and clarify the response heterogeneity under different irrigations with wastewaters from different sources.

2. Materials and methods

2.1. Study area and soil sampling

The study area is located near the Shijiazhuang City in Hebei Province, North China (Fig. 1). Climate is typically temperate continental with a mean annual rainfall of 556 mm (75% in June–August) and mean annual temperature of 13.1 °C. The main soil type at the site is Cambisol. Shijiazhuang area is an important field of cereal crop in the North China Plain. In this area, summer maize (*Zea mays* L.)–winter wheat (*Triticum aestivum* L.) rotation (covering approximately 60% of the arable land) is the predominant crop system.

With high demand and shortage of freshwater, wastewater is a pervasive option for agricultural irrigation in the Shijiazhuang area, where farmlands have been irrigated with wastewater for > 30 years (Wu et al., 2004). Agricultural irrigations with domestic, industrial, and pharmaceutical wastewaters are all distributed in Shijiazhuang area because of the simultaneous presences of domestic sewage treatment, chrome tanning, and pharmaceutical factories. This condition facilitates the assessment of the responses of soil HS ETC to irrigations with wastewaters from different sources.

Soil sampling was conducted in June 2014 in three zones, namely, irrigated with domestic, industrial, and pharmaceutical wastewaters (Fig. 1). One zone was irrigated with groundwater as control (Fig. 1). The domestic, industrial, and pharmaceutical wastewaters were secondary treatment effluents discharged from domestic sewage treatment, chrome tanning, and pharmaceutical factories, respectively. The average physicochemical properties of wastewaters and groundwater collected in March, June, September, and November 2014 are provided in Table 1. Five soil sampling sites at each zone were selected. At each site, 10 randomized uppermost 10 cm of soils were collected and mixed. A total of 20 composed soil samples were sieved (2 mm diameter) to remove soil fauna, fine roots, and rock fragments. All pretreated soil samples were stored at −20 °C until analysis.

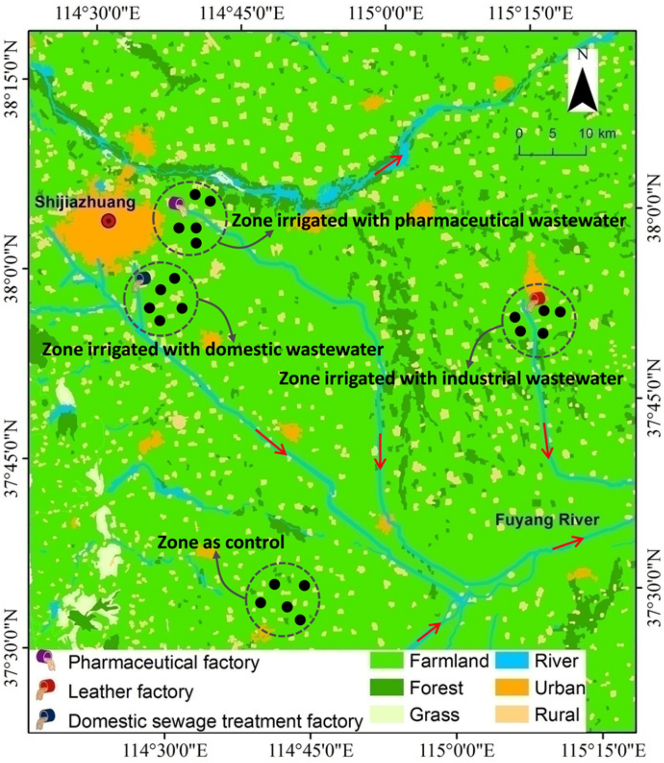

Fig. 1. Study area and sampling locations. Black solid circles indicate the sampling sites. Red arrows indicate the river flow directions.