



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Effect of long-term fertilization on humic redox mediators in multiple microbial redox reactions[☆]

Peng Guo^{a, b, 1}, Chunfang Zhang^{a, 1}, Yi Wang^b, Xinwei Yu^d, Zhichao Zhang^d, Dongdong Zhang^{a, c, *}

^a Institute of Marine Biology, Ocean College, Zhejiang University, Zhoushan 316021, Zhejiang, China

^b Institute of Agricultural Products Processing and Nuclear Agriculture Technology Research, Hubei Academy of Agricultural Sciences, Wuhan 430064, China

^c School of Fisheries, Zhejiang Ocean University, Zhoushan 316022, Zhejiang, China

^d Zhoushan Municipal Center for Disease Control and Prevention, Zhoushan 316021, Zhejiang, China

ARTICLE INFO

Article history:

Received 18 September 2017

Received in revised form

22 October 2017

Accepted 26 October 2017

Keywords:

Organic fertilization

Redox activity

Humic substance

Microbial respiration

Polychlorinated biphenyl

ABSTRACT

This study investigated the effects of different long-term fertilizations on humic substances (HSs), humic acids (HAs) and humins, functioning as redox mediators for various microbial redox biotransformations, including 2,2',4,4',5,5'-hexachlorobiphenyl (PCB₁₅₃) dechlorination, dissimilatory iron reduction, and nitrate reduction, and their electron-mediating natures. The redox activity of HSs for various microbial redox metabolisms was substantially enhanced by long-term application of organic fertilizer (pig manure). As a redox mediator, only humin extracted from soils with organic fertilizer amendment (OF-HM) maintained microbial PCB₁₅₃ dechlorination activity (1.03 μM PCB₁₅₃ removal), and corresponding HA (OF-HA) most effectively enhanced iron reduction and nitrate reduction by *Shewanella putrefaciens*. Electrochemical analysis confirmed the enhancement of their electron transfer capacity and redox properties. Fourier transform infrared analysis showed that C=C and C=O bonds, and carboxylic or phenolic groups in HSs might be the redox functional groups affected by fertilization. This research enhances our understanding of the influence of anthropogenic fertility on the biogeochemical cycling of elements and *in situ* remediation ability in agroecosystems through microorganisms' metabolisms.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Redox mediators can be reversibly oxidized and reduced, thereby conferring the capacity to transfer electrons between reduction and oxidation reactions. Redox mediators are very important during the electron transfer process of anaerobic microbial respiration. They accelerate reactions by lowering the activation energy (Liu et al., 2012), resulting in enhanced microbial transformation of pollutants and nutrients in ecosystems (Watanabe et al., 2009). Naturally occurring humic substances (HSs) are redox-active organic macromolecules that are widely distributed in the environment (i.e., in all types of soils, sediments, peatlands, and wetlands; Chin et al., 1994; Lovley et al., 1999). HSs

are composed of recalcitrant decomposition products derived from plant, animal, and microbial biomass, and make up 60–70% of the total organic carbon in soils (Hernandez-Montoya et al., 2012).

The roles of soluble HSs, such as humic acid (HA), and quinoid model compounds as redox mediators for various microbial redox reactions has been studied extensively during the past two decades (Aranda-Tamaura et al., 2007; Van der Zee and Cervantes, 2009; Watanabe et al., 2009). The immobilization of soluble HSs and quinoid model compounds on anion exchange resin (Cervantes et al., 2011, 2013; Martinez et al., 2013), alumina nanoparticles (Cervantes et al., 2015), and polyethylene terephthalate (Xu et al., 2015) has been demonstrated to be an effective solid-phase redox mediator accelerating several reductive biotransformations, such as dechlorination, decolorization, and denitrification. We recently reported on the redox-mediating ability of humin (Zhang and Katayama, 2012), a fraction of HSs that is more stable and not water-soluble at any pH. It has been established that various humins obtained from soils and sediments function as solid-phase redox mediators in the microbial reductive dehalogenation of

[☆] This paper has been recommended for acceptance by B. Nowack.

* Corresponding author. Institute of Marine Biology, Ocean College, Zhejiang University, Zhoushan 316021, Zhejiang, China.

E-mail address: zhangdongzju@zju.edu.cn (D. Zhang).

¹ These authors contributed equally to this study.

pentachlorophenol (PCP), tetrabromobisphenol A (TBBPA), and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB₁₅₃), dissimilatory iron reduction, nitrate reduction to ammonium, and denitrification (Xiao et al., 2016; Zhang and Katayama, 2012; Zhang et al., 2013, 2015b, 2017). Solid-phase humin is also versatile as a redox mediator for various microbial reactions. It is noteworthy that, for these microbial reductive dehalogenation reactions, humin was able to maintain the activities as a redox mediator, whereas dissolved HA could not. Therefore, humin as a solid-phase redox mediator might play a more important role for microbial reductive dehalogenation among the HSs in soil. Naturally originating HSs might significantly affect the microbial redox metabolisms in soil, including some bioremediation and nutrient recycling processes, thereby having important environmental implications for soil biogeochemistry.

Although HSs as the major organic matter component in soil are highly stable, they are most affected by the types of long-term fertilizer application (Naidja et al., 2002), and maintaining fertilization is an essential management approach for preserving and increasing HSs levels in arable soils (Liu et al., 2010). Therefore, HSs have generally been used for evaluating the changes in soils promoted by different fertilizing practices. However, previous studies have focused on the effects of fertilization and management systems in relation to soil humification, the elemental composition and physicochemical characterization of HSs, and soil fertility and quality (Galantini and Rosell, 2006; Huang et al., 2009; Simonetti et al., 2012); in contrast, the effect on the electron transfer ability of HSs as redox mediators has been poorly explored. A study of the effects of fertilization on electron transfer ability in HSs, especially for solid-phase humins, can be useful for assessing the influence on multiple microbial redox reactions in soils, which are ubiquitous and thought to play an important role for cycling elements and biodegrading contaminants in agroecosystems.

Therefore, this study evaluated the effects of differing long-term fertilization regimes (i.e., no fertilizer, chemical fertilizer, or organic fertilizer) on humification, and the functions of HAs and humins as redox mediators for multiple microbial respiration reactions with different terminal electron acceptors, namely reductive dechlorination of PCB₁₅₃, dissimilatory iron reduction, and nitrate reduction to ammonium. Chemical, spectroscopic, and electrochemical analyses of HAs and humins were also conducted to gain insights into their electron-mediating nature affected by fertilizing practices. It is generally accepted that the role of soil in cycling elements, mitigating contamination, and structuring the Earth's climate is largely driven by microorganisms that exist in soil environments (Pepe-Ranney et al., 2016). A better understanding of the electron transfer ability of naturally originating HSs in soil for environmentally relevant microbial metabolisms, as affected by different fertilizing practices, has significant implications for the role of anthropogenic fertility in elemental cycles, *in situ* remediation ability in soil, and even the Earth's climate construction.

2. Materials and methods

2.1. Experimental design and soil sampling

Since 1981, four plots (plot size: 5 × 8 m; typical yellow-brown soil) have been maintained at the Nanhu experimental station of the Hubei Academy of Agricultural Sciences (Wuhan, China) and subjected to specific fertilization practices: unfertilized soil, soil amended with chemical fertilizers (150 kg N ha⁻¹y⁻¹, 75 kg P₂O₅ ha⁻¹y⁻¹, 150 kg K₂O ha⁻¹y⁻¹), and soil amended with organic fertilizer (22.5 t ha⁻¹y⁻¹ of pig manure: 69% water ratio, used after composting for 1 week). The characteristics of pig manure were listed in our previous study (Ren et al., 2014). The field has two annual cropping seasons of rice and wheat. The soil in each plot was

sampled at five different sites and homogeneously mixed, then air-dried and passed through a 2 mm sieve. The soil samples were stored at room temperature in darkness until HSs extraction.

2.2. Extraction and physicochemical characterization of HSs

HSs were obtained from soils as previously described by Zhang and Katayama (2012). Briefly, air-dried soils were extracted with 2% hydrofluoric acid (HF) to remove clay minerals and silicates. The HF-treated residue was treated with 0.1 M NaOH, then centrifuged, and the supernatant was collected as the extract. This alkaline treatment process was repeated at least 10 times until there was no obvious dark color in the extract. This collected extract was acidified to pH < 2 with 2 M HCl, forming a flocculent precipitate (termed HA). The HA was further purified by redissolving and reprecipitating to remove any residual inorganic matter. The soil residue remaining after alkaline treatment was termed humin, and was further treated with 2% HF to concentrate the organic matter. Finally, the obtained HA and humin were thoroughly rinsed with distilled water to neutralization and then freeze-dried. All centrifugation steps were carried out at 8000 × g for 10 min. Humic acid (HA) and humin (HM) extracted from the soils subjected to different fertilizers were designated as UF-HA/UF-HM for unfertilized soil, CF-HA/CF-HM for chemical fertilizers, and OF-HA/OF-HM for organic fertilizer.

The carbon, hydrogen, and nitrogen contents of HAs and humins were determined via elemental analysis (Yanaco MT-5 CHN-corder; Yanaco New Science, Inc., Kyoto, Japan) with antipyrine as a standard. Metal species in HAs and humins were analyzed using inductively coupled plasma-atomic emission spectroscopy (Optima 3300DV; PerkinElmer, Yokohama, Japan) after perchloric acid and nitric acid digestion.

2.3. Effect of fertilizations on HSs functioning as redox mediator

An anaerobic humin-dependent PCB₁₅₃-dechlorinating culture was used as the source culture for evaluating the roles of HAs and humins as redox mediators for reductive dechlorination. The culture was maintained as described by Zhang et al. (2017). The influence of HSs, extracted from differently fertilized soils, on microbial reduction of amorphous Fe (III) oxide (FeOOH) (Lovley and Phillips, 1986) and nitrate was examined using *Shewanella putrefaciens* strain CN32 (China Center for Type Culture Collection) under anaerobic conditions. The anaerobic HSs medium was prepared in 60 mL serum bottles containing 20 mL of mineral medium, 5 g L⁻¹ HA/humin, filter-sterilized vitamin solution (Holliger et al., 1998), 10 mM formate (30 mM when evaluating the nitrate reduction reaction), and 1.38 μM PCB₁₅₃, 10 mM FeOOH, or 5 mM nitrate as the electron acceptor, all flushed with N₂. The bottles with a N₂ headspace were sealed using Teflon-coated butyl rubber stoppers and crimped by an aluminum cap. The mineral medium consisted of (per liter): 1.0 g NH₄Cl, 0.05 g CaCl₂·2H₂O, 0.1 g MgCl₂·6H₂O, 0.4 g K₂HPO₄, 1 mL trace element SL-10 solution, 1 mL Se/W solution, and 15 mM MOPS buffer of pH 7.2 (Widdel et al., 1983). After appropriate incubation periods at 30 °C, the microbial redox activities were analyzed. PCB₁₅₃ and its metabolites were analyzed using a gas chromatography–mass spectrometer (GC MSD 5975; Agilent Technologies, United States) equipped with a HP-5MS column (Agilent Technologies, United States) (Zhang et al., 2017). Recovery rates of PCB₁₅₃ (1.38 μM) during the extraction process were also examined. Ferrous ion concentration in the culture was determined spectrophotometrically using a ferrozine method (Rodén et al., 2010). Measurements of nitrate and nitrite concentrations were obtained using a Metrohm 761 ion chromatograph (Herisau, Switzerland) equipped with a SI-90 4E

Download English Version:

<https://daneshyari.com/en/article/8857183>

Download Persian Version:

<https://daneshyari.com/article/8857183>

[Daneshyari.com](https://daneshyari.com)