Chemosphere 95 (2014) 317–323

Contents lists available at ScienceDirect

Chemosphere

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

Photosensitizing properties of water-extractable organic matter from soils

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HIGHLIGHTS

- Organic matter was extracted by pure water from two black soils and IHSS Elliott soil.
- Reactive species generated upon irradiation of these WEOMs were quantified.
- The quantum yields are comparable to those of IHSS humic substances or even higher.
- WEOMs photosensitized the degradation of bisphenol A.

ARTICLE INFO

Article history:
Received 23 June 2013
Received in revised form 23 August 2013
Accepted 2 September 2013
Available online 29 September 2013

Keywords:
Water-soluble soil organic matter
Sensitizing properties
Singlet oxygen
Hydroxyl radicals
Triplet excited states
Bisphenol A

ABSTRACT

Water-extractable organic matter (WEOM) was extracted using pure water from two black soils and from the Elliott reference soil of the International Humic Substances Society (IHSS). WEOMs were characterized by chemical and spectroscopic methods. The apparent quantum yields of singlet oxygen, triplet excited states and hydroxyl radicals formation upon irradiation within the wavelength range 290–450 nm were determined using chemical probes and compared to those of standard Elliott humic substances. In general, the aromatic content, as measured by the SUVA value, was close in WEOMs and humic substances, while the E_2/E_3 was higher and the humification index lower in the former. Quantum yield values measured for WEOMs fell within the range of those found for basic medium extracted humic substances or were even higher in one case. Thus, water soluble aromatic moiety of the soil organic matter, especially those with low humification degree, is important for the photosensitizing properties. We also found that WEOMs sensitized the bisphenol A phototransformation with rates of the same order of magnitude for all the samples.

1. Introduction

The organic matter accumulated in soils, sediments or terrestrial waters offers interesting photochemical properties as they are able to promote the photodegradation of organic micropollutants. Many examples of such reactions are reported in the literature (Stangroom et al., 1998; Vialaton and Richard, 2002; Buschmann et al., 2005; Boreen et al., 2008; Ge et al., 2009; Han et al., 2009; Golanoski et al., 2012; Chen et al., 2012) even though in some cases natural organic matter inhibits rather than enhances the micropollutant photodecomposition. Most of the reported photochemical studies are conducted on aquatic samples collected from surface waters, on natural organic matter (NOM) isolated from lake and river water or from humic substances (HSs) extracted from soils or sediments. Whatever their origin these complex mixtures are found to photogenerate reactive species such as oxidant excited states, singlet oxygen and hydroxyl radicals under exposure to solar light (Zepp et al., 1981; Haag and Hoigné, 1986; Canonica et al., 1995; Aguer et al., 1999; Paul et al., 2004).

As far as soil is concerned, the typical extraction of organic matter is made in basic medium and aims the recovering of two humic fractions: the humic acids (HAs) which are soluble in basic medium and precipitate in acidic solution and the fulvic acids (FAs) wich are soluble at all pH and recovered after a series of desalting steps involving cation exchange and dialysis. Another fraction of soil is also the subject of a great interest: the water-extractable organic matter (WEOM) (Corvasce et al., 2006; Rennert et al.,

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.09.023

2007; Hassouna et al., 2010). This is the fraction of soil organic matter that can be obtained by simply agitating soil in neutral water. The WEOM is composed of the water-soluble organic compounds and minerals present in the soil pores and of the additional organic matter and minerals whose dissolution is favored by the breakdown of soil aggregates during agitation. This corresponds to a variety of labile molecules, intermediary between the plant residues and the humic end-products, and of stable molecules corresponding to humic compounds. Basically, the WEOM soil fraction is expected to be distinct from the soil base-extracted HAs and FAs. In particular, the WEOM should be much less concentrated than HSs in the high molecular weight polyelectrolytes material only extractable by base, but enriched in small molecules compared to HSs because the WEOM recovery protocol does not include purification steps in contrast to the HSs extraction protocol.

Contrary to HAs, FAs, NOM and aquatic samples collected from surface waters which were intensively studied for their photoreactivity, WEOMs were poorly investigated for their potential sensitizing properties until quite recently (Jia et al., 2013). It is however important to note that Navarro et al. (2004) and Sanches et al. (2011) pointed out that the photosensitized phototransformations of polycyclic aromatic hydrocarbons and of some pharmaceuticals were found faster in the presence of groundwater than of surface water. As groundwaters are expected to contain WEOMs or a fraction of their constituents, this implies that WEOMs show significant photosensitizing properties. In other works focused on the waste-derived bioorganic substances (compost) which are materials enriched in organic matter, it was found that the organic matter extracted from the compost by pure water showed higher efficiency to generate reactive species than the humic-like substances extracted in basic medium by the same protocol as that used to extract HAs from soils (Amine-Khodja et al., 2005; Trubetskoj et al., 2008; Bianco Prevot et al., 2010; Coelho et al., 2011; Avetta et al., 2012). Again, this result underlines the potential photosensitizing properties of water-soluble organic compounds.

In this work, we aimed to study the photosensitizing properties of WEOMs. WEOMs were extracted by pure water from two black soils and from a reference soil of the international humic substances society (IHSS), the Elliott soil, for which standard HA and FA are also available. We measured the apparent quantum yields of reactive species formation from irradiated WEOMs using the scavenging technique to determine the capacity of pure water to extract sensitizing chromophores from soil. We also investigated the ability of WEOMs to photosensitize the photodegradation of bisphenol A, a commonly studied aquatic micropollutant.

2. Experimental

2.1. Materials

Two black soils, enriched in organic carbon, were selected. The first soil (L-BS) was sampled in the Limagne plain (France) which is closed to Auvergne volcanoes. This fertile black soil shows similarities with chernozem soil. Soil was taken in May 2010 in the agricultural parcel of the Lycée Agricole of Marmilhat, Auvergne, France at 45°46′42″N and 3°10′45″E and collected between 5 and 20 cm. The soil sample was air-dried at 25 °C for 15 d. The second black soil (P-BS) was sampled in Płońsk (Poland) near to Water Voluntary Rescue Service at geographic area 20°23′15″N and 52°38′20″E in 2010. Material was taken from the depth 0–40 cm, dried at room temperature and stored in the dark. The last soil, Elliott soil 1BS102M, was purchased from the International Humic Substances Society (IHSS). Standard Elliott FA (E-FA) and HA (E-HA) were also obtained from IHSS, 2S102F and 1S102H, respectively. Data on these compounds are available on the web page www.humicsubstances.org. The chemical probes furfuryl alcohol (FFA), 2,4,6-trimethylphenol (TMP), terephthalic acid (TA), hydroxyterephthalic acid (TAOH) and bisphenol A (BPA) as well as all other chemicals (sodium nitrate, phosphate buffers and HPLC solvents) were of the highest grade available and were used as received. The ultra-pure water used was from a Millipore Milli-Q system.

2.2. Organic matter extraction

WEOMs were extracted using the previously described procedure (Nkhili et al., 2012). Twelve grammes of dried soil were suspended in Milli-Q water in a ratio (soil/water = 1/10 in weight). Extractions were conducted at room temperature or at 60 °C. Samples extracted at room temperature were named L-WEOM20, P-WEOM20 and E-WEOM20 for Limagne, Płońsk and Elliott soil, respectively. Samples extracted at 60 °C were named L-WEOM60, P-WEOM60 and E-WEOM60. For extraction at room temperature, suspended soils were mechanically shaken for 24 h. For extractions at 60 °C, they were put in a flask equipped with a cooled column, mechanically shaken and heated for 30 min. After the extraction process, suspensions were centrifuged at 5600 rpm for 60 min. Finally, the supernatant was lyophilized and stored in amber bottles. Each extraction was made in triplicate. The percentage of extraction, defined as the mass of recovered WEOM divided by the mass of initially weighted soil, was 0.34% for L-WEOM60, 0.20% for L-WEOM20, 0.15% for E-WEOM60 and less than 0.10% for E-WEOM20, P-WEOM60 and P-WEOM20. This is small compared to the amounts obtained by basic extraction.

2.3. Solutions preparation

Stock solutions of WEOMs or HSs were prepared by dissolution of 5 mg of powder in 500 mL of Milli-Q water under stirring. Appropriate mixture of potassium phosphate monobasic and sodium phosphate dibasic was added to buffer the solutions at pH 6.5; the final buffer concentration was 10^{-3} M. In the case of poorly soluble P-WEOMs, it was necessary to dissolve the powder in the dibasic phosphate solution first and to add the mono basic phosphate after the full P-WEOM dissolution.

2.4. Irradiations

Irradiations were conducted in a device equipped with six fluorescent tubes (TLAD 15W05 Philips, Eindhoven, The Netherlands) emitting between 290 and 450 nm. The emission spectrum of these

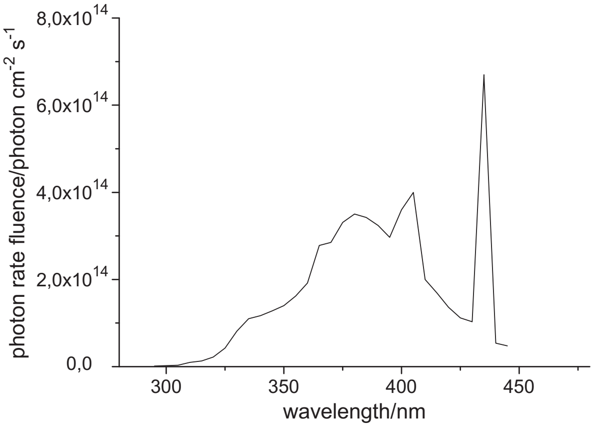

Fig. 1. Emission spectrum of the fluorescent tubes.