



Photodegradation of polycyclic aromatic hydrocarbons in soils under a climate change base scenario



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HIGHLIGHTS

- PAH photodegradation depends on exposure time, molecular weight and soil texture.
- Semiconductor minerals in fine-textured regosol soil enhance PAH photodegradation.
- Microtox[®] shows a higher detoxification over time in fine-textured soil.
- $\delta^2\text{H}$ confirmed benzo(a)pyrene degradation, highlighting the potential of CSIA.

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ABSTRACT

The photodegradation of polycyclic aromatic hydrocarbons (PAHs) in two typical Mediterranean soils, either coarse- or fine-textured, was here investigated. Soil samples, spiked with the 16 US EPA priority PAHs, were incubated in a climate chamber at stable conditions of temperature (20 °C) and light (9.6 W m⁻²) for 28 days, simulating a climate change base scenario. PAH concentrations in soils were analyzed throughout the experiment, and correlated with data obtained by means of Microtox[®] ecotoxicity test. Photodegradation was found to be dependent on exposure time, molecular weight of each hydrocarbon, and soil texture. Fine-textured soil was able to enhance sorption, being PAHs more photodegraded than in coarse-textured soil. According to the EC₅₀ values reported by Microtox[®], a higher detoxification was observed in fine-textured soil, being correlated with the outcomes of the analytical study. Significant photodegradation rates were detected for a number of PAHs, namely phenanthrene, anthracene, benzo(a)pyrene, and indeno(123-cd)pyrene. Benzo(a)pyrene, commonly used as an indicator for PAH pollution, was completely removed after 7 days of light exposure. In addition to the PAH chemical analysis and the ecotoxicity tests, a hydrogen isotope analysis of benzo(a)pyrene was also carried out. The degradation of this specific compound was associated to a high enrichment in ²H, obtaining a maximum $\delta^2\text{H}$ isotopic shift of +232‰. This strong isotopic effect observed in benzo(a)pyrene suggests that compound-specific isotope analysis (CSIA) may be a powerful tool to monitor *in situ* degradation of PAHs. Moreover, hydrogen isotopes of benzo(a)pyrene evidenced a degradation process of unknown origin occurring in the darkness.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of semi-volatile organic compounds composed of two or more fused aromatic rings. Although these chemicals are mostly released to air, soil is considered as one of the major sinks of atmospheric PAHs

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(Nadal et al., 2011; Wang et al., 2014), being deposited via dry and wet processes (Nadal et al., 2004). PAH fate in the environment includes volatilization, adsorption on soil particles, leaching, microbial degradation, chemical oxidation, and photo-oxidation (Hartiash and Kaushik, 2009). Photodegradation is an important transformation pathway for most PAHs in the environment (Zhang et al., 2006), having been largely studied in water (Bertilsson and Widenfalk, 2002; de Bruyn et al., 2012; Fasnacht and Blough, 2003; García-Martínez et al., 2005; Jacobs et al., 2008; Jing et al., 2014; Luo et al., 2014; Rivas et al., 2000; Shemer and Linden, 2007; Singh et al., 2013; Xia et al., 2009). In contrast, the knowledge regarding the photodegradation process of PAHs in soils is rather limited (Balmer et al., 2000; Frank et al., 2002; Gong et al., 2001; Xiaozhen et al., 2005). It has been reported that soil depth has an important role in the photodegradation of these chemicals, enhancing the resistance of PAHs to be photodegraded. In addition, temperature, soil particle size and humic acids also have a significant influence on photodegradation in soils under UV-B radiation (Zhang et al., 2010). Photodegradation of PAHs in soils has been shown to be not only limited by the light penetration capacity in soils, but also by its wavelength (Cavoski et al., 2007; Xiaozhen et al., 2005). Consequently, photodegradation depends on a number of variables, such as soil type, thickness of the soil layer, as well as light absorption spectrum of each compound (Zhang et al., 2010). This degradation process may play a key role on the fate of PAHs in areas such as the Mediterranean region, with high sunlight presence during the whole year. In turn, some PAH metabolites, which can even be more toxic than their parental compounds, may be generated during the degradation process. Overall, although PAH levels might be reduced in soils exposed to sunlight, toxicity may be increased (Huang et al., 1995; Mallakin et al., 1999; McConkey et al., 1997).

Compound-specific isotope analysis (CSIA) is a very valuable tool, which can be used to monitor *in situ* degradation processes of chemical pollutants, and as a source identification technique (Elsayed et al., 2014; Imfeld et al., 2014). CSIA is capable of discriminating degradation from other attenuation processes naturally occurring in the environment, that do not generate destruction of pollutants, such as dispersion, volatilization or sorption. CSIA is based on the isotopic effect produced during a degradation process, which is known as isotopic fractionation (Meckenstock et al., 2004). This effect is based on the enrichment of heavy isotopes in the reacting compound, which is linked to the different strength of the bonds that contain heavy and light isotopes. Since non-destructive natural attenuation processes frequently do not entail significant isotope fractionation, a significant enrichment of the heavy isotope of organic pollutants confirms that a degradation process is occurring. Unfortunately, research on the hydrogen isotopic fractionation of PAHs during degradation is very scarce. To the best of our knowledge, the only precedent is the study of Bergmann et al. (2011), who reported a high hydrogen isotopic shift of naphthalene in two different microbial cultures.

The present investigation aimed at assessing the photodegradation of 16 US EPA priority PAHs in two types of Mediterranean soils. Laboratory experiments were conducted in a climate chamber to simulate the current Mediterranean environmental conditions, keeping temperature and sunlight stable. Temporal changes of PAH concentrations and ecotoxicity levels were investigated, and jointly evaluated. Moreover, hydrogen isotopic analysis of benzo(a)pyrene, considered one of the most toxic PAHs and probably carcinogenic to humans (Aina et al., 2006), was complementarily performed to verify the findings.

2. Materials and methods

2.1. Soil characteristics

Two common Mediterranean soils were selected to perform the photodegradation experiments. Physicochemical properties of both soils are given in Table 1. Soil samples were collected from the A horizon of remote areas of Catalonia (NE of Spain). The Arenosol soil, with granitic origin, is an acidic and coarse-textured soil that can be classified as Haplic Arenosol, according to the (FAO-UNESCO, 1998). It is commonly used for ecotoxicity tests in terrestrial environments. In turn, Regosol soil is an alkaline calcareous fine-textured soil formed of sedimentary materials, being classified as Calcaric Regosol (FAO-UNESCO, 1998). Both soils are characterized by owing a low organic matter content (Table 1). In order to quantify titanium, iron, aluminum and manganese oxides, ammonium oxalate was used as extractant, according to the method described by Drees and Ulery (2008).

2.2. Experimental design

Photodegradation experiments were carried out in a Binder KBWF 240 climate chamber (Binder GmbH, Tuttlingen, Germany) with constant lighting, temperature and humidity. Temperature and daylight were set at 20 °C and 9.6 W m⁻², respectively, as current environmental conditions in the Mediterranean area. Because photodegradation reactions occur mainly in the surface, soil was air-dried. Consequently, to avoid the presence of water and any potentially associated biodegradation process, humidity was kept constant at 40%. Ten grams of air-dried soil were deployed in uncovered glass Petri dishes forming a thick layer of 1 mm of soil. A stock solution containing 16 US EPA priority PAHs at 2000 µg mL⁻¹ in dichloromethane:benzene was provided by Supelco® (99.0% purity, Bellefonte, PA, USA). Each sample was 10-times spiked with 25 µL of this stock solution diluted with an hexane/dichloromethane (1:1) mixture (Scharlau Chemie S.A., Barcelona, Spain; hexane: 96% purity, dichloromethane: 99.5% of purity) to an individual PAH concentration of 100 µg mL⁻¹, leading to a Σ16 PAHs concentration of 40 µg g⁻¹ in soil. Afterwards, samples were incubated inside the climate chamber. In order to differentiate concentration decreases due to slow sorption and/or volatilization processes from photodegradation, a number of dark control samples covered with aluminum foil were exposed to the same environmental conditions. Duplicates of irradiated samples and dark

Table 1
Physico-chemical properties of the selected Mediterranean soils.

	Arenosol soil	Regosol soil
pH	5.8	8.0
Electrical conductivity at 25 °C (dS m ⁻¹) ^a	0.06	0.13
Organic C (%) ^b	0.71	1.70
Total Kjeldahl N (%)	0.07	0.18
C/N	10.1	9.44
CaCO ₃ (%)	0.10	23.20
Texture: sand/silt/clay (%) ^c	74.1/14.0/11.9	43.4/22.3/34.3
Cation exchange capacity (meq 100 g ⁻¹) ^d	12.60	18.23
Exchangeable calcium (mg CaO kg ⁻¹) ^d	4.80	12.55
TiO ₂ (mg kg ⁻¹)	429	41.3
MnO ₂ (mg kg ⁻¹)	573	648
Al ₂ O ₃ (mg kg ⁻¹)	3008	6070
Fe ₂ O ₃ (mg kg ⁻¹)	6686	13492

Analytical methods.

^a Aqueous extracts 1:2.5.

^b Oxidizable C by Walkley-Black method.

^c Robinson Pipette method.

^d 1 N ammonium acetate extracts.

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