CLIMATE CHANGE IMPACT ON THE PAH PHOTODEGRADATION IN MEDITERRANEAN SOILS

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Introduction

Climate scientists have widely demonstrated that human-caused greenhouse gases will drive to an increase of the global temperature. The Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC 2013) predicted, under different expected scenarios[1], that the mean global temperatures will increase by 1 to 1.5 °C in the period 2016–2035 with respect to those registered between 1850 and 1900, resulting in an increase up to 4.8ºC at the end of the century. Although the high latitude regions will suffer the greatest warming[2], the Mediterranean basin has been identified as one of the most vulnerable regions, since it lies in a transition zone between arid and temperate/rainy climates[3-7].

One of the consequences of the climate change is its potential to alter the environmental distribution and biological effects of chemical toxicants[2], including persistent organic pollutants (POPs) and other semi-volatile organic compounds. Thus, climate change is expected to affect the environmental fate of organic contaminants, which is largely governed by temperature[8-10]. The increase of the temperature may enhance the mobilization of organic contaminants from reservoirs such as natural waters, soils and sediments, therefore altering their rates of accumulation, sorption and degradation[10]. Polycyclic aromatic hydrocarbons (PAHs) are a group of semi-volatile organic compounds composed of two or more benzene and/or pentacyclic aromatic rings[11]. PAHs in the environment may have a petrogenic or a pyrogenic origin[12], being emitted by a number of natural or anthropogenic sources[13]. In recent years, PAHs have become an issue of concern due to their potential to cause adverse effects on the global environment and human health, owning some of them carcinogenic and mutagenic properties. The environmental fate and transport of PAHs, similarly to some POPs, is highly influenced by temperature and solar radiation[14], which, in turn, are subjected to the effects of the climate change. This study was aimed at estimating the photodegradation rate of PAHs in Mediterranean soils over time, considering the current climate conditions as well as an IPCC-based climate change scenario in the Mediterranean region.

Materials and methods

Soil samples were taken from the A horizon of two representatives Mediterranean remote areas. Arenosol soil is an acidic and coarse-textured soil with granitic origin and classified as Haplic Arenosol according to the FAO classification[15]. It is commonly used for ecotoxicity testing in terrestrial environments. By contrast, Regosol soil corresponds to a Calcaric Regosol, which is a fine-textured soil formed by sedimentary materials. The main properties of both soils are summarized in Table 1.

Two climate scenarios were simulated in a Binder KBWF 240 climatic chamber (Binder GmbH, Tuttlingen, Germany), with controlled lighting, temperature and humidity. An actual Mediterranean climate scenario was set by considering a temperature of 20ºC and a daylight of 9.6 W/m^2. In turn, an extreme IPCC-based climate change scenario (RCP 8.5) was simulated by assuming a temperature and daylight of 24ºC and 24 W/m^2, respectively. Prior to the initiation of the experiment, soils were analyzed to confirm the absence of PAHs. Moreover, soils were incubated at the same conditions in manometric respirometers (Oxitop®, WTW) to discard the presence of any biotic reaction. Afterwards, 10 grams of soil were deployed in uncovered Petri dishes forming a thick layer of 1 mm of soil. Samples were 10-times spiked with 25 µL of a stock solution containing 16 US EPA priority PAHs at a concentration of 100 µg/mL. Subsequently, samples were incubated inside the climate chamber. Simultaneously, dark control samples covered with aluminum foil were exposed to the same environmental conditions for each scenario to differentiate concentration decreases due to sorption and volatilization processes from those associated to photodegradation. Irradiated samples and dark controls were daily removed by duplicate after 1, 2, 3, 4, 5, 6, 7, 14 and 28 days.

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

	Arenosol soil	**Regosol soil**
pH	5.8	8.0
Electrical conductivity at 25ºC (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_2O_3 (mg kg^{-1})	3008	6070
Fe_2O_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.

PAHs were extracted by using an hexane/dichloromethane (1:1) mixture in a Milestone Start E Microwave Extraction System (Milestone S.r.l., Sorisole, Italy), according to the US EPA method 3546 or by Ultrasonic extraction following the US EPA method 3550. Subsequently, the extracts were filtered and further concentrated down to 1 mL in a rotatory evaporator. Finally, they were dried with a gentle stream of purified N_2, being further dissolved with 500 µL of solvent. All samples were analyzed by means of gas chromatography-mass spectrometry (GC-MS) in accordance to the US EPA method 8270. A Hewlett-Packard G1099A/MSD5973 equipment was used to quantify the content of the 16 PAHs under study. Regarding to the quality control, a mixture of 6 deuterated PAHs (d_4-1,4-dichlorobenzene, d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene, and d_{12}-perylene) was spiked prior to the extraction to check any potential losses during the process. In turn, d_{10}-fluorene and d_{12}-benzo(a)pyrene were used as internal standards and added before GC-MS injection.

Results and discussion

A different behavior for the 16 PAHs in coarse and fine-textured soils was observed, leading to different photodegradation rates, which were calculated as the difference of PAH levels between irradiated samples and dark controls, in each simulated climate scenario (Table 2). Three main processes might be related to the observed concentration decreases: volatilization, sorption, and photodegradation. However, the contribution of each process was different according to the physicochemical properties of each compound, soil texture, climate conditions, and time of exposure.

In Arenosol soil, higher photodegradation rates of PAHs were found in the climate change scenario, with higher temperature and lighting. Naphthalene and acenaphthylene, the most volatile hydrocarbons, were quickly volatilized irrespective of the environmental conditions. In the current Mediterranean climate scenario, acenaphthene, anthracene and fluorene were completely removed after 1, 4 and 7 days of exposure, respectively, while fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(b+k)fluoranthene were not photodegraded. In contrast, the latter PAHs experienced photodegradation rates up to 60% in the climate change scenario after 28 days of exposure. Furthermore, benzo(a)pyrene, benzo(ghi)perylene, dibenzo(ah)anthracene and indeno(123cd)pyrene underwent a photodegradation approximately 30% higher in the climate change scenario than in the current climate scenario.

Table 2. Photodegradation rates (%) of the 16 PAHs under study after 28 days in Arenosol and fine-textured Regosol soil when simulating current Mediterranean and extreme IPCC-based climate change scenarios.

PAH	**Arenosol soil**		**Regosol soil**	
	Current climate scenario	**Climate change scenario**	**Current climate scenario**	**Climate change scenario**
Naphthalene	0	0	0	0
Acenaphthylene	0	0	0	0
Acenaphthene	1.5	21.3[a]	2.0	2.5
Fluorene	3.0	15.4[c]	9.5	7.8
Phenanthrene	11.2	16.0	33.2	30.5
Anthracene	19.7	85.4[b]	39.8	41.3[d]
Fluoranthene	0	28.9	12.5	14.1
Pyrene	0	60.1	17.1	18.6
Benzo(a)anthracene+ Chrysene	0	41.0	30.0	34.2
Benzo(b+k)fluoranthene	0	20.2	30.0	8.0
Benzo(a)pyrene	23.0	54.6	4.9[c]	37.8[d]
Benzo(ghi)perylene	3.6	27.1	24.6	19.4
Dibenzo(ah)anthracene	2.0	37.0	28.3	23.2
Indeno(123cd)pyrene	11.7	39.1	68.9	43.2

[a]Complete degradation after: [a]1 day, [b]4 days, [c]7 days, and [d]14 days.

Similarly to Arenosol soil, naphthalene and acenaphthylene were also quickly volatilized in the fine-textured Regosol soil in both climate scenarios. In turn, similar photodegradation rates were observed in both climate scenarios for 3-, 4-, 5- and 6-ringed PAHs, being the differences non-significant. The similar degradation rates in Regosol soil may be explained by two reasons: 1) the soil particle size plays a key role, since photolysis increases from sand through silt to clay[16], 2) the presence of photocatalysts (iron, aluminum and manganese oxides) in soil (Table 1) may enhance the photodegradation in any climate conditions[17,18]. Although the content of titanium oxide (TiO_2) in fine-textured Regosol soil is lower than that in Arenosol soil, the total amount of oxides of iron, aluminum and manganese, which are related to the fine fraction, is much higher in Regosol soil. Because of the lower amount of catalysts, excepting TiO_2, the coarse soil requires more activation energy to induce PAH photodegradation, presenting an important role in the climate change scenario, when temperature and light conditions are increased.

Finally, it must be highlighted that metabolites, potentially more toxic than their parental compounds, are likely to be generated due to the photodegradation of PAHs[19]. Future studies will be focused on byproducts identification, having been quinones, such as 9,10-anthracedione and benzo(a)anthracene-7,12-dione, already detected in the same reported chromatograms.

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