

# CLIMATE CHANGE EFFECTS ON PAH PHOTODEGRADATION IN MEDITERRANEAN SOILS: A PILOT STUDY

Marquès M<sup>1,2</sup>, Mari M<sup>1</sup>, Sierra J<sup>1,3</sup>, Schuhmacher M<sup>1,2</sup>, Domingo JL<sup>2</sup>, Nadal M<sup>2\*</sup>

<sup>1</sup>Environmental Engineering Laboratory, Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain; <sup>2</sup>Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain; <sup>3</sup>Laboratory of Soil Science, Faculty of Pharmacy, Universitat de Barcelona, Avda Joan XXIII s/n, 08028 Barcelona, Catalonia, Spain

## Introduction

The periodical assessments of the Intergovernmental Panel on Climate Change (IPCC) have demonstrated that, mostly due to the increasing air release of greenhouse gases, the Earth's climate system is changing<sup>1</sup>. Global warming has become one of the most important worldwide problems to face in the 21<sup>st</sup> century. A rise of the sea level and an increased frequency of extreme climatic events, including intense storms, heavy rainfalls and droughts, are expected to occur<sup>2,3</sup>. The planetary mean temperature is projected to increase 1.8-4.0°C by the end of the century under a range of probable greenhouse gas emission scenarios, being the greatest warming expected at high latitudes<sup>4</sup>. Since it is a transition zone between arid and temperate/rainy climates<sup>5-9</sup>, the Mediterranean basin has been pointed out as one of the most vulnerable regions in the world to the effects of the climate change.

One of the consequences of climate change that has recently attracted most attention is its potential to alter the environmental distribution and biological effects of chemical toxicants<sup>4</sup>, including persistent organic pollutants (POPs) and other semi-volatile organic compounds. Polycyclic aromatic hydrocarbons (PAHs) form a well known family of widespread environmental pollutants, whose chemical structure is based on two or more fused benzene rings. PAHs are released from a variety of natural and anthropogenic combustion processes<sup>10</sup>. Human exposure to PAHs may pose important adverse health effects, while some of them have carcinogenic and mutagenic properties. Environmental fate and transport of PAHs, similarly to some POPs, is highly influenced by temperature and solar radiation<sup>11</sup>, which, in turn, are subjected to the effects of the climate change. This study was aimed at estimating the loss rate of PAHs in two Mediterranean soils in a base scenario, according to IPCC estimations.

## Materials and methods

Soil samples were taken from the A horizon of two common Mediterranean soils with different physicochemical properties (texture, pH, calcium carbonate content, etc.). Arenosol soil samples belonged to Haplic Arenosol, an acidic and coarse-textured soil with granitic origin and commonly used for ecotoxicity testing in terrestrial environments. In turn, Regosol soil samples corresponded to Calcaric Regosol, which is formed of sedimentary materials and fine-textured soil. The main properties of both soils are summarized in Table 1.

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 <sup>-1</sup> ) <sup>a</sup>	0.06	0.13
Organic C (%) <sup>b</sup>	0.71	1.70
Kjeldahl (%)	0.07	0.18
C/N	10.14	9.44
CaCO <sub>3</sub>	0.1	23.20
Texture: sand/silt/clay (%) <sup>c</sup>	74.1/14.0/11.9	43.4/22.3/34.3
Cation exchange capacity (meq 100 g <sup>-1</sup> ) <sup>d</sup>	12.60	18.23
Exchangeable calcium (mg CaO kg <sup>-1</sup> ) <sup>d</sup>	4.803	12.554

Analytical methods: <sup>a</sup>Aqueous extracts 1:2.5; <sup>b</sup>Oxidizable C by Walkley-Black method;

<sup>c</sup>Sedimentation method; <sup>d</sup>1 N ammonium acetate extracts.

Experiments were performed in a Binder KBWF 240 climatic chamber (Binder GmbH, Tuttlingen, Germany) with constant lighting, temperature and humidity conditions. An IPCC-based base scenario of average climate conditions in the Mediterranean area was set by assuming a temperature of 20 °C and a daylight of 9.6 W/m<sup>2</sup>. Prior to irradiation tests, soils were analyzed to assure they did not contain PAHs. Ten grams of soil were deployed in 8 uncovered glass Petri dishes. Every sample was spiked with 25 µL of a stock solution containing 16 US EPA priority PAHs at a concentration of 100 µg/mL. Samples were kept for one hour in the darkness at room temperature before being incubated inside the climate chamber. In order to assess any potential changes in PAH concentrations over time, a soil sample was daily removed from the climate chamber during one week. Dark controls with the same climatic conditions for each scenario were also performed to assess slow sorption processes.

PAHs were analyzed by gas chromatography/mass spectrometry (GC/MS). Firstly, PAHs were extracted from soil samples by using a hexane/dichloromethane (1:1) mixture in a Milestone Start E Microwave Digestion System (Milestone S.r.l., Sorisole, Italy), in accordance to the US EPA method 3546. Subsequently, a clean-up procedure based on columns containing activated ICN alumina B - Super I was carried out to eliminate interfering chemicals. A first fraction was collected by elution of 25 mL of hexane, while a second PAH-containing fraction was obtained after eluting 40 mL of hexane/dichloromethane (1:1)<sup>12</sup>. Subsequently, the extract was evaporated with a gentle stream of purified N<sub>2</sub>. The analytical determination was performed by means of a Hewlett-Packard G1099A/MSD5973 equipment, following the US EPA method 8270. Two surrogate standards, d<sub>10</sub>-fluorene and d<sub>12</sub>-benzo(a)pyrene, were spiked prior to microwave extraction to check any potential losses. In addition, d<sub>8</sub>-naphthalene was used as internal standard for calibration and quantification.

## Results and discussion

The results of the present study showed that the concentration of PAHs in both soils clearly reduced over time. However, different patterns were noted depending on the molecular weight of each hydrocarbon and the properties of each soil. PAH concentrations after one week of light radiation in Regosol soil are depicted in Figure 1. In general terms, PAHs could be classified in three different groups, according to the number of benzene rings. The first group included 2-ringed PAHs, whose high volatility is a limitation factor to report PAH losses exclusively due to photodegradation. Naphthalene could not be quantified in any soil. In addition, although the levels of acenaphthene and acenaphthylene were above the limit of detection, values showed a high variability over time. Both compounds presented very low concentrations at the beginning of the experiment, possibly linked to the effect of other loss processes such as volatilization. In turn, no significant changes of concentration were found after 7 days of exposure, therefore suggesting that acenaphthene and acenaphthylene could be partially formed as photodegradation products of larger PAHs. Three-ringed PAHs, which encompass medium molecular weight PAHs, suffered a notable photodegradation after one week. Anthracene showed the most significant loss (80%) in Arenosol soil, while the highest reduction of phenanthrene (60%) was found in Regosol soil. Finally, 4- and 5- ringed PAHs presented slightly slower photodegradation rates, with losses of up to 50%. The only exception was benzo(a)pyrene, whose levels reduced 75% and 70% in Regosol and Arenosol soils, respectively, being its behavior similar to that of medium molecular weight PAHs.

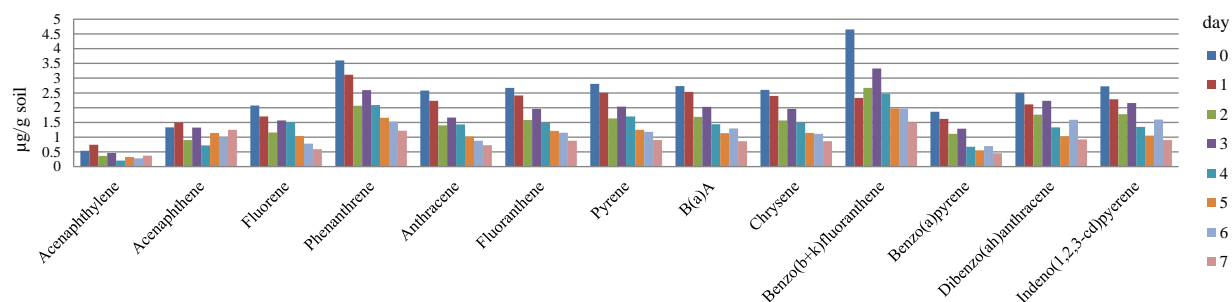


Figure 1. Trends of PAH concentrations in Regosol soil samples subjected to light exposure for one week.

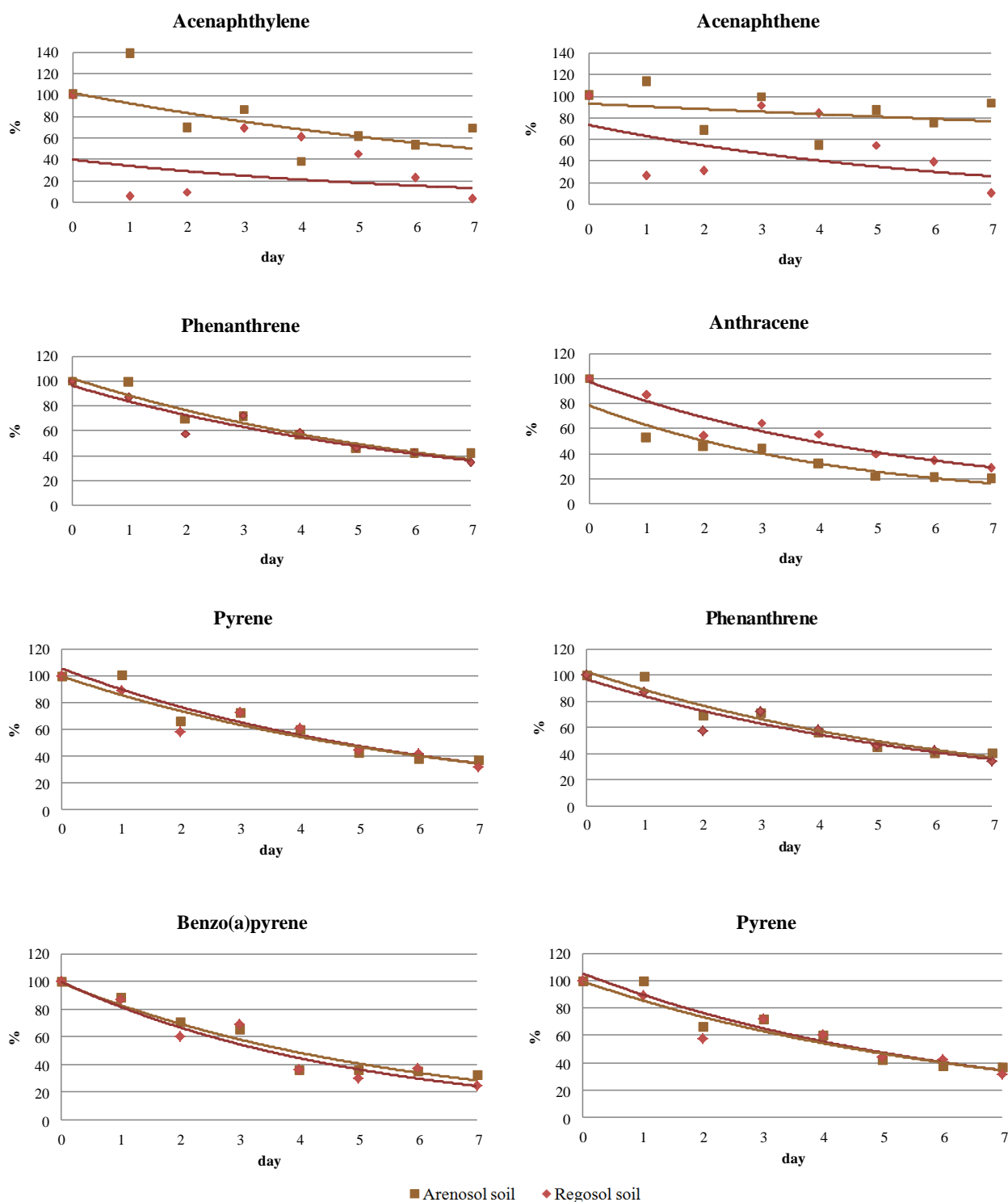


Figure 2. Comparison of PAH photodegradation rates in a number of 2-, 3-, 4- and 5- ringed PAHs in typically Mediterranean Arenosol and Regosol soils.

As previously reported<sup>12</sup>, these findings show the clear impact of temperature and light exposure on the behavior of PAHs. Some differences in the PAH loss were noted according to the type of soil, especially for low molecular weight PAHs. Acenaphthylene, acenaphthene and anthracene showed more notable different photodegradation rates, being the reduction of chemicals more pronounced in Regosol soil. In agreement with the results from previous PAH biodegradation studies, low molecular weight PAHs seem to be more easily degraded in soils containing high clay contents than in less sorptive soils<sup>13</sup>. However, the relationship between the PAH loss according to soil properties should be further investigated, including the role of other degradation processes of PAHs (i.e., biodegradation or volatilization).

Future studies will be focused on assessing the PAH photodegradation in other IPCC-based climate change scenarios for the Mediterranean area. These data will be essential to estimate the medium- and long-term environmental burdens of PAHs, taking into account current and projected emissions of PAHs to air. Furthermore, longer experiments will have to be performed to accurately assess the photodegradation of high molecular weight PAHs, as well as the formation of byproducts, paying special attention to benzo(a)pyrene, a hydrocarbon of high carcinogenic potential.

### Acknowledgements

The authors thank the Spanish Ministry of Economy and Competitiveness for its financial support through the project CTM2012-33079. Montse Marquès also received a PhD fellowship from AGAUR (Commissioner for Universities and Research of the Department of Innovation, Universities and Enterprise of the “Generalitat de Catalunya” and the European Social Fund).

### References:

1. IPCC. (2013) IPCC Fifth Assessment Report: Climate Change 2013 (AR5)
2. Kusangaya S, Warburton ML, Archer van Garderen E, Jewitt GPW. (2013); *Phys Chem Earth Parts A/B/C*, in press; doi: 10.1016/j.pce.2013.09.014
3. McBean G, Ajibade I. (2009); *Curr Opin Environ Sustainability*. 1: 179-86
4. Noyes PD, McElwee MK, Miller HD, Clark BW, Van Tiem LA, Walcott KC, Erwin KN, Levin ED. (2009); *Environ Int*. 35: 971-86
5. Sánchez-Canales M, López Benito A, Passuello A, Terrado M, Ziv G, Acuña V, Schuhmacher M, Elorza FJ. (2012); *Sci Total Environ*. 440: 140-53
6. Schröter D, Cramer W, Leemans R, Prentice IC, Araújo MB, Arnell NW, Bondeau A, Bugmann H, Carter TR, Gracia CA, De La Vega-Leinert AC, Erhard M, Ewert F, Glendining M, House JI, Kankaanpää S, Klein RJT, Lavorel S, Lindner M, Metzger MJ, Meyer J, Mitchell TD, Reginster I, Rounsevell M, Sabaté S, Sitch S, Smith B, Smith J, Smith P, Sykes MT, Thonicke K, Thuiller W, Tuck G, Zaehle S, Zierl B. (2005); *Science* 310: 1333-7
7. Bangash RF, Passuello A, Hammond M, Schuhmacher M. (2012); *Sci Total Environ*. 440: 60-71
8. Marquès M, Bangash RF, Kumar V, Sharp R, Schuhmacher M. (2013); *J Hazard Mater*. 263: 224-32
9. Terrado M, Acuña V, Ennaanay D, Tallis H, Sabater S. (2014); *Ecol Indic*. 37: 199-209
10. Li A, Schoonover T M, Zou Q, Norlock F, Conroy L M, Scheff P A. (2005); *Atmos Environ*. 39: 3491-501
11. Nadal M, Wargent JJ, Jones KC, Paul ND, Schuhmacher M, Domingo JL. (2006) *J Atmos Chem*. 55: 241-52
12. Nadal M, Schuhmacher M, Domingo JL. (2004); *Environ. Pollut*. 132: 1-11
13. Crampon M, Bureau F, Akpa-Vinceslas M, Bodilis J, Machour N, Le Derf F, Portet-Koltalo F. (2014) *Environ Sci Pollut Res.*, in press, doi: 10.1007/s11356-014-2799-6