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Hydrocarbon pollution from domestic oil recycling industries in peri-urban soils. Lipid molecular assemblages

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ABSTRACT

The impact of continuous inputs of hydrocarbons from domestic waste oil recycling industries and further remediation practices, like inertization (liming and addition of ashes), have been studied in peri-urban soils in Spain in order to monitor the fate and spatial distribution patterns of potentially hazardous organic compounds. Physical and chemical properties of undisturbed soils or contaminated with waste-oil were determined. Lipid fractions were extracted using a dichloromethane:methanol mixture and analyzed by gas chromatography–mass spectrometry (GC/MS) in search for environmental proxies. A pollution gradient (distance to the waste oil spill) was accompanied by the following chromatographic features: (i) the increasing extent of the unresolved 'hump' caused by branched/cyclic alkanes with non-biogenic signature, (ii) the depletion of fatty acids and alkanol series, and (iii) the accumulation of phenols and polycyclic hydrocarbons. An increase in the C-preference index (odd-C/even-C numbered homologues) of fatty acids was also detected with an opposed trend in alkane chains. Concerning alkanes and fatty acids chain length, there was a generalized decrease whereas a progressive increase of alien long-chain (>C_{20}) homologues was observed. Signature compounds found in waste oil (mainly squalene, steroids and waxes) were almost absent from neighbor soils, either undisturbed or inertized, suggesting the occurrence of rapid biodegradation or condensation processes in the soil matrix probably aided by the remediation practices or by abiotic humification processes.

1. Introduction

The fate of lipid compounds in terrestrial and aquatic environments is a complex process related to the ecosystem biogeochemical performance, which in turn also depends on the geological sources and the general climatic conditions [1,2]. In some circumstances, massive inputs of lipid compounds following environmental disasters, spills or uncontrolled dumping of industrial by-products may lead to dramatic local or diffuse pollution. The spatial variability of the composition of the molecular assemblages present in the soil lipid fraction [3] may vary both in terms of the distance from the pollution focus, as well as in terms of the local application of 'inertizing' treatments or other remediation practices aiming at enhancing soil function as 'environmental filter' able to immobilize hazardous compounds that otherwise could enter the biogeochemical cycle [4].

This study was carried out in a well-publicized peri-urban contaminated site located in an industrial area near Madrid at Arganda del Rey municipality, i.e., the Boca Alta Lagoon system, including a waste oil spill, i.e., Laguna Negra or 'Black Lagoon' (Fig. 1a and b). Although oil spilling is currently discontinued a series of industries in the vicinity continued were spilling for the last 30 years that has resulted in severe landscape perturbation and the death of thousands of birds [5].

The current situation began at the 1980s at the so called Boca Alta Lagoon, when oil recycling companies were dumping wastes in the lake with little control or concern about possible environmental consequences. Since the discontinuation of activities of the main recycling plant in 1997 and for more than 20 years Boca Alta Lagoon has been covered by a layer of non-volatile floating black fluid. Nonetheless, dumping of residues at the lagoon systems has continued with additions from industrial extraction companies pouring pitch-like fluid wastes generated during a number of not publicized activities. In fact, the information available suggests that the industrial activities consisted of a large variety of waste-generating operations including the mentioned domestic oil recycling, petroleum, grease, lubricants and other

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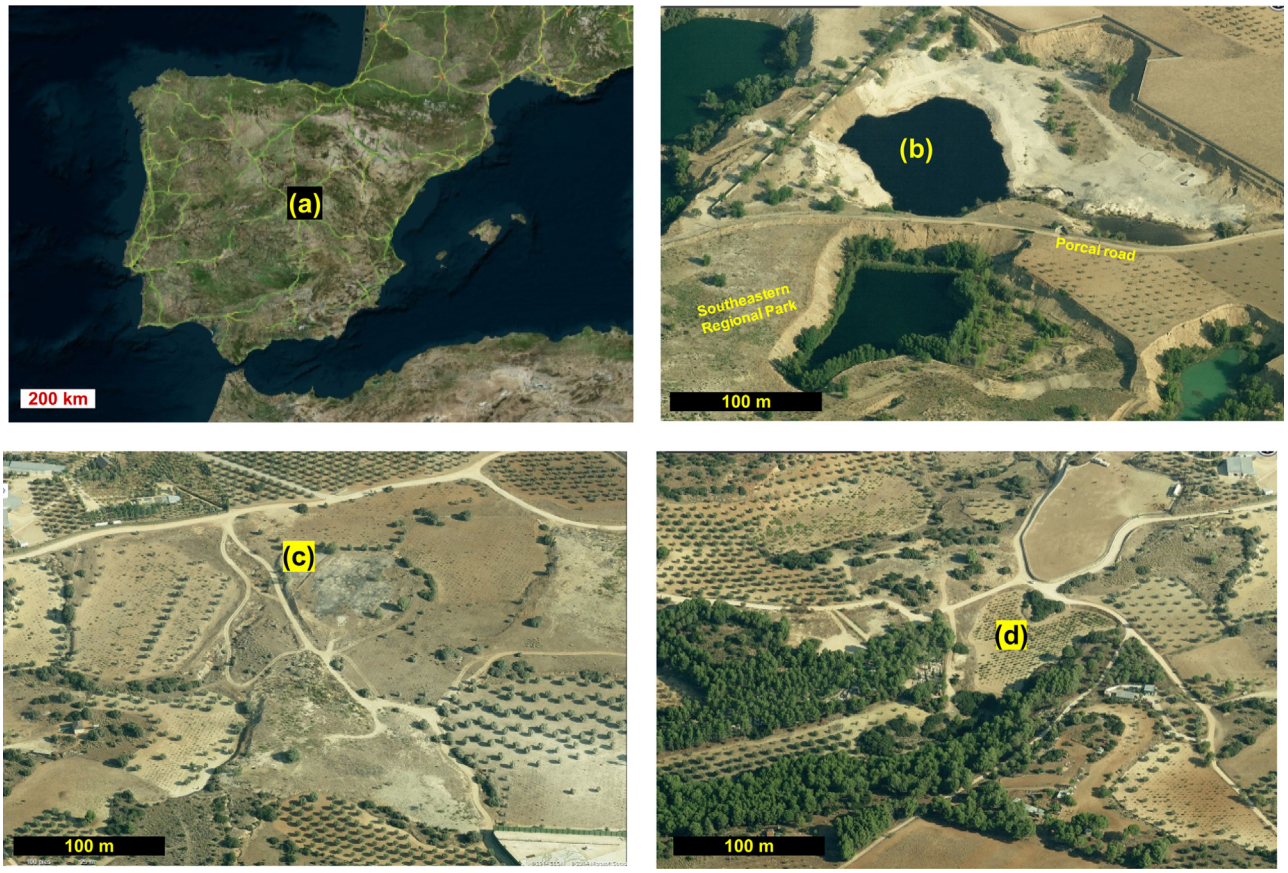

Fig. 1. Lagoon system used as oil dumping (Arganda del Rey, Madrid): (a) geographical location of the sampling sites in the Iberian Peninsula, (b) Black Lagoon (sampling series T) and soils neighbor to the Black Lagoon (series L), (c) sampling sites at sealed, inertized, lagoon plots (series C), (d) and control soils in middle zone (series M) and a seminatural soil (series R).

industrial manufactures like oil and petroleum sulfates and insulators [6]. Remediation practices comprise an inertization process in which the waste oil (originally an emulsion with low pH) is treated with a mixture of ash and lime, with the consequent formation of secondary salts [7].

The aim of this work is to monitor the fate and changes in spatial distribution patterns of the potentially hazardous organic compounds, in order to assess the environmental impact of the Boca Alta Lagoon oil spill on the surrounding soil physical and chemical properties. A comparative study including both the molecular composition study of the extractable lipids in the oil floating with those extracted from the soils was conducted. This would inform about lipid transformations resulting either from remediation activities in sealed lagoon sites or from biodegradation and organo–mineral stabilization processes in sealed, abandoned contaminated lagoons at comparatively higher distances from the main Black Lagoon. It is also expected that the chemical characterization of these soil lipid fractions extracted from peri-urban contaminated sites would lead to define a series of molecular proxies with use in assessing the degree of diagenetic transformation of the organic matter in the waste oil spill and their resilience to natural hazards.

2. Material and methods

2.1. Location and context

The main pollution source, the pitch lake (or Black Lagoon) is located in Arganda del Rey, in the Southeast Regional Park in Madrid (40°18′10.1″N, 3°29′46.8″W). This site was early a wide natural lagoon system of high ecological value (Boca Alta Lagoon). The scenario is located at the confluence of Manzanares and Jarama rivers forming a wetland with high wildlife density and diversity (Fig. 1a).

The seminatural ecosystems include typical kermes oak (*Quercus coccifera*) and oak forests (*Quercus ilex* ssp. *ballota*) accompanied by brushwood with *Retama sphaerocarpa*,*Cistus albidus* and other aromatic plants, including endemic species of the gypsiferous limestone substrate.

The studied area includes two large sets of geological formations: (i) lacustrine, predominantly with Neogene sediments and, (ii) coarse riverine sedimentary materials mainly Quaternary. The former Neogene lacustrine formations include gypsum and limestone, whereas the latter consists of Quaternary colluvial materials in the river channels. The soil sampled in the area corresponded to: Leptic Kastanozems (Arenic) (referred to as series R); Hortic Anthrosols (Eutric) (series M); Spolic Technosols (Toxic Densic) (series C) and Spolic Technosols (Toxic) (series L) [6]. The climate in the area is Mediterranean with continental features and tendency to aridity; average annual rainfall of 450 mm and an