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Polyaromatic hydrocarbons (PAHs) in a paleolake sediment core from eastern Romania

Denisa Igescu[*1,2], Virgil Drăguşin[1,3], Sorin Avramescu[4], Alina E. Olaru[1,2,4]

1 . "Emil Racoviţă" Institute of Speleology of the Romanian Academy, Calea 13 Septembrie 13, 050711 Bucharest, Romania
2 . Faculty of Biology, University of Bucharest, Bucharest, Romania
3 . Reaseach Institute of the University of Bucharest, University of Bucharest, Romania
4 . PROTMED Research Centre, University of Bucharest, Bucharest

In southern Dobrogea, around the town of Mangalia, there is an important karst area where large dolines are dominating the landscape. The presence of mesothermal groundwater rich in H_2S and CH_4 created conditions for the development of hypogene karst (Sârbu & Lascu, 1997; Onac & Drăguşin, 2017; Drăguşin *et al.*, 2021), while also providing the basis of a chemoautotrophic ecosystem (Sârbu & Lascu, 1997; Sârbu *et al.*, 2019; Brad *et al.*, 2021).

Large collapse dolines present in this area functioned as lakes during the Pleistocene and into the present, allowing for the accumulation of lake sediments for extensive periods of time. Such a doline, Obanul Mare, was recently cored throughout its sediment infill and we present here data on the content of polyaromatic hydrocarbons (PAHs) in these sediments.

PAHs are a class of chemical compounds consisting of two or more condensed aromatic rings, which can be used as proxies for the intensity and frequency of biomass burning. Under certain circumstances, several PAHs can be created by geogenic processes and are frequently found in hydrocarbon formations (Stogiannidis & Laane, 2015).

By studying PAHs from the Obanul Mare paleolake, we intend to reconstruct local fire activity in parallel with paleo-fire reconstructions based on microcharcoal from the same sediment core. Thus, we focused on measuring 15 PAHs from 26 samples that were selected in order to cover the entire sediment sequence. While the level of the mesothermal sulphidic aquifer is controlled by that of the neighboring Black Sea, we intend to identify periods with geogenic PAH input that would help us identify sea level high stands.

Sediment samples were allowed to dry at ambient temperature in order to prevent the loss of low molecular weight PAHs (e.g. naphthalene) by sublimation. Prior to the extraction step, the sediment was ground into a fine powder using an agate mortar and pestle, in order to enhance the contact between the sample and the solvent [acetone-dichloromethane (1:1)] and to insure a high extraction yield. Extraction was performed using the accelerated solvent extraction method in a Dionex ASE 200 system at 100 °C and 1500 psi.

The accelerated solvent extraction method takes advantage of the fact that solubility increases with temperature and, at the same time, liquids can penetrate more effectively into different matrices under higher pressure. Higher temperatures allow for more effective extraction of analytes that have been encapsulated in the matrix, as well as of chemicals that have been adsorbed on the surface of some matrices.

After extraction, sample concentration was performed using a Cole Parmer Type 28100 Dri-Bath Thermolyne concentrator in a stream of nitrogen, until the sample dried. Afterwards, a fixed volume of 2 mL of acetonitrile was added in order to retrieve the sample from the vial. Samples were stored in 2 mL vials at −20 °C prior to chromatographic analyses.

Samples were analyzed on a Varian ProStar HPLC fitted with a fluorescence detector, as it is favorable in the detection of PAHs at trace level due

*Corresponding author. *E-mail address*: d.igescu20@s.bio.unibuc.ro (D. Igescu).

to its high sensitivity and selectivity. A significant challenge was to obtain a good separation of these PAHs taking into account that matrices of samples were not always similar, and that other compounds present in the sample were overlapping with the signal of the PAHs.

Our preliminary results show that low molecular weight PAHs (LWPAHs) had concentrations of less than $0.1\,ng\,g^{-1}$, significantly less than high molecular PAHs (HWPAHs), that showed concentrations between $1\,ng\,g^{-1}$ and $10\,ng\,g^{-1}$. Dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-C,D)pyrene were the three HWPAHs that were most frequently found in our samples. However, the distribution of HWPAHs varied considerably and in order to better understand the variety of pyrogenic PAHs and their geogenic delimitation, we will use paleofire data inferred from microcharcoal studied from the same sediment samples.

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