CHARACTERIZATION OF SOIL ORGANIC MATTER AND PAHs CONCENTRATION IN SOILS AT LIVINGSTON ISLAND, ANTARCTICA

Denitsa Apostolova[1], Ekaterina Filcheva[2], Achim Bechtel[3],
Kalinka Markova[1], Irena Kostova[1]
[1]Faculty of Geology and Geography, St. K. Ohridski Sofia University
[2]N. Poushkarov Institute of Soil Science, Agrotechnologies and Plant Protection - Sofia
[3]Department of Applied Geosciences and Geophysics, University of Leoben

Abstract

Three soil samples from sites situated near the Bulgarian Antarctic Base (BAB) have been studied for better understanding of soil formation processes and for determining the concentration of polycyclic aromatic hydrocarbons (PAHs). The content and composition of soil organic matter showed that the processes of humus formation are at a very initial stage. Twelve from totally sixteen PAHs defined by US EPA as priority pollutants are registered in soils studied. The highest concentration of PAHs (6.38 µg/g TOC) is established in the first sample (1s_2016) located nearest to the BAB. According to the calculated B(a)P equivalent carcinogenic power (BaPE) for PAHs no toxicity value (< 1) for all samples, respectively 1s_2016 (0.55 µg/g TOC), 15s_2016 (0.12 µg/g TOC) and 19s_2016 (0.09 µg/g TOC, were determined.

Key words: Antarctic soil, PAHs, humic acids, fulvic acids

INTRODUCTION

The Bulgarian Antarctic Base 'St. Kliment Ohridski' (BAB) is situated at the eastern coast of the South Bay of Livingston Island, South Shetland Archipelago. There are three more detailed investigations describing the composition, properties and some ecological aspects concerning soil sampling around it (Sokolovska et al., 1996, 2015; Kostova et al., 2015). Soil organic matter (SOM) content in Antarctica is low. Its sources are scarce vegetation (lichens, mosses and rarely grasses). Birds (eg penguin) excrements also play an important role in the humus formation processes.

During the last years scientists pay a great attention to human impacts to the Antarctic environment. Apart from regular human activity accidental contaminations and PAHs emission from regional sources are also possible. Since the soils are a major recipient of contamination from anthropogenic sources, there are a number of studies focusing on various aspects of soil disturbances (Ugolini, Bockheim, 2008).The low temperatures and abundant snow/rain events in some regions such as the Southern Shetlands and Antarctic Peninsula, favour the atmospheric deposition of organic pollutants and their persistence in soils. They are free of snow/ice cover only in coastal areas and for few

weeks/months during the austral summer. High concentrations of polycyclic aromatic hydrocarbons (PAHs) have been measured in soil and sediment samples collected in the vicinities of the research stations or where oil spills, fossil fuel combustion, or sewage discharge have been occurred (Cabrerizo et al., 2012; Bícego et al., 2009).

MATERIALS AND METHODS

Soil samples were collected in the vicinity of BAB from Livingstone Island during the 25th Bulgarian Antarctic expedition. The first sample (sample 1s_2016) was collected north-east, with 14 m elevation. The soil sample point was clear of snow, ice and sample was characeried by a gray-brown colour. Mosses and lichens were observed around the sampling area. The second sample (sample 15s_2016) was taken from the Johnson Dock area, on a cliff over the sea and with 8-10 m elevation. The soil sample was dug under the grass and has a dark brown colour. Thick grass vegetation, lichens, mosses and remains of mussels can be observed near to the place of sampling. The third sample (sample 19s_2016) was taken to the south-west of the base from Punta Esperides area, in the highest point with 95-98 m elevation. Many mosses and rocks were observed at the sampling site. The soil has a dark brown colour. The rock bottom of the first and second soil samples was represented by sedimentary and the third by volcanic rocks.

Total organic carbon and composition of SOM were determined according to the modified method of Turin (120°C, 45 min, with catalyst Ag_2SO_4) and method of Kononova, Belchikova (Kononova, 1966; Filcheva, Tsadilas, 2002). Optical characteristics, in E_4/E_6, the ratio between extinctions of Humic acids at 465 and 665 nm.

Gas chromatography-mass spectrometry (GC-MS) was used for identification and quantification of PAHs in samples studied. For the determination of the molecular composition of hydrocarbons, approximately 5 g of each sample were extracted by dichloromethane for 1 h at 75°C and a pressure of 75 bar in a Dionex ASR 200 instrument. After concentration, the extracts were dissolved in a solvent mixture of hexane:dichloromethane (80:1) and asphaltenes were subsequently separated by centrifugation. The hexane-soluble organic compounds (maltenes) were subdivided into saturated and aromatic hydrocarbons and polar components using a Köhnen-Willsch MPLC (medium pressure liquid chromatography) instrument according to Radke et al. (1980). The fractions of aromatic hydrocarbons were analyzed by GC-MS Finnigan MAT GCQ, equipped with a DB-5MS silica capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Oven temperature was programmed from 70-300°C with steps of 4°C/min, followed by an isothermal period of 15 min. Helium was used as carrier gas. The device was set in electron impact mode with a scan rate of 50-650 Daltons (0.7 s/scan). Identification of biomarkers is based on retention time and comparison of mass spectra with published data. The determination of absolute concentrations of biomarkers was done using internal standards (deuterated *n*-tetracosane for the aliphatic fractions and 1,1'-binaphthyl for the aromatic fractions).

RESULTS AND DISCUSSION

Data for the content and composition of soil organic matter are presented in Table 1. The results demonstrate that the three soil samples are different at a large extent. Total organic carbon content follows the descending order: 15s_2016 > 19s_2016 > 1s_2016, as already suggested by the colour of the samples, reflecting differences in vegetation and elevation of the sampling site. Humic acids prevail over fulvic ones in samples 15s_2016 and 19s_2016, especially in sample 15s_2016, where thick grass vegetation, lichens, mosses and remains of mussels were observed. In contrast, to these samples, SOM in the first sample is of fulvic type.

The low molecular humic substances show a low degree of condensation. The ratios Ch/Cf and E_4/E_6 describe more condensed humic acids for sample 19s_2016. An interesting result was obtained for the humic substances extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH and those extracted with 0.1M NaOH for the both soil samples – 15s_2016 and 19s_2016. About a half of the humic substances was extracted with 0.1M NaOH for the sample 15s_2016 compare to those for the pyrophosphate extract, probably due to the remains of mussels. The extracted portions of humic acids were equal for both extracts in the studied sample 19s_2016 and 20% of humic acids were found to be bound with Ca.

Twelve from the sixteen PAHs defined by US EPA as priority pollutants were registered in soils studied, i.e. phenanthrene, anthracene, fluoranthene, pyrene, benzo(ghi) fluoranthene, benzo(a)anthracene, triphenylene, chrysene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene and perylene (Fig. 1 a, b, c). The concentrations of all US EPA PAHs increase from 15s_2016 (0.93 µg/g TOC) to 19s_2016 (1.04 µg/g TOC), and the highest values is registered for sample 1s_2016 (the closest to BAB) (6.38 µg/g TOC). In almost all samples PAHs comprised hydrocarbons with 2–5 rings. Five ring PAHs were not found in sample 19s_2019. PAHs of high molecular weight (HMW) (i.e., 4, 5 ring PAHs) are dominate in all samples studied (Fig. 2).

For the studied soil samples was calculated B(a)P equivalent carcinogenic power (BaPE) according to the formula proposed by Cecinato (1997):

BaPE=B(a)P+BFa x 0.07+ B(a)A x 0.06+ DB(ah)A x 0.06 + IPy x 0.08,

where BFa is the sum of all benzofluoranthene isomers

The degree of carcinogenic power for PAHs determined by calculation of B(a)PE has assumed no toxicity as value < 1 for all samples were calculated, respectively 1s_2016 (0.55 µg/g TOC), 15s_2016 (0.12 µg/g TOC) and 19s_2016 (0.09 µg/g TOC).

The type of PAHs distribution registered in our study is common for the most fossil fuels, and was previously described for Antarctica soils and marine sediments by Green, Nichols (1995). It is generally assumed by the authors that their origin is Special Antarctic Blend (SAB) and contains predominantly 2-3 ring PAHs. However, in emissions from incomplete combustion also heavier PAHs are formed. Human activity related to combustion of fossil fuels and their products, as well as the fire accidents in the
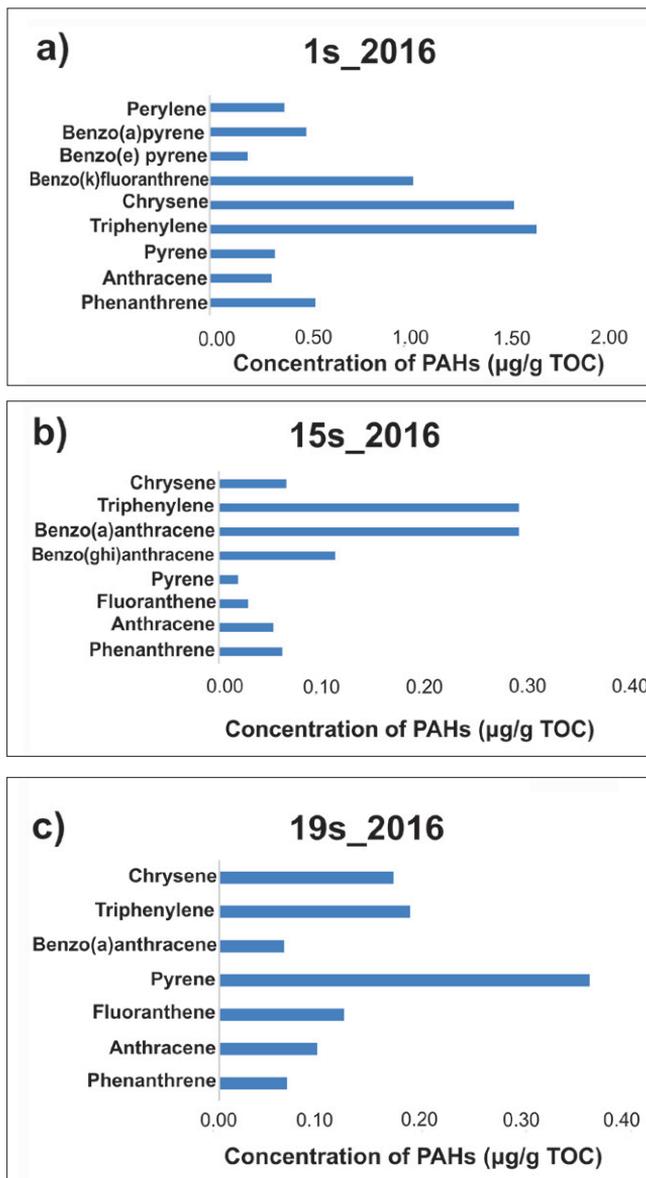
Fig. 1. Concentration and distribution of PAHs in soil samples studied

Brazilian Scientific Antarctic Station in 2012 resulted in PAHs emission. It can migrate over long distances adsorbed on particulate matter (Ravindra et al., 2008; Guerra et al., 2013). Our data gave us ground to assume that the high concentration of PAHs in 1s_2016 sample could be explained by emissions from the countries surrounding the Antarctica or by potential local sources.

In view to clarify the humus matter formation process and possible sources of PAHs in Antarctic soils the present investigation will continue.

120

Table 1. Content and composition of soil organic matter

Sample	Ct,%	Ch,%	Cf,%	Ch/Cf	Cres.,%	Optical characteristics E_4/E_6
1s_2016	0.96	0.00	0.22/22.92	-	0.74/77.08	-
15s_2016	4.12	1.45[a]/35.19[b]	0.70[a]/16.99[b]	2.07	1.97[a]/47.82[b]	7.78
19s_2016	2.70	0.90[a]/33.33[b]	0.36[a]/13.34[b]	2.50	1.44[a]/53.33[b]	6.46

Note: Ct – total organic carbon; %Ch - carbon in Humic acids, %; Cf - carbon in Fulvic acids, %; (a-% of soil mass, b - % of the total carbon); Optical characteristics – Ratio between extinction of Humic acids (465 and 665 nm)
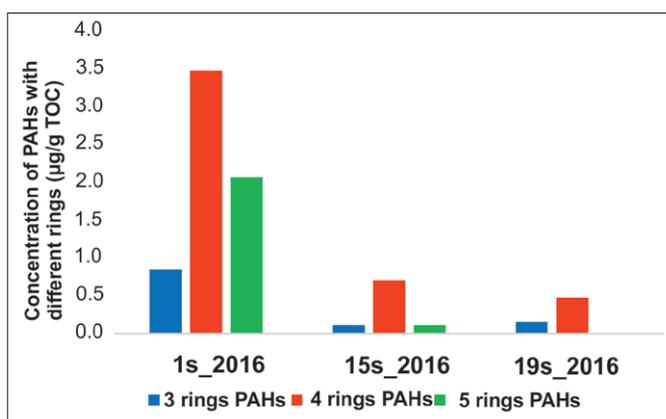
Fig. 2. Distribution of PAHs with different number of rings in soil samples studied

REFERENCES

Bícego, M.C., Zanardi-Lamardo, E., Taniguchi, S., Martins, C.C., da Silva, D.A.M., Sasaki, S.T., Albergaria-Barbosa A. C. R., Paolo F. S., Weber R. R., Montone R. C. 2009. Results from a 15-year study on hydrocarbon concentrations in water and sediment from Admiralty Bay, King George Island, Antarctica. Antarct. Sci., 21 (03), 209–220.

Cabrerizo, A., Dachs, J., Damià Barceló, D., Jones, K.C. 2012. Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. Environ. Sci. Technol., 46, 1396–1405.

Cecinato, A. 1997. PAH, BaPy and N-PAH in suspended particulate matter. Annali di Chimica, 87, 483-496.

Filcheva E., C. Tsadilas. 2002. Influence of Clinoptilolite and Compost on Soil Properties. Communications of Soil Science and Plant Analysis, 33 (3-4), 595-607.

Green, G., Nichols, P.D. 1995. Hydrocarbons and sterols in marine sediments and soils at Davis Station, Antarctica: a survey for human-derived contaminants. Antarctic Sci., 7, 137–144.

Guerra, M.B.B., Neto, E.L., Prianti, M.T.A., Pereira-Filho, E.R., Schaefer, C.E.G.R. 2013. Postfire study of the Brazilian Scientific Antarctic Station: toxic element contamination and potential mobility on the surrounding environment. Microchem. J. 110, 21–27.

Kononova, M.M. 1966. Soil Organic Matter. 2nd Ed. Pergamon press, Inc., M. V., 544.

Kostova, I., Apostolova, D., Filcheva, F., Klain, L., Popov, M. 2015. Geochemical composition and properties of Antarctic soil samples from Livingston Island. Annual of the University of mining and geology 'St. Ivan Rilski', 58, I, Geology and Geophysics, 107-116.

Radke, M., Schaefer, R.G., Leythaeuser, D., Teichmüller, M. 1980. Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. Geochimica et Cosmochimica Acta, 44, 1787–1800.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895- 2921.

Sokolovska, M., L. Petrova, N. Chipev. 1996. Particulars of Humus Formation in Antarctic Soils: Factors, Mechanisms, Properties. – Bulgarian Antarctic Research: Life Sciences, 1, 7–12.

Sokolovska, M., N. Chipev, R. Ilieva, M. Nustorova, L. Petrova, Z. Vergilov, R. Hristova, J. Bech. 2015. Soils in Livingston Island: Composition and properties, and ecological aspects. - In: Bulgarian Antarctic Research, A Syntesis (Eds. Pimpirev, C. N. Chipev), 'St. K. Ohridski' University Press, 308-319.

Ugolini, F., J. Bockheim. 2008. Antarctic soils and soil formation in a changing environment: A review. Geoderma, 144, 1-8.

E-mail: dapostolova@gea.uni-sofia.bg