MUNI | RECETOX

Nitrated and Oxygenated Polycyclic Aromatic Hydrocarbons in the atmosphere – distributions, air-surface exchange and long-range transport potential

Mariam Tannous[1], Céline Degrendele[1] & Gerhard Lammel[1,2]

[1]Masaryk University, Research Centre for Toxic Compounds in the Environment, Brno, Czech Republic

[2]Max Planck Institute for Chemistry, Multiphase Chemistry Department, Mainz, Germany

E-mail: 504127@mail.muni.cz

Introduction

Over the last years, air quality had become a major concern for the environmental scientists. Polycyclic Aromatic Hydrocarbons PAHs and their derivatives (NPAHs and OPAHs) are a class of organic substances containing two or more rings. These compounds are mostly emitted by incomplete combustion. Once emitted, PAHs partition between two phases (gaseous and particulate) depending on their physico-chemical properties and the meteorological conditions. Their reaction with the atmospheric oxidants (OH, O_3, NO_3) in the atmosphere lead to the NPAHs and OPAHs secondary formation. Regarding their toxicity, many NPAHs and OPAHs are classified as possible carcinogens and exhibit a higher toxicity than the parent compounds.

Unfortunately, NPAHs and OPAHs remains understudied and rarely addressed in remote sites. Furthermore, their vertical fluxes have never been investigated in seawater almost never in soils.

Therefore, the purposes of this study is to build a thorough knowledge of their large-scale distribution in the remote atmospheric environment as well as their air-surface cycling. Our priority list mainly includes the following compounds: 3-nitrobenzanthrones (3-NBAN), 2-nitro-FLT, 2-nitro-PYR, 1-nitro-PYR, 6-nitro-BAP, benzo-a-pyrenequinones (O_2BAPs), dibenz-a,l-pyrenequinones, anthraquinones, and many others.

Objectives

- Characterize the distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) in ambient air in central Europe and in remote atmospheric environments.
- Characterize the processes which determine the NPAHs and OPAHs long-range transport potential (gas-particle partitioning, mass size distribution, air-surface mass exchange).

Methodology

Study area

- Košetice – Czech Republic – Central European background site
- Thessaloniki – Greece – urban site
- Thermaikos Gulf – northwestern Aegean Sea – polluted site subject to pollution from ships and industrial discharges
- Atlantic ocean – remote site
- Arctic ocean – Svalbard – remote site

- Air & soil samples
- Air & seawater samples
- Air samples

Scheduled campaigns

Fall 2019	Winter 2020	Summer 2020	Winter 2021	Spring 2021	Fall 2021
Atlantic	Košetice	Košetice	Košetice	Mediterranean	Mediterranean
	Thessaloniki	Thessaloniki	East west subtropical Atlantic		Atlantic
		Arctic - Svalbard			

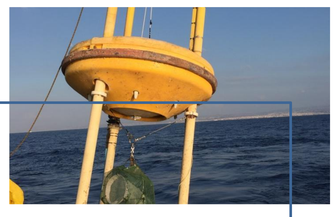
Sampling devices

Active low volume sampler

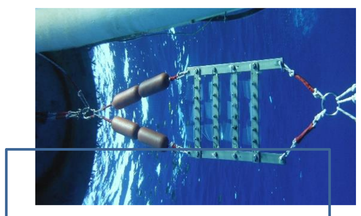
Polyurethane foams PUFs collect the gaseous phase

Quartz fiber filters collect the particulate phase

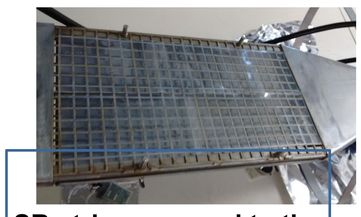
Passive seawater sampler



Buoy deployment (Aegean)



SR strips exposed to the seawater directly, fixed to a buoy (Aegean)



SR strips exposed to the seawater within a drum constantly flushed by seawater (Atlantic)

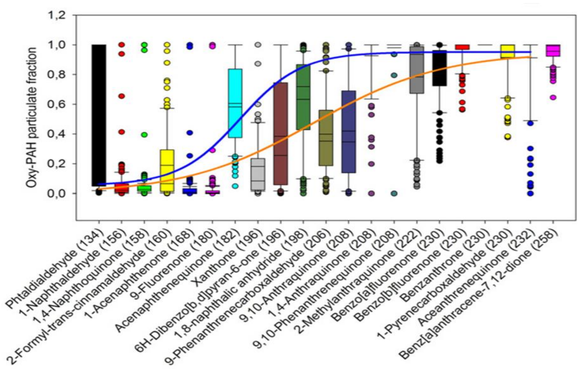
Silicone Rubber SR (**surface area: 392 cm²**) sorbs hydrophobic carbons

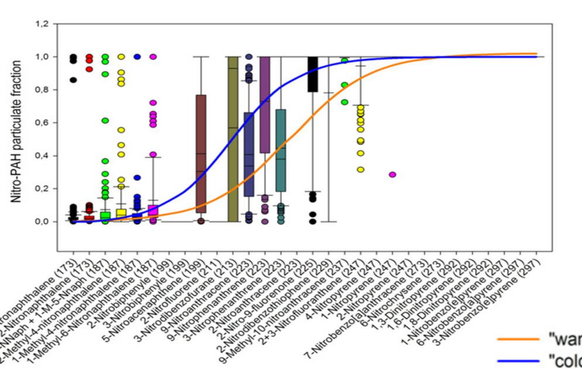
Samples preparation steps & Analysis

	Polyurethane foams & Quartz fiber filters	Silicone rubber sheets
➢ ***Spiked by***	Surrogate recovery standards	Performance Reference Compounds PRC
➢ ***Soxhlet extraction***	Dichloromethane DCM	Ethyl acetate
➢ **Clean up**	Silica gel column to separate the target compounds from the interfering compounds	
➢ **Analysis**	Gas chromatography coupled to mass spectrometry (GC / MS)	

Possible results

Seasonal variations (Tomaz et al., 2016)





- NPAHs and OPAHs are expected to be higher in winter than in summer. Wintertime concentrations can be affected by domestic heating. Another reason is the meteorological conditions represented by a lower atmospheric mixing height and less photochemical degradation.
- Individual NPAHs-to-PAHs and OPAHs-to-PAHs ratios should be higher in summer because of the sunlight intensity favoring the secondary formation through atmospheric reactions occurring between the PAH and the chemical oxidant (OH, O_3, NO_3).

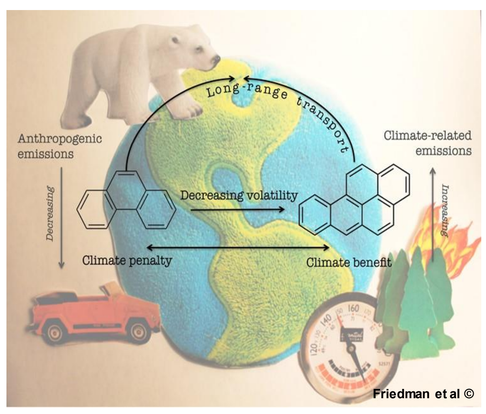
Partitioning in the environment (Cabrerizo et al., 2011 ; Idowu et al., 2019)

- OPAHs compared to NPAHs are expected to be more prevalent in seawater due to their high solubility and mobility, low lipophilicity.
- The soil is the major reservoir of High Molecular Weight HMW PAHs.

Long-Range Transport (Nežiková et al., 2020)

A spatial gradient has been reported between the Central European background and Svalbard stations, suggesting a long-range transport to the Arctic.

This gradient will be predicted throughout this project, using 3D Eulerian coupled chemistry-transport model.



References

- Tomaz, S., Shahpoury, P., Jaffrezo, J. L., Lammel, G., Perraudin, E., Villenave, E., & Albinet, A. (2016). One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation. *Science of the Total Environment*, *565*, 1071–1083. https://doi.org/10.1016/j.scitotenv.2016.05.137
- Cabrerizo, A., Dachs, J., Moeckel, C., Ojeda, M. J., Caballero, G., Barceló, D., & Jones, K. C. (2011). Ubiquitous net volatilization of polycyclic aromatic hydrocarbons from soils and parameters influencing their soil?air partitioning. *Environmental Science and Technology*, *45*(11), 4740–4747. https://doi.org/10.1021/es104131f
- Idowu, O., Semple, K. T., Ramadass, K., Connor, W. O., & Hansbro, P. (2019). Beyond the obvious : Environmental health implications of polar polycyclic aromatic hydrocarbons. *Environment International*, *123*(October 2018), 543–557. https://doi.org/10.1016/j.envint.2018.12.051
- Nežiková, B., Degrendele, C., Bandowe, B. A. M., Holubová, A., Kukučka, P., Martiník, J., … Lammel, G. (2020). *Atmospheric concentrations of nitrated and oxygenated polycyclic aromatic hydrocarbons and oxygen heterocycles are declining in Central Europe*. 1–39.

Acknowledgements

This project will be carried out at Masaryk University RECETOX, supported by the **Czech Ministry of Education, Youth and Sports** and in collaboration with the following partners: **Max Planck Institute for Chemistry MPIC-Germany, Aristotle University, Thessaloniki AUT-Greece, Norwegian University of Life Sciences NUMB, University Institute in Svalbard UNIS, Czech Hydrometeorological Institute CHMI.** The authors would like to express their gratitude to all these organizations for their financial and logistic support, providing access to ship platform, observatories, meteorological data and coastal sites and off-shore sites.

MUNI SCI