Three years of atmospheric concentrations of nitrated and oxygenated polycyclic aromatic hydrocarbons and O-heterocycles at a central European background station

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their nitrated (N-PAHs) and oxygenated (O-PAHs) derivatives are products of incomplete combustion and they are emitted for example from traffic, heavy industries and biomass burning (1, 2; Fig. 1). N-PAHs and O-PAHs can be also formed in photochemistry (2; Fig. 1). All these pollutants are ubiquitous in the atmosphere in both phases, gaseous and particulate (2). Many PAH derivatives are more toxic than the parent compounds, e.g. N-PAHs are often more mutagenic (1). Despite the health hazard they pose, N-PAHs and O-PAHs were rarely included in air monitoring and to the best of our knowledge, this is the first study covering their concentrations in both particulate and gaseous phases for longer than one year.

Aims of this study are:

- Characterise atmospheric levels and seasonal variations of N-PAHs and O-PAHs
- Describe gas-particle partitioning and multi-year variations of N-PAHs and O-PAHs

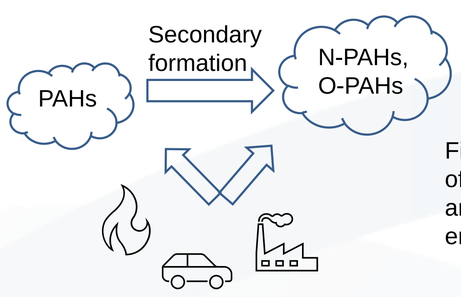


Figure 1 Scheme of PAHs, N-PAHs and O-PAHs emissions

Figure 2 Map of sampling site, Košetice observatory

Methodology

Sampling:

- 78 air samples (each consisting from 2 PUF discs and quartz microfiber filters) collected every other week in years 2015 to 2017
- Sampling site – Košetice observatory – regional background station in Central Europe (Fig. 2)
- Sampling period 7 days, average volume 5200 m^3
- High-volume sampler (Digitel DH77 with PM10 pre-separator, Fig. 3)

Sample processing:

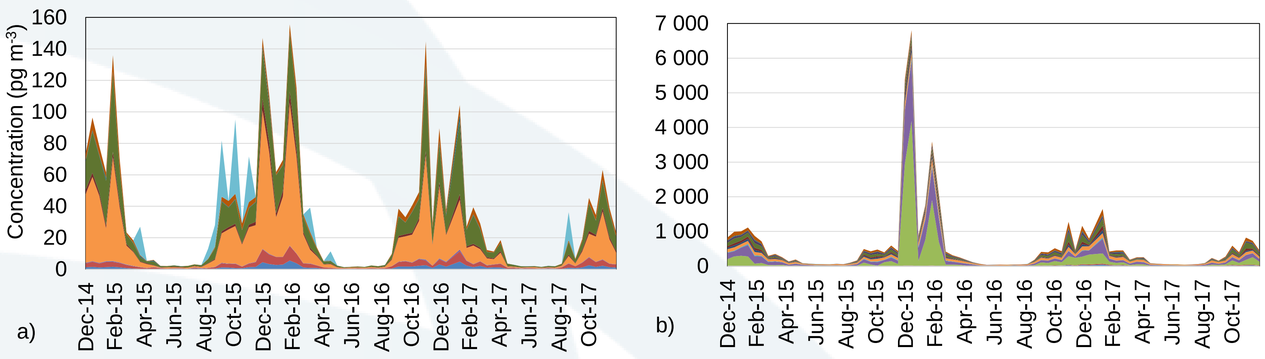
- Warm Soxhlet extraction in dichloromethane
- Cleaning on silica column
- Gas chromatography connected to a mass spectrometer

The target compounds in this study were 16 PAHs, 17 N-PAHs, 10 O-PAHs and 2 O-heterocycles.

Figure 3 Photo of air sampler

Results

- The total air concentrations ranged from 1.3 to 160 pg m^{-3} (average: 36 pg m^{-3}) for Σ_{17}N-PAHs, from 32 to 2600 pg m^{-3} (average: 380 pg m^{-3}) for Σ_{10}O-PAHs and from 5.1 to 4300 pg m^{-3} (average 209 pg m^{-3}) for Σ_{2}O-heterocycles, Fig. 4
- Ratios between different compounds (e.g. $c_{2\text{-NFLT}}/c_{1\text{-NPYR}}$) showed high importance of photochemistry sources
- 3-NBAN included for first time in longer time series, showed lower concentration than in other studies
- DBF is suspected to be prone to long-range atmospheric transport
- Main contributors to Σ_{17}N-PAHs concentration – 9-NANT (35 %) and 2-NFLT (29 %)
- Main contributors to Σ_{12}(O-PAHs and O-heterocycles) concentration – 9-OFLN (23 %), 9,10-O_2ANT (23%) and DBF (17 %)
- N-PAHs, O-PAHs and O-heterocycles showed significantly ($p<0.05$) higher concentrations in winter than in summer (Fig. 4)
- Lowest winter-to-summer ratios were found for compounds with significant secondary sources (1,4-O_2NAP, 6-OBCC, 9,10-O_2ANT, 1-NNAP)
- The mean particulate mass fraction of individual N-PAHs and O-PAHs was generally increasing with molecular weight of compound (Fig. 5)
- Significantly ($p<0.05$) highest particulate mass fraction of individual compounds was found in winter (Fig. 5)
- Significant downward trends were found for some 3-5 rings compounds (i.e. 2-NFLN, 9-NANT, 1-NPYR, 6-OBCC, BaOFLN, BbOFLN and 7,12-O_2BAA) with halving times of 2.0-4.6 years (Fig. 6)
- Significant upward trends were found for some 2-rings compounds (i.e. 1-NNAP, 1,4-O_2NAP and 1(CHO)NAP) with doubling times of 0.5-2.5 years (Fig. 6)



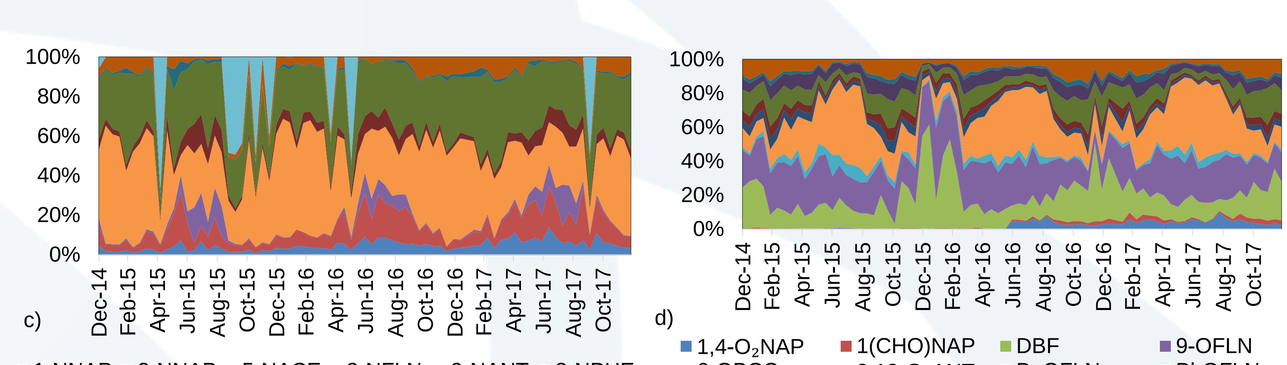


Figure 4 Total air concentrations of Σ_{17}N-PAHs (a) and Σ_{12}(O-PAHs and O-heterocycles) (b) with individual compounds contribution of N-PAHs (c) and O-PAHs and O-heterocycles (d).

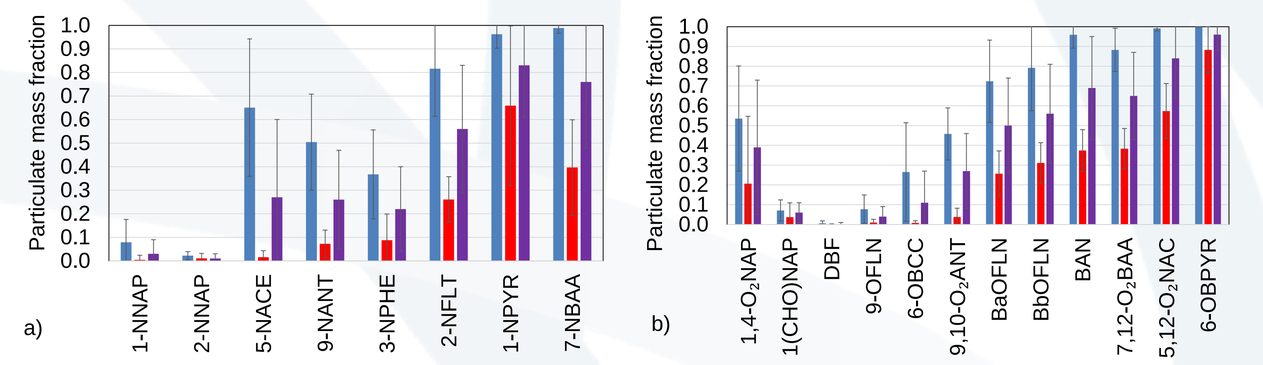


Figure 5 Average particulate fraction of individual N-PAHs (a), O-PAHs and O-heterocycles (b) for samples collected in winter (blue colour), in summer (red colour) and for all samples (purple colour).

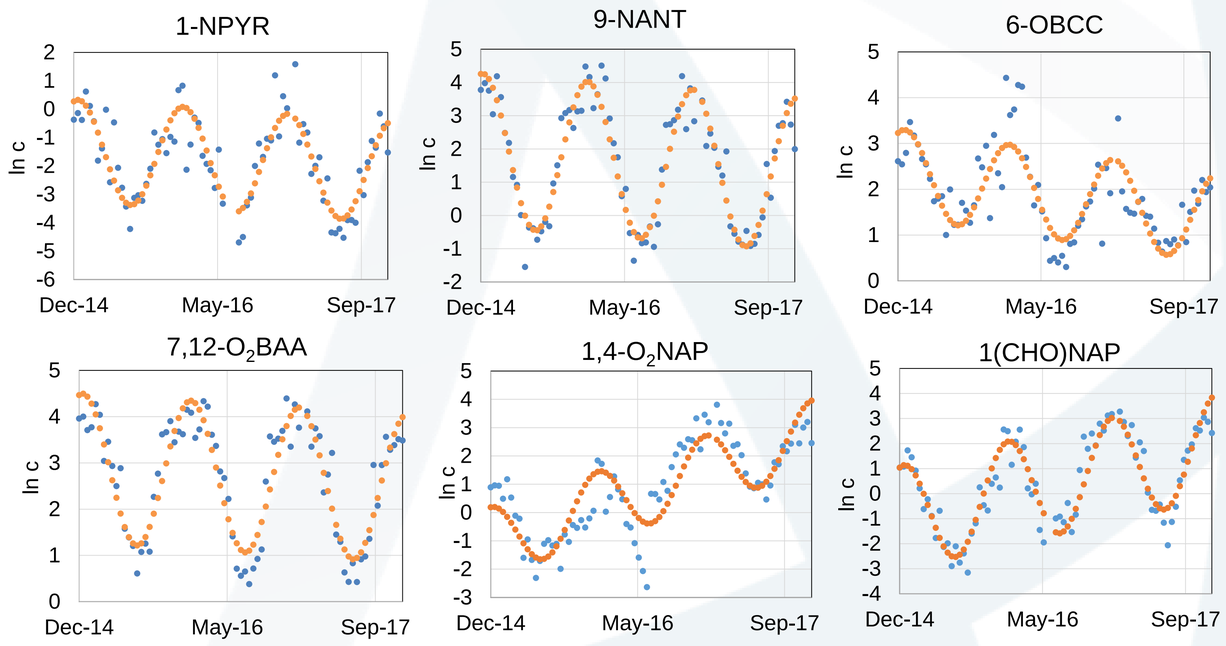


Figure 6 Multi-years trends of individual N-PAHs, O-PAHs and O-heterocycle. Blue line is measured concentration, orange line is fitted concentration.

Conclusions

- 5-NACE, 9-NANT, 3-NPHE, DBF, 9-OFLN and 6-OBCC predominantly found in the gaseous phase → implication that studies addressing only the particulate phase of N-PAHs and O-PAHs are incomplete and not conclusive (possible underestimation of exposure)
- Significant halving times for 2-NFLN, 9-NANT, 1-NPYR, 6-OBCC, BaOFLN, BbOFLN and 7,12-O_2BAA

→ prevailing decreasing trends suggest that on-going emission reductions of PAHs are effective also for co-emitted N- and O-PAHs and O-heterocycles

- Significant doubling times for 1-NNAP, 1,4-O_2NAP, and 1(CHO)NAP

→ apparent positive trends possibly suggest either inter-annually different meteorological and advection conditions or inter-annual variability of specific sources

List of compounds

N-PAHs: 1-nitronaphthalene (1-NNAP), 2-nitronaphthalene (2-NNAP), 3-nitroacenaphthene (3-NACE), 5-nitroacenaphthene (5-NACE), 2-nitrofluorene (2-NFLN), 9-nitroanthracene (9-NANT), 9-nitrophenanthrene (9-NPHE), 3-nitrophenanthrene (3-NPHE), 2-nitrofluoranthene (2-NFLT), 3-nitrofluoranthene (3-NFLT), 1-nitropyrene (1-NPYR), 7-nitrobenzo(a)anthracene (7-NBAA), 6-nitrochrysene (6-NCHR), 1,3-dinitropyrene (1,3-N_2PYR), 1,6-dinitropyrene (1,6-N_2PYR), 1,8-dinitropyrene (1,8-N_2PYR), 3-nitrobenzanthrone (3-NBAN); O-PAHs: 1,4-naphthoquinone (1,4-O_2NAP), naphthalene-1-aldehyde (1(CHO)NAP), 9H-fluoren-9-one (9-OFLN), 9,10-anthraquinone (9,10-O_2ANT), 11H-benzo(a)fluoren-11-one (BaOFLN), 11H-benzo(b)fluoren-11-one (BbOFLN), benzanthrone (BAN), benz(a)anthracene-7,12-dione (7,12-O_2BAA), 5,12-naphthacenequinone (5,12-O_2NAC), 6H-benzo(c,d)pyren-6-one (6-OBPYR); O-heterocycles: dibenzofuran (DBF), 6H-benzo(c)chromen-6-one (6-OBCC).

References

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Acknowledgements

This research was supported by the Ministry of Education, Youth and Sports of the Czech Republic (ACTRIS-CZ and RECETOX Research Infrastructures LM2015037 CZ.02.1.01/0.0/0.0/16_013/0001315 and LM2018121), by the Czech Science Foundation (503/12/G147) and by the European Commission H2020 (CETOCOEN EXCELLENCE Teaming 2, #857560). The authors are also thankful for the data provided by the EBAS data bank, Norwegian Institute for Air Research.