Investigation of primary and secondary processes in the formation of oxy-PAHs and nitro- PAHs in Paris (France) by conjoining on-line and off-line measurements

D. Srivastava^{1, 2}, O. Favez¹, N. Bonnaire³, E. Perraudin², V. Gros³, E. Villenave², A. Albinet¹

¹INERIS, Parc Technologique Alata, BP 2, 60550 Verneuil-en-Halatte, France

²Université de Bordeaux, EPOC, UMR 5805 CNRS, 33405 Talence, France

³LSCE - UMR8212, CNRS-CEA-UVSQ, Gif-sur-Yvette, France

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Presenting author email: deepchandra.srivastava-etudiant@ineris.fr

Severe implications of air pollution can be considered as a significant role in altering the chemistry and the radiative balance of the Earth's atmosphere, and in adversely affecting human health. Impacts of particulate matter (PM) on health are mainly linked to its chemical composition, and precisely depend on the presence of compounds such as polycyclic toxic aromatic (PAHs), hydrocarbons mostly considered as anthropogenic and emitted by incomplete combustion processes. Atmospheric oxidation of PAHs induces the formation of oxidized compounds such as oxygenated-PAHs (oxy-PAHs) and nitrated-PAHs (nitro-PAHs). The study of these PAH derivatives have become a prime concern as most are speculated or considered to be carcinogenic and potentially more mutagenic than PAHs (IARC 2013). In addition, these compounds may also instigate the formation of secondary organic aerosol (SOA), which may represent a large source of SOA in urban areas (Chan et al. 2009). However, the determination of the sources of oxy-PAHs and nitro-PAHs appears arduous as such compounds may be formed either through secondary processes (Keyte et al. 2013) or primarily emitted.

The main objective of this study was to develop the right understanding to make the discrimination between primary and secondary processes taking place in the formation of oxy-PAHs and nitro-PAHs. This was accomplished by utilizing information obtained from intensive filter measurements along with online measurements as well. To the best of our knowledge, this unique approach has not been explored yet. Measurements were conducted at SIRTA-LSCE, a well arranged atmospheric ACTRIS supersite. This site features the suburban background conditions of the Ilede-France region and is located about 25 km southwest of Paris city center. PM₁₀ samples were collected at every 4 hour over a period from 6-24, March 2015, concomitantly with online measurements, carried out using ACSM, Aethalometer 7\u03b2, TEOM-FDMS, PTR-MS, NOx and O_3 analyzers. Filter samples were analyzed to quantify species such as OC/EC, ions/cations, levoglucosan, PAH, oxy-PAHs and nitro-PAHs...

Results highlight high concentrations of oxy-PAHs and nitro-PAHs during the period 14-21, March 2015, including specific secondary PAH derivatives as 6H-dibenz[b,d]pyran-6-one, acenaphthenequinone and 2-nitrofluoranthene. This suggests that these species could be generated through secondary processes due to high NO₃⁻ and SO₄²⁻ concentrations, and can be explicitly observed considering ASCM results (Figure 1). Besides,

the formation of 6H-dibenz[b,d]pyran-6-one seems to be highly influenced by the daytime chemistry while 2nitrofluoranthene may formed during nighttime (NO₃ radical chemistry). Interestingly, fossil-fuel-based BC_{ff} and 1-Nitropyrene (1-NP, a promising marker for diesel emissions) present similar temporal profiles. Discussion will further accentuate diurnal variations, information about the day- and nighttime chemistry, and also usefulness of combining off-line and on-line measurements to have comprehensive understanding about the prevalent atmospheric processes and organic aerosol sources.

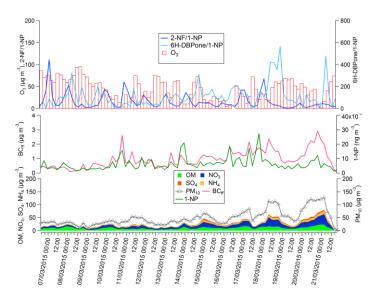


Figure 1. Temporal variation of the ratios 2-NF/1-NP and 6H-DBPone/1-NP along with the concentrations of PM₁₀ (chemical composition), O₃, 1-NP, BC_{ff} identified at SIRTA (France).

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References

Chan, Arthur Wing Hong, et al. (2009), Atmospheric Chemistry and Physics, 9 (9), 3049-60.

IARC (2013), vol.105.

Keyte, Ian J., Harrison, Roy M., and Lammel, Gerhard (2013), *Chemical Society reviews*, 42 (24), 9333-91.