Assessment of atmospheric air pollution in Himalaya through simultaneous determination of oxidation PAHs products using lichens as bioindicators

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Abstract
The method has implied the DSASE extraction with toluene as solvent; the SPE as clean-up step using NH₂ cartridge and GC-MS ion trap system was used as detection method in chemical ionization mode. The final concentrations were around 7.694 to 0.833 μg g⁻¹ for oxoPAHs and 1.627 to 0.332 μg g⁻¹ for nitroPAHs.

Materials and methods

Sampling
Lichen samples (45) have been collected by researchers from the Department of Botany (Garhwal Central University), city of Rishikesh (Dehradun), India, and sent to the University of Zaragoza. Each sample was received in sealed bag, perfectly coded and in sufficient quantity (about 2 grams). All the samples were collected in the state of Uttarakhand with the exception of one sample, which was collected in Himachal Pradesh. The collection sites of all samples correspond to the Districts of Chamoli, Rudraprayag and Kangra. The sampling points are located in an altitude range of 1353 - 3678 meters above sea level (m.a.l.s). The predominant varieties were: Heterodermia diademata sp Parmotrema reticulatum sp and Dermatocarpon vellerum sp, and the predominant substrate were rocks.

Chemical and standards
All eight (8) nitroPAHs and nine (9) oxoPAHs were purchased separately from Sigma-Aldrich Germany. Naphthalene-d₈ (Np-d₈) from Isotec USA, acenaphthene-d₁₀ from Supelco, and benzo[a]-7,8-pyrene-d₂ (BaP-d₂) from Aldrich were used as internal standard in all analysis.

Processing and analysis
9 oxoPAHs and 8 nitroPAHs were extracted from Himalayan lichens samples by the DSASE extraction method (Dynamic sonication-Assisted Solvent Extraction) and the obtained extracts were purified and enriched by SPE (Solid Phase Extraction) (see figure 1). The detection and quantification of oxoPAHs and nitroPAHs was carried out simultaneously by GC-MS chemical ionization mode before developing and optimizing the analytical method.
Results and discussion

From the 45 samples, fifteen (15) showed a total concentration of nitroPAHs higher than 1.0 $\mu$g g$^{-1}$, 23 samples of Himalayan lichens contain a concentration between 0.5 and 1.0 $\mu$g g$^{-1}$ and 9 of them showed a total concentration of nitroPAHs lower than 0.5 $\mu$g g$^{-1}$. The sample with the highest concentration of total nitroPAHs with 1.627 $\mu$g g$^{-1}$ where 49% corresponds to 3-nitrofluoranthene, in this site the automobile movement is mild and the main land use type is secondary scrubland. This sample was collected on the rocks. In the case of oxoPAHs from the 45 samples, nineteen (19) showed a total concentration of oxoPAHs higher than 4.0 $\mu$g g$^{-1}$, 24 samples of Himalayan lichens contain a concentration between 1.0 and 4.0 $\mu$g g$^{-1}$ and 2 of them showed a total concentration of oxoPAHs lower than 1.0 $\mu$g g$^{-1}$. The sample with the highest concentration of total oxoPAHs with 7.694 $\mu$g g$^{-1}$ (see figure 2) where 34% corresponds to benzo[a]anthracene-7,12-dione, in this site the locomotive exhaust is the main source of anthropogenic activity and the main land use type is the iron rail tracks. This sample was collected directly on railway track. In all the samples always the amount of oxoPAHs has been higher than the amount of nitroPAHs. In other words, between 48% and 94% of total sum of both derivatives correspond to oxoPAHs (see the figure 3). This is a very important aspect considering that the nitroPAHs have a mutagen potential higher than oxo and PAHs.$^{9}$

Conclusions

An analytical method capable to analyze simultaneously nitroPAHs and oxoPAHs compounds by GC-MS ion trap system from Himalayan lichens was developed. This method has shown a good analytical performance based on the high sensitivity of the ion trap mass detector using the ionization mode for these families. All measurements were confirmed by the powerful method APGC-Q-TOFMS$^{10}$ assuring the robustness of obtained data.

REFERENCIAS

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Figure 1. Laboratory assembly of extraction, clean-up and analysis of oxoPAHs and nitroPAHs in lichens from Himalaya

Figure 2. Some chromatograms about two samples and calibration standard of current study

Figure 3. Concentrations of total oxidation PAHs products at different Himalayan sampling stations.