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 NH_2 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 $\mu g \ g^{-1}$ for oxoPAHs and 1.627 to 0.332 $\mu g \ g^{-1}$ for nitroPAHs

Introduction

The lichens, mosses and pine leaves have been the most habitually bioindicators used for the assessment of atmospheric pollution. Biomarkers are organisms that respond to a certain level of pollution by changing their natural behavior or pollutant accumulation in their tissues. In addition, the advantages of using these kind of vegetable materials include: the real and temporal information of the area of study, not requiring additional instrumental devices, the widespread and natural distribution of sample points; an easy and fast access to the area, the low cost of monitoring and they also give multiparametral characteristics about the region of analysis[1-5]. Polycyclic aromatic hydrocarbons PAHs and their oxidation products, such as nitrated polycyclic aromatic hydrocarbons, nitroPAHs and oxygenated PAHs oxoPAHs are catalogued as carcinogenic and mutanogenic compounds for the internacional environmental and health agencies and represents potential health risks[6]. Because of its toxicity, interest in the presence and source of these contaminants in remote areas is of great importance. The aim of this work was the analytical evaluation of 45 samples of lichens in triplicate analysis as biomonitors of atmospheric pollution contained in the Himalayan natural ecosystem through the determination of 9 oxoPAHs and 8 nitroPAHs in each sample. For this purpose we have developed an analytical method that includes extracting, cleaning and detection simultaneously all 17 prioritary pollutants with chemical ionization mode using a GC-MS ion trap system.

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-d_8 (Np-d_8) from Isotec USA, acenaphthalene-d_{10} from Supelco, and benzo[*a*]-7,8-pyrene-d_2 (BaP-d_2) 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)[7] and the obtained extracts were purified and enriched by SPE (Solid Phase Extraction)[8] (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 disscusion

From the 45 samples, fifteen (15) showed a total concentration of nitroPAHs higher than 1.0 μg g⁻¹, 23 samples of Himalayan lichens contain a concentration between 0.5 and 1.0 μg g⁻¹ and 9 of them showed a total concentration of nitroPAHs lower than 0.5 μg g⁻¹. The sample with the highest concentration of total nitroPAHs with 1.627 μg 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 μg g⁻¹, 24 samples of Himalayan lichens contain a concentration between 1.0 and 4.0 μg g⁻¹ and 2 of them showed a total concentration of oxoPAHs lower than 1.0 μg g⁻¹. The sample with the highest concentration of total oxoPAHs with 7.694 μg 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 powerfull method APGC-Q-TOFMS[10] assuring the robustness of obtained data.

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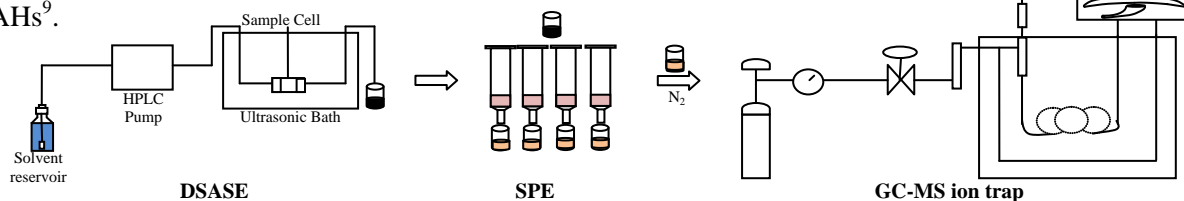
Figure 1. Laboratory assembly of extraction, clean-up and analysis of oxoPAHs and nitroPAHs in lichens from Himalaya
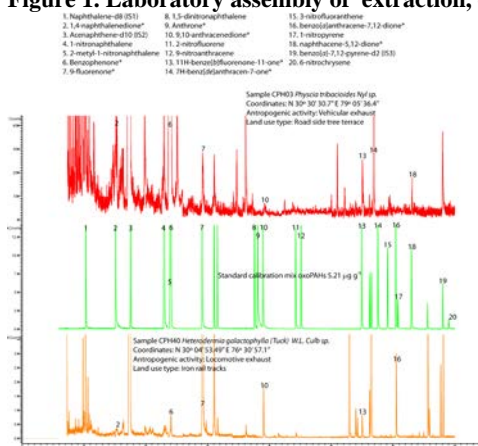

Figure 2. Some chromatograms about two samples and calibration standard of current study
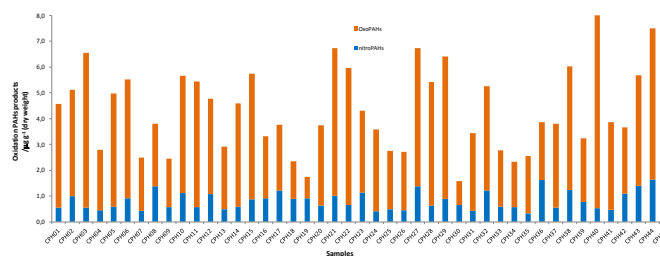

Figure 3. Concentrations of total oxidation PAHs products at different Himalayan sampling stations.