PAHS IN NEEDLES AND HUMUS OF ALPINE ECOSYSTEMS (PROJECT MONARPOP)

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) were determined in humus layer and needles samples, collected in 40 sites of the Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants (MONARPOP). Samples were analysed using high resolution gas chromatography (HRGC) combined with high resolution mass spectrometry (HRMS). The median of total PAHs in humus was 189 µg kg^{-1} d.w. while the same parameter in needles was 19 µg kg^{-1} d.w. Data has been arranged on maps and vertical profiles aiming at describing the spatial distribution of PAH'S in the Alps. The toxicity of the matrices have been estimated using potency equivalency factors (PEF).

Introduction

PAHs (Polycyclic Aromatic Hydrocarbons) include hundreds of chemical compounds consisting of two or more aromatic rings which derive from incomplete combustion of organic matter such as coal, petroleum, oil and wood. The physical properties of PAHs, in particular vapour pressure and K_{ow} vary with the number of rings and the molecular weight. PAHs are semivolatile substances transported by air masses both in gaseous and solid phases, the latter being predominant. They are subject to dry or wet deposition and as many other persistent compounds tend to accumulate in environments with low temperatures and high precipitations like mountainous regions. Due to their lipophilic properties PAHs accumulate in soil, sediment and living organisms, and are transferred along the food chain to the higher trophic levels including human beings. These compounds are of toxicological and ecotoxicological concern since some of them have been classified as probable or possible carcinogens (cPAHs).[1]

The present survey was conducted within the framework of the Interreg III B Project Monarpop aiming at measuring the load of PAHs in remote sites and their distribution across the alpine region and at assessing their long range transport. In order to ensure comparability of results have been selected sites with the same characteristics widespread over the Alps and all the samples have been analysed in a single laboratory.

Materials and Methods

Concentrations of 20 PAHs (including 16 EPA PAHs) were measured in Norway spruce needles and forest humus samples collected in 40 alpine sites including 7 vertical profiles in the Alpine area (7° - 16°E; 46° - 48°N)

Site selection procedures are formulated in order to obtain a set of homogeneous remote sites from the vegetational and altitudinal point of view. Excepting the vertical profiles, site altitudes range between 1300 and 1600 m a.s.l. and their minimum distances to local pollution sources are coherent with the EMEP Guidance to the Air Quality Directive. All the sampling sites are placed in 30 or more years old Norway spruce forests (>80% specific purity) of at least 0.5 ha. surface.

The sampling campaign was performed in autumn 2004 and repeated in selected sites in autumn 2005. The entire humus layer was collected using metallic 0.3 x 0.3 m squared frames in 6 to 10 pits regularly distributed in 5 x 20 m rectangular grids (30 sites). Needles were obtained from the youngest shoots near the top of the tree (7^{th} whorl) of healthy dominant specimens (40 sites).

Both needles and humus samples were transported in cool and dark conditions in air-tight glass jars and stored a –20 °C. Needles were separated from twigs after freezing them with liquid nitrogen in inert atmosphere and then ground and lyophilized. After lyophilization humus sub-samples were pooled per site and ground to particle diameter < 0.5 mm.

PAHs in ground samples were spiked with deuterium labelled standards and extracted using acetone and cyclohexane. The cyclohexane phase was concentrated by rotary evaporation and the extracts were cleaned-up in silica gel and reverse phase column.

PAHs were measured using a high resolution mass spectrometer (HRMS) coupled to a high resolution gas chromatograph (HRGC). Limits of detection are reported in table 1. Recovery rate ranged between 40% and 115%. In needles only the 16 EPA PAHs are presented since the additional ones felt always below the L.O.D.

All the humus and needle PAHs concentrations refer to dry weight determined by oven-drying at 105°C.

The toxicity equivalent concentrations (TEC) of the PAHs fraction in each matrix has been calculated using the potency equivalency factors (PEF) referred to BaP .[2,3]

Table 1. Limits of detection for the 20 analized PAHs

PAHs	Abbreviation	L.O.D. (µg kg^{-1})	PAHs	Abbreviation	L.O.D. (µg kg^{-1})
Acenaphthene	ACNATHE	0.5	Fluoranthene	FLNTE	0.1
Acenaphthylene	ACNATHY	0.5	Fluorene	FLENE	0.5
Anthracene	ANT	0.5	Indeno(1,2,3-c,d)pyrene	IcdP	0.1
Benz(a)anthracene	BaA	0.1	Naphthalene	NAPH	0.5
Benzo(b)fluoranthene	BbF	0.1	Phenanthrene	PHEN	0.5
Benzo(k)fluoranthene	BkF	0.1	Pyrene	PYR	0.1
Benzo(g,h,i)perylene	BghiP	0.1	Dibenzo(a,l)pyrene	dBalP	0.5
Benzo(a)pyrene	BaP	0.1	Dibenzo(a,e)pyrene	dBaeP	0.5
Chrysene	CHR	0.1	Dibenzo(a,i)pyrene	dBaiP	0.5
Dibenz(a,h)anthracene	dBahA	0.1	Dibenzo(a,h)pyrene	dBahP	0.5

Results and Discussion

The median of total PAHs in humus (Σ20 PAHs) and needles (Σ16 PAHs) are 189 µg kg^{-1} d.w. and 19 µg kg^{-1} d.w. respectively. Benzo(b)fluoranthene, Chrysene and Fluoranthene are the most abundant PAHs in the humus layer with means between 30 and 37 µg kg^{-1} d.w. (Figure 2). In needles the most abundant PAHs are Naphtalene and Phenantrene with means between 5 and 7 µg kg^{-1} d.w. (Figure 3).

In humus the highest total PAHs concentrations (Σ20 PAHs >75° Percentile) are observed in the samples of the northern slope of the Alps and some in the western side of the study area while the lowest concentrations (Σ20 PAH <25° Percentile) are observed in the central and southern Alps. Needle samples with the highest PAHs total concentrations (Σ16 PAHs >75° Percentile) belong to the western zone of the study area, with the exception of one site in north-western Slovenia, while the lowest concentrations (Σ16 PAHs <25° Percentile) are observed in the middle Alps (i.e. the intermediate longitudes in the area under study).

With the exception of one site in the southern Alps, the vertical profiles of total PAHs in humus present two maxima, the first of which in the lowermost altitudes and a second one, often more evident, at a relative height ranging between 350 and 700 m above the valley floor.

In central and northern Alps PAHs concentrations in needles are slightly higher in the lowermost altitudes and tend to decrease with height while those in the southern Alps present one peak at intermediate or high altitudes. In humus the spatial pattern of the most toxic PAHs is coherent with the one observed in total PAHs. In this matrix carcinogenic PAHs represent one third of the total PAHs (Σ6 cPAHs/Σ20 PAH = 0.34 ± 0.05) and the mean toxicity equivalent concentration (TEC) is 17.8±10 µg kg^{-1} d.w. In needles the contribution of carcinogenic PAHs falls to one tenth (Σ6 cPAHs/Σ16 PAH = 0.10 ± 0.08) and the mean TEC is 0.7±0.4 µg kg^{-1} d.w. Surprisingly needle samples with the highest total PAHs concentrations, mostly located in the west of the

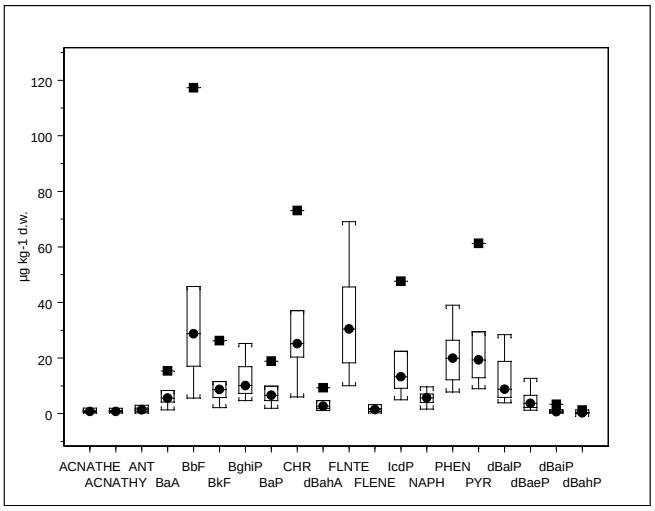

Figure 1. Concentration of PAHs in humus samples

Circles: median, boxes: 25° and 75° Percentiles, whiskers: minimum and maximum values, solid squares: outliers.

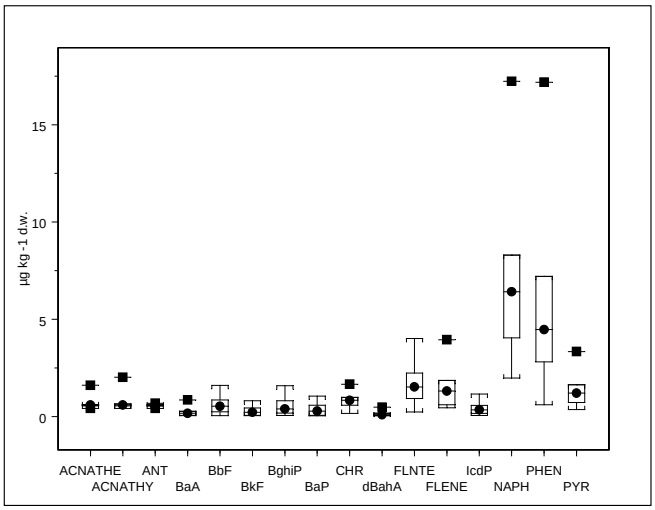

Figure 2. Concentration of PAHs in needle samples

Circles: median, boxes: 25° and 75° Percentiles, whiskers: minimum and maximum values, solid squares: outliers.

study area, present the lowest toxicities (Σ6 cPAHs/Σ16 PAH and TEC < 25° Percentile) while the samples with the highest toxicities are located in the east of the study area (Σ6 cPAHs/Σ16 PAH and TEC > 75° Percentile). The only needle samples departing from the described pattern are those in western Tyrol where high total PAHs match high TEC.

The median of the total PAHs concentrations in needles of Austrian remote sites (18 µg kg^{-1} d.w.) observed in the present study is less than the half of the one observed in 1993 using a comparable methodological approach (48 µg kg^{-1} d.w.).[4] Such a decreasing trend in PAHs levels coincides with the findings of a recent study on PAHs concentration in needles in several German sites.[5] A similar, trend even if less evident, was observed in humus. In contrast to the temporal trend, the geographic pattern in the two studied matrices differs. In humus differences are related to the latitude while needles present a clear est-west gradient. In the first case differences may be related to the different temperatures and insolation between the southern and the northern slopes of the Alps that influence gas/aerosol partitioning and photodegradation. On the other hand, the longitudinal gradient is probably associated to differences in the sources between eastern and western European countries. In both cases the area in the center of the domain turn out to be the least polluted. The difference in the matrices may also indicate that the input of pollutants is evolving in time considering that PAHs concentrations in humus represent the average of several years while needles provide information on the last vegetative season.

The presence of a peaks in the PAHs concentrations at relatively low altitudes with respect to the valley floor

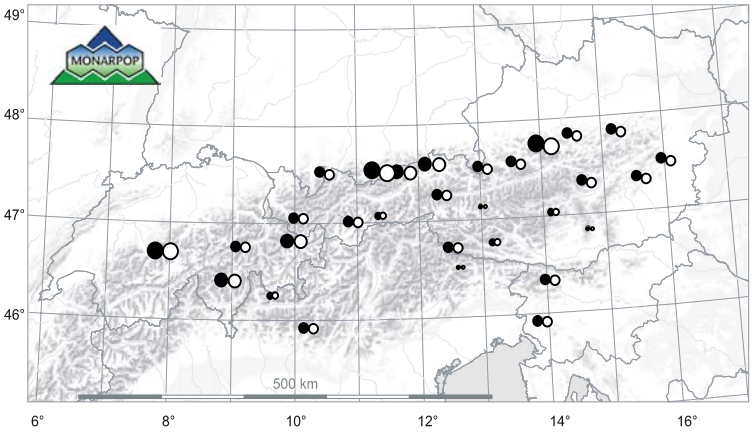

Figure 3. Map of humus sampling locations in the European Alps. Solid circles: Σ20 PAHs, Empty circles: toxicity equivalent concentration referred to BaP.

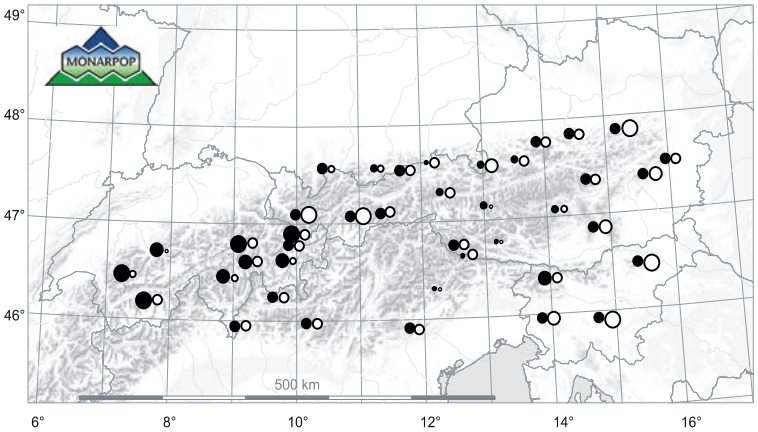

Figure 4. Map of needle sampling locations in the European Alps. Solid circles: Σ16 PAHs, Empty circles: toxicity equivalent concentration referred to BaP.

may be associated to local sources while peaks at higher altitude are probably connected to the height of the mixing layer.

The dominance of BbF, a carcinogenic compound, in PAHs in humus is an indication about the potential toxicity of the mixture. The observed data indicate that the fraction of cPAHs in each matrix is relatively constant throughout the study area. Despite differences in PAHs concentrations between needles and humus of one order of magnitude the TEC in humus are only twice as much as those in needles. The enrichment in toxic PAHs in the humus may be the consequence of (a) losses of lighter congeners by evaporation or degradation and (b) deposition of toxic aerosol from the atmosphere.

Acknowledgment

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References

1. IARC. Monograph 32, International Agency for Research on Cancer, Lyon 1984.
2. OEHHA. *Benzo(a)pyrene as a toxic air contaminant.* Air Toxicology & Epidemiology Sect, Berkeley, 1993.
3. Collins JF, Brown JP, Alexeeff GV, Salmon AG. Regul. Toxicol. Pharmacol. 1998; 28:45
4. Weiss P, Lorbeer G, Scharf S. Environ. Sci. & Pollut. Res. 1998 Special issue 1: 46
5. Schröter-Kermani C, Kreft D, Schilling B, Herrchen M, Wagner G. J. Environ. Monit. 2006; 8:806