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Absorption of polycyclic aromatic hydrocarbons by *Pinus* bark: Analytical method and use for environmental pollution monitoring in the Palermo area (Sicily, Italy)

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ABSTRACT

In the light of using biomaterial as pollutants sorbents for the environmental biomonitoring, we report here the results of the absorption of polycyclic aromatic hydrocarbons (PAHs) by pine bark. Quantitative analysis of 19 different polycyclic aromatic compounds was performed, after Soxhlet extraction in dichloromethane, by means GC–MS technique. *Pinus* was chosen due to its wide distribution in the Mediterranean area. The passive absorption of PAH by pine bark in the metropolitan areas allowed us to evaluate the air quality of Palermo. The obtained results showed a very high range of PAHs concentrations, from 33 μg/kg (bark dry weight), as ΣPAHs, at the control site to 1015 μg/kg along a road with high traffic flow.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) may enter the atmosphere from both natural and anthropogenic sources, the latter prevailing in industrialized and urban areas. The primary natural sources of airborne PAHs are forest fires and volcanoes (Kim et al., 2003). Natural sources of PAHs also include biosynthesis by microbes and plants under anaerobic conditions (Neff, 1979). The commercial production of PAHs is not a significant source of these compounds in the environment (Law and Biscaya, 1994; Howsam and Jones, 1998). PAHs are a class of chemicals that result from the incomplete combustion of fuels. In rural areas the residential burning of wood and the agricultural activities (combustion of grass, crop residues, etc.) represent the main source of atmospheric PAHs, which result from inefficient combustion and uncontrolled emissions. Other important stationary anthropogenic sources include industrial power generation, incineration, production of coal tar, coke, and asphalt and petroleum catalytic cracking (Neff, 1979; Kim et al., 2003). The anthropogenic mobile sources are represented especially by vehicular traffic in large urban areas (Nielsen, 1996; Caricchia and Chiavarini Pezza, 1999; Dumbar et al, 2001).

The health effect of concern associated with PAH exposure is cancer (de Meagd and Vethaak, 1998). According to the International Agency for Research on Cancer (IARC, 1991), benzo[a]anthracene and benzo[a]pyrene are probable human carcinogens, and benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3,-c,d]pyrene are possible human carcinogens (IARC, 1991). Some researchers have suggested that 1–10% of the incidence of lung cancer is caused by air pollution.

Toxicological investigations showed different cancerogenic potency for various PAH mixtures, individual PAH and different application paths (oral, dermal and inhalative) which at present cannot be predicted quantitatively (Schneider et al., 2002). Of all EPA–PAH analysed in this content of some PAHs—especially the slightly volatile ones—are not regarded cancerogenic. Within the remaining PAHs there are substantial differences of potency of several orders of magnitude—the most potent possibly is benzo(a)pyrene BaP. Through several different studies it became evident that it is possible to specify the cancerogenic effect of individual PAH compared with BaP and to weigh it by means of a conversion factor. These factors are called toxicity equivalence factors (TEF, Table 1) (Larsen and Larsen, 1998; Nisbet and La Goy, 1992; Malcom and Dobson, 1994; Schneider et al., 2002).

There are numerous references in the literature concerning the PAHs concentration in the atmosphere of large urban areas and of zones particularly exposed to this type of emissions (Nielsen, 1996; Caricchia and Chiavarini Pezza, 1999; Dumbar et al., 2001).

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Table 1
Polycyclic aromatic hydrocarbons analysed and classification regarding their carcinogenic potentials (Toxic equivalence factors (TEF)) hydrocarbons (mean of three analysis) in Pine Bark samples

	TEF (a) Larsen and Larsen, (1998)	TEF (b) Schneider et al., (2002)		TEF (a) Larsen and Larsen, (1998)	TEF (b) Schneider et al., (2002)		TEF (a) Larsen and Larsen, (1998)	TEF (b) Schneider et al., (2002)
Acenaphythylene		0.001	Fluoranthene	0.05	0.001	Penzo (a) pyrene	1	1
Acenaphythene		0.001	Pyrene	0.005	0.001	Perylene		
Fluorene		0.001	1 Methyl pyrene			Indeno (1,2,3-cd)pyrene	0.1	0.1
Phenanthrene	0.0005	0.001	Benzo (a) anthracene	0.005	0.1	Dibenzo (a,h) nthracene	1.1	
Anthracene	0.0005	0.01	Chrysene	0.03	0.01	Benzo (g,h,i0 perylene	0.02	0.01
2 Methyl anthracene			Benzo (b) fluoranthene	0.1	0.1			
9 Methyl anthracene			Benzo (k) fluoranthene	0.05	0.1			

Animal and vegetal organisms including lichens have been widely used for environmental biomonitoring purposes (Rühling and Tyler, 1968; Walkenhorst et al., 1993; Raffaelli, 1996; Baumard et al., 1998; Catsky et al., 2001; Cortés, 2004; Madejon et al., 2006). Some studies, carried out by our research group using lichens and leaves as bioaccumulators (Giovenco et al, 1996; Alaimo et al., 2000; Macaluso et al., 2000; Lombardo et al., 2001; Culotta et al., 2002, 2005) showed a general increasing of heavy metals and/or PAHs concentration in the urban areas under investigation owing to human activities.

Tree bark has also been used as a bioaccumulator of both heavy metals and organic toxicants in a study comparing the bioaccumulation capacity of moss and pine bark samples towards heavy metals in an industrialized area of Turkey (Türkan et al., 1995). Schultz et al. (1999) used pine barks to characterize temporal variations and spatial patterns of some inorganic and organic substances and clearly showed the suitability of this biomonitoring tool. Some authors (Böhm et al., 1998) used oak tree bark for determining the distribution of air pollution by heavy metals and other elements in Bohemia. Schulz et al. (1999) analysed the concentrations and natural isotope ratios of both N and individual compounds in bark samples from various locations to obtain information on the origin of atmospheric N depositions (Schulz et al., 2001).

Due to its very porous surface, tree bark is well recognized to be an excellent biosorbent material of airborne pollutants. In this work, we optimize an analytical method for the bark of pine trees, which are widespread in Palermo town, as well as throughout the Mediterranean area, and use it as a bioaccumulator of PAHs, with the aim of evaluating the air quality of Palermo.

2. Material and methods

Among the various steps of the procedure for the detection of PAHs in whatever environmental sample, the sampling, the extraction and the quantitative recovery are by far most important. First, the repeatability of the sampling was checked by analysing for PAHs in four different samples of bark collected from different points of the same tree, giving a relative standard deviation of about 7%, while analysing four bark samples taken from different trees of the same site gave a relative standard deviation of about 8%. Therefore, we can consider the standard deviation from sampling to be negligible relative to that of the analytical process. For the subsequent analyses, we collected about 25–50 g bark from each station and homogenized it before extraction in the laboratory.

Particular attention was paid in this study to the extraction method in order to obtain the best recovery of PAHs from barks under investigation. The PAHs concentration in the various bark samples and their distribution in the different sampling sites were related to hypothesize the possible origin of PAHs in the urban area of Palermo. Qualitative and quantitative analysis of PAHs was carried out by the GC–MS technique using reference standards and spectra libraries. As recommended by the USA Environmental Protection Agency, in each sample 19 PAHs were analysed, with particular attention to 16 recognized as priority pollutants (Table 1).

2.1. Chemicals

All chemicals used were of analytical grade with high purity. In particular, organic solvents (dichloromethane, cyclohexane, pentane), supplied by Sigma Aldrich (Milano, Italy), were of 99.8% purity. Standard reference PAHs mixture (EPA 610 PAHs mixture) and perdeuterated internal standards (fortification solution B) were from Supelco (Milano, Italy).

2.2. Sampling and sites

Palermo is a densely populated town (more than 1 million habitants) with a heavy load of vehicular traffic and major industrial activities are located within the urban area. *Pinus sylvestris* L., a vegetal species common in the entire Mediterranean region, is widespread both in the city and in the outskirts. Pine bark samples were collected, between April 2004 and February 2005, from 50- to 60-year-old pine trees, free of mosses and lichens. When it was possible three trees for every sampling station were chosen. Sampling sites are shown in the maps reported in Figs. 1 and 2.

In order to compare analytical results obtained in sites having different meteorological conditions and vehicular traffic, some pine barks samples were also collected in sites far from the city. Detailed information about the characteristics of sampling sites are reported in Table 2.

Using a hard steel knife, the external surface of the bark, not exceeding 2 mm in depth, was removed from different areas of the whole circumference of each tree, at 1–1.5 m height, obtained by combining the sub-samples of 5–10 g. For analysis we used the laboratory sample obtained by combining the sub-samples of the same tree into one mixed sample. Barks were collected using rubber gloves and were immediately refrigerated (4 °C), stored avoiding exposure to light, and then rapidly carried to the laboratory where they were frozen before analysis.

Two samples of bark for each site were dried to a constant weight in an oven at a temperature of 70 °C to report PAH values on a dry weight basis.

2.3. Sample treatment

The dried samples were pulverised to uniform size with a laboratory mill. The mill was scrupulously cleaned and dried after each grinding to avoid contamination. About 5 g of bark was added to pre-cleaned (Soxhlet extracted with dichloromethane for 24 h) anhydrous Na_2SO_4 (Carlo Erba, Milano). A solution of a perdeuterated surrogate standard (benzo(a)anthracene-d_{12}) was added to the sample of bark.

2.4. Extraction of PAHs

To find the best extraction method to obtain the maximum recovery percentage of PAHs under investigation, different recovery tests were carried out on tree bark samples. These were preventively extracted for 48 h, using a Soxhlet apparatus and successively spiked with a known quantity of PAHs using different methods. The average recoveries calculated for all the compounds and the relative standard deviations are reported in Table 3.