Spatial Variation of Polycyclic Aromatic Hydrocarbons (PAHs) in Air, Soil and Tree Components in Iskenderun Industrial Region, Turkey

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***Abstract*—** Iskenderun is one of the hot spots of Turkey due to the several industrial activities located in the area. The spatial distribution of air pollution in this area was investigated by measuring polycyclic aromatic hydrocarbons (PAHs) in air, soil, leaf litter and tree components (bark, needle and branch) of two pine species (*Pinus brutia* and *Pinus pinea*). To investigate the concentrations and profiles of PAHs, tree component samples were collected from different forested areas (27 sites) in Iskenderun, Turkey during the period of November 7-14, 2010. Soil and ambient air samples were also collected at the same sites to investigate the relationships between the soil, tree components and air. Passive air samplers (PAS) consisting of polyurethane foam (PUF) disks were used to measure ambient air concentrations during a three-month deployment period (November 2010 – February 2011). All collected samples were processed using commonly accepted methods and they were analyzed using gas chromatography / mass spectrometry (GC/MS). Concentrations in ambient air (ng m^{-3}) ranged from 21.0 to 314 (average ± S.D., 133 ± 106 ng m^{-3}) for $\sum_{16}$-PAHs. Phenanthrene, fluorene, pyrene and chrysene were the dominating compounds in all samples. The spatial distribution of ambient air PAH concentrations indicated that the major PAH sources in the region were iron-steel plants. PAH concentrations for all air, soil and tree samples decreased with distance from the major sources. The highest concentrations were observed near industrial sites and lowest concentrations were observed in background sites indicating that industries in the area were the major sources of PAHs. The highest and lowest PAH concentrations were observed in 2-year needles and branch samples, respectively. Air, soil and tree component PAH concentrations were correlated significantly indicating the interaction of these compartments. Results of this study indicated that tree components and soil could be used to assess the spatial distribution of ambient air PAHs in a region.

***Keywords*—** Air pollution, polycyclic aromatic hydrocarbons, tree components, Turkey

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I. Introduction

POLYCYCLIC aromatic hydrocarbons (PAHs) have become a substantial environmental issue during the past decades, because of their persistence, bioaccumulation and toxicity in the environment. Several PAHs also exhibit mutagenic and/or carcinogenic properties [1]. PAHs are emitted from both natural and anthropogenic sources into the environment. Natural sources include forest fires, volcano activities and biosynthesis by bacteria and plants. However, anthropogenic sources such as incomplete combustion of fossil fuels, waste incineration, vehicle exhausts and industrial processes are the predominant emission sources of PAHs [2].

The atmosphere is a major pathway for the transportation and deposition of PAHs. Plants accumulate environmental pollutants by atmospheric depositions to their components and root uptake from soil. The level of accumulation depends on the pollutants' physicochemical properties, plant characteristics and environmental conditions [3]. Pine trees, due to retention properties exhibited by their waxy layer of needles, can be used for biomonitoring to assess the occurrence of POPs in the environment [4].

Iskenderun is an industrialized city situated at the southern part of Turkey and it is one of the hot spots of the country because of the several industries, especially iron-steel plants located in the area. Recent studies based on soil, ambient air, and stack-gas sampling have shown that the ferrous scrap and iron ore processing steel plants are important local sources of PAHs in the region [5], [6], [7]. The objective of this study was to investigate the spatial distribution of air pollution in Iskenderun industrial region in Turkey by measuring polycyclic aromatic hydrocarbons (PAHs) in air, soil, leaf litter and tree components (bark, needle and branch) of two pine species (*Pinus brutia* and *Pinus pinea*).

II. Experimental

A. Sample Collection

The field studies were conducted in the forested areas of Iskenderun industrial region. The area contains several air pollutant sources including a large integrated steel plant (with a sintering plant, coke ovens, blast furnaces, a lime plant, and rolling mills), a cement plant, a fertilizer plant, and several scrap processing iron-steel plants with electric arc furnaces (EAFs), scrap iron storage and classification sites, steel rolling mills, a very dense transportation activity of scrap iron trucks, sampling sites were selected to represent locations affected by the industrial emissions and the background locations. The selection was based on preliminary field studies and the results of a recent study carried out in this region [7]. Pine needles (1 and 2 years of age), bark, branch, leaf litter and soil samples were collected from all sampling sites during the period of November 7-14, 2010. Air samples were collected on polyurethane foam (PUF) disks using passive samplers (PAS) during a three-month deployment period (November 2010 – February 2011). Collected samples were brought to the laboratory in their pre-cleaned containers (tightly closed glass jars and vials) and stored at 4°C until analysis.

B. Sample Preparation and Analysis

Prior to extraction, all samples were spiked with PAH surrogate standards. Ambient air PUFs were Soxhlet extracted for 12 hours with a mixture of 1:1 acetone:hexane. Ten grams of soil and tree component samples were soaked in 40 mL of 1:1 acetone:hexane mixture overnight. Then, they were ultrasonically extracted for 30 min. After concentrating to 2 mL, samples were cleaned up using gel permeation chromatography. Samples further cleaned up and fractionated on an alumina-silicic acid column. All samples were analyzed for PAHs with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) using electron impact ionization. PAHs were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. Further details for sample preparation and instrumental analysis could be found elsewhere [6], [8].

III. Results

$\sum_{16}$PAH concentrations for tree components, soil, leaf litter and ambient air samples are summarized in Table I. All sample concentrations measured in this study were reported on the basis of dry weight.

Concentrations in ambient air (ng/m^3) ranged from 21.0 to 314 ng/m^3 (average ± SD, 133 ± 106 ng/m^3) for $\sum_{16}$PAHs. The highest and lowest PAH concentrations were observed in 2-year needles (1838 ± 2818 µg/kg) and branch samples (147 ± 108 µg/kg), respectively. On the average, PAH concentration in 2-year needles was 2.4 times higher than 1-year needles as a result of longer exposure to polluted air. The lowest PAH levels in needles were found in background sites without specific local PAH sources (88.8 – 692 µg/kg) and the highest concentrations were found in industrial sites (654 – 12161 µg/kg). A similar observation was reported by Piccardo *et al.* [9], the lowest PAH levels in needle samples were found in a rural area (10.4 – 39.1 µg/kg dry wt) while the highest concentrations were found in an industrial area (201.6 – 817.4 µg/kg dry wt.). Measured PAH concentrations in pine needles at different locations in Portugal and Spain ranged between 213–1773 µg/kg [4]. Another recent study conducted in Portugal has reported that the mean values for $\sum_{16}$PAHs ranged from 96 ± 30 µg/kg (dw) for remote sites to 866 ± 304 µg/kg (dw) for industrial sites for *Pinus pinaster* needles and from 188 ± 117 µg/kg (dw) for rural sites to 337 ± 153 µg/kg (dw) for urban sites for *Pinus pinea* [10]. A similar spatial distribution was observed in the present study and the levels of PAHs in pine needles were comparable to those measured in different sites in Portugal. PAH concentrations in bark samples ranged between 13 – 1523 µg/kg and were generally higher than those observed in Portugal and Spain (22 – 196 µg/kg) by Ratola *et al.* [4].

Sampling sites were grouped according to their distance from the area that the major sources (iron-steel plants) are located (i.e., within 2 km, 2-5 km, and background sites). PAH concentrations in all samples decreased substantially with the distance from the sources (Fig. 1).

TABLE I
PAH Concentrations In Soil, Tree Components And Ambient Air

	$\sum_{16}$-PAHs Concentrations						
	1-year needle (µg/kg)	2-year needle (µg/kg)	Branch (µg/kg)	Bark (µg/kg)	Leaf Litter (µg/kg)	Soil (µg/kg)	Ambient air (ng/m^3)
Minimum	89	120	6	13	113	89	21
Maximum	6524	12161	451	1523	7848	43481	314
Median	374	1129	109	119	636	532	50
Mean	844	1838	147	204	1131	3424	106
Standard Deviation	1500	2818	108	342	1793	10176	109

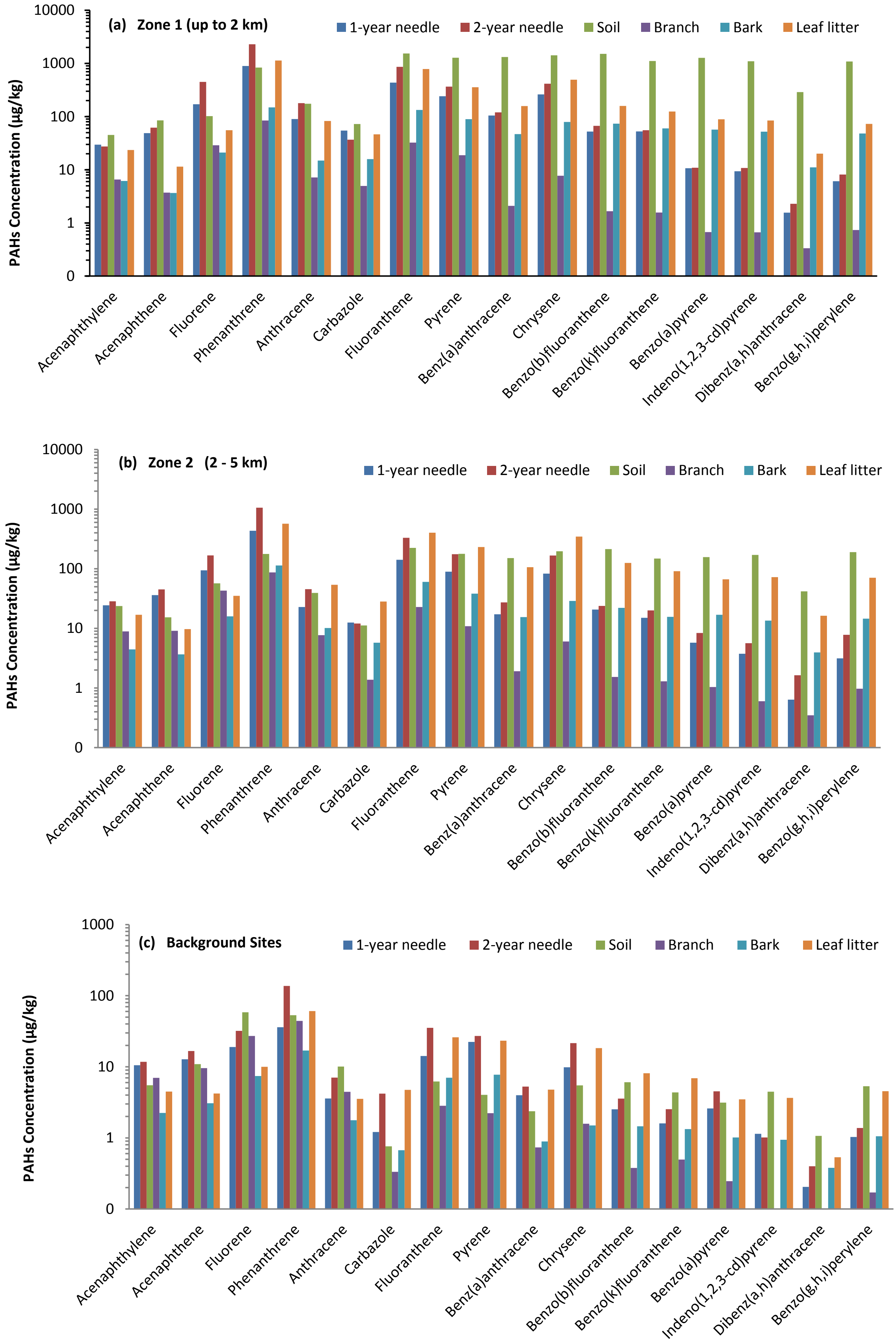

Fig. 1 Variations of individual PAHs with distance from the source area, (a) within 2 km, (b) 2-5 km, (c) background sites

Phenanthrene, fluorene, pyrene and chrysene were the dominating compounds in all types of samples and sites. Phenanthrene consisted of 40% to 70% of the $\sum_{16}$PAHs in most cases. However, medium to high volatility PAHs dominated the soil concentrations (Fig. 1). Similar to the present study, pine needles sampled across the UK [11] showed that phenathrene was the predominant compound. Phenanthrene, fluoranthene and pyrene were also previously found to be among the predominant PAHs in pine needles in UK [11], in leaves of *Quercus ilex L*. in Italy [12] and in tree bark from urban areas in Brazil [1]. PAH profiles observed in the present study were also similar to those reported by Migaszewski *et al.* [13], Piccardo *et al.* [9] and Netto *et al.* [1].

Spatial variations of PAHs in the study area are illustrated in Fig. 2 and Fig. 3 using the measured concentrations in ambient air and in pine needles as examples. PAH concentrations for air, soil and tree samples decreased with distance from the major sources. Generally, substantially higher concentrations were measured near industrial sites and the lowest ones in background sites (not shown in Fig. 2 and Fig. 3).

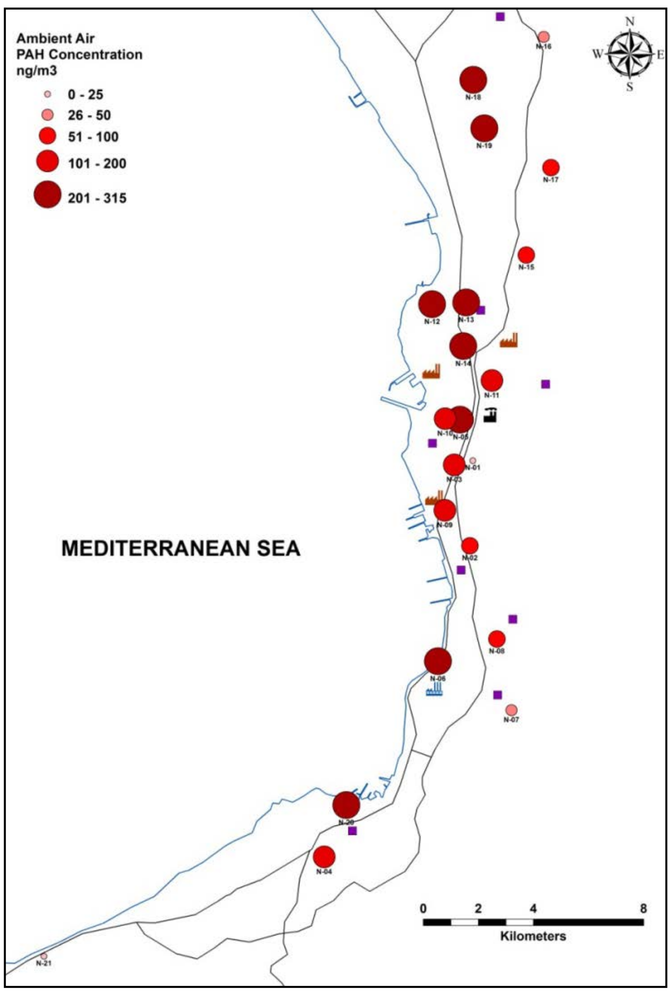

Fig. 2. Spatial variations of ∑16PAH concentrations in ambient air

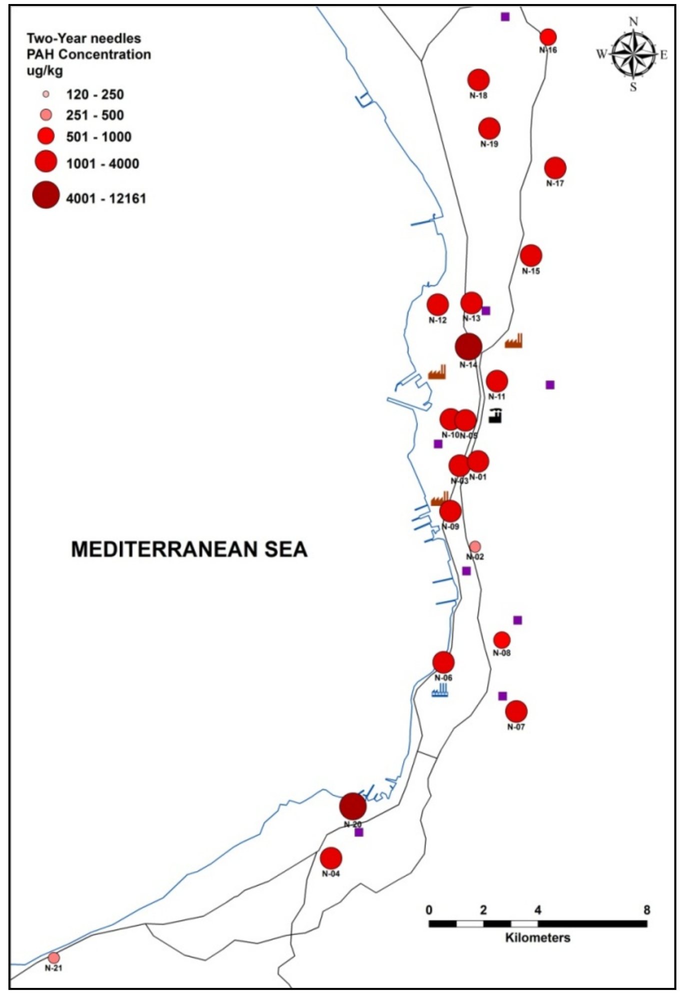

Fig 3. Spatial variations of ∑16PAH concentrations in 2-year needles

It was reported that the prevailing wind directions in the area are southerly [7]. The highest concentrations were measured at sites located north of the iron-steel plants with EAFs (sites 5 and 10) and the integrated steel plant (sites 12, 13, 14) where their emissions are transported by the prevailing winds. Results indicated that the iron-steel plants were the major sources of PAHs in the study area (Fig. 2 and Fig. 3). This is consistent with the recent studies reporting that iron-steel production from scrap is a significant source for PAHs [6], [7]. PAHs may be present in the scrap and are thermally desorbed during the production processes or they may form as a result of incomplete combustion of scrap organic matter, fuels, and additives like coal. PAH emissions of the integrated steel plants are even higher due to the presence of coke ovens.

The relationships between PAHs measured in different samples were investigated by constructing a correlation matrix (Table II). The statistically significant correlations ($p<0.01$) between ambient air, soil, tree components and leaf litter indicated the interaction of these compartments. PAHs in most of the samples (soil, needle, bark and leaf litter) were well correlated with ambient air suggesting that they could be used for biomonitoring of air pollution. These correlations further support the finding that measured PAHs in the area are emitted by common sources (i.e., iron-steel plants).

TABLE II
CORRELATION MATRIX FOR THE PAHS MEASURED IN DIFFERENT SAMPLES (SIGNIFICANT CORRELATIONS ARE SHOWN IN BOLD, P<0.01)

	Air	Soil	Bark	Branch	1-Year Needle	2-Year Needle	Leaf litter
Air	1.00						
Soil	**0.55**	1.00					
Bark	**0.66**	**0.76**	1.00				
Branch	0.46	0.42	0.48	1.00			
1-Year Needle	**0.67**	**0.52**	**0.75**	0.21	1.00		
2-Year Needle	**0.77**	**0.53**	**0.62**	0.30	**0.88**	1.00	
Leaf litter	**0.68**	**0.57**	**0.67**	0.09	**0.79**	**0.68**	1.00

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