MONITORING PAHs IN A PETROCHEMICAL AREA IN CATALONIA, SPAIN

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Introduction

Petrochemical industries potentially release a considerable number of environmental pollutants. Higher concentrations of polycyclic aromatic hydrocarbons (PAHs), as well as other organic contaminants such as polychlorinated biphenyls (PCBs) and volatile organic compounds (VOCs), have been found in ambient air surrounding oil refineries[1]. A correlation between the presence of these facilities and an increase of adverse health effects has been also observed for workers and the local population[2].

In 2002, a wide monitoring study was carried out in various areas of Tarragona County (Catalonia, Spain) by analyzing the levels of environmental pollution. The zone is characterized by the presence of a number of potentially important industrial (a large oil refinery, a chlor-alkali plant, several plastic-manufacture chemical companies, and two incineration plants) and urban (traffic, heating) sources of pollution. In that baseline study, the concentrations of several PAHs and those of some chlorinated pollutants were determined in soil and vegetation samples[3, 4]. Although pollution levels were relatively low, considering the high amount of potential emission sources, concern among the local population is still present. Because of that, in 2005 a 5-year environmental surveillance program was initiated in order to assess the temporal trend of these pollutants. In 2005 and 2006, PAH levels were determined in samples of soil and herbage, respectively[5, 6]. In the present survey, the concentrations of PAHs were again analyzed in both monitors, and the temporal trends were determined. Additionally, the PAH content in ambient air was also measured and correlated with the concentrations found in soil and vegetation.

Materials and methods

In winter of 2007, 24 samples of soil, 15 of vegetation, and 8 of ambient air were collected at 4 different sites in the industrial area of Tarragona County. Sampling locations were the same as previous surveys, being classified according to the emission sources of pollutants: a) petrochemical; b) chemical; c) urban/residential; and d) unpolluted (blank). The sampling methodology of surface soil (0-5 cm) and vegetation (*Piptatherum L.*) has been described previously[3]. Ambient air was collected by using an active air sampling device TE-1000-PUF (Tisch Environmental, Cleves, OH, USA). A quartz fiber filter and polyurethane foam (PUF) were used to collect the PAHs associated to the particulate and gaseous phases, respectively. A total volume of 1533-1864 m^3 was taken during the 24-h sampling.

The environmental concentrations of PAHs were determined by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS). The analytical determination of PAHs in soil and vegetation followed a combination of US EPA 1625 and CARB 429 methods. In turn, PAH analysis in air samples was done according to the German VDI 3499 method. Prior to the pre-treatment, some deuterated-PAHs were spiked to check potential losses during the process. An accelerated solvent extraction (ASE) was carried out with toluene. The clean-up and fractionation of the crude extract consisted on size exclusion chromatography. Finally, PAHs were analyzed by means of an Agilent 6890 capillary gas chromatograph equipped with a DB5-MS capillary column and coupled to a Waters Autospec Ultima High Resolution Mass Spectrometer, with selected ion recording at resolution of 8,000.

The statistical software package SPSS 15.0 was used for data treatment. The Levene test was applied to establish whether the data followed a normal distribution or not. Subsequently, ANOVA or Kruskal Wallis test were used depending on the equality of variances. In the cases in which the concentration of a specific compound was below their respective limit of detection (LOD), the value was considered as one-half of that limit (ND=1/2 LOD).

Results and discussion

PAH concentrations in soil, vegetation, and ambient air

The individual concentrations of PAHs in soil, vegetation, and immission air samples of Tarragona County are summarized in Table 1 according to the area of collection. Higher (although not significant) levels of the sum of the 16 US EPA priority PAHs were observed in the urban/residential area (446 ng/g dw). It is well established that traffic is one of the most important emission sources of PAHs, contributing more than one-half of the total emissions[7]. In contrast, the lowest PAH levels were found near the oil refinery. Although the petrochemical industries are catalogued as releasers of PAHs, these facilities usually have high stacks and torches which make easier for the deposition of pollutants to greater distances. In addition, the most volatile PAHs, such as naphthalene and acenaphthene, have a great long-range transport capacity[8]. In the present survey, the highest concentrations of these compounds were found in unpolluted soils (71.6 and 21.6 ng/g dw, respectively). Although naphthalene has been identified as a typical PAH marker of background pattern[9], the current PAH levels in the unpolluted soils are still higher than those reported for remote and not directly impacted areas over the world (i.e., the poles[10]). This means that some confounding factors (e.g., agricultural burning and forest fires) deriving to changes in the PAH concentrations could be present in the evaluated zones.

Total PAH concentrations in vegetation were very similar among the different sampling areas, with relatively higher concentrations in the chemical and urban areas. In most samples, the most volatile PAHs presented values below their respective limits of detection. Acenaphthylene was not detected in any sample, while naphthalene could be detected in only one (30 ng/g dw). Significant higher concentrations of acenaphthene and anthracene were observed near the oil refinery ($p < 0.05$). In turn, significant higher levels of the most toxic PAHs (benzo(a)pyrene and dibenzo(a,h)anthracene) were noted in the chemical zone ($p < 0.05$). Finally, phenanthrene was the individual PAH showing a highest concentration in the urban/residential area, being significantly higher than that found in the petrochemical zone ($p < 0.05$). Phenanthrene has been previously identified as an important contributor to total PAHs in traffic-impacted urban areas[11].

Regarding to PAH concentrations in ambient air, the 4 areas under evaluation presented similar levels. Notwithstanding, the concentration of the 7 carcinogenic PAHs in the petrochemical and urban/residential zones was slightly higher. Because of the most weighted contaminants are likely deposited closer to the emission sources[12], comparatively higher concentrations of those PAHs were expected as a consequence of the oil refinery and the traffic. Anyhow, PAH concentrations in samples of ambient air, as well as in soil and vegetation collected at different zones of Tarragona County, are similar to those reported in the literature for similar areas[13, 14]. On the other hand, no significant Pearson correlations were found among the PAH levels in the 3 studied environmental monitors (soil, vegetation, and air).

Temporal trends of PAH levels in soil and vegetation

The temporal trends in PAH levels in samples of soil and vegetation collected in Tarragona County are depicted in Figures 1 and 2, respectively. In comparison to the baseline (2002) study, an important decrease of the levels of total PAHs and carcinogenic PAHs was observed in the chemical area (1002-130 and 397-42 ng/g dw, respectively). A remarked reduction of the PAH concentrations was also noted between 2005 and 2006 in the petrochemical and unpolluted soils (281-97 and 241-160 ng/g dw, respectively). Although the behavior of the individually studied PAHs differed, no significant differences were noted in soils with respect to the year of collection. The trends of PAHs in soils, assessed as a whole mixture, were also evaluated by calculating the PAH levels in benzo(a)pryene-equivalents (b(a)p-eq). The PAH concentrations given in these units, which can be considered as similar to dioxins and furans' toxicity equivalents (TEQ), are obtained by multiplying the individual concentration of each PAH and its toxicity, referred to that of benzo(a)pyrene[15]. In our first survey, the PAH levels in soil were 24, 124, 96 and 25 ng b(a)p-eq/g dw in the petrochemical, chemical, residential and unpolluted areas, respectively[3]. In the current survey (2007), the PAH levels dramatically decreased to 16, 11, 69 and 10 ng b(a)p-eq/g dw in the same 4 areas. The reduction of PAHs in the chemical area was due to the decrease of toxic PAHs (mainly benzo(a)pyrene and dibenzo(ah)anthracene). The decrease of these compounds in the urban/residential area was not so notable.

The marked increase of the total PAH concentrations in herbage is especially remarkable. In fact, the amount of PAHs in vegetation significantly increased between 2005 and 2007 in the petrochemical area (from 59 to 94 ng/g dw; $p < 0.05$), and between 2002 and 2007 in the unpolluted area (from 28 to 108 ng/g dw; $p < 0.05$). However, this increase was not constant for all PAHs. For instance, the levels of naphthalene were drastically reduced between the last 2 surveys. It is known that PAHs, and especially low molecular weight PAHs, may suffer a quick degradation according to different meteorological and climatological parameters, such as solar radiation and temperature[16]. These pollutants may fluctuate notably depending on the environmental conditions of each specific area and time. One possible explanation for this naphthalene decrease might be the 2°C increase of temperature registered between January 2005 and January 2007.

In conclusion, the notably higher levels of total PAHs in soils, and carcinogenic PAHs in ambient air, would point out traffic as one of the most important emission sources of PAH contamination in Tarragona County. The study of the PAH levels in different environmental compartments leaded to distinguish different pollution patterns. Consequently, the use of various complementary monitors is essential to evaluate the real state of pollution impacted by a high number of potential emission sources of PAHs and other organic pollutants.

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Table 1: PAH concentrations in soil (ng/g), vegetation (ng/g) and ambient air (ng/m³) in petrochemical (P), chemical (C), urban/residential (U/R) and unpolluted (Un) areas of Tarragona County (Catalonia, Spain)

	Soil				Vegetation				Ambient air			
	P	**C**	**U/R**	**Un**	**P**	**C**	**U/R**	**Un**	**P**	**C**	**U/R**	**Un**
Naphthalene	9.9	36.8	67.6	71.6	<8.0	<8.0	<8.0	12.7	3.6	4.9	4.4	2.7
Acenaphthylene	1.9	1.8	4.1	2.2	<2.0	<2.0	<2.0	<2.0	0.2	0.2	1.1	1.8
Acenaphthene	1.7^a	3.3^a	17.8^{ab}	21.6^b	4.0^a	4.8^{ab}	3.6^{ab}	3.1^b	0.8	1.4	2.0	1.5
Fluorene	<1.8	2.2	6.4	6.8	7.7	11.5	8.6	7.8	0.4	2.1	0.4	0.4

Table 1 (cont.)

	Soil				Vegetation				Ambient air			
	P	**C**	**U/R**	**Un**	**P**	**C**	**U/R**	**Un**	**P**	**C**	**U/R**	**Un**
Phenanthrene	7.5	9.1	34.4	10.1	29.5[a]	49.0[ab]	44.3[b]	40.0[ab]	5.2	8.1	7.7	5.6
Anthracene	2.1	2.1	4.7	<2.0	3.0[a]	2.4[ab]	1.4[ab]	<2.0[b]	0.5	0.7	0.8	0.5
Fluoranthene	11.5	12.6	43.0	6.8	15.9	20.8	19.5	17.3	1.5	2.2	2.9	3.3
Pyrene	11.9	12.8	44.4	6.2	14.5	17.4	14.9	12.8	1.1	1.9	2.9	2.3
Benzo(a)anthracene	3.8	4.2	26.3	2.9	2.0	1.4	1.7	1.3	0.1	0.3	0.2	0.1
Chrysene	7.2	9.0	33.1	4.4	4.8	4.9	3.9	4.2	0.3	0.8	0.5	0.3
Benzo(b)fluoranthene*	11.8	10.8	35.2	7.2	2.4	3.1	3.0	2.6	2.4	1.3	2.6	1.0
Benzo(k)fluoranthene	5.0	3.8	16.4	2.9	0.9	1.3	1.1	1.1				
Benzo(a)pyrene	8.1	6.6	41.8	4.9	1.0[ab]	1.7[a]	1.2[ab]	0.7[b]	1.5	1.0	1.1	0.8
Indeno(123-cd)pyrene	5.8	5.1	25.2	4.4	1.2	1.8	1.2	1.0	0.1	0.3	0.2	0.1
Dibenzo(ah)anthracene	1.5	1.9	11.0	1.5	0.2[a]	0.6[b]	0.2[a]	<0.2[a]	0.2	0.5	0.4	0.2
Benzo(ghi)perylene	6.5	7.4	35.0	5.4	2.2	3.6	2.2	1.2	0.03	0.08	0.03	<0.03
16 PAHs	97.2	129.5	446.2	160.1	94.2	128.8	111.4	107.9	18.1	25.8	27.5	20.6
7 carcinogenic PAHs	43.3	41.5	189.0	28.2	12.5	14.8	12.2	11.0	4.5	3.8	4.6	2.4

* In air, benzo(b)fluoranthene and benzo(k)fluoranthene were concurrently analyzed.

Different superscripts indicate significant differences between areas ($p < 0.05$).

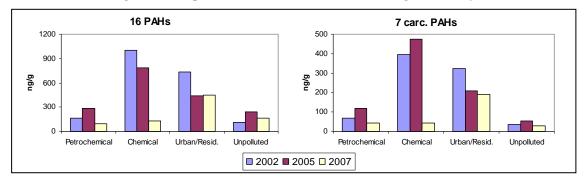**Figure 1: Temporal trend of PAHs in soils of Tarragona County**

Figure 2: Temporal trend of PAHs in vegetation of Tarragona County. Different superscripts indicate significant differences ($p < 0.05$)