

ENVIRONMENTAL MONITORING OF ORGANIC POLLUTANTS IN A PETROCHEMICAL AREA. TEMPORAL TRENDS IN VEGETATION

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Introduction

A number of industrial activities emit polycyclic aromatic hydrocarbons (PAHs) into the environment. Among anthropogenic sources, in recent years power generation and petroleum manufacturing have become very important¹. In addition to stationary sources, traffic has also been suggested to be a remarkable contributor to pollution by PAHs.² Moreover, other industries involving thermal processes may be potentially releasers of other organochlorine compounds such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs).^{3,4}

The most important chemical/petrochemical industrial complex in Southern Europe is located in Tarragona (Catalonia, Spain). In 2002, after approximately 40 years of operations, a wide environmental monitoring program was carried out in various industrial and residential areas of Tarragona.⁵⁻⁷ Three years later (2005), a 5-years surveillance program was started in order to state the temporal variation of the environmental levels of some pollutants. The results concerning the levels of PAHs, PCBs and PCNs in herbage samples collected during the second year of the program are here presented.

Materials and Methods

In winter of 2006, 15 samples of herbage (*Pipatherum paradoxum* L.) were collected in 4 different areas of Tarragona: 4 in the chemical area (Southern complex), 4 in the petrochemical zone (Northern complex), 4 in urban areas, and finally, 3 in presumably unpolluted points. Between 100 and 150 g of herbage were collected by cutting the plants at 5 cm above ground. All samples were kept in double aluminium foils. Once in the laboratory, they were dried at room temperature until analyses.

The determination of PCBs, PCNs and PAHs was carried out following a derivation of the US EPA 1625 method. Prior to extraction, several ¹³C₁₂-labelled PCDD/Fs and PCBs, as well as deuterated PAHs, were spiked as internal standards. The pollutants were extracted by ASE (Accelerated Solvent Extraction) in toluene for 24 h. The extract was concentrated up to 2 mL and divided into 2 parts for the determination of PAHs, and for PCBs and PCNs. The clean-up was based on a multistep adsorption chromatography, consisting on consecutives columns of multilayer silica and alumina. The final extract was dried with a gentle stream of nitrogen and another internal standard was added to check the feasibility of the analytical equipment. The resulting cleaned samples were analyzed by High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC/HRMS).

Data were assessed by using the SPSS 12.0 statistical software. Statistical significance was established at p<0.05 and studied by applying an analysis of variance (ANOVA) or a Kruskal-Wallis test. In the cases in which a pollutant presented a level below the limit of detection (LOD) (no detected = ND), its concentration was assumed to be one-half of the LOD.

Results and Discussion

The concentrations of the 16 individual analyzed PAHs, their aggregation and the sum of the 7 carcinogenic PAHs are summarized in Table 1. The levels concerning the chlorinated compounds (7 PCB congeners and 5 PCN homologues) are also given.

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Table 1. Concentrations of PAHs (ng/g) as well as PCBs and PCNs (ng/kg) in herbage collected in different areas of Tarragona (Catalonia, Spain).

	Chemical n=4	Petrochemical n=4	Residential n=4	Unpolluted n=3
Naphthalene	18.5 ± 2.6 ^a	9.5 ± 1.2 ^b	24.5 ± 4.5 ^{ac}	27.5 ± 0.7 ^c
Acenaphthylene	0.78 ± 0.35	<1.2	<1.2	<1.2
Acenaphthene	3.3 ± 4.5	0.8 ± 0.3	1.2 ± 0.4	1.6 ± 0.1
Fluorene	4.2 ± 0.4	3.6 ± 0.9	5.0 ± 1.3	6.4 ± 0.3
Phenanthrene	3.7 ± 2.1	4.7 ± 3.1	5.0 ± 2.5	6.5 ± 0.9
Anthracene	1.5 ± 0.7	2.0 ± 1.4	2.2 ± 0.6	1.9 ± 0.7
Fluoranthene	10.5 ± 5.0	10.5 ± 5.4	16.9 ± 7.9	14.6 ± 7.6
Pyrene	16.2 ± 9.4	12.1 ± 4.0	23.8 ± 13.3	13.9 ± 8.7
Benzo(a)anthracene	2.1 ± 0.9	2.6 ± 1.7	3.4 ± 1.5	1.9 ± 1.3
Chrysene	5.8 ± 2.4	4.4 ± 1.6	5.1 ± 2.1	3.4 ± 2.3
Benzo(b)fluoranthene	3.7 ± 1.2	2.7 ± 0.1	4.5 ± 1.5	2.1 ± 1.0
Benzo(k)fluoranthene	1.6 ± 0.6	1.2 ± 0.3	1.9 ± 0.7	0.9 ± 0.4
Benzo(a)pyrene	1.8 ± 0.9	1.0 ± 0.3	1.8 ± 0.5	0.5 ± 0.2
Indeno(123-cd)pyrene	1.8 ± 0.9	1.1 ± 0.2	1.7 ± 0.5	0.7 ± 0.3
Dibenzo(ah)anthracene	0.40 ± 0.17	0.21 ± 0.05	0.40 ± 0.20	0.09 ± 0.06
Benzo(ghi)perylene	4.8 ± 3.3	2.3 ± 1.4	3.5 ± 1.0	0.9 ± 0.3
16 PAHs	80.5 ± 28.2	59.3 ± 11.4	101.3 ± 30.9	83.3 ± 22.7
7 carcinogenic PAHs	17.2 ± 6.9	13.1 ± 3.0	18.8 ± 6.4	9.6 ± 5.4
PCB-28	220 ± 59	198 ± 62	298 ± 38	273 ± 40
PCB-52	113 ± 40	120 ± 71	188 ± 43	187 ± 35
PCB-101	185 ± 45	145 ± 61	263 ± 98	163 ± 15
PCB-118	179 ± 78	121 ± 40	248 ± 85	137 ± 12
PCB-153	308 ± 82	203 ± 67	355 ± 73	183 ± 38
PCB-138	390 ± 139 ^a	180 ± 45 ^b	345 ± 153 ^{ab}	118 ± 29 ^{ab}
PCB-180	170 ± 58	127 ± 53	160 ± 41	69 ± 20
Sum PCBs	1563 ± 450	1093 ± 337	1855 ± 406	1131 ± 126
Tetra-CN	32.3 ± 6.2	28.8 ± 6.9	64.3 ± 51.8	40.7 ± 16.3
Penta-CN	10.2 ± 2.3	9.0 ± 2.0	22.0 ± 21.1	10.5 ± 3.1
Hexa-CN	3.7 ± 1.5	2.8 ± 0.3	3.8 ± 2.0	2.6 ± 1.2
Hepta-CN	1.3 ± 1.1	<1.0	0.7 ± 0.4	<1.0
Octa-CN	0.8 ± 0.7	0.7 ± 0.6	<0.50	<0.50
Sum PCNs	48.3 ± 10.2	41.7 ± 8.8	90.6 ± 75.2	53.3 ± 20.6

A common superscript (a, b, c) indicates no significant differences between areas ($p > 0.05$).

In relation to PAHs, the residential area showed the highest concentration of $\Sigma 16$ PAHs (101.3 ng/g d.m.) and $\Sigma 7$ carcinogenic PAHs (18.8 ng/g d.m.). In contrast, the lowest levels of the sum of 16 PAHs and the sum of the 7 carcinogenic PAHs (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123-cd)pyrene, dibenzo(ah)anthracene) corresponded to the petrochemical and the unpolluted areas, 59.3 and 9.6 ng/g d.m., respectively. However, the differences did not reach the level of statistical significance. When the PAHs were individually assessed, only naphthalene showed significant different concentrations according to the area of sampling. Thus, the levels obtained in the unpolluted area were significantly higher than those collected near the chemical and petrochemical areas. It is well known that naphthalene is a very volatile compound, and it tends to be present as vapour phase in the atmosphere. Consequently, its long range transport capacity is quite important, as it has been demonstrated by the fact of having found important concentrations of naphthalene in remote areas of the planet.⁸

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Regarding to PCBs, the levels of the sum of 7 PCB congeners were very similar in the 4 areas of collection, ranging between 1093 and 1855 ng/kg d.m. A significant difference was registered for the levels of the PCB-138 congener between the chemical and the petrochemical zones (390 and 180 ng/kg d.m., respectively). In contrast, the residential area presented the highest PCN concentration (90.6 ng/g d.m.), whereas the remaining zones showed similar values (48.3, 41.7 and 53.3 ng/kg d.m. for the chemical, petrochemical and unpolluted zones, respectively). In fact, traffic has been suggested as an important contributor of PCNs in densely populated areas.⁹

In any case, the present levels of organic pollutants found in herbage are similar or even lower than those obtained in other industrial and urban zones. Currently, the number of investigations regarding to the levels of organic pollutants in vegetation is quite scarce. Among the different kinds of vegetal species, pine needles have been frequently used as a biomonitor of pollution. Lehndorff and Schwark (2004)¹⁰ found a PAH concentration ranging between 61 and 185 ng/g in pine needles of the urban area of Cologne (Germany). In turn, Martínez et al. (2000)¹¹ reported a mean PCB concentration of 298 ng/kg in pine bark of an unburned forest in Catalonia, and ranges of PCN levels in pine needles of 165-925 and 250-2100 ng/kg have been reported in Poland and Japan, respectively.^{12,13} Notwithstanding, in spite of a general lack of comparative studies, it has been suggested that the individual plant characteristics might lead to a different PAH accumulation.¹⁴

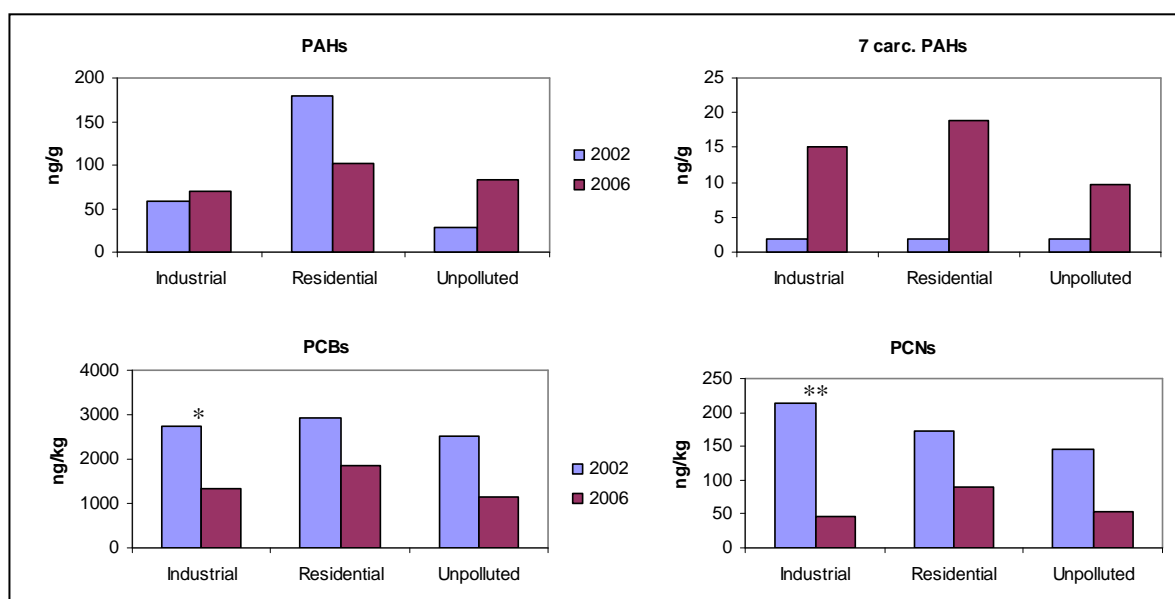


Figure 1. Temporal variation of $\Sigma 16$ PAHs, $\Sigma 7$ carcinogenic PAHs, PCBs and PCNs in herbage collected in Tarragona (* $p < 0.05$; ** $p < 0.01$).

The results of the current study (2006) were compared to those found in the baseline survey (2002). The temporal trends of the organic pollutants in herbage, according to the area of sampling, are depicted in Figure 1. Regarding to the sum of 16 PAHs, the tendencies were different according to the zone of collection. Thus, the PAH concentration in the residential area diminished, whereas that of the unpolluted zone increased. In contrast, the levels of the industrial (chemical and petrochemical) area remained nearly invariable. However, these differences did not reach the level of statistical significance ($p < 0.05$). By contrast, the levels of the 7 carcinogenic PAHs notably increased in the last survey. In 2002, none of the carcinogenic PAHs could be detected in vegetation (LOD=2 ng/g). Due to practical reasons, the kind of vegetation used as a monitor in the baseline study (chard) was substituted by common herbage. The inter-species differences could explain a different retention of compounds depending on each plant characteristics. Moreover, another possibility could be that the experiment (storage and analysis) duration (greatly longer in the baseline study) would have been able to allow the PAHs to degrade.¹⁵

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With respect to the chlorinated compounds PCBs and PCNs, a similar tendency in the three areas of sampling could be observed. For both compounds, the industrial area presented a significant reduction of concentrations between the baseline (2002) and the current (2006) study. PCB levels decreased from 2744 to 1328 ng/kg d.m., while PCN concentrations diminished from 214 to 45 ng/kg d.m. ($p < 0.05$ and $p < 0.01$, respectively). In the residential and the unpolluted areas, the concentrations also notably decreased, but without reaching the level of statistical significance. Since PCBs were included in the Stockholm Convention for the Regulation of POPs, and PCNs are by-products of PCB formulations, this decrease was quite expectable.

In conclusion, the results of the present investigation indicate that the current levels of PAHs, PCBs and PAHs in vegetation of the chemical/petrochemical industrial area of Tarragona are relatively low. In addition, a notable decrease of the chlorinated compounds levels has been found. However, a slight (although not significant) increase of the carcinogenic PAHs has also been noted. Therefore, special attention must be paid to these pollutants in future surveys of 2005-2009 surveillance program.

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