

Monitoring persistent organic pollutants in an industrial area of Tarragona (Catalonia, Spain)

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Introduction

It is well known that combustion of different materials is one of the most important sources of environmental contamination by persistent organic pollutants (POPs)¹⁻³. Therefore, environments affected by this kind of processes should be strictly controlled. In relation to it, the 2001 Stockholm Convention for the regulation of POPs was undertaken in order to establish agreements and mechanisms to erase the release of 12 POPs on a global scale⁴. While polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) were included in this list, other pollutants such as polychlorinated naphthalenes (PCNs) and polycyclic aromatic hydrocarbons (PAHs) can be added in a near future.

Since more than 30 years ago, one of the largest chemical and petrochemical industrial complexes in Southern Europe is located in Tarragona County (Catalonia, Spain). Several chemical industries (such as a PVC production facility and a chlor-alkali plant) and a big oil refinery are located in this residential area (up to 300,000 inhabitants), together with a municipal solid waste incinerator (MSWI) and a hazardous waste incinerator (HWI). Moreover, the presence of a highway and several roads with an important traffic density influences also the environment of the zone.

The current study is a preliminary investigation to assess the levels of several POPs (PCDD/Fs, PCBs, PCNs and PAHs) in soil and vegetation samples collected in Tarragona's industrial and residential areas and to compare them with data obtained in unpolluted sites as well as in other industrial and residential zones.

Materials and methods

Sampling: In Winter 2002, 24 soil and 12 wild chard (*Beta vulgaris*) samples were collected in several sampling points of Tarragona County. Soil sampling points were chosen as follows: 15 in the industrial complex divided into industrial-1 (8 samples collected in the vicinity of chemical industries) and industrial-2 (7 samples collected near a large oil refinery and petrochemical industries), 5 in urban (Tarragona downtown) and residential (several suburbs of Tarragona city) zones, and finally, 4 outside the study area in presumably unpolluted zones. Soil samples were taken from the upper 3 cm of soil and kept in polyethylene bags. They were dried at room temperature until constant weight and sieved through a 2-mm mesh screen.

Chard samples were collected in 12 of the 24 sampling points in which soil samples were taken. Six samples were collected in the industrial (industrial-1 and industrial-2) zone, 3 samples in the residential/urban zones, and 3 samples in unpolluted sampling points. Chard samples were obtained by cutting the aerial part of the plant, and subsequently they were packed in aluminum foils. Samples were dried at room temperature and shredded with a domestic shredder. They were kept in a double aluminum foil, packed in labeled plastic bags, and stored at room temperature until analysis.

Analytical procedure: The compounds whose concentrations were assessed in soil and chard samples were the 17 most toxic PCDD/F congeners, 7 PCB environmental markers (PCB28, PCB52, PCB101, PCB118, PCB153, PCB138 and PCB180), PCN homologues (tetra-, penta-, hexa-, hepta- and octaCN) and the 16 EPA priority PAH.

Two subsamples were taken in order to analyze separately chlorinated and non-chlorinated compounds. PCDD/F, PCB and PCN concentrations were determined following US EPA method 1625, as previously reported^{5,6}. Samples were spiked with a mixture of ¹³C-labeled internal standards and Soxhlet-extracted. Clean-up process was performed with adsorption chromatography, consisting on consecutive multilayer silica and alumina columns. For chard samples, additionally, a 70g BioBead-SX3- gel permeation chromatography column and gel permeation columns were used. The final step involved the reduction to the volume necessary for the analysis. Prior to analysis, a ¹³C-labeled standard was added for calculation of recovery ratios. The cleaned extract was analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

The concentrations of the 16 PAH were determined according to US EPA method 8100. Samples were spiked with two deuterated internal standards and extracted with dichloromethane/hexane. All the extracts were concentrated by rotary vacuum evaporation before clean-up in an alumina column. Naphthalene was recovered in the first fraction and the remaining 15 PAHs in the second one. Finally, all fractions were concentrated with a gentle stream of purified N₂ to the desirable volume. Prior to injection, d₈-naphthalene was added as an internal standard. The samples were analyzed by a gas chromatograph using FID as detector.

Quality control was performed by determining the recovery percentage of those internal standards spiked before extraction. Recovery rates ranged from 42 to 138%. Additionally, a blank was run up every 6 samples.

The values of pH and organic matter content of the soil samples were also determined. Fifteen grams of sample were dissolved in 15 ml of deionized water and after mixing for 24 h the measurement of pH was done with a pH-meter. Organic matter content was evaluated according to the Loss on Ignition (LOI) method. Samples were dried in order to eliminate water content. Subsequently, they were heated for 2 h at 600°C and the weight loss was assessed.

Data analysis: Statistical analysis of the results was carried out with the SPSS 11.0 statistical package. In those samples in which a compound was not detected (ND), its concentration was assumed to be one-half of the limit of detection (ND = ½ LOD). Statistical significance of the differences was determined by one-way analysis of variance (ANOVA) for variables with normal distribution, and the Kruskal-Wallis test for those with no normal distribution. A $p < 0.05$ was considered as significant. Correlation between variables was carried out using Pearson analysis. Principal Component Analysis (PCA) was used to establish relations among levels in soil samples according to the different zones of collection.

Results and discussion

The mean pH of soils was 7.66 (7.03-8.22), while the mean content of organic matter in the 24 soil samples was 5.8% (2.6-9.5%). Levels of PCBs and PCNs were significantly correlated with organic matter in soil ($p < 0.01$ and $p < 0.05$, respectively), while no correlation was found for the remaining compounds.

In soils, mean PCDD/F concentrations ranged from 2.65 ng I-TEQ/kg d.m. (chemical area) to 0.16 ng I-TEQ/kg d.m. (unpolluted sites). PCDD/F levels of the residential soils were one-half of those from the industrial-1 area (1.31 ng I-

TEQ/kg d.m.), whereas the samples collected near the oil refinery showed a closer concentration to blank (0.45 ng I-TEQ/kg d.m.). Significant differences were noted between the most concentrated samples (industrial-1 and residential) and the less concentrated (industrial-2 and unpolluted). The tendency of PCB concentrations according to the sampling area was very similar to that presented by dioxins and furans. The highest levels were found in the industrial-1 and residential areas (12038 and 10342 ng/kg, respectively), followed by the industrial-2 and unpolluted ones (1965 and 657 ng/kg, respectively). Significant differences in individual PCB and Σ PCB concentrations in soils were found between those of the industrial-1 area and industrial-2 and unpolluted zones. With respect to Σ PCNs, industrial-1 and urban samples showed also the highest concentrations (121 and 180 ng/kg, respectively), followed by industrial-2 and unpolluted soils (70 and 32 ng/kg, respectively). However, the differences were not statistically significant ($p > 0.05$).

PAH profile was very similar to the presented by chlorinated compounds. Industrial-1 and residential soils were the most concentrated (1002 and 736 ng/g, respectively), while industrial-2 and unpolluted samples showed the lowest levels (166 and 122 ng/g, respectively). The same profile was obtained for the 7 carcinogenic PAHs (chrysene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[123-cd]pyrene and dibenzo[ah]anthracene)⁷: 397, 322, 70 and 37 ng/g for industrial-1, residential, industrial-2 and unpolluted sites, respectively. PCDD/Fs, PCBs, PCNs and PAHs profiles in soils are depicted in Figure 1.

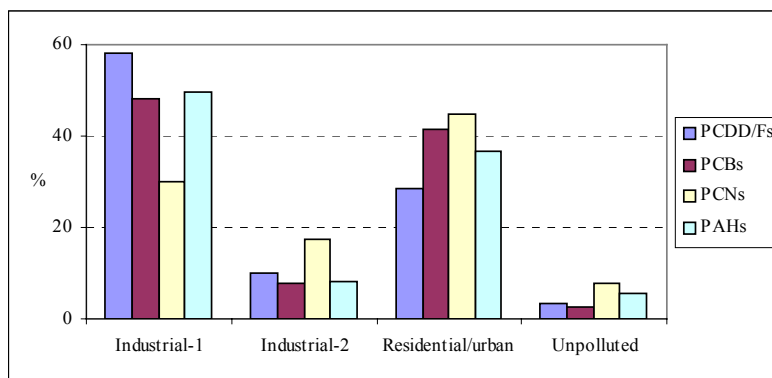


Figure 1: Levels of POPs in soils according to the area of collection (the value in each zone is expressed as the percentage respect to the sum of concentrations found in all the areas).

The profile of concentrations of POPs in chards is shown in Figure 2. Unlike soils, there were no significant differences according to the sampling area. The levels of the chlorinated compounds were very similar in the 3 zones. PCDD/F concentrations found in unpolluted sites (0.54 ng I-TEQ/kg) were higher than those of industrial and urban areas (0.46 and 0.33 ng I-TEQ/kg). It would confirm that long-range transport of PCDD/Fs plays an important role in the environmental levels of these pollutants⁸. Σ PCBs and Σ PCNs concentrations in chard samples were 2744 and 214 ng/kg, respectively, near the chemical/petrochemical industries, 2943 and 172 ng/kg, respectively, in the urban area, and 2503 and 146 ng/kg, respectively, in unpolluted zones. Σ PCBs, tetra- and pentaCN concentrations in chards were higher than those observed in soils. The physico-chemical characteristics of the most volatile compounds, in special their high K_{oa} (octanol-air coefficient), let a high plant storage capacity because they are easily adsorbed by leaves⁹.

PAH tendency was slightly different from those of the remaining pollutants. Residential chards showed the highest concentration (179 ng/g as Σ PAH), followed by industrial and unpolluted samples (58 and 28 ng/g, respectively). Anyway, no significant differences were found between the areas of study. None of the 7 carcinogenic PAH showed concentrations above the limit of detection. Phenanthrene was the individual hydrocarbon which presented a higher concentration (35 and 79 ng/g in industrial and urban areas, respectively), and the only one detected in unpolluted samples (13 ng/g).

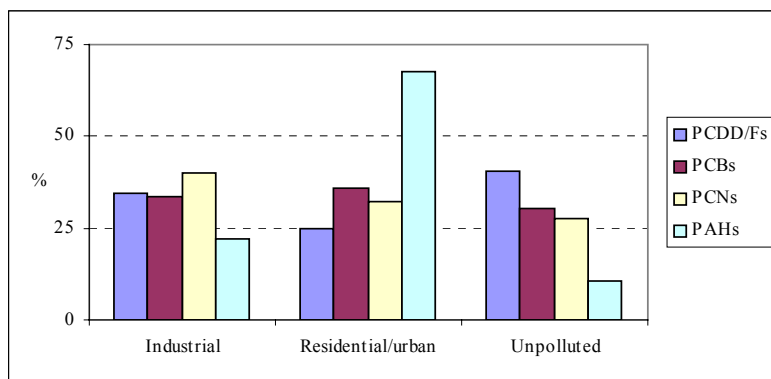


Figure 2: Levels of POPs in chards according to the area of collection (the value in each zone is expressed as the percentage respect to the sum of concentrations found in all the areas).

The results of the present study would corroborate that urban zones are environments with remarkable levels of persistent organic pollutants (POPs), mainly due to traffic, heating and other minor sources¹⁰. Anyhow, the concentrations observed in soils and chards collected in the area of study are comparatively low in relation to those previously found in other industrial and urban sites¹¹⁻¹⁴.

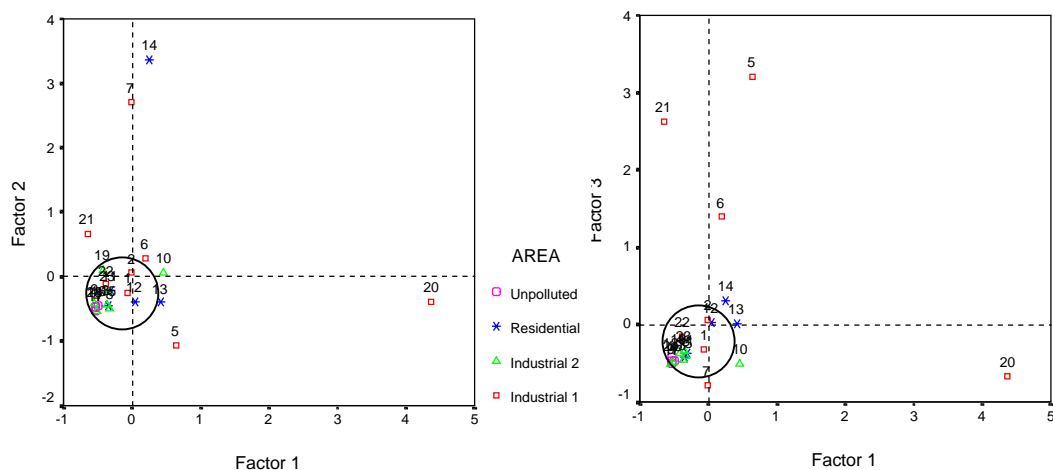


Figure 3: Principal component (PC1/PC2 and PC1/PC3) analysis loading plot for soil samples.

Since there were several emission sources in the area of study, a multivariate statistical analysis was carried out in order to handle the data and identify the main sources^{15,16}. PCA was applied to the 24 soil and 12 chard samples, respectively, reducing them into a few variables. In soils, PCA provided a three-dimensional model, which would explain 71.5% of the variance in the data. The first main principal component (PC), which would explain 27.4% of the variance, was correlated with most PCDD/F congeners. The second PC (25.7% of the variance) was positively correlated with PAHs. Finally, the third PC (18.4% of the variance) was correlated with PCBs, PCNs and indeno(123-cd)pyrene. The scatterplot of the component scores on PC1/PC2 and PC1/PC3 is depicted in Figure 3. Sample #20 (collected in a site where no direct emission sources are known) showed the highest level of component 1. This fact would mean that some uncontrolled fires were probably carried out in that sampling point. Samples #14 and #7 were directly influenced by a heavy traffic. Finally, samples #5 and #21 were located in

the South-eastern part of the chemical complex, where important concentrations of industrial origin could be expected.

With regard to chards, PCA showed also a three-dimensional model, with 77.1% of the variance explanation. The first PC (39.6% of the variance) was correlated with high-chlorinated dioxins and furans and the most weighted PCBs. The second PC (23.0% of the variance) was correlated with low-substituted dioxins and furans. In turn, the third PC (14.5% of the variance) was correlated with PAHs, PCNs and light PCBs. The scatterplot scores are depicted in Figure 4. Sample #6, located in the Southern-eastern corner of the chemical area, showed the highest level of component 1. No clusters for chard samples collected in a same zone were noted.

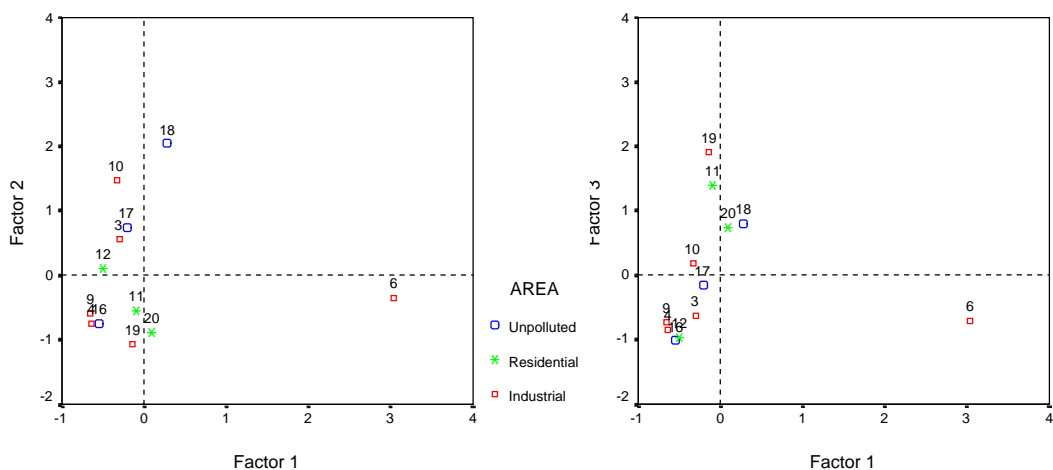


Figure 4: **Principal component (PC1/PC2 and PC1/PC3) analysis loading plot for vegetation samples.**

In summary, the current concentrations of POPs in soil and vegetation samples collected in the chemical and the petrochemical complex of Tarragona do not mean a significant level of pollution when they are compared with data from unpolluted sites. However, this is only a preliminary study including a relatively low number of samples. Consequently, further investigations should be carried out in order to establish the tendency of these pollutants in the environment.

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