

## PASSIVE AIR SAMPLING OF PAHs AT LOCAL SCALE: PRELIMINARY RESULTS IN TARRAGONA COUNTY, SPAIN

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### Introduction

The need to monitor the occurrence of contaminants in the environment has led to the development of a large range of methods and devices for sampling<sup>1</sup>. Passive air samplers (PAS) have become a viable alternative to commonly used active air sampling equipment, since those devices are cheaper, smaller, simpler to handle, and they do not require electricity and maintenance. These characteristics assist the deployment in remote areas and the simultaneous collection of samples at different locations and/or scales<sup>1-7</sup>. PAS are based on the theory of physical advection and diffusion to capture the compounds<sup>10</sup>. Although different designs have been developed according to the adsorbent material<sup>8</sup>, polyurethane foam (PUF) is the mostly used design for air monitoring worldwide<sup>4,8</sup>. PAS were the preferred samplers by the United Nations Environment Program for global air monitoring<sup>12</sup>, while other initiatives such as the Global Atmospheric Passive Sampling (GAPS)<sup>3</sup> are also based on the same approach. The GAPS is a worldwide ambitious monitoring program for investigating the spatial and temporal trends of persistent organic pollutants (POPs) on a global-scale<sup>3,13-17</sup>. However, few international efforts have been conducted in order to study the suitability of PUF-PAS for monitoring POPs at a local scale<sup>6,7</sup>.

POPs are transboundary chemicals with long-range atmospheric transport (LRAT), therefore capable to reach remote and sensitive regions of the planet, away from the origin source<sup>3,5,15</sup>. According to the UNECE Protocol, POPs include a wide variety of compounds, including some polycyclic aromatic hydrocarbons (PAHs) such as benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and indeno[1,2,3-*cd*]pyrene. In recent years, the toxic character of these compounds has been recognized<sup>5</sup>, and the United States Environment Protection Agency (USEPA) has developed a list of 16 priority PAHs<sup>9,19,21</sup>. Furthermore, some PAHs have been classified as carcinogens or possible carcinogens to humans by the International Agency for Research on Cancer (IARC), being benzo[*a*]pyrene and dibenzo[*a,h*]anthracene two of the most relevant<sup>20,21</sup>.

PAHs can be released by natural (e.g., volcanoes, forests fires and grassland combustion) or anthropogenic sources (e.g., oil refineries, power generation, domestic heating and traffic)<sup>18-20</sup>. Therefore, the environmental PAH burdens are expected to be different depending on the proximity of emission sources. This preliminary investigation was aimed at studying the viability of PAS-PUF for sampling PAHs at local scale, prior to the creation of a PAH monitoring network. Air concentrations of 16 priority PAHs were determined in different areas of Tarragona County, Spain, using PAS-PUF, and resulting data were compared with international studies.

### Materials and methods

PUFs (diameter: 14 cm; thickness: 1.2 cm; surface area: 360 cm<sup>2</sup>; density: 0.035g cm<sup>-3</sup>) were purchased to Newterra (Beamsville, ON, Canada). Prior to deployment, PUFs were pre-cleaned by Soxhlet extraction for 24 hours by using dichloromethane (DCM) (99.9% purity, Merck, Darmstadt, Germany)<sup>4</sup>. Subsequently, they were dried in a vacuum desiccator, and stored in brown glass jars which were pre-cleaned with DCM and sealed with high density polyethylene caps<sup>4</sup>. Once in the field, PUFs were inserted between two aluminum chambers to protect them from the external air, precipitation and light<sup>8,9,11</sup>.

PUF-PAS were deployed at three sampling points in Tarragona County for 2 months (October - December of 2013). Sampling sites were Roda de Berà, an urban/residential area, Vilallonga del Camp, a village under the potential influence of the emissions of a petrochemical complex (industrial area), and ETSQ University Campus, a presumably unpolluted or slightly polluted site (rural area). The geographical distribution of sampling sites is depicted in Figure 1.

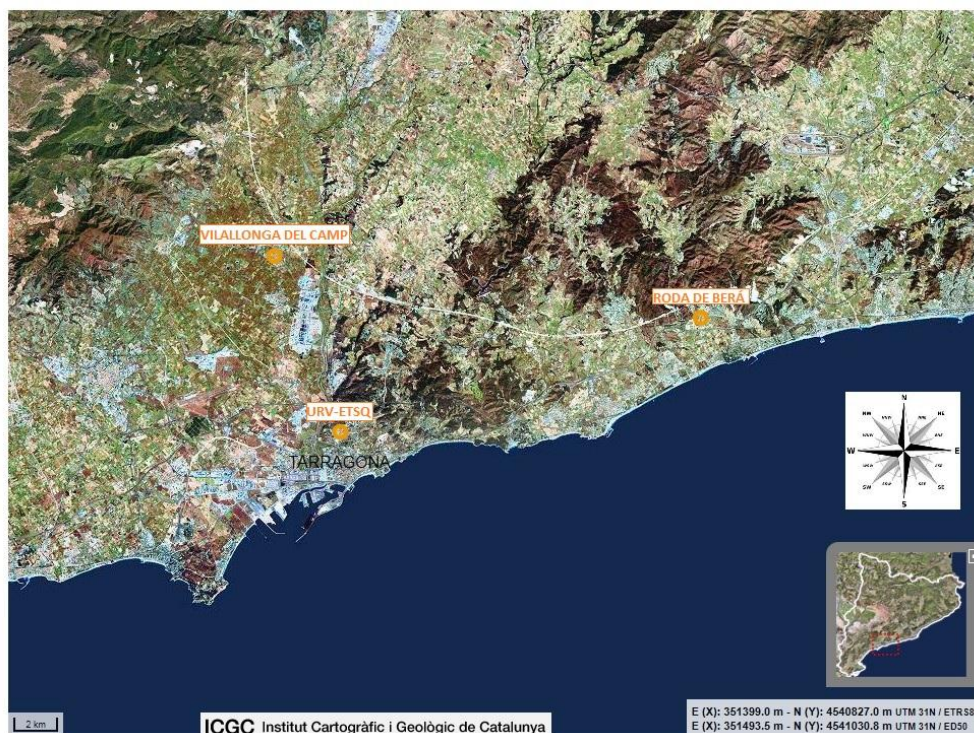


Figure 1. Location of sampling points in Tarragona County (Spain) where PUF-PAS were deployed.

The determination of PAHs was based on the CARB Method 429. Appropriate isotope-labeled extraction standards (i.e., deuterated PAHs) were added to each sample in order to control the whole sample preparation process. The sample was extracted using dichloromethane as solvent. The extract was concentrated and analyzed by HRGC/HRMS using Agilent GCs (5890 and 6890) coupled to Waters Autospec Ultima HRMS systems with selected ion recording at resolution 8000. Samples were injected onto non-polar DB5MS-type GC columns. The quantification was carried out by using the corresponding isotope-labeled compounds as internal standards. Additional QA/QC measures consisted on analyzing blanks and recovery standards inserted in every batch of samples. Recovery percentages differed according to individual PAHs, ranging 89-123%, 99-134% and 108-141% in the urban, industrial and rural areas, respectively. For those hydrocarbons presenting levels below the limit of detection (LOD), a concentration equal to one-half of that limit was assumed.

### Results and discussion

Airborne concentrations of PAHs as well as the sum of 16 US EPA priority PAHs ( $\Sigma_{16}$ PAHs) in different areas of Tarragona County (Catalonia, Spain), are summarized in Table 1.  $\Sigma_{16}$ PAHs concentrations ranged from 17.30 to 66.62 ng m<sup>-3</sup> (rural and industrial areas, respectively). Acenaphthylene and benzo[a]anthracene were not detected in any sample, while acenaphthene and anthracene only showed levels above the LOD in the industrial area. None of the 16 PAHs were detected in the rural zone, excepting naphthalene and fluorene, showing concentrations very close to their respective detection limit (4.47 and 1.08 ng m<sup>-3</sup>, respectively). Therefore, if calculated in a lower-bound scenario (this is, assuming a level of zero for undetected compounds), the  $\Sigma_{16}$ PAHs concentration in the rural site would be only 5.55 ng m<sup>-3</sup>. Anyhow, these levels are very similar to the  $\Sigma_{14}$ PAHs concentrations in air samples collected in winter of 2010 in different regions of Australia<sup>22</sup>, where values ranged from 1.99 to 60.06 ng m<sup>-3</sup>. Furthermore, they are very similar to those previously reported in a number of countries<sup>9,23,24</sup>, such as Canada (range: 8.33-18.46 ng m<sup>-3</sup>), South Korea (mean: 42.6 ng m<sup>-3</sup>) and Bolivia (range: 15.67- 36.03 ng m<sup>-3</sup>).

The highest  $\Sigma_{16}$ PAHs concentrations were detected in Vilallonga del Camp sampling point, located relatively nearby a big oil refinery and well under the potential influence of petrochemical emissions. This fact is in agreement with the results showed in other monitoring studies, where the highest values were also associated to the presence of chemical industries<sup>25</sup>. Air  $\Sigma_{16}$ PAHs concentrations showed a strong industrial>urban>rural

gradient, showing the industrial area 2- and 4-times higher PAH levels than urban and rural zones, respectively. This pattern has been also found in other international studies<sup>23,25</sup>. The PAH profile was dominated by 2-4 ringed PAHs, which accounted for more than 90% of the  $\Sigma_{16}$ PAH concentrations (Figure 2). Phenanthrene was the predominant hydrocarbon, with a mean percentage of 35% of the total (range: 26-44%), while high contributions were also noted for naphthalene and fluoranthene (21% and 13%, respectively). The profile observed in this study was consistent with the results reported by other authors<sup>4,9,25</sup>, who showed a predominance of 3-4 ringed PAHs. This group may reach contributions of up to 90%, being phenanthrene the most contributive compound to the total PAH concentration. PAHs with 2-4 benzene rings are compounds with low molecular weight and high volatility. They are predominantly present in gas phase, and maybe therefore more easily captured by the PUF-PAS<sup>5,9,25</sup>. In contrast, PAHs with 5-6 benzene rings have a higher molecular weight and lower volatility, tending to remain in particulate phase<sup>5,9,25</sup>. In this study, a higher concentration of molecular weight PAHs was observed in urban and industrial areas, more potentially affected by traffic and petrochemical emissions, respectively.

Table 1. PUF-derived air concentrations (in ng m<sup>-3</sup>) for PAHs in 3 areas of Tarragona County in 2013.

	Area			Sampled volume <sup>a</sup>	Sampling rate <sup>b</sup>
	Urban	Industrial	Rural		
Naphthalene	5.93	10.69	4.47	102.92	1.66
Acenaphthylene	<1.25	<1.25	<1.25	159.96	2.58
Acenaphthene	<2.43	3.64	<2.43	82.46	1.33
Fluorene	2.00	3.44	1.08	194.68	3.14
Phenanthrene	16.40	28.25	<9.11	109.74	1.77
Anthracene	<2.21	2.87	<2.21	90.52	1.46
Fluoranthene	3.98	9.72	<3.89	102.92	1.66
Pyrene	2.70	5.14	<2.57	155.62	2.51
Benzo[ <i>a</i> ]anthracene	<0.81	<0.81	<0.81	123.38	1.99
Chrysene	0.60	0.84	<0.60	166.16	2.68
Benzo[ <i>b</i> ]fluoranthene	0.59	0.44	<0.14	141.36	2.28
Benzo[ <i>k</i> ]fluoranthene	0.09	<0.07	<0.07	279.00	4.50
Benzo[ <i>a</i> ]pyrene	0.33	<0.13	<0.13	150.66	2.43
Indeno[123- <i>cd</i> ]pyrene	0.28	0.14	<0.11	190.34	3.07
Dibenzo[ <i>ah</i> ]Anthracene	0.24	0.11	<0.10	203.98	3.29
Bengo[ <i>ghi</i> ]perylene	0.41	0.22	<0.09	229.40	3.70
$\Sigma_{16}$ PAHs	36.91	66.62	17.30	-	-

<sup>a</sup>In m<sup>3</sup>, <sup>b</sup>Sampling rates, according to He and Balasubramanian<sup>29</sup>, are given in m<sup>3</sup> day<sup>-1</sup>.

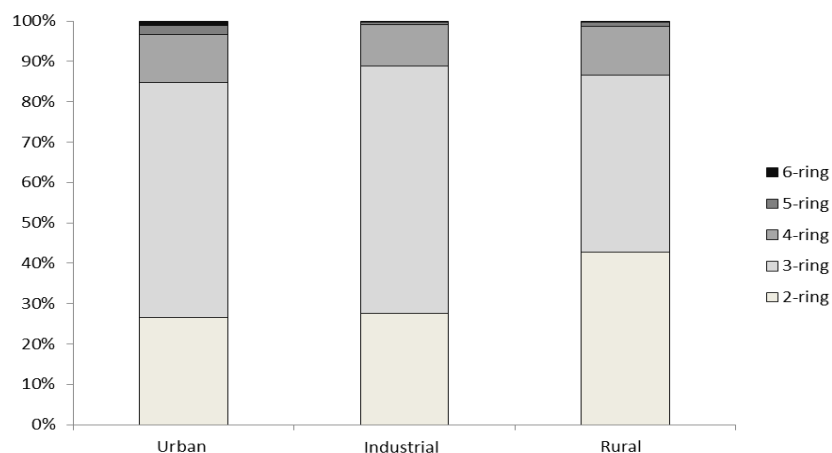


Figure 2. PAH profile in air samples collected in Tarragona County using PUF-PAS.

Despite being this is the first approach to analyze airborne PAHs in Tarragona County by using PUF-PAS, previous research based on active air samplers has been already conducted in the same area of study. Data on PAHs in air coming from passive and active air sampling methods are very comparable, when monitoring campaigns are conducted in the same season. Nadal et al.<sup>26</sup> reported that the mean  $\Sigma_{16}$ PAH concentration in 4 different areas of Tarragona County ranged 18.08 to 27.45 ng m<sup>-3</sup>, while Ramírez et al.<sup>27</sup> found  $\Sigma_{16}$ PAH levels ranging from 10.4 to 59.5 ng m<sup>-3</sup> respectively, in the same 3 kinds of area here considered (industrial, urban, and rural). In summary, these results confirm that PUF-PAS may be a good option for PAH monitoring at local scale. The next step will be to design and deploy a PUF-based monitoring network for the periodical assessment of PAHs in air of Tarragona County as a complement to existing data on PAHs in soil and vegetation<sup>26,28</sup>.

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