Temporal trend in the levels of polycyclic aromatic hydrocarbons emitted in a big tire landfill fire in Spain: Risk assessment for human health

JOAQUIM ROVIRA[A,B], NOELIA DOMÍNGUEZ-MORUECO[A,B], MARTÍ NADAL[A], MARTA SCHUHMACHER[A,B], and JOSÉ L. DOMINGO[A]

[a]Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain; [b]Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain

CONTACT José L Domingo e-mail: joseluis.domingo@urv.cat Adress: Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain.

ABSTRACT

In May 2016, a big fire occurred in an illegal landfill placed in Seseña (Toledo, Spain), where between 70,000 and 90,000 tons of tires had been accumulated during years. Just after the fire, and because of the increase of airborne PAHs, we found that cancer risks for the population living in the neighborhood of the landfill were 3-5 times higher than for the rest of inhabitants of Seseña. Some months after our initial (June 2016) study, two sampling campaigns (December 2016 and May 2017) were performed to assess the temporal trends of the environmental levels of PAHs, as well as to reassure these chemicals did not pose any risk for the human health of Seseña inhabitants. In soils, the total concentrations of the 16 PAHs (December 2016), as well as the sum of the 7 carcinogenic PAHs, showed values between 8.5 and 94.7 ng/g and between 1.0 and 42.3 ng/g, respectively. In May 2017, a significant decrease (between 4 and 38 times) in the levels of PAHs in air was observed, with total concentrations ranging between 3.49 and 5.06 ng/m^3. One year after the fire, the cancer risk at different zones of Seseña was similar, being lower than that found in June 2016, and negligible according to national and international agencies.

KEYWORDS

Seseña tire landfill fire; PAHs; soils; air; cancer risks

Introduction

In May 13th 2016, an uncontrolled fire occurred in one of the largest landfills in Europe, located in the village of Seseña (Castilla-La Mancha/Madrid, Spain). With a total surface of 117,000 m^2, the landfill was estimated to contain around 70,000-90,000 tons of used tires, illegally accumulated for a period of more than 15 years. Three weeks after starting, the fire was extinguished, having consumed >75% of the landfilled products. Tire landfill fires involve the combustion of highly flammable materials, including different types of natural and synthetic rubbers such as styrene-butadiene rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber and polybutadiene rubber, as well as other types of components such as steel belt and cord (metals), carbon and different types of additives. [1] As a result, a wide range of environmental contaminants (e.g., particulate matter (PM), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides (NO_x) and volatile organic compounds (VOCs)) may be released to the environment. [2,3] In addition, highly hazardous pollutants such as benzene, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), as well as some metals and metalloids (e.g., arsenic, cadmium, nickel, zinc, mercury, chromium and vanadium), may be also emitted to the atmosphere. [4]

PAHs are organic compounds composed of multiple aromatic rings. They are associated with incomplete combustions, either of natural origin (e.g., volcanic eruptions or forest fires) or from anthropogenic sources (e.g., emissions from industrial complexes, traffic, domestic heating), including tire landfill fires like that of Seseña. [5,6] The International Agency for Research on Cancer (IARC) has classified some PAHs as carcinogenic to humans. In addition, the US Environmental Protection Agency (US EPA) has established a list of 16 priority PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a,h*)anthracene, benzo(*g,h,i*)perylene and indeno(1,2,3-*cd*)pyrene), being 7 of them considered as probable human carcinogens. Benzo(*a*)pyrene (BaP) and dibenzo(a,h)anthracene are the two most potentially toxic, being also carcinogenic. Based on the toxicological profiles of the PAHs, the emission of these organic compounds during the tire landfill fire could mean relevant health risks, both non-carcinogenic and carcinogenic, for the population living in the vicinity.

In June 2016, just after the fire was extinguished, our research group conducted a preliminary survey in the area under potential influence of the tire landfill fire. [5] For that purpose, soil and air samples were collected at different areas around the landfill, as well as in 2 reference sites. In each one of the samples, the concentrations of several organic chemicals (PAHs, PCDD/Fs and PCBs) and trace elements were determined. [5] According to the results of that preliminary investigation, PAHs were identified as the pollutants showing the greatest concern, in terms of health risks for the population closest to the landfill site. [5] Some months after that study, new sampling campaigns were performed to assess the temporal trends of PAH environmental levels, as well as to reassure these chemicals did not pose any risk for the human health of Seseña inhabitants.

The concentrations of PAHs in soil and air samples, as well as the comparison with the data obtained in the first survey, conducted in June 2016, are here presented. The results of the human health risk assessment for the residents in the area potentially affected by the tire landfill fire, are also shown.

Materials and methods

Study area

The tire landfill under study occupied a surface of 117,000 m^2, being located in the village of Seseña (Toledo, Spain). It was more exactly located in the border of 2 Spanish Autonomous Communities: Castilla-La Mancha (73%) and Madrid (27%). The fire was active for three weeks. In June 2nd, 2016, it was declared extinct in the area of Castilla-La Mancha, while five days later, it was completely extinguished in the area corresponding to the Community of Madrid. From the initially calculated amount, only 15,000 tons were estimated to remained unburned. A day after of the extinction (June 7th, 2016), we started an environmental (air and soil) sampling to evaluate the air release of chemical contaminants and to assess the exposure by the local population.[5] Six months later (December 2016), a first follow-up investigation was conducted, with the sampling of soils in the same points of the initial study. A second follow-up sampling was performed approximately 12 months after the extinction of the fire (May 2017), including the collection and analysis of air samples.

Sampling

In May 2017, 3 air samples were collected in the same sampling points of the first investigation (Figure 1): El Quiñón, Seseña Nuevo, and Seseña Viejo. [5] For the collection of air samples, the TO-13A procedure of the US EPA was followed. [7] Air samples were collected with TE-1000-PUF high volume active samplers (Tisch Environmental, Cleves, OH, USA). The gas and particle phases were separately collected in polyurethane foams

(PUFs) and quartz fiber filters (QFFs), respectively. The sampling lasted for approximately 24 h, collecting volumes of air between 250 and 290 m^3. The PUFs and QFFs were stored separately in amber glass bottles and kept at -20°C until PAH analysis.

Previously, in December 2016, 14 samples of soils were collected in different areas around the old tire landfill, including the same 8 sampling points used in the first investigation, [5] and 6 new sampling sites (Figure 1). These additional points were located in Seseña Nuevo (1 sampling point), Seseña Viejo (2 sampling points), Aranjuez (1 sampling point) and Ciempozuelos (2 sampling points) (Figure 1). A total of 500 g of surface soil was collected for each sampling point. Each sample consisted of four subsamples collected in an area of 25 m^2 and a depth of 0-5 cm. They were stored in individual plastic bags. Once in the laboratory, all samples were dried at room temperature and sieved through a 2 mm mesh sieve.

Chemical analysis

The compounds analyzed in the present study were the 16 priority PAHs established by the US EPA: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a,h*)anthracene, benzo(*g,h,i*)perylene, and indeno(1,2,3-*cd*)pyrene. For air samples, both PUFs and QFFs were Soxhlet-extracted with toluene for 24 h. Once the extraction was completed, a clean-up process was performed. Each extract was run through multilayer silica columns followed by graphitized carbon micro-columns. Subsequently, each of the extracts was concentrated to a final volume of 2 mL. Finally, the concentrated extract was injected to a high resolution gas chromatograph coupled to a mass spectrometer with electron impact/selected ion monitoring (HRGC-MS EI/SIM).

With respect to soils, 15 g of dry sample were used, being subjected to an Accelerated Solvent Extraction (ASE) with a mixture of acetone/hexane (1:1 v/v), at 120°C over a period of 8 min. Two extraction cycles were performed. As for the air samples, each of the extracts was concentrated to a final volume of 2 mL, and subsequently injected to HRGC-MS (EI/SIM). In both air and soil samples, a standard solution corresponding to a mixture of 9 PAHs supplied by Dr. Ehrenstorfer (Augsburg, Germany) was used. The identification of each compound was performed by comparison of retention times and ion ratio (m/z), while the quantification was done by interpolation in a calibration line covering a concentration range between 10 and 1000 ng/mL.

Detection limits were calculated for each individual PAHs in each sample as the concentration that generated a signal equivalent to three times the baseline noise. Detection limits in air (gas phase) were 0.10 ng/m^3 for Naphthalene, Acenaphthylene, Fluorene, and Anthracene; 0.27 ng/m^3 for Acenaphthene; and 0.03 ng/m^3 for the rest of PAHs. Detection limits in air (particle phase) were 0.10 ng/m^3 for Naphthalene, Acenaphthylene, and Acenaphthene; and 0.03 ng/m^3 for the others of PAHs. Meanwhile in soil, detection limits was 1.0 ng/g for all PAHs analyzed. In previous study, [5] detection limits of 0.15 ng/m^3 and 1.0 ng/g were reported in air and soil, respectively.

To check the absence of interferences in the quantification, several wavelengths were recorded. Additionally, for the same purpose, results were compared to those obtained after the injection in a GC–MS equipment (Agilent, Santa Clara, CA, USA). Analytical blanks, following the whole analytical procedure without sample, were performed with each series of samples. Most congeners were not detected, or they were below the limit of detection. Finally, the method performance was assessed through successful participation in international inter-laboratory tests and the analysis of reference materials.

Results and discussion

Levels of PAHs in air

In our initial sampling (June 2016), [5] the concentrations of PAHs ranged between <0.15 ng/m^3 (detection limit), for various individual hydrocarbons, and 112 ng/m^3, for chrysene in El Quiñón, the sampling point closest to the landfill. Chrysene, together with benzo(*a*)anthracene (9.77 ng/m^3), were the main contributors to the total concentrations of Σ16 PAHs in El Quiñón. The levels of the 7 PAHs considered as carcinogenic -or potential carcinogenic- for humans by the IARC (benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, dibenzo(*a,h*)anthracene, and benzo(*g,h,i*)perylene) achieved relatively high contribution percentages with respect to total PAHs, with values ranging 86%-97%. In that first study (June 2016), the maximum concentration of Σ16 PAHs in air (gas + particle phases) was found in the closest point to the tire landfill (El Quiñón, 500 m), with a level of 134 ng/m^3. It means an amount at least 6-times than values reported in other neighborhoods of Seseña (19.5 and 22.7 ng/m^3 in Seseña Nuevo and Seseña Viejo, respectively), both located at approximately 4 km from the landfill. The gas phase mostly contributed (>98%) to the total concentration of PAHs.

The concentrations of PAHs in air samples collected approximately 12 months after the fire (May 2017) are shown in Tables 1 and 2. The PAH concentrations in the gas phase ranged between values below the detection limit and a maximum of 2.08 ng/m^3, which corresponded to phenanthrene at Seseña Nuevo sampling point. Most of the individual PAHs showed levels below their detection limit, with the only exception of fluorene, phenanthrene, fluoranthrene, pyrene and chrysene. In the particle phase (Table 2), the concentrations of PAHs ranged between values below the detection limit and a maximum value of 0.14 ng/m^3 for dibenzo(*a,h*)anthracene and indeno(1,2,3-*cd*)pyrene in El Quiñón.

The total concentrations of the 16 PAHs in air (gas and particle phases) samples collected in the 3 sampling sites are depicted in Figure 2. The highest total levels for the 16 PAHs were observed in Seseña Nuevo and Seseña Viejo, with concentrations of 5.06 and 5.05 ng/m^3, respectively. Unlike the initial sampling, El Quiñón samples presented the lowest level (3.49 ng/m^3). The gas phase contributed between 66% and 80% to the total sum of PAHs.

When comparing the total air concentrations of PAHs detected a few days after the fire (range: 19.5-134 ng/m^3) with those found after 12 months (3.49-5.06 ng/m^3), a significant decreased was observed. The reduction was found to be 38-fold at El Quiñón (Figure 3). Comparatively, the levels found in the campaign carried out in May 2017 are well below those reported in other studies conducted in Spain, such as those reported in Tarragona County, [8,9] an area characterized by the presence of the largest chemical and petrochemical industrial complex in southern Europe. In Tarragona County, atmospheric concentrations of the same 16 PAHs ranged in average between 5.52 and 67.2 ng/m^3 in the gas phase and between 0.67 and 7.00 ng/m^3 in the particle phase. [8] This study collected more than 150 samples during 1 year (June 2008 to June 2009) in three sites, a semirural at less than 0.5 km from a petrochemical complex, and two suburban sites at less than 0.5

km and less than 1 km from Chemical complex. Other study determine in winter 2007, the levels of 16 PAHs in urban (n=2) and background (n=2) areas. [9] They were 27.5 ± 2.83 ng/m^3 and 20.6 ± 1.68ng/m^3 (mean ± standard deviation) in urban and background areas, respectively. Urban samples were collected in the center of the two main cities of Tarragona region (around 100,000 and 130,000 inhabitants) meanwhile background samples were collected in two towns (around 5,000 and 30,000 inhabitants) outside the influence, according prevailing winds, of chemical and petrochemical industries, respectively.

Levels of PAHs in soils

In our initial survey (June 2016), the levels of PAHs ranged from values under the detection limit (<1.0 ng/g) in most samples, and a maximum of 4.5 ng/g for benzo(*b*)fluoranthene in the sample collected in Morata de Tajuña (reference/control minimum affected by the fire). Total concentrations of the 16 PAHs in soils ranged from 8.76 to 33.2 ng/g, while the levels of the 7 carcinogenic PAHs were within the range 3.50-19.3 ng/g. The highest concentrations were detected in samples from agricultural soils at El Quiñón (located less than 500 m from the fire), an urban garden in Seseña Viejo (located about 4 km from the landfill), and in one of the samples from the reference/control sites (minimum affected by the fire), located in Morata de Tajuña. The high PAH levels in soils from the background area might suggest that this zone could be under the direct influence of a cement factory in that area. A number of studies have shown that PAHs are compounds associated with emissions from cement industries. [10–13]

The concentrations of PAHs in soils 6 months after the fire (December 2016) are summarized in Table 3. The levels of PAHs ranged from below the limit of detection (<1.0 ng/g) in most samples, and a maximum of 17.0 ng/g for indeno(1,2,3-cd)pyrene in in the industrial area of Ciempozuelos (highly affected by fire emissions). This zone is under the impact of dense traffic, being located very close to the one of the most important highways connecting Madrid and Andalusia. As noted in the initial sampling (June 2016), certain low molecular weight PAHs, such as acenaphthylene, acenaphthene or fluorene, showed soil values below the limit of detection (1.00 ng/g) in most of the samples.

Total concentrations of the 16 PAHs, as well as the sum of the 7 carcinogenic PAHs, in each one of the 14 sampling points selected in the current survey, are depicted in Figure 4. The levels of Σ16 PAHs in soils ranged from 8.50 to 94.7 ng/g. In turn, the concentrations of the 7 carcinogenic PAHs ranged from 3.50 to 42.3 ng/g. The highest levels of PAHs were found in Ciempozuelos, highly affected by fire emissions due prevailing winds, and in the reference/control sample collected in Morata de Tajuña, minimum affected by the emissions of the tire landfill fire. Both locations, Morata de Tajuña and Ciempozuelos, are characterized by the presence of several industries, which may mean a potentially higher release of PAHs and other environmental pollutants. On the other hand, the third sampling point with the highest concentration of PAHs was the reference/control sample collected in the town of Collado Villalba. It could be explained because in this municipality, single-family dwellings are predominant. In a number of cases, they have wood-burning heating, which has been identified as an important source source of PAH emissions. As in the initial sampling, no correlations were observed between the concentrations of PAHs at the different sampling points and the distance to the landfill.

The temporal trends of PAHs in soils in each one of the same 8 locations between the initial sampling (June 2016) and that conducted six months later (December 2016), are depicted in Figure 5. The concentrations of PAHs were generally higher in the second survey, conducted in December 2016. This is especially evident in the two reference/control points, being also in agreement with the seasonal patterns already reported in the scientific literature for these chemicals. [14–17] PAHs concentrations tend to be higher in cold seasons, mainly due to a higher consumption in heating systems, increase of biomass burning, increase PAH emissions from automobile exhaust due to low ambient temperatures, etc. [6,18,19] In addition, meteorological conditions in winter, such as low height of mixing layer or solar radiation, conduct to a reduce the dispersion of pollutants and their atmospheric reactivity. [18] Collado Villalba, a town which is characterized by numerous single-family homes, would be a clear example. Large differences of PAHs in soil were found between the first (June) and second (December) surveys, being likely related to the wide use of heating systems in winter. On the other hand, it should be noted that PAHs are compounds that are sensitive to environmental factors. Recent studies in soil have demonstrated that an increase of temperature and solar radiation can lead to an increased degradation of these compounds. [20–22] The initial sampling was conducted after a few days just after the fire, under typical summer temperature conditions (June 2016). However, the survey of December 2016 was carried out under typical winter conditions. Consequently, changes of PAH environmental levels would be mainly linked to changes of environmental conditions.

In contrast to air samples, the levels of PAHs obtained in the Seseña soils in both samplings were below the concentrations reported in other Spanish areas. [23–25] They are also lower than the levels found by our group in Tarragona County, where PAH levels in soils ranged between 166 and 1,002 ng/g. [26] Although values have shown some fluctuations over time, other investigations conducted in the same region also reflected higher levels of PAHs (281, 129 and 212 ng/g in 2005, 2007 and 2009, respectively) [9,27,28] than those found in Seseña. In fact, soil is a long-term indicator of environmental pollution, as contaminants may be accumulated for long periods of time (months or years). The emissions of PAHs due to the tire landfill fire were certainly important, as noted by the notably higher levels found in air samples just after tire landfill than Tarragona air levels. However, soil levels in Seseña were lower than those found in Tarragona country where emissions of PAHs were started long time ago and continue until nowadays.

Human health risk assessment

The concentrations of PAHs in air and soils of El Quiñón, Seseña Nuevo and Seseña Viejo, in the initial and follow-up samplings, were used to evaluate the exposure and the health risks for the population living in those 3 areas. For exposure calculations, three main routes were considered: inhalation, soil ingestion and dermal contact with soils, using previously validated methodologies. [5,11] Once the human exposure was calculated, the non-carcinogenic risks were characterized by calculating the Hazard Quotient (HQ), which is defined as the relationship between exposure and the reference dose (RfD). If the HQ is lower than the unit (HQ <1), exposure is lower than its reference dose, and therefore, there are no health risks, or at least, levels may be considered as acceptable. Cancer risks through ingestion and dermal contact were calculated by multiplying the exposure (ingestion and dermal) with the oral and dermal carcinogenic slope factors, respectively. In turn, cancer risks due to inhalation were calculated based on the most up-to-date RAGS methodology of the US EPA. [29] Unlike non-carcinogenic risk, cancer risk is expressed as a probability of developing cancer, which although small is unavoidable. Values less than 10^{-6} (1 in 1,000,000) are considered negligible, while levels below 10^{-5}

are considered as acceptable. [30] On the other hand, since dermal reference doses (RfD_d) for PAHs have not been established yet, the RfD_d for the calculation of the non-carcinogenic risk was obtained by multiplying the RfD_o by the corresponding gastrointestinal absorption factor (GI_{ABS}). In turn, the dermal carcinogenic factors were calculated by dividing the corresponding oral carcinogenic potency by the GI_{ABS}. [31]

The environmental exposure to PAHs for the population living in El Quiñón, Seseña Nuevo and Seseña Viejo is summarized in Table 4. In June 2016, chrysene was pointed out as the hydrocarbon with the maximum exposure, ranging between $3.5\cdot10^{-6}$ and $3.1\cdot10^{-5}$ mg/(kg·day)). In the follow-up sampling, phenanthrene was identified as the most relevant PAH, with an exposure ranging between $2.9\cdot10^{-7}$ mg/(kg·day) in El Quiñón and $5.9\cdot10^{-7}$ mg/(kg·day) in Seseña Nuevo. The main route of exposure was air inhalation, with average contributions of 99% and 87%, in the first and second surveys, respectively. The non-carcinogenic risks -based on the HQ- due to exposure to PAHs at the 3 Seseña neighborhoods were much lower than the unit. None of the hydrocarbons exceeded the safety limit. The PAH with a higher quotient was naphthalene ($HQ<10^{-4}$), while for the remaining PAHs, the HQ was lower than 10^{-6}.

Figure 6 shows the carcinogenic risks of PAHs for the sum of the three routes of exposure (ingestion, dermal contact and inhalation) in the three areas studied in the initial (June 2016) and subsequent studies, performed 6 (for soils) and 12 (for air) months after the fire. As above-mentioned, a risk below 10^{-6} is considered as negligible, [29] while values below 10^{-5} are considered as acceptable. [30] The mean contribution to the total carcinogenic risk corresponded to dibenzo(*a,h*)anthracene (50%) and benzo(*a*)pyrene (34%). The carcinogenic risks due to PAHs, six and twelve months after the fire, were lower than those observed just after the event. They are below the limit of 10^{-6}, and consequently, cancer risks could be considered as negligible. Cancer risks in El Quiñón dramatically decreased between both investigations.

Conclusions

In May 2017, approximately 12 months after the fire, a significant decrease (between 4 and 38 times) in the levels of PAHs in air was observed, with total concentrations ranging between 3.49 and 5.06 ng/m^3. They were also considerably lower than those reported in various air monitoring studies performed in Tarragona area. [8,9] In the present case, the samples collected in Seseña Nuevo and Seseña Viejo showed similar levels for the total

PAHs in air: about 5 ng/m^3, being El Quiñón the zone with a lower concentration (3.49 ng/m^3) of the 16 PAHs. In soils, in the follow-up sampling (December 2016), the total concentrations of the 16 PAHs, as well as the sum of the 7 carcinogenic PAHs in each of the 14 sampling points, showed values between 8.5 and 94.7 ng/g and between 1.0 and 42.3 ng/g, respectively. No correlations were found between the concentrations of PAHs at the different sampling points and the distance to the landfill. In contrast to air samples, the concentrations of PAHs in soils were generally similar in the three neighborhoods of Seseña, and higher in the reference/control points when the initial (June 2016) and the follow-up sampling (December 2016) were compared. Anyhow, the concentrations of PAHs recorded in the Seseña's soils are in the lower part of the range of levels reported for other Spanish areas. [9,23–28]

Environmental exposure to PAHs occurred mainly (99% in 2016 and 87% in 2017) through the inhalation route. Non-carcinogenic risks due to exposure to PAHs, one day and one year after the fire of the tire landfill, were within the limits established by national and international agencies. However, the carcinogenic risks in El Quiñón, estimated one day after of the extinction of the fire, were not negligible (more than one case of cancer per million of inhabitants). One year after the fire, the cancer risk in Seseña Viejo, Seseña Nuevo and El Quiñón was similar in the three neighborhoods, being lower than that found in June 2016, and negligible according to national and international agencies.

Acknowledgement

The authors are especially grateful to Miguel Angel Hernández and his colleagues of Ecologistas en Acción, for their valuable help in the experimental design of the study. J. Rovira has a fellowship of the Department of Health of Catalonia (Generalitat de Catalunya), "Pla Estratègic de Recerca i Innovació en Salut" (PERIS 2016–2020, fellowship SLT002/16/00094). N. Domínguez Morueco received a PhD fellowship (BES-2013-066313) from the Spanish Ministry of Economy and Competitiveness, through the project CTM2012-33079.

Funding

This study was financially supported by the Municipality of Seseña, Castilla-La Mancha, Spain.

References

[1] Evans, A.; Evans, R. The Composition of a Tyre: Typical Components. Waste Resources Action Program: Bandbury, 2006; 1-5.

[2] Downard, J. M. Particulate emissions of tire combustion. Masther thesis. University of Iowa. Iowa City **2014**. Available at: http://ir.uiowa.edu/etd/4615 (accessed July 2017).

[3] Artíñano, B.; Gómez-Moreno, F.J.; Díaz, E.; Amato, F.; Pandolfi, M.; Alonso-Blanco, E.; Coz, E.; García-Alonso, S.; Becerril-Valle, M.; Querol, X.; Alastuey A.; van Drooge B.L. Outdoor and indoor particle characterization from a large and uncontrolled combustion of a tire landfill. Science of the Total Environ. **2017**, *593-594***,** 543-551.

[4] Reisman, J. I. Air Emissions From Scrap Tire Combustion. EPA-600/R-97-115. U.S. Environmental Protection Agency, Office of Research and Development: Washington, DC, 1997; 1-117.

[5] Nadal, M.; Rovira, J.; Díaz-Ferrero, J.; Schuhmacher, M.; Domingo, J. L. Human exposure to environmental pollutants after a tire landfill fire in Spain: Health risks. Environ. Int. **2016**, *97***,** 37–44.

[6] Domínguez-Morueco, N.; Augusto, S.; Trabalón, L.; Pocurull, E.; Borrull, F.; Schuhmacher, M.; Domingo, J.L.; Nadal, M. Monitoring PAHs in the petrochemical area of Tarragona County, Spain: comparing passive air samplers with lichen transplants. Environ. Sci. Pollut. Res. Int. **2017**, *24*(13)**,** 11890–11900.

[7] Winberry, W.T.; Jungclaus, G. Compendium Method TO-13A. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). EPA/625/R-96/010b. U.S. Environmental Protection Agency, Office of Research and Development: Cinncinati, 1999; 1-84.

[8] Ramírez, N.; Cuadras, A.; Rovira, E.; Marcé, R. M.; Borrull, F. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. Environ. Health Perspect. **2011,** *119*(8)**,** 1110–1116.

[9] Nadal, M.; Mari, M.; Schuhmacher, M.; Domingo, J. L. Multi-compartmental environmental surveillance of a petrochemical area: Levels of micropollutants. Environ. Int. **2009**, *35*(2)**,** 227–235.

[10] Ercan, Ö.; Dinçer, F. Atmospheric concentrations of PCDD/Fs, PAHs, and metals in the vicinity of a cement plant in Istanbul. Air Qual. Atmos. Heal. **2006**, *9*(2)**,** 159–

172.
[11] Rovira, J.; Nadal, M.; Schuhmacher, M.; Domingo, J. L. Alternative Fuel Implementation in a Cement Plant: Human Health Risks and Economical Valuation. Arch. Environ. Contam. Toxicol. **2016**, *71*(4)**,** 473–484.
[12] Sánchez-Soberón, F. van Drooge, B.L.; Rovira, J.; Grimalt, J.O.; Nadal, M.; Domingo, J.L.; Schuhmacher, M. Size-distribution of airborne polycyclic aromatic hydrocarbons and other organic source markers in the surroundings of a cement plant powered with alternative fuels. Sci. Total Environ. **2016**, *550***,** 1057–1064.
[13] Schuhmacher, M.; Domingo, J. L.; Garreta, J. Pollutants emitted by a cement plant: health risks for the population living in the neighborhood. Environ. Res. **2004**, *95*(2)**,** 198–206.
[14] Brown, A.S.; Brown, R.J.C.; Coleman, P.J.; Conolly, C.; Sweetman, A.J.; Jones, K.C.; Butterfield, D.M.; Sarantaridis, D.; Donovan, B.J.; Roberts, I. Twenty years of measurement of polycyclic aromatic hydrocarbons (PAHs) in UK ambient air by nationwide air quality networks. Environ. Sci. Process. Impacts **2013**, *15*(6), 1–30.
[15] Zhang, L.; Chen, R.; Lv, J. Spatial and Seasonal Variations of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Particulate Matter (PM_{10}, $PM_{2.5}$) in Three Mega-Cities in China and Identification of Major Contributing Source Types. Bull. Environ. Contam. Toxicol. **2016**, *96*(6)**,** 827–832.
[16] Wang, X.; Thai, P.K.; Li, Y.; Li, Q.; Wainwright, D.; Hawker, D.W.; Mueller, J.F. Changes in atmospheric concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls between the 1990s and 2010s in an Australian city and the role of bushfires as a source. Environ. Pollut. **2016**, *213***,** 223–231.
[17] Liu, B.; Xue, Z.; Zhu, X.; Jia, C. Long-term trends (1990–2014), health risks, and sources of atmospheric polycyclic aromatic hydrocarbons (PAHs) in the U.S. Environ. Pollut. **2017**, *220***,** 1171–1179.
[18] Delhomme, O.; Millet, M. Characterization of particulate polycyclic aromatic hydrocarbons in the east of France urban areas. Environ. Sci. Pollut. Res. **2012**, *19*(5)**,** 1791–1799.
[19] Jyethi, D. S.; Khillare, P. S.; Sarkar, S. Risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in school children. Environ. Sci. Pollut. Res. **2014,** *21*(1)**,** 366–378.
[20] Marquès, M.; Mari, M.; Audí-Miró, C.; Sierra, J.; Soler, A.; Nadal, M.; Domingo, J. L. Photodegradation of polycyclic aromatic hydrocarbons in soils under a climate

change base scenario. Chemosphere **2016,** *148***,** 495–503.

[21] Marquès, M.; Mari, M.; Audí-Miró, C.; Sierra, J.; Soler, A.; Nadal, M.; Domingo, J. Climate change impact on the PAH photodegradation in soils: Characterization and metabolites identification. Environ. Int. **2016**, *89-90***,** 155–165.

[22] Marquès, M.; Mari, M.; Sierra, J.; Nadal, M.; Domingo, J. L. Solar radiation as a swift pathway for PAH photodegradation: A field study. Sci. Total Environ. **2017**, *581-582***,** 530-540.

[23] Zuazagoitia, D.; Garcia-Arrona, R.; Millán, E. Evaluation of soil contamination by Polycyclic aromatic hydrocarbons in Gipuzkoa (Northern Spain). Soil Sediment Contam. **2011**, *20*(5)**,** 525–534.

[24] Navarro-Ortega, A.; Ratola, N.; Hildebrandt, A.; Alves, A.; Lacorte, S.; Barceló, D. Environmental distribution of PAHs in pine needles, soils, and sediments. Environ. Sci. Pollut. Res. **2012**, *19*(3)**,** 677–688 (2012).

[25] Plaza-Bolaños, P.; Padilla-Sánchez, J. A.; Garrido-Frenich, A.; Romero-González, R.; Martínez-Vidal, J. L. Evaluation of soil contamination in intensive agricultural areas by pesticides and organic pollutants: South-eastern Spain as a case study. J. Environ. Monit. **2012**, *14*(4)**,** 1182–1189.

[26] Nadal, M.; Schuhmacher, M.; Domingo, J. L. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ. Pollut. **2014**, *132*(1)**,** 1–11.

[27] Nadal, M.; Schuhmacher, M.; Domingo, J. L. Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: Temporal trend. Chemosphere **2007**, *66*(2)**,** 267–276.

[28] Nadal, M.; Schuhmacher, M.; Domingo, J. L. Long-term environmental monitoring of persistent organic pollutants and metals in a chemical/petrochemical area: Human health risks. Environ. Pollut. **2011**, *159*(7)**,** 1769–1777.

[29] United States Environmental Protection Agency (US EPA). Risk Assessment Guidance for Superfund (RAGS), Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). Office of Superfund Remediation and Technology Innovation: Washington D.C., 2009; 1-68.

[30] Ministerio de Medio Ambiente. Guía Técnica de aplicación del RD 9/2005, de 14 de enero, por el que se establece la relación de actividades potencialmente contaminantes del suelo y los criterios y estándares para la declaración de suelos contaminados. Dirección General de Calidad y Evaluación Ambiental: Madrid, 2007; 1-122.

[31] United States Environmental Protection Agency (US EPA). Risk Assessment

Guidance for Superfund Volume I: Human Health Evaluation Manual , EPA/540/1-89/002. Office of Emergency and Remedial Response: Washington D.C., 1989; 1-291.

FIGURE CAPTIONS

Figure 1. Location of the sampling points. (U: Urban; CP: Children’s park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

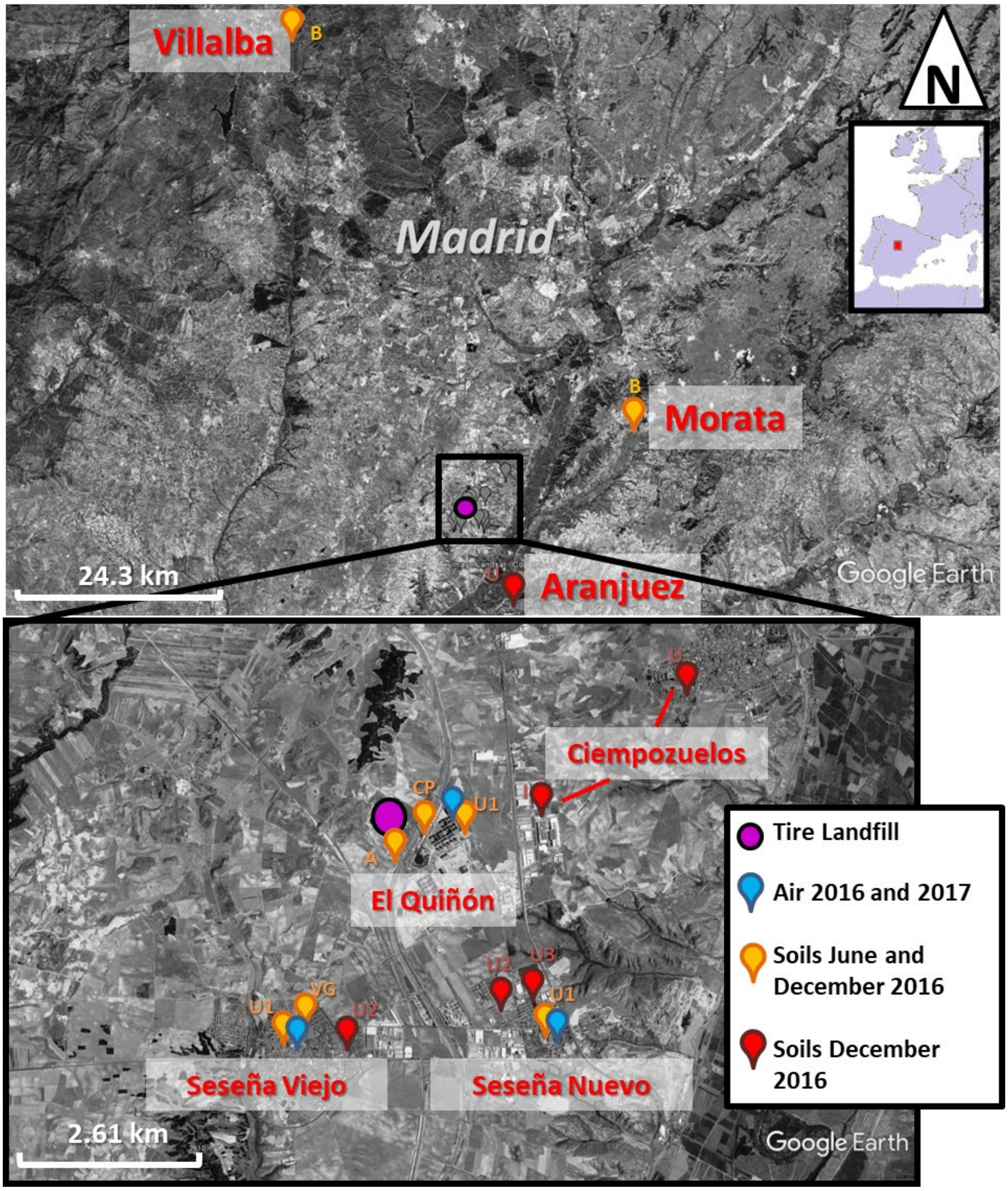
Figure 2. Total concentrations of the sum of 16 PAHs in air samples (gas and particulate phases) collected in May 2017.

Figure 3. Total levels of 16 PAHs in air samples collected in 2016 and 2017, approximately one year after the fire.

Figure 4. Total concentrations of the sum of 16 PAHs, as well as the sum of the 7 carcinogenic PAHs, in soil samples collected in December 2016. (U: Urban; CP: Children’s park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

Figure 5. Sums of the 16 PAHs in soils in the first (June 2016) and second (December 2016) surveys. (U: Urban; CP: Children’s park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

Figure 6. Cancer risks due to exposure to PAHs one day (June 2016) and approximately one year (May 2017) after the fire was extinguished.

514 

515 **Figure 1.** Location of the sampling points. (U: Urban; CP: Children's park; A:
516 Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

517

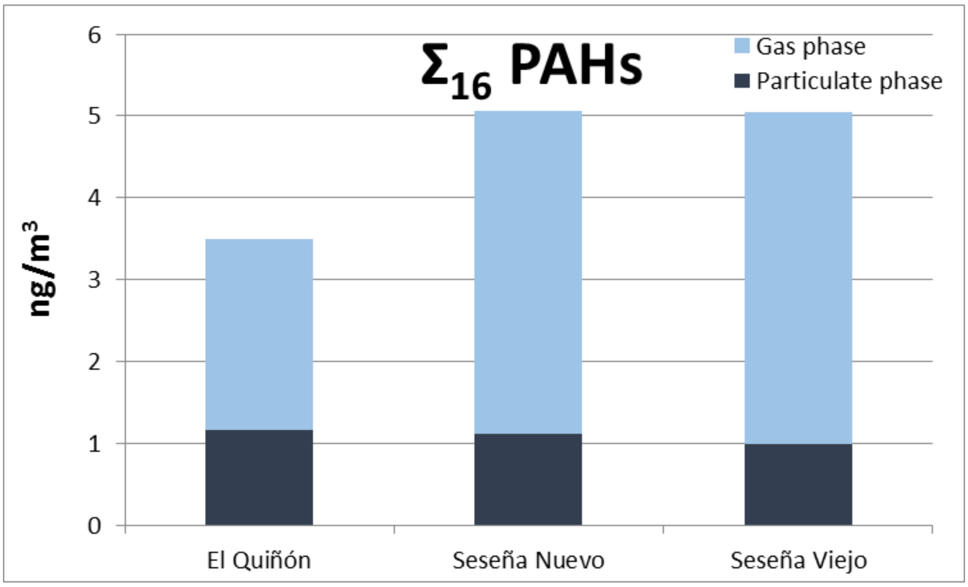


Figure 2. Total concentrations of the sum of 16 PAHs in air samples (gas and particulate phases) collected in May 2017.

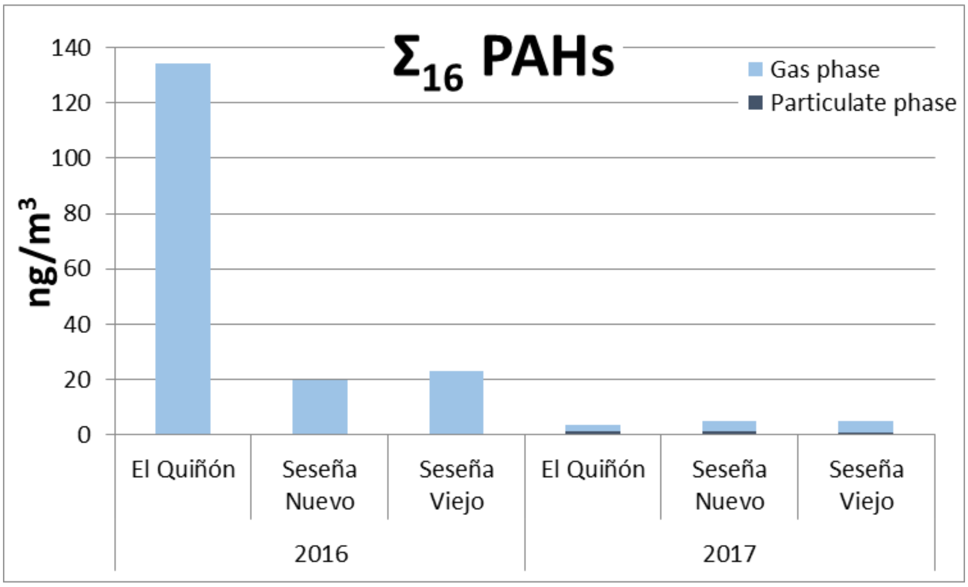


Figure 3. Total levels of 16 PAHs in air samples collected in 2016 and 2017, approximately one year after the fire.

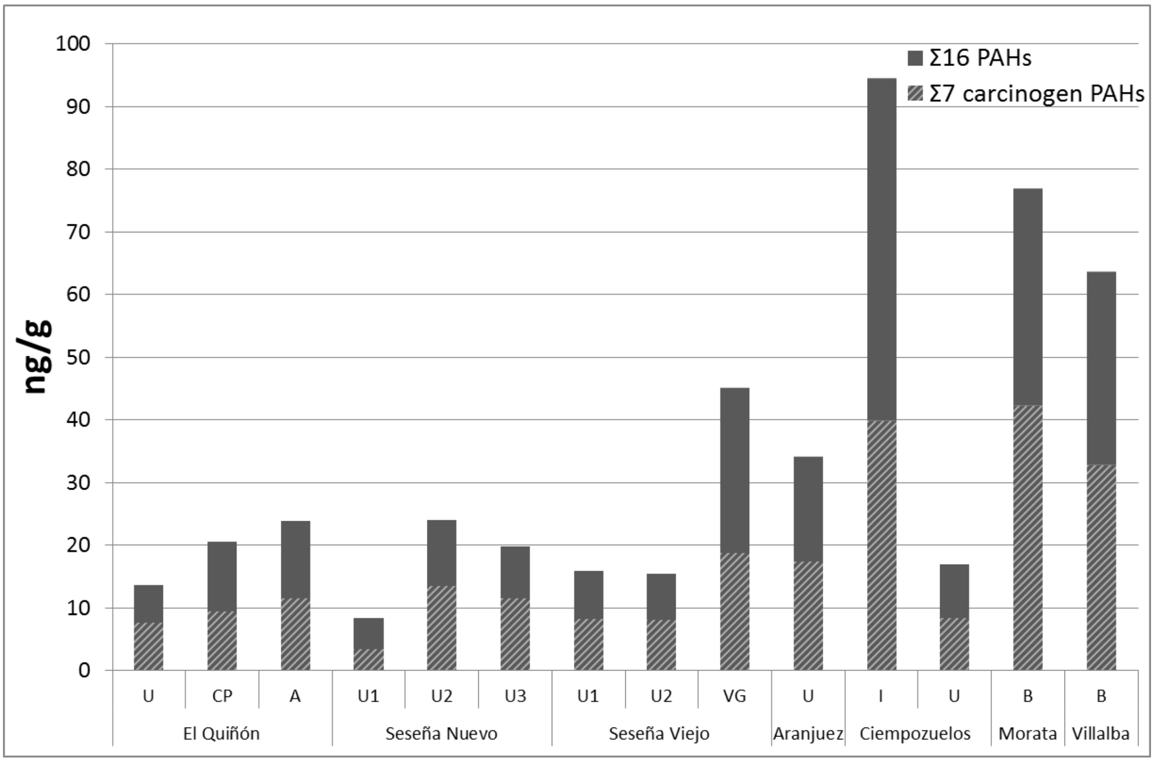


Figure 4. Total concentrations of the sum of 16 PAHs, as well as the sum of the 7 carcinogenic PAHs, in soil samples collected in December 2016. (U: Urban; CP: Children's park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

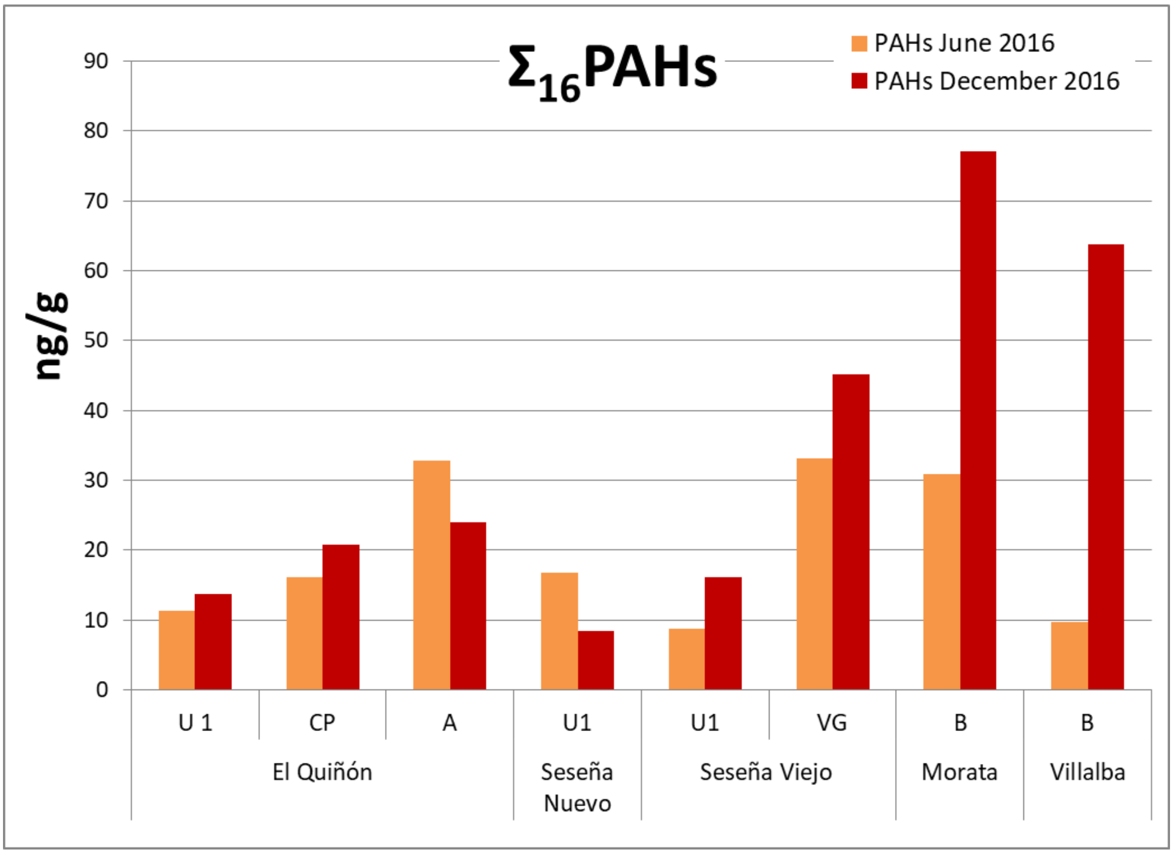


Figure 5. Sums of the 16 PAHs in soils in the first (June 2016) and second (December 2016) surveys. (U: Urban; CP: Children's park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background).

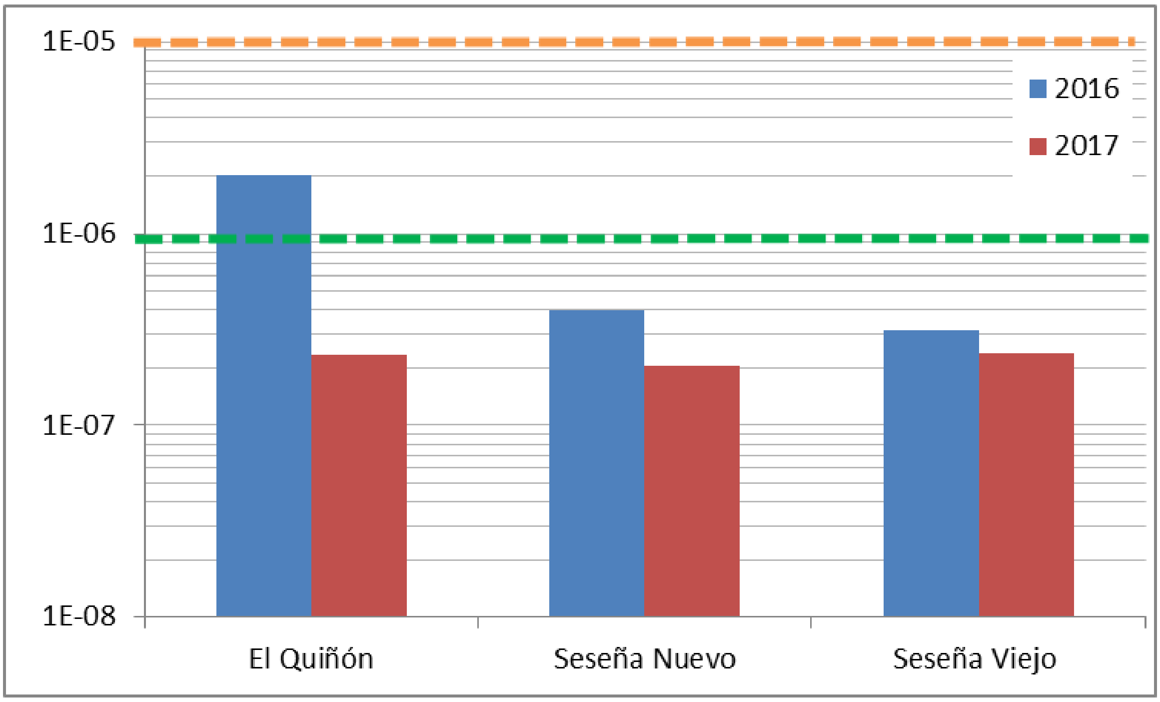


Figure 6. Cancer risks due to exposure to PAHs one day (June 2016) and approximately one year (May 2017) after the fire was extinguished.

Table 1. Concentrations (ng/m^3) of PAHs in air (gas phase) in the sampling campaign conducted in May 2017

	El Quiñón	Seseña Nuevo	Seseña Viejo
Naphthalene	<0.10	<0.10	<0.10
Acenaphthylene	<0.10	<0.10	<0.10
Acenaphthene	<0.27	<0.27	<0.27
Fluorene	0.24	0.46	1.48
Phenanthrene	0.98	2.08	1.50
Anthracene	<0.10	<0.10	<0.10
Fluoranthene	0.26	0.43	0.26
Pyrene	0.29	0.52	0.38
Benzo(*a*)anthracene	<0.03	<0.03	<0.03
Chrysene	0.08	<0.03	<0.03
Benzo(*b*)fluoranthene	<0.03	<0.03	<0.03
Benzo(*k*)fluoranthene	<0.03	<0.03	<0.03
Benzo(*a*)pyrene	<0.03	<0.03	<0.03
Dibenzo(*a.h*)anthracene	<0.03	<0.03	<0.03
Benzo(*g,h,i*)perylene	<0.03	<0.03	<0.03
Indeno(1,2,3-*cd*)pyrene	<0.03	<0.03	<0.03

Table 2. Concentrations (ng/m^3) of PAHs in air (particulate phase) in the sampling campaign conducted in May 2017

	El Quiñón	**Seseña Nuevo**	**Seseña Viejo**
Naphtalene	<0.10	<0.10	<0.10
Acenaphthylene	<0.10	<0.10	<0.10
Acenaphthene	<0.10	<0.10	<0.10
Fluorene	<0.03	<0.03	<0.03
Phenanthrene	<0.03	<0.03	<0.03
Anthracene	<0.03	<0.03	<0.03
Fluoranthene	0.09	0.09	0.08
Pyrene	0.09	0.10	0.08
Benzo(*a*)anthracene	0.09	0.08	0.07
Chrysene	0.08	0.09	0.07
Benzo(*b*)fluoranthene	0.11	0.10	0.09
Benzo(*k*)fluoranthene	0.11	0.10	0.09
Benzo(*a*)pyrene	0.06	0.05	0.05
Dibenzo(*a.h*)anthracene	0.14	0.13	0.12
Benzo(*g,h,i*)perylene	<0.03	<0.03	<0.03
Indeno(1,2,3-*cd*)pyrene	0.14	0.14	0.11

Table 3. Concentrations (ng/g) of PAHs in soil samples collected in December 2016

	El Quiñón			Seseña Nuevo			Seseña Viejo			Ciempozuelos		Aranjuez	Morata	Villalba
	U	CP	A	U1	U2	U3	U1	U2	VG	I	U	U	B	B
Naphthalene	1.3	2.2	2.4	<1.0	1.2	<1.0	<1.0	<1.0	4.8	3.9	<1.0	4.8	3.9	2.3
Acenaphthylene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.4	<1.0
Acenaphthene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.8	<1.0	<1.0	<1.0	<1.0	<1.0
Fluorene	<1.0	<1.0	1.6	<1.0	1.3	<1.0	<1.0	<1.0	<1.0	<1.0	1.9	1.7	1.7	1.9
Phenanthrene	1.1	2.3	2.6	1.0	1.2	1.6	<1.0	1.6	5.1	7.2	1.6	2.3	7.4	5.2
Anthracene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.6	15.8	<1.0	<1.0	1.8	1.8
Fluoranthene	<1.0	2.4	2.2	<1.0	1.2	2.1	2.4	1.9	5.9	10.0	1.7	2.3	8.4	10.1
Pyrene	<1.0	1.9	1.7	<1.0	<1.0	1.6	1.8	1.2	5.7	13.9	1.0	1.0	6.3	8.1
Benzo(*a*)anthracene	<1.0	1.2	1.5	<1.0	<1.0	<1.0	<1.0	1.9	3.2	3.4	<1.0	3.2	5.0	3.4
Chrysene	1.3	2.3	2.1	<1.0	1.4	2.0	1.6	2.2	4.8	<1.0	2.1	2.3	6.9	7.7
Benzo(*b*)fluoranthene	1.8	<1.0	1.6	<1.0	1.0	1.4	1.7	1.6	<1.0	5.6	1.3	2.3	6.5	5.6
Benzo(*k*)fluoranthene	<1.0	<1.0	<1.0	<1.0	1.7	2.0	<1.0	2.5	3.2	3.9	1.3	2.9	4.0	3.5
Benzo(*a*)pyrene	<1.0	1.4	1.9	<1.0	1.6	1.8	1.3	2.2	3.3	4.7	<1.0	2.3	6.0	3.2
Dibenzo(*a.h*)anthracene	1.4	2.0	1.7	<1.0	<1.0	1.4	1.5	<1.0	3.5	4.9	<1.0	2.5	6.3	3.5
Benzo(*g,h,i*)perylene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	3.3	<1.0	2.5	<1.0	3.2	3.5	<1.0
Indeno(1,2,3-*cd*)pyrene	1.8	1.7	2.6	<1.0	1.6	2.6	1.3	2.7	<1.0	17.0	2.3	2.1	7.8	6.2

U: Urban; CP: Children's park; A: Agricultural; VG: Vegetable garden; I: Industrial; B: Background

Table 4. Total exposure to PAHs (mg/(kg day)) and contribution (%) of each exposure route between December 2016 and May 2017

	El Quiñón	Seseña Nuevo	Seseña Viejo	Contribution (%)		
				Soil ingestion	Dermal contact	Inhalation
Naphthalene	5.0E-08	3.3E-08	4.8E-08	5	25	70
Acenaphthylene	3.7E-08	3.3E-08	3.3E-08	2	10	88
Acenaphthene	6.4E-08	5.7E-08	6.1E-08	2	7	91
Fluorene	8.0E-08	1.4E-07	4.2E-07	1	2	97
Phenanthrene	2.9E-07	5.9E-07	4.3E-07	1	3	96
Anthracene	2.6E-08	2.4E-08	2.7E-08	4	18	79
Fluoranthene	1.1E-07	1.6E-07	1.2E-07	3	11	86
Pyrene	1.2E-07	1.8E-07	1.5E-07	2	8	90
Benzo(*a*)anthracene	3.8E-08	3.6E-08	3.7E-08	5	22	73
Chrysene	6.0E-08	4.3E-08	4.6E-08	6	29	65
Benzo(*b*)fluoranthene	4.6E-08	4.4E-08	3.9E-08	4	20	76
Benzo(*k*)fluoranthene	3.9E-08	4.6E-08	4.6E-08	5	22	73
Benzo(*a*)pyrene	3.3E-08	3.3E-08	3.7E-08	7	34	59
Dibenzo(*a.h*)anthracene	5.8E-08	4.7E-08	5.3E-08	4	19	77
Benzo(*g,h,i*)perylene	1.5E-08	2.2E-08	1.4E-08	7	34	59
Indeno(1,2,3-*cd*)pyrene	6.0E-08	5.9E-08	4.6E-08	5	22	73
Σ16 PAHs	**1.1E-06**	**1.5E-06**	**1.6E-06**	**2**	**11**	**87**