

1 **Human exposure to environmental pollutants after a tire**
2 **landfill fire in Spain: Health risks**

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31 HIGHLIGHTS

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33 ➤ A fire occurred recently in the largest tire landfill in Europe (Seseña, Toledo, Spain).

34 ➤ After the fire, the environmental levels of most pollutants were not of concern.

35 ➤ Airborne PAH concentrations near the landfill were substantially higher.

36 ➤ Cancer risks were higher for the population living near the landfill.

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38

39 ABSTRACT

40

41 In May 2016, a fire occurred in one of the largest landfills in Europe (Seseña, Toledo,
42 Spain), where 70,000-90,000 tons of tires had been illegally accumulated for more than
43 15 years. Because of the proximity of population nuclei and the duration of the episode
44 (>20 days), we conducted a preliminary human health risk assessment study just after the
45 tire fire. Samples of air and soil were collected in 3 areas surrounding the landfill (El
46 Quiñón, at only 500 m, and Seseña Nuevo and Seseña Viejo, both at 4 km), as well as in
47 background sites. In addition, samples of crops (barley, wheat, cabbage and lettuce) were
48 also obtained from local farmers. The concentrations of polychlorinated dibenzo-*p*-
49 dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polycyclic
50 aromatic hydrocarbons (PAHs) and a number of trace elements (As, Cd, Co, Cr, Cu, Hg,
51 Mn, Ni, Pb, Sb, Sn, Tl, and V) were analyzed in all the samples. The concentrations of
52 all the target pollutants, excepting PAHs, were relatively similar at the different sampling
53 zones, irrespective of the distance to the landfill. In turn, a significant increase of PAHs
54 was noted near the tire landfill, with air levels up to 6-times higher than those found at 4
55 km (134 vs. 19.5-22.7 ng/m³). Similarly, PAH concentrations in lettuce were relatively
56 higher than those typically found in monitoring programs of food safety. Because of the
57 increase of airborne PAHs, cancer risks due to exposure to environmental pollutants for
58 the population living at El Quiñón, near the landfill, were between 3- and 5-times higher
59 than those estimated for the inhabitants of Seseña. After this preliminary study, further
60 investigations, focused only on PAHs, but more extensive in terms of number of samples,
61 should be conducted to assure that PAHs have been progressively degraded through time.

62

63 *Keywords:*

64 Tire landfill fire

65 Seseña, Spain

66 Human exposure

67 Polycyclic aromatic hydrocarbons

68 Cancer risks

69 1. Introduction

70

71 In recent decades, the number of tires globally produced and, therefore, to be
72 disposed as waste at the end of their lives, has dramatically increased. The total
73 production of tires in the European Union, which are manufactured in about 90 plants, is
74 approximately 355 million per year, which corresponds approximately to 24% of the total
75 world production (ETRMA, 2014), with over 450 factories. In the next few years the
76 annual number of tires produced in the world is expected to reach 1.7 billion of units. It
77 means that each year over 290 million of tires are discarded only in the USA (Earth911,
78 2016), while in the EU plus Norway and Switzerland, about 3.2 million tons of used tires
79 (part worn + end of life tires) are generated, of which 2.5 million tons are either recycled
80 or recovered (ETRMA, 2016). Consequently, this increasing number of used tires means
81 a serious threat to the natural environment (Jang et al., 1998; Hennebert et al., 2014).

82 With respect to the typical compositions of tires (Evans and Evans, 2006), the rubber
83 component of the tire is a mixture of several rubbers strengthened with carbon black filler
84 material. The construction of the tire involves a composite of several layers of the rubber.
85 For it, different synthetic and natural rubbers are used, including styrene–butadiene
86 rubber, natural rubber (polyisoprene), nitrile rubber, chloroprene rubber, polybutadiene
87 rubber), textile material, steel belt and cord (metal), carbon black and additives.
88 Obviously, it means that tires are flammable materials. In relation to this, it is well
89 established that uncontrolled open tire fires produce a number of air pollutants, including
90 "criteria" pollutants, such as particulates, carbon monoxide (CO), sulfur oxides (SO₂),
91 oxides of nitrogen (NO_x), and volatile organic compounds (VOCs). "Non-criteria"
92 hazardous air pollutants such as benzene and polycyclic aromatic hydrocarbons (PAHs),
93 polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated
94 biphenyls (PCBs), as well as some trace elements such as arsenic, cadmium, nickel, zinc,
95 mercury, chromium, and vanadium, are also generated (Reisman, 1997; Stefanov et al.,
96 2013). The emission of these pollutants from an open tire fire can mean significant acute
97 and chronic health hazards to the population living near the fire.

98 Although a search via Internet shows that in recent years there have been various
99 large tire fires over the world, to the best of our knowledge, only four papers are available
100 in the scientific literature (PubMed and Scopus) regarding uncontrolled tire fires and their
101 potential environmental and health effects. These articles report details on two tire fires
102 occurred in Canada: Ontario (Steer et al., 1995) and Quebec (Wang et al., 2007), and in

103 USA: Iowa City, Iowa (Downard et al., 2015; Singh et al., 2015). The last uncontrolled
104 large tire fire occurred recently in Seseña (Toledo, Spain), where in May 13, 2016, started
105 the fire of a landfill with approximately 70,000-90,000 tons of tires illegally accumulated
106 for 15 years. The facility is placed between the villages of Valdemoro (Madrid) and
107 Seseña (Toledo), with more than 72,000 and 22,000 inhabitants, respectively. Madrid the
108 capital of Spain is located at 44 km of the illegal landfill. The fire was officially
109 extinguished about three weeks after the onset.

110 The tremendous magnitude of the fire and the fact that an important part of the
111 population of Seseña lives in a neighborhood placed only at 500 m of the landfill made
112 essential to know the human health risks. Therefore, this study was aimed at determining
113 the levels of PAHs, PCDD/Fs, PCBs, and toxic metals in air and soil samples collected
114 at various points of the area under the influence of the emissions, as well as to assess the
115 health risks for the local population. Some local crop samples were also analyzed for the
116 same pollutants.

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118 **2. Materials and methods**

119

120 *2.1. Sampling*

121

122 The landfill is located in Seseña (Toledo, Spain) and it has an extension of 117.000
123 m². It is located in the border of two Spanish Autonomous Communities: Castilla-La
124 Mancha (73%) and Madrid (27%). The fire lasted uninterruptedly for 20 days. In June 2,
125 2016, the fire was declared as extinguished in the zone of Castilla-La Mancha, while five
126 days later, the fire was completely extinguished in the zone of Madrid. It was estimated
127 that only 15,000 tons of the initially calculated (70,000-90,000 tons) remained unburnt.

128 In June 6-10, 2016, just after the fire was extinguished, we conducted a preliminary
129 environmental sampling. Six soil samples were collected in 3 main areas surrounding the
130 landfill: El Quiñón, a residential neighborhood located at only 500 m, as well as Seseña
131 Nuevo and Seseña Viejo, both situated at approximately 4 km from the landfill. In
132 addition, two soil samples were collected in the villages of Morata de Tajuña and Collado
133 Villalba, both located at the Community of Madrid at a distance of 25 and 70 km,
134 respectively. These samples were used as reference or background. Around 500 g of bulk
135 samples of surface soil, formed of 4 subsamples within an area of 25 m², were collected

136 in each sampling site. Once in the laboratory, they were dried at room temperature and
137 sieved through a 2 mm mesh screen.

138 Air samples were also collected in schools for children of El Quiñón, Seseña Nuevo
139 and Seseña Viejo. Since the study covered a wide spectrum of target pollutants (PAHs,
140 PCDD/Fs, PCBs, and toxic metals), two different equipments were used. On one hand, a
141 TE-1000-PUF active sampling device (Tisch Environmental, Cleves, OH, USA) was used
142 for the sampling of organic pollutants. Particulate- and gas-phases were separately
143 collected by using a quartz fiber filter (QFF) and a polyurethane foam (PUF),
144 respectively. Sampling lasted for approximately 48 h, being collected an air volume of
145 481-588 m³. For the sampling of trace elements, a TE-6070-DV active sampler (Tisch
146 Environmental, Cleves, OH, USA) was deployed. Particulate matter was trapped in QFFs.
147 Two headings, intended for a separate collection of PM₁₀ and PM_{2.5} fractions, were used.
148 Volumes ranged 1290-1519 m³ for PM₁₀, and 1300-1537 m³ for PM_{2.5}.

149 Due to its capacity to register short-term environmental contamination, vegetation is
150 known to be a suitable monitor for chemical pollutants (Rovira et al., 2016). As a
151 complementary matrix to soil and air, samples of local crops, were also collected. Four
152 different varieties were included: lettuce and cabbage, as leafy vegetables, and barley and
153 wheat, as cereals. Vegetables were supplied by local farmers, while cereals were directly
154 harvested from the field. The distribution of sampling points for each one of the matrices
155 is depicted in Fig. 1.

156

157 2.2. Chemical analysis

158

159 The content of trace elements was determined by inductively coupled plasma mass
160 spectrometry (ICP-MS). Details on the methodological procedure have been recently
161 reported (Nadal et al., 2016). The digestion of soils and vegetation was conducted in a
162 Milestone Start D Microwave Digestion System, where 0.5 g of sample were treated with
163 5 mL of HNO₃ (65% Suprapur, E. Merck, Darmstadt, Germany) for 30 min. Air filters
164 were treated for 16 h with 5 mL of a mixture (1.5:1 v:v) containing HF (37.5%, Panreac
165 SA, Barcelona, Spain) and HNO₃ (65% Suprapur, E. Merck, Darmstadt, Germany) in
166 hermetic Teflon bombs. Subsequently, the extract was evaporated in a sand bath, and
167 reconstituted with HNO₃. The levels of the following 13 elements were determined in
168 each extract: arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu),
169 mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), thallium

170 (Ti), and vanadium (V). The quality control was assessed by analyzing blanks and a
171 number of standards: Trace Metals - Loamy Clay 1 (CRM052 Sigma-Aldrich), Trace
172 element in spinach leaves (SRM 1570a, NIST, USA) and Urban Particulate Matter (SRM
173 1648a, NIST, USA). Recovery percentages of the standards ranged 91-140%, 87-132%
174 and 79-98% for soil, vegetation, and air, respectively.

175 The levels of PCDD/Fs, dioxin-like PCBs (dl-PCBs) and non-dioxin-like PCBs (ndl-
176 PCBs) were determined by high-resolution mass chromatography coupled to high-
177 resolution mass spectrometry (HRGC/HRMS). For dioxin-like compounds, an aliquot of
178 40 g of sample was weighed and $^{13}\text{C}_{12}$ -labelled extraction standards (Wellington
179 Laboratories, Ontario, Canada) were added: 2,3,7,8-substituted PCDD/Fs and dl-PCBs
180 (PCB 81, PCB 77, PCB 123, PCB 118, PCB 114, PCB 105, PCB 126, PCB 167, PCB
181 156, PCB 157, PCB 169 and PCB 189). PUFs and QFFs were analyzed together. All the
182 samples were Soxhlet-extracted with toluene for 24 h. Prior to the extraction, lettuce and
183 cabbage samples were freeze-dried to remove water contents. The extract was
184 subsequently subjected to multilayer silica column cleanup procedure followed by
185 microcolumns of graphitized carbon. Two fractions were obtained: one for PCBs and one
186 for PCDD/Fs. The fraction containing PCBs was concentrated and injected in a high
187 performance liquid chromatography (HPLC) system equipped with a pyrenyl column to
188 separate dl-PCBs from the bulk of PCBs. For the analysis of ndl-PCBs, an aliquot of 5 g
189 of sample was weighed and $^{13}\text{C}_{12}$ -labelled extraction standards were added: PCB 28, PCB
190 52, PCB 101, PCB 138, PCB 153 and PCB 180. Sample were extracted with a 41:59 (v:v)
191 mixture of hexane (LGC Standards, Wesel, Germany) and acetone (VWR, Radnor, PA,
192 USA) for 3 h in a Soxhlet apparatus. The extracts were subsequently subjected to
193 multilayer silica column cleanup and concentrated.

194 PCDD/Fs, dl-PCBs and ndl-PCBs were analyzed in a 7890N gas chromatograph
195 (Agilent, Santa Clara, CA, USA) coupled to an Autospec Premier high resolution mass
196 spectrometer (Micromass-Waters, Manchester, UK), operating in electronic impact
197 ionization mode and at 10,000 resolving power. For the PCDD/F analysis, samples were
198 injected (2 μl) on splitless mode (1 min) into the injector at 280 °C. The chromatograph
199 was fitted with a RTX-5MS column (60 m x 0.25 mm i.d., 0.25 μm) from Restek
200 (Bellefonte, PA, USA). The carrier gas was helium at 250 kPa constant pressure mode.
201 The temperature program was 150 °C (held for 1 min), increased at 30 °C min^{-1} to 200
202 °C, increased at 3 °C min^{-1} to 235 °C (held for 10 min) and increased at 6 °C min^{-1} to 300
203 °C (held 17 min). Monitored masses were those proposed by the US EPA 1613 method.

204 For dl-PCB and ndl-PCB analysis, samples were injected (1 μ l) on splitless mode (3 min)
205 into the injector at 250 °C. The chromatograph was equipped with a RTX-5MS column
206 (60 m x 0.25 mm i.d., 0.25 μ m) from Restek (Bellefonte, PA, USA). The carrier gas was
207 helium at 250 kPa constant pressure mode. The temperature program was 120 °C (held
208 for 3 min), being increased at 20 °C min⁻¹ to 180°C, and then at 2 °C min⁻¹ to 270 °C (held
209 19 min). Monitored masses were [M]⁺ and [M+2]⁺ for tetra- and penta-CBs and [M+2]⁺
210 and [M+4]⁺ for hexa- and hepta-CBs. Samples were quantified according to the isotopic
211 dilution method, with the use of ¹³C₁₂-labelled PCDD/F, dl-PCB and ndl-PCB mixtures
212 as internal standards. PCDD/F and dl-PCB concentrations were also expressed as TEQ
213 concentrations, which were calculated for each sample by multiplying the individual
214 congener concentrations quantitated in each sample by the corresponding toxic
215 equivalency factor (TEF). The used TEFs were those established by the World Health
216 Organization (WHO) for humans in 2005 (van den Berg et al. 2005).

217 The levels of the 16 US EPA priority PAHs (naphthalene, acenaphthylene,
218 acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene,
219 benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene,
220 benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-
221 cd)pyrene) were analyzed. For vegetation and air, an aliquot of the PCDD/F cleaned-up
222 extract was used. For soil, 5 g were extracted in a pressurized-liquid extractor (ASE,
223 Dionex) with hexane:acetone (1:1). The extracts were subsequently subjected to clean-up
224 in polymeric microcolumns, concentrated and reconstituted in acetonitrile (LGC
225 Standards, Wesel, Germany). The instrumental determination of PAHs was performed by
226 HPLC with a fluorescence detector (Waters, Milford, MA, USA), and equipped with a
227 Pursuit 3-PAH column (100x4.6 mm i.d., 3 μ m) from Agilent (Santa Clara, CA, USA).
228 Acetonitrile and water were used as mobile phases in gradient mode at 1.2 ml min⁻¹ flow
229 rate. Two pairs of excitation and emission wavelengths for each compound were used to
230 record fluorescence signal. PAHs were quantified by external standard method using a
231 standard stock solution supplied by Dr. Ehrenstorfer (Augsburg, Germany).

232 A quality control/quality assurance (QC/QA) method was properly applied to assure
233 the validity of the results regarding organic pollutants. For chlorinated compounds,
234 retention time and intensity ratios of the monitored ions were used as identification
235 criteria. A deviation of the ion intensity ratios within 20% of the theoretical values was
236 considered as acceptable. Recoveries of the labelled ¹³C₁₂ surrogate were in the range
237 from 60% to 110%. The quantification through the isotopic dilution method directly

238 corrected analyte concentrations for surrogate recoveries. With respect to PAHs, different
239 wavelengths were recorded to check the absence of interferences in the quantification.
240 Additionally, for the same purpose, results were compared to those obtained after the
241 injection in a GC-MS equipment (Agilent, Santa Clara, CA, USA). Detection limits were
242 determined for each compound in each sample as the concentration that generated a signal
243 equivalent to three times the baseline noise. Analytical blanks, following the whole
244 analytical procedure without sample, were performed with each series of samples. Most
245 congeners were not detected, or they were below the limit of detection. Additionally, the
246 method performance was assessed through successful participation in international
247 interlaboratory studies and the analysis of reference materials.

248

249 *2.3. Human health risk assessment*

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251 Human exposure to each target pollutants was evaluated, and the health risks for the
252 adult population living near the landfill were characterized. Details on the procedure to
253 assess the exposure and the risk were previously reported (Nadal et al., 2016; Rovira et
254 al., 2016). Basically, three exposure pathways were considered: soil ingestion (Exp_{ing}),
255 dermal contact (Exp_{derm}), and air inhalation (Exp_{inh}). Details on the equations and input
256 data can be found elsewhere (Nadal et al., 2016; Rovira et al., 2015, 2016). Following
257 exposure assessment, non-cancer (Hazard Quotient-HQ) and cancer risks associated to
258 exposure through each pathway, as well as the total risk, were characterized.

259

260 **3. Results and discussion**

261

262 *3.1. Environmental concentrations of target pollutants*

263

264 The levels of 13 trace elements in soil samples collected in the surroundings of the
265 illegal tire landfill are summarized in Table 1. The highest concentrations of most metals
266 were found in El Quiñón, the closest populated nuclei, being substantially higher those of
267 As, Cd, Cr, Hg, and Tl. In turn, Sb in Seseña Nuevo, and Cu and Pb in Seseña Viejo,
268 presented the greatest levels. Finally, Mn and Sn concentrations were relatively higher in
269 the background sites. Although a general increase of metal concentrations was found in
270 the soils nearest to the landfill, the levels of all trace elements in El Quiñón were lower
271 than threshold concentrations, according to regional and national legislations (Table 1).

272 A different profile was observed for metal concentrations in air, since only Cd presented
273 the highest concentrations in El Quiñón. The concentrations of the 4 elements for which
274 Air Quality Standards (AQS) have been established by the EC are shown in Fig. 2. In
275 general terms, airborne levels of metals were very similar independently on the area of
276 sampling. They were also far below the AQS (6, 5, 20 and 500 ng/m³ for As, Cd, Ni and
277 Pb, respectively), and very close to those reported by other researchers. Thus, Downard
278 et al. (2015) evaluated the emissions of a fire that occurred in a landfill with 1.3 million
279 shredded tires in Iowa City (Iowa, USA). They found ambient concentrations of Pb in
280 PM₁₀ ranging from undetected values to 4 ng/m³ during the fire, and 3 ± 2 ng/m³ post-
281 fire. In the Seseña landfill, the mean airborne level of Pb in El Quiñón was 5.12 ng/m³,
282 being lower than those found in Seseña Nuevo and Seseña Viejo (6.76 and 7.51 ng/m³,
283 respectively). When characterizing the size fractionation, a higher abundance of PM_{2.5}
284 was found for most elements, with mean percentages ranging from 54% to 87% (for Cd
285 and Ni, respectively).

286 After the landfill fire, PM₁₀ values in El Quiñón, Seseña Nuevo and Seseña Viejo
287 were 44, 24 and 60 µg/m³, respectively, while those of PM_{2.5} were 18, 15 and 21 µg/m³,
288 respectively. During the episode, several PM₁₀ peaks, of up to 390 µg/m³, were registered
289 in El Quiñón (JCCM, 2016). Similarly, a maximum concentration of PM_{2.5} of 141 µg/m³
290 was also observed one week after the fire started.

291 The soil concentrations of the sum of 16 PAHs, as well as the sum of the 7
292 carcinogenic PAHs in each one of the 8 sampling sites, are depicted in Fig. 3. Mean levels
293 of the 16 PAHs in soils ranged from 8.8 to 33.2 ng/g. In turn, the concentration of the 7
294 carcinogenic PAHs ranged from undetected values to 18.0 ng/g. An individual analysis
295 of the results shows specially low concentrations in the samples of Seseña Viejo and a
296 background site (Villalba), where only 1 of the 16 PAH at each site could be detected
297 (indeno(1,2,3-cd)pyrene and pyrene, respectively). On the other hand, the highest PAH
298 values were found in different areas: an agricultural soil in El Quiñón, a vegetable garden
299 in Seseña Viejo, and the second background site (Morata de Tajuña). The high PAH levels
300 in this area could be potentially related to the presence of a big cement factory in this
301 village, as these chemicals have been largely identified as potential releases by cement
302 factories (Ercan and Dinçer, 2016; Rovira et al., 2016; Sánchez-Soberón et al., 2016). In
303 any case, no correlations were observed between PAH concentrations and the distance to
304 the landfill. Furthermore, when these data were compared with values from the scientific
305 literature, it was observed that PAH levels in soils collected in the vicinity of Seseña were

306 in the lowest part of the range. Since 2002, our laboratory has been periodically
307 monitoring the environmental burdens of PAHs in the largest chemical/petrochemical
308 industrial complex in Southern Europe, located in Tarragona County (Catalonia, Spain).
309 In the first survey of the series, PAH levels in soil ranged between 166 and 1002 ng/g
310 (Nadal et al., 2004). Despite PAH levels have shown some fluctuations through the time,
311 subsequent studies reflected higher levels than those found near the Seseña landfill (281,
312 129 and 212 ng/g in 2005, 2007 and 2009, respectively) (Nadal et al., 2007, 2009, 2011).
313 Moreover, soil concentrations of PAHs in Seseña are in the lowest part of the range in
314 comparison to levels found in other Spanish areas (Zuazagoitia et al., 2011; Navarro-
315 Ortega et al., 2012; Plaza-Bolaños et al., 2012).

316 The concentrations of the 16 analyzed PAHs in air samples, collected at 3 different
317 sites around the Seseña landfill, are summarized in Table 2. Notably higher levels of the
318 sum of the 16 PAHs (134 ng/m^3) were found in El Quiñón, the closest location to the
319 landfill (at only 500 m). This value was up to 6-times higher than those found in Seseña
320 Nuevo and Seseña Viejo (19.5 and 22.7 ng/m^3 , respectively), both of them situated at
321 around 4 km from the landfill. A high abundance of the 7 carcinogenic PAHs was
322 observed in the 3 sampling sites, with contribution percentages ranging from 86% to 97%.
323 Individually, chrysene and benzo(a)anthracene were identified as the main responsible of
324 the increase of PAHs in El Quiñón, where the levels of these two PAHs were 112 and
325 9.77 ng/g , respectively. In turn, the 4 most volatile (naphthalene, acenaphthylene,
326 acenaphthene, and fluorene) and the heaviest (benzo(a)pyrene, benzo(g,h,i)perylene and
327 indeno(123-cd)pyrene) PAHs were not detected in any sample. Unlike soils, PAH levels
328 in air were dramatically higher than those previously found in other areas of Spain. When
329 evaluating the atmospheric concentrations of 18 PAHs across the chemical/petrochemical
330 industrial area of Tarragona County, Ramírez et al. (2011) reported mean values ranged
331 from 5.52 to 67.2 ng/m^3 in the gas phase, and from 0.67 to 7.00 ng/m^3 in the particle
332 phase. PAHs in the vapor phase tend to be more predominant than in the gas phase
333 (Barrado et al., 2013). Furthermore, a clear seasonal trend was detected, being the levels
334 clearly higher in winter than those registered in summer. In a previous study, Nadal et al.
335 (2009) found similar air concentrations of PAHs (mean: 18.1 ng/m^3) in both (gas and
336 particle) phases, from samples collected at different locations around the same
337 petrochemical area.

338 The number of investigations focused on the environmental consequences of a tire
339 landfill fire is extremely limited. However, PAHs have been identified as one of the most

340 relevant groups of pollutants released in natural combustion processes, such as forest
341 fires, for example (Choi, 2014; Simon et al., 2016). In the above-mentioned fire occurred
342 in a shredded tire landfill located in Iowa City, a dramatic increase of 19 PAHs in PM_{2.5}
343 was observed during the fire period. PAH levels in PM_{2.5} samples collected prior to the
344 event, averaged 0.24 ng/m³ (range: 0.15-0.42 ng/m³), while 1 week after the fire started,
345 the PAH concentration peaked at 33.2 ng/m³. However, it must be highlighted that the
346 data found in these studies are not entirely comparable, because the present investigation
347 was focused on total concentrations of PAHs in air, while that conducted in the USA
348 analyzed PAHs only in the PM_{2.5} fraction. In turn, data from the Iowa City landfill fire
349 were in agreement with the values reported by the regional authorities a few days the fire
350 at Seseña started (JCCM, 2016). In May 16, PAHs reached a concentration peak of 314
351 and 246 ng/m³ in PM₁₀ and PM_{2.5}, respectively. Furthermore, the levels of benzo(a)pyrene
352 were exceeding the threshold, set at 1 ng/m³, during the whole event. Three days after the
353 fire was initiated, benzo(a)pyrene concentrations in PM₁₀ and PM_{2.5} were 17.97 and 14.62
354 ng/m³, respectively, while those reported 15 days after the start were even higher (25.09
355 and 24.18 ng/m³ in PM₁₀ and PM_{2.5}, respectively) (JCCM, 2016).

356 Since PCDD/Fs are pointed out as one of the most hazardous chemicals released in
357 tire fires (Steer et al., 1995), environmental levels of PCDD/Fs and other chlorinated
358 compounds, such as PCBs, were also analyzed in samples surrounding the Seseña landfill
359 after the fire episode. The concentrations of PCDD/Fs and PCBs in air and soil samples
360 collected in different locations in the vicinity of the facility, are depicted in Fig. 4. In air,
361 all the chlorinated compounds presented very similar levels irrespectively of the sampling
362 site. PCDD/Fs and dl-PCBs showed concentrations ranging 14.6-16.9 fg WHO-TEQ/m³,
363 being PCDD/Fs the main contributors (91%). Only 2 of the PCDD/F congeners (OCDD
364 and 2,3,7,8-TCDF) could be detected in all the samples, while 1,2,3,4,6,7,8-HpCDF could
365 be also quantified in Seseña Nuevo. The remaining 14 PCDD/F congeners, as well as
366 PCB-169, presented concentrations below their respective limits of detection. These
367 values are relatively low in comparison to data from the scientific literature. Steer et al.
368 (1995) investigated the occurrence of PCDD/Fs in air, soil, vegetation and oily runoff
369 from a fire at a used tire storage facility near Hagersville (Ontario, Canada). Around 8-9
370 days after the fire started, PCDD/F levels in ambient air were found to be one order of
371 magnitude higher near the plant (<1 km) than at 3 km from the site (2500 vs. 270 I-TEQ
372 fg/m³). However, air concentrations dramatically decreased one week later, when the fire
373 was extinguished, being reported a level of 120 fg I-TEQ/m³. The concentrations of

374 PCDD/Fs and PCBs near Seseña are currently similar to those found in areas not impacted
375 by a fire. Since 2007, the environmental impact of a hazardous waste landfill located in
376 Castellolí (Catalonia, Spain) is being monitored (Nadal et al., 2016). PCDD/Fs air
377 concentrations inside the facility, and in the surroundings, were of the same order of
378 magnitude than those observed in the different Seseña neighborhoods, with levels of up
379 to 12.7 fg WHO-TEQ/m³. Similar data regarding PCDD/Fs and PCBs in air have been
380 reported in other industrial and urban areas across Spain (Rovira et al., 2015; Vilavert et
381 al., 2015). Non-dioxin-like PCBs presented a similar pattern to other chlorinated
382 compounds. Airborne levels of ndl-PCBs fell within a range between 34.1 and 44.9 fg/m³
383 (Fig. 4a), very similar to those found in other urban zones (Rovira et al., 2015).

384 The concentrations of PCDD/Fs and dl-PCBs in soils ranged between 0.11 to 1.66
385 ng WHO-TEQ/kg, with a mean concentration of 0.43 ng WHO-TEQ/kg. Similarly to the
386 air matrix, PCDD/Fs in soils were more abundant than dl-PCBs, being the mean
387 contribution percentage 81%. Furthermore, there were no correlations between soil levels
388 and the distance to the landfill. This is a clear indicator that the fire did not lead to an
389 increase of the environmental burdens of PCDD/Fs in the closest area. Furthermore, the
390 maximum concentration was found in a sample of an agricultural soil collected in a
391 vegetable garden of Seseña Viejo. The PCDD/F congener profile was dominated by high-
392 chlorinated PCDDs, with OCDD showing the highest contribution to the total
393 concentration (range: 35%-87%). On the other hand, PCB-118 was the predominant dl-
394 PCB congener in all the samples. In general, the pattern of ndl-PCBs in soil was quite
395 similar to that of dioxin-like compounds, with very low levels in all the samples,
396 excepting the soil sample from the vegetable garden. However, there was an important
397 difference between air and soil profile, as the soil from El Quiñón showed the highest
398 concentration of ndl-PCBs in soil (0.84 ng/g). Furthermore, this sample was the only one
399 with detectable amounts of the 6 ndl-PCB congeners, which ranged from 0.12 to 0.16
400 ng/g (PCB-153 and PCB-52, respectively). Anyhow, in terms of PCDD/Fs and PCBs,
401 data relative to the Seseña environment after the tire landfill fire, are not of concern. These
402 values are relatively low in comparison to levels reported by other researchers,
403 corresponding to areas impacted by a tire fire (Steer et al., 1995), or not (Rovira et al.,
404 2015; Vilavert et al., 2015).

405 In addition to air and soil, samples of local crops were also collected, being the
406 concentrations of the same target pollutants were analyzed. The levels of trace elements,
407 PCDD/Fs, PCBs and PAHs in barley, wheat, cabbage and lettuce, harvested just after the

408 fire was extinguished, are summarized in Table 3. Regarding heavy metals, Mn and Cu
409 showed the greatest concentration, being wheat the species with the highest value (36.1
410 and 4.77 mg/kg, respectively). In turn, no traces of As, Cd, Hg, Sb, Sn, Tl and V were
411 found in any of the vegetal samples. With respect to organic pollutants, lettuce presented
412 the highest concentrations of PCDD/Fs + dl-PCBs and ndl-PCBs (0.33 ng WHO-TEQ/kg
413 and 0.52 ng/g, respectively), while barley showed the highest level of PAHs (1800 ng/g).
414 Because of their physiological differences, the comparison of pollutant concentrations in
415 the different vegetal species cannot be performed. However, results were compared with
416 those from the scientific literature. The levels of some particular target pollutants, such
417 as Pb and PAHs in lettuce, were slightly higher than those previously found in a number
418 of food safety studies conducted in Spain (Martorell et al, 2010; Capdevila et al., 2014;
419 Perelló et al., 2014), but lower than those reported in other international studies (Waqas
420 et al., 2014). In contrast, similar concentrations of PCDD/Fs and PCBs were reported in
421 lettuce from commercial markets (Perelló et al., 2012).

422

423 *3.2. Human health risk assessment*

424

425 The post-fire environmental concentrations of the target pollutants here analyzed in
426 the 3 populated nuclei around the Seseña landfill, were used to assess human health risks
427 associated to exposure to those chemicals. Air inhalation was the most important
428 exposure pathway for all the chemicals, with contributions >99% for PCDD/Fs, PCBs
429 and PAHs, and >95% for trace elements. The only exceptions were As and Mn, for which
430 inhalation accounted for 87% and 92%, respectively, of the total environmental exposure.
431 In turn, soil ingestion and dermal absorption were minor routes.

432 The non-cancer risks were evaluated for each chemical with a well-defined reference
433 dose (RfD). The calculated HQ in the 3 sampling sites is shown in Table 4. None of the
434 pollutants exceeded the threshold level, which is set at the unity (HQ=1). Furthermore,
435 the HQ estimated for the inhabitants of El Quiñón was not higher than that calculated for
436 other 2 neighborhoods (Seseña Nuevo and Seseña Viejo). Slightly different results were
437 found for cancer risks (Fig. 5). The health risks associated to the exposure to carcinogenic
438 substances were, in El Quiñón, from 3- to 5-times higher than those in the other two
439 locations. It was especially relevant for PAHs, as exposure to all the PAHs, excepting
440 benzo(a)pyrene and indeno(123-cd)pyrene, was higher in El Quiñón. Despite there cannot
441 be recommendations with respect to exposure to carcinogenic substances, cancer risks

442 below 10^{-5} , according to the Spanish legislation (MMA, 2007), and 10^{-6} , according to
443 some international organizations, are considered as acceptable. In a post-fire scenario,
444 neither PAHs, nor any of the other organic pollutants exceeded the most restrictive of
445 these thresholds, being all $<10^{-6}$. On the other hand, exposure to As and Cr raised the
446 levels above 10^{-5} . As it is well known, only inorganic As and Cr-VI are carcinogenic.
447 However, since a metal speciation was not conducted, total concentrations of As were
448 here used for risk assessment calculations, while Cr-VI was considered as one sixth of
449 total Cr (Nadal et al., 2016). This may lead to a potential overestimation of the risk, which
450 could be refined in further studies. In any case, cancer risk values for trace elements are
451 typical of urban areas not impacted by a fire episode. In any case, it must be highlighted
452 that the working scenario was based on a post-fire situation. Because of the lack of
453 environmental information, health risks for the inhabitants of El Quiñón as well as the
454 other populated nuclei, could not be assessed during the episode. Therefore, the real
455 exposure degree of the people to PAHs and the rest of analyzed chemicals, could not be
456 properly evaluated.

457

458 **4. Conclusions**

459

460 Preliminary data regarding the human health impact of the tire fire occurred in the
461 Seseña landfill were obtained. Most of the target pollutants did not show increased
462 concentrations in the environment surrounding the facility after the fire. Moreover, the
463 concentrations of trace elements, PCDD/Fs and PCBs fell in the lowest part of the range,
464 compared with data from the scientific literature relative to urban areas not impacted by
465 fire. In contrast, airborne levels of PAHs were substantially higher in El Quiñón, which
466 led to an increase of cancer risks for the population living in that neighborhood.
467 Furthermore, a certain impact on local crops was observed, as PAH levels in lettuce were
468 somehow higher than those from the literature.

469 The current results are indicative of the post-fire situation, just when the sampling
470 was conducted. However, this is only a preliminary study based certainly on a limited
471 number of samples, which means the most important limitation of this investigation. It
472 was performed in response to the notable social concern, as well as for evident scientific
473 interest linked to the lack of information and protocols in front of serious tire fire
474 episodes. Therefore, our results must be considered as a basic “screening”. Anyway, the
475 present survey must be also considered as a successful case-study of risk communication,

476 as neighbors were the first receivers of these results. The screening was also useful for
477 the optimization of economic resources, as it remarked that further efforts should be made
478 on those chemicals of most concern, PAHs, being excluded trace elements and
479 chlorinated compounds of a more complete investigation.

480

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482

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485

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487

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593

TABLES AND FIGURES

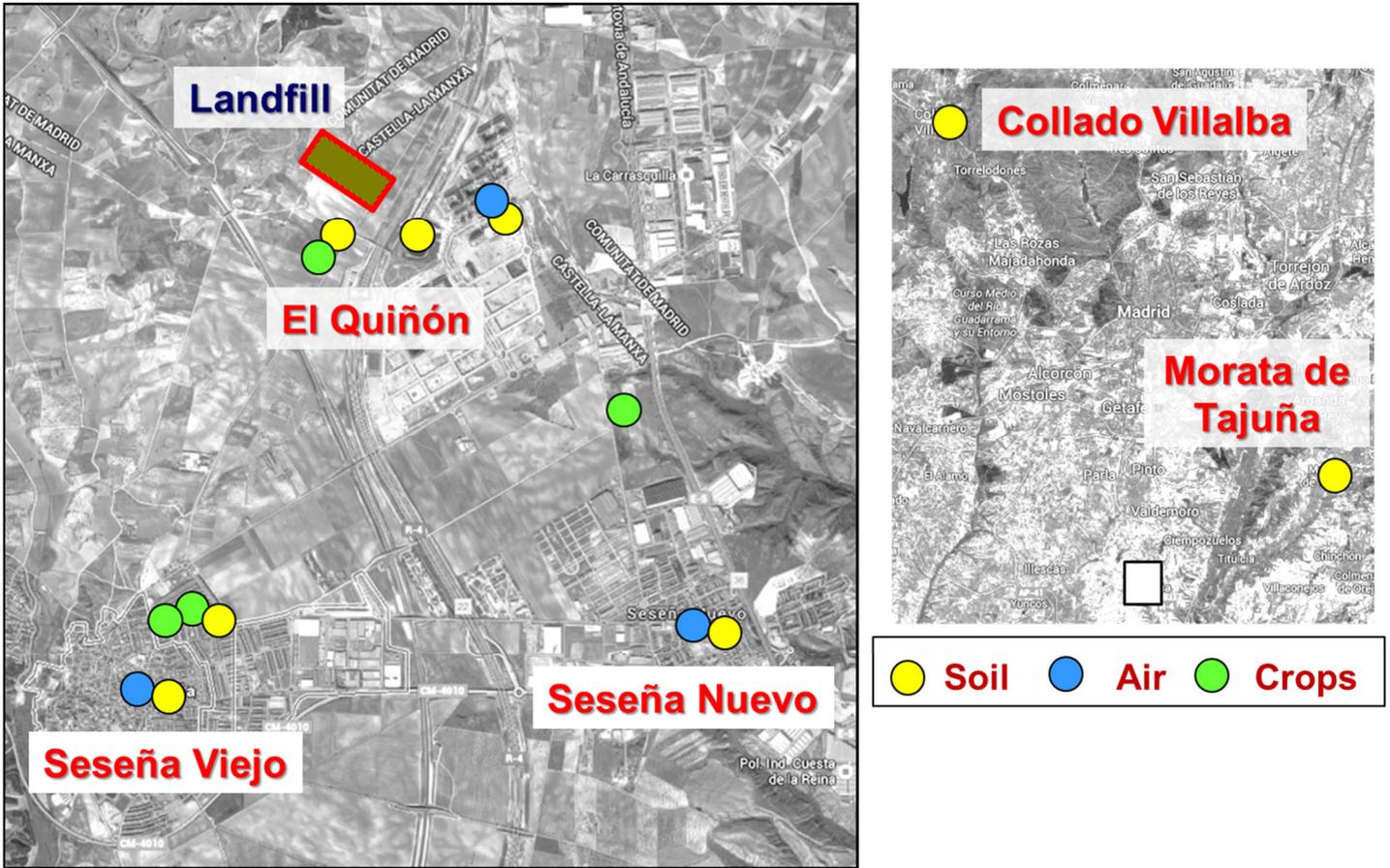


Fig. 1. Area of sampling

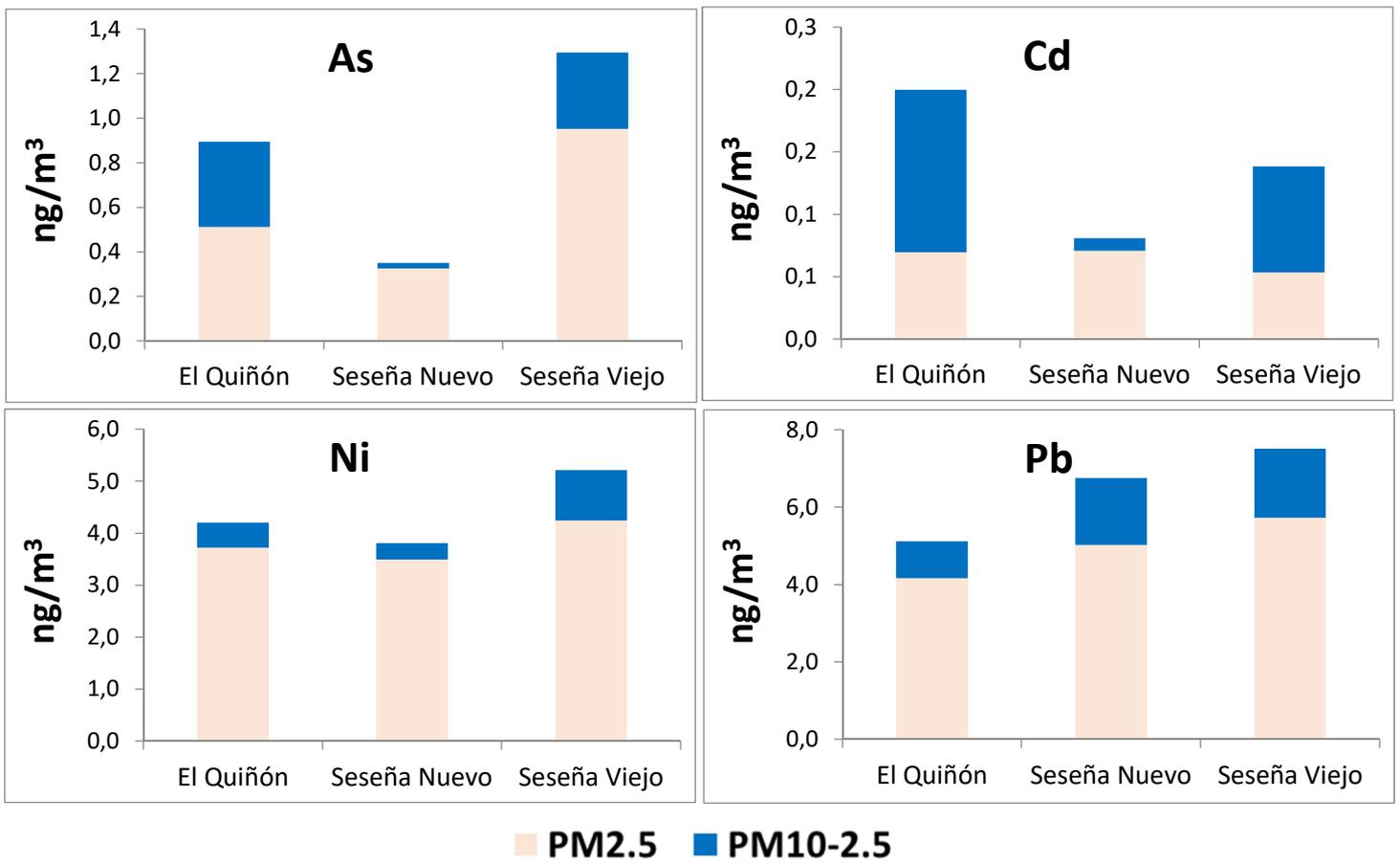


Fig. 2. PM₁₀ levels and size-fractionation of trace elements with Air Quality Standards established by the European Commission, in samples collected near the Seseña landfill.

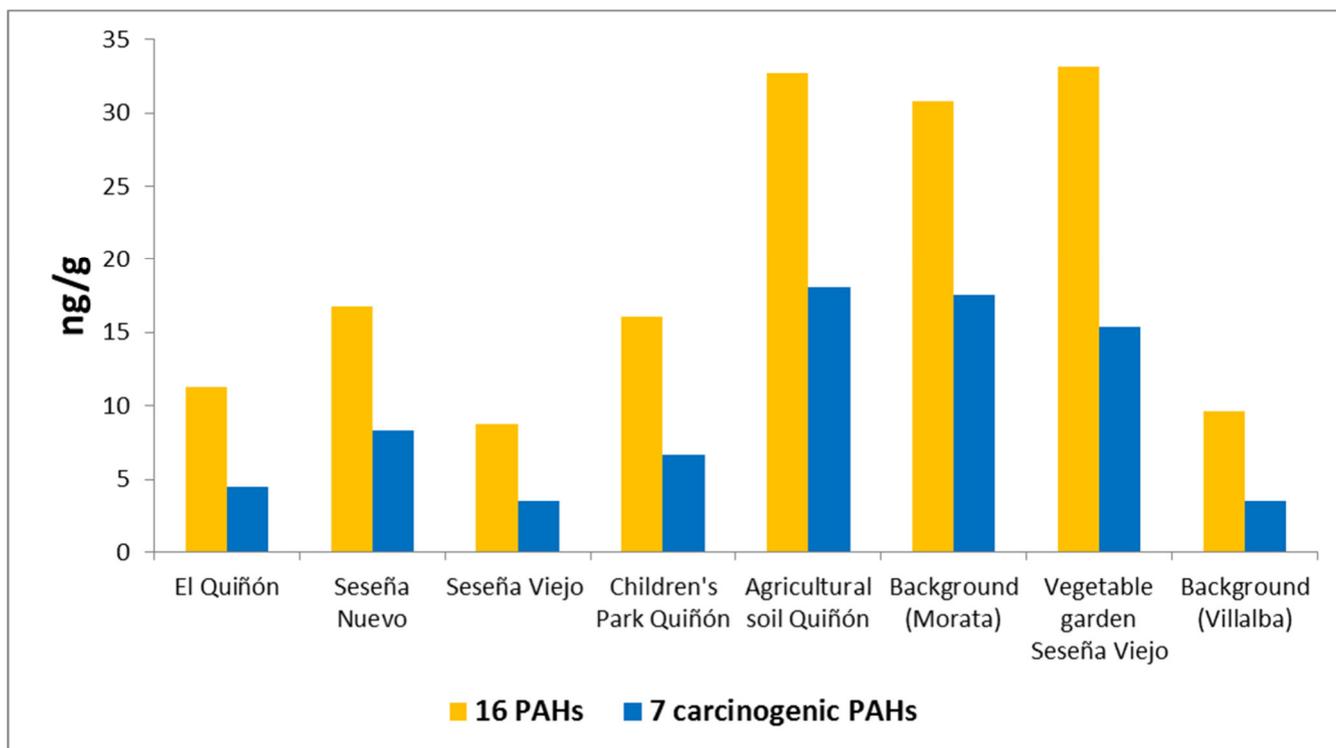
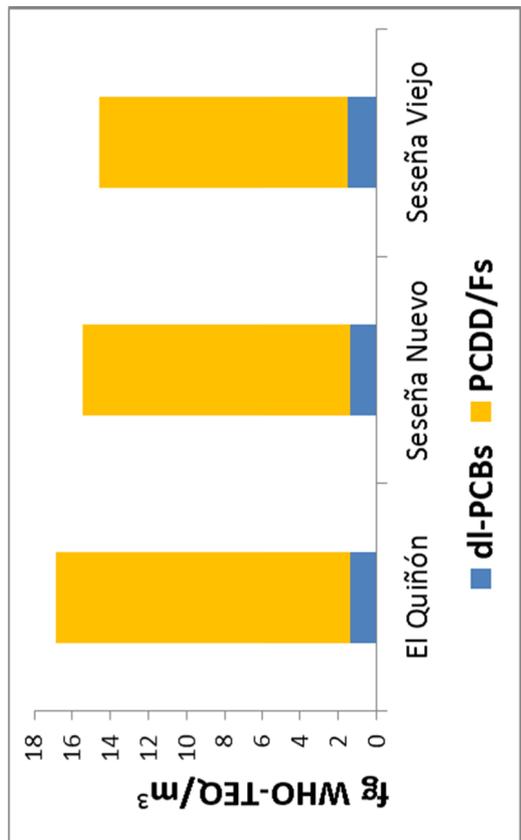
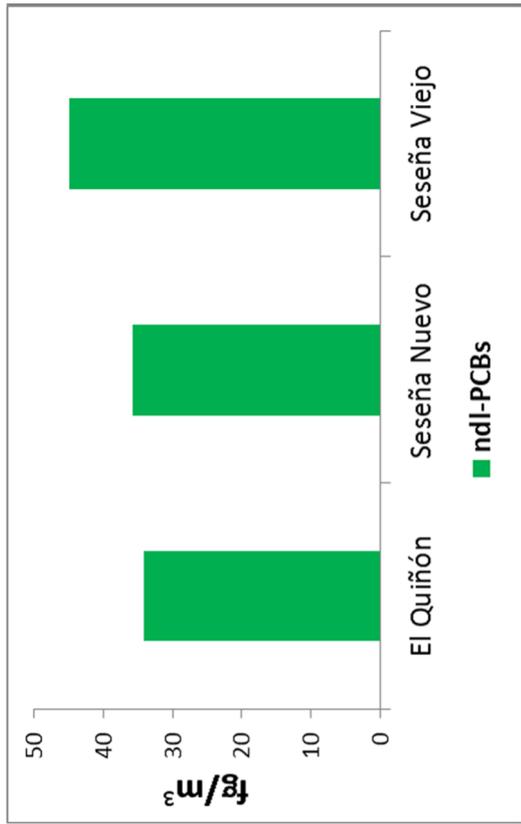
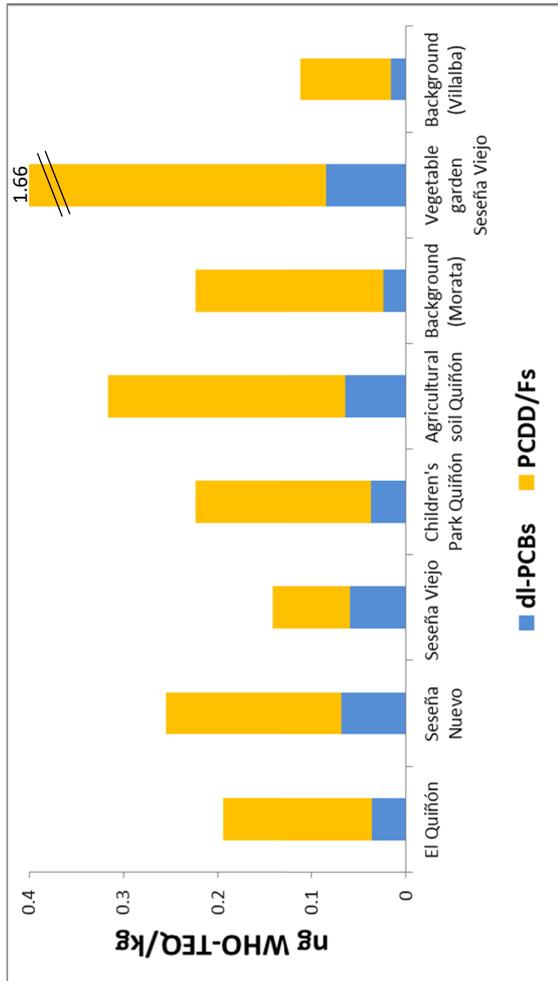
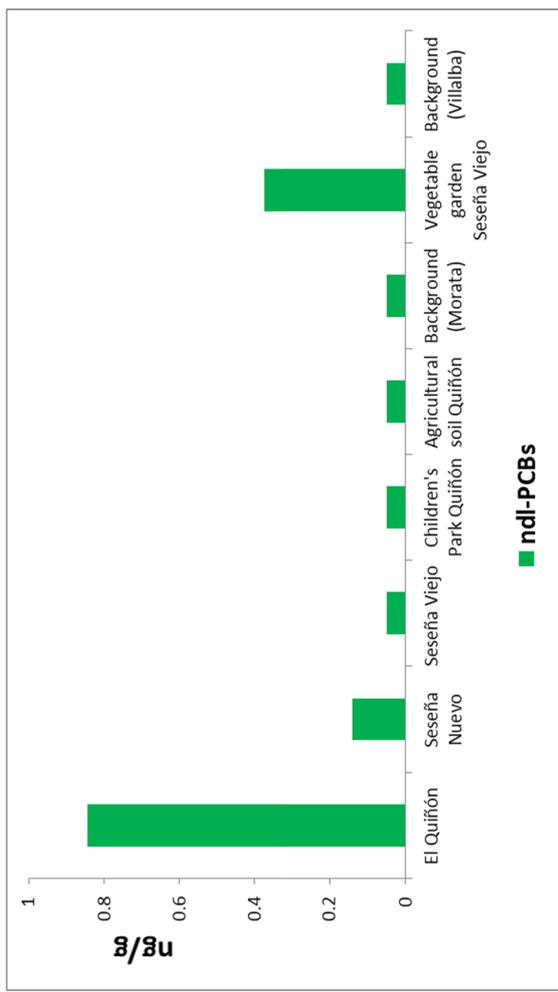


Fig. 3. PAH concentrations in 8 soil samples collected in the vicinity of the Seseña landfill in June 2016.



(a) AIR



(b) SOIL

Fig. 4. Concentrations of PCDD/Fs, dl-PCBs and ndl-PCBs in air (a) and (b) soil samples collected around the Seseña landfill in June 2016.

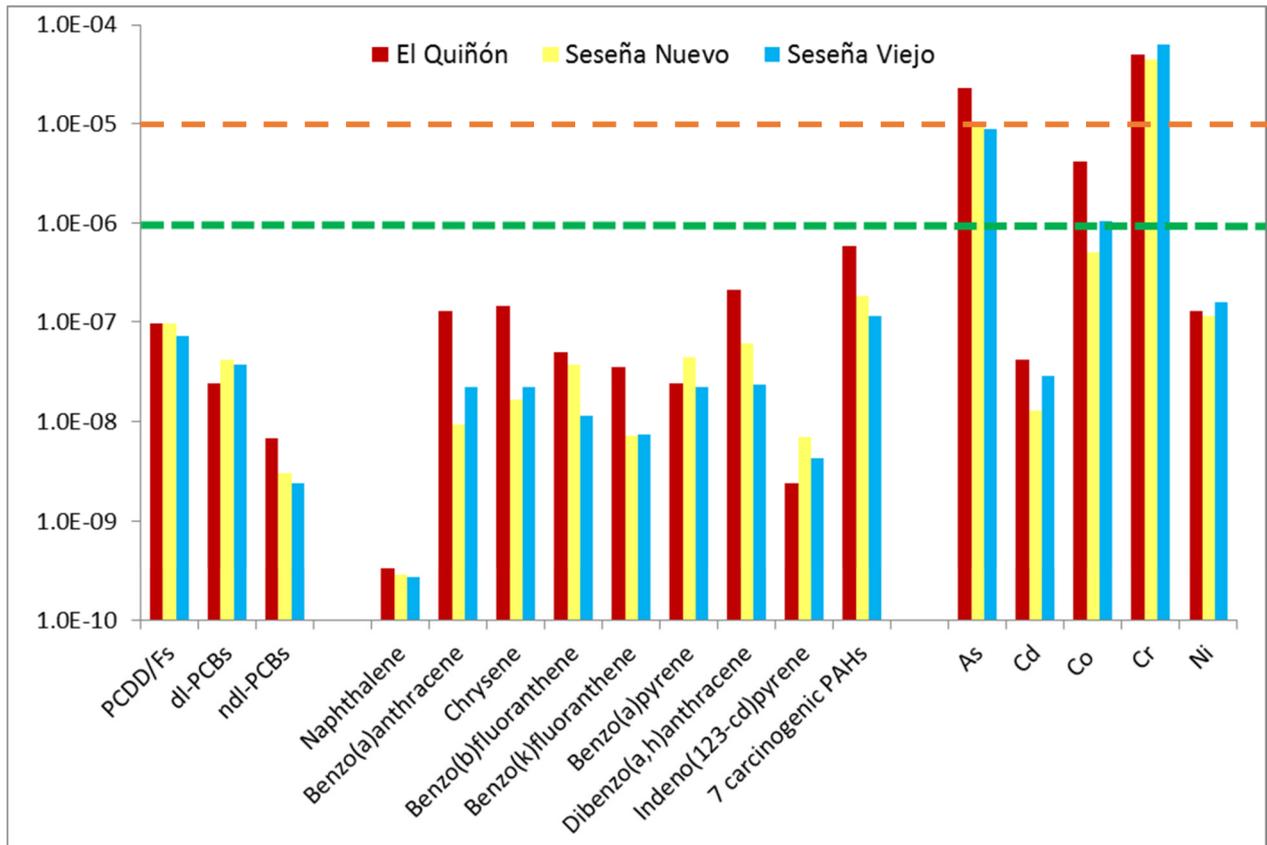


Fig. 5. Cancer risk of exposure to a number of carcinogenic pollutants in 3 populated nuclei around the Seseña landfill in June 2016.

Table 1

Metal concentrations in soil samples collected in the surroundings of the Seseña landfill in June 2016.

| | El Quiñón | Seseña Nuevo | Seseña Viejo | Background | Reference values* |
|----|--------------|--------------|--------------|--------------|-------------------|
| As | 16.6 ± 10.3 | 4.46 | 10.5 ± 9.2 | 5.39 ± 1.39 | 24 |
| Cd | 0.13 ± 0.06 | 0.04 | 0.08 ± 0.06 | 0.05 ± 0.03 | 3 |
| Co | 3.94 ± 0.85 | 1.8 | 2.97 ± 2.69 | 2.86 ± 0.42 | 15 |
| Cr | 12.14 ± 2.75 | 5.86 | 10.53 ± 7.67 | 8.08 ± 4.69 | 90 |
| Cu | 6.16 ± 1.34 | 5.1 | 8.18 ± 7.63 | 8.02 ± 4.06 | 80 |
| Hg | 0.17 ± 0.28 | <0.10 | <0.10 | <0.10 | 5 |
| Mn | 209 ± 46 | 97.0 | 174 ± 161 | 267 ± 160 | 690 |
| Ni | 6.35 ± 1.55 | 3.52 | 5.62 ± 4.84 | 4.28 ± 2.59 | 405 |
| Pb | 9.99 ± 2.20 | 5.47 | 10.70 ± 5.42 | 10.18 ± 1.35 | 75 |
| Sb | 0.03 ± 0.00 | 0.06 | 0.03 ± 0.02 | 0.02 ± 0.02 | 0.8 |
| Sn | 1.07 ± 0.20 | 0.39 | 0.64 ± 0.56 | 1.74 ± 0.79 | 46730 |
| Tl | 0.30 ± 0.07 | 0.1 | 0.20 ± 0.20 | 0.17 ± 0.02 | 2 |
| V | 20.47 ± 4.81 | 8.92 | 16.1 ± 16.4 | 13.69 ± 2.79 | 37 |

Data are given as mean ± standard deviation, except for Seseña Nuevo, where only 1 sample was collected.

*Soils with no industrial or urban use at the Community of Madrid, according to the Regional Government (Consejería de Medio Ambiente y Ordenación del Territorio, 2006).

Table 2
Concentrations of 16 PAHs (in ng/m³) in air samples collected around the Seseña landfill in June 2016.

| | El Quiñón | Seseña Nuevo | Seseña Viejo |
|----------------------------|------------------|---------------------|---------------------|
| Naphthalene | <0.15 | <0.15 | <0.15 |
| Acenaphthylene | <0.15 | <0.15 | <0.15 |
| Acenaphthene | <0.15 | <0.15 | <0.15 |
| Fluorene | <0.15 | <0.15 | <0.15 |
| Phenanthrene | 1.31 | 0.76 | 0.78 |
| Anthracene | <0.15 | 0.40 | <0.15 |
| Fluoranthene | 0.50 | 0.49 | 0.37 |
| Pyrene | 1.70 | 0.72 | 0.49 |
| Benzo(a)anthracene | 9.77 | 0.61 | 1.63 |
| Chrysene | 112 | 12.8 | 17.4 |
| Benzo(b)fluoranthene | 3.74 | 2.62 | 0.78 |
| Benzo(k)fluoranthene | 2.70 | 0.54 | 0.56 |
| Benzo(a)pyrene | <0.15 | <0.15 | <0.15 |
| Dibenzo(a,h)anthracene | 1.39 | <0.15 | <0.15 |
| Benzo(g,h,i)perylene | <0.15 | <0.15 | <0.15 |
| Indeno(123-cd)pyrene | <0.15 | <0.15 | <0.15 |
| ∑16 PAHs | 134 | 19.5 | 22.7 |
| 7 carcinogenic PAHs | 130 | 16.8 | 20.6 |

For the calculation of the sum of 16 PAHs and the 7 carcinogenic PAHs, compounds with undetected levels were assumed to have a concentration equal to one-half of the detection limit.

Table 3

Concentrations of trace elements, PCDD/Fs, PCBs and PAHs in crops around the Seseña landfill in June 2016.

| | Barley | Wheat | Cabbage | Lettuce |
|----------------------|---------------|--------------|----------------|----------------|
| As | <0.10 | <0.10 | <0.10 | <0.10 |
| Cd | <0.025 | <0.025 | <0.025 | <0.025 |
| Co | <0.05 | <0.05 | 0.08 | <0.05 |
| Cr | <0.05 | <0.05 | 0.11 | <0.05 |
| Cu | 2.56 | 4.77 | 0.64 | 1.34 |
| Hg | <0.10 | <0.10 | <0.10 | <0.10 |
| Mn | 9.31 | 36.1 | 6.80 | 3.97 |
| Ni | <0.10 | 0.78 | 0.21 | 0.17 |
| Pb | 0.15 | <0.025 | 0.11 | 0.26 |
| Sb | <0.010 | <0.010 | <0.010 | <0.010 |
| Sn | <0.05 | <0.05 | <0.05 | <0.05 |
| Tl | <0.025 | <0.025 | <0.025 | <0.025 |
| V | <0.05 | <0.05 | <0.05 | <0.05 |
| PCDD/Fs | 0.05 | 0.05 | 0.10 | 0.23 |
| Dioxin-like PCBs | 0.05 | 0.03 | 0.10 | 0.13 |
| Non-dioxin-like PCBs | <0.05 | 0.10 | 0.20 | 0.52 |
| 16 PAHs | 1800 | 885 | 20.75 | 29.5 |

Units: trace elements, in mg/kg; PCDD/Fs and dl-PCBs, in ng WHO-TEQ/kg dry weight; ndl-PCBs and PAHs, in ng/g. For calculations, chemicals with undetected levels were assumed to have a concentration equal to one-half of the detection limit.

Table 4

Hazard Quotient (unitless) due to the environmental exposure to a number of pollutants in 3 areas around the Seseña landfill in June 2016.

| | El Quiñón | Seseña Nuevo | Seseña Viejo |
|--------------|------------------|---------------------|---------------------|
| PCDD/Fs | 8.37E-04 | 9.56E-04 | 4.73E-04 |
| PCB 81 | 7.76E-07 | 2.79E-06 | 9.31E-07 |
| PCB 77 | 1.64E-06 | 5.15E-06 | 1.62E-06 |
| PCB 123 | 9.41E-08 | 2.72E-07 | 1.50E-07 |
| PCB 118 | 2.06E-06 | 8.28E-06 | 3.85E-06 |
| PCB 114 | 5.95E-08 | 3.17E-07 | 9.49E-08 |
| PCB 105 | 1.17E-06 | 5.78E-06 | 2.04E-06 |
| PCB 126 | 4.50E-04 | 8.60E-04 | 7.49E-04 |
| PCB 167 | 5.08E-07 | 1.09E-06 | 9.95E-07 |
| PCB 156 | 6.46E-07 | 1.86E-06 | 1.48E-06 |
| PCB 157 | 1.66E-07 | 3.05E-07 | 3.35E-07 |
| PCB 169 | 2.31E-05 | 3.62E-05 | 3.67E-05 |
| PCB 189 | 3.85E-07 | 6.46E-07 | 5.56E-07 |
| Sum PCBs | 4.81E-04 | 9.23E-04 | 7.98E-04 |
| Naphthalene | 7.81E-06 | 6.82E-06 | 6.43E-06 |
| Acenaphthene | 7.31E-08 | 7.31E-08 | 7.31E-08 |
| Fluorene | 1.10E-07 | 1.10E-07 | 1.10E-07 |
| Anthracene | 1.46E-08 | 1.46E-08 | 1.46E-08 |
| Fluoranthene | 1.10E-07 | 3.42E-07 | 1.10E-07 |
| Pyrene | 3.57E-07 | 3.42E-07 | 1.46E-07 |
| As | 1.17E-01 | 4.79E-02 | 4.30E-02 |
| Cd | 3.89E-04 | 1.46E-04 | 1.38E-04 |
| Co | 2.24E-02 | 1.27E-02 | 7.56E-03 |
| Cr | 7.52E-02 | 4.64E-02 | 4.05E-02 |
| Cu | 2.54E-04 | 2.70E-04 | 1.47E-04 |
| Hg | 6.62E-04 | 6.62E-04 | 6.62E-04 |
| Mn | 1.05E-01 | 6.24E-02 | 3.88E-02 |
| Ni | 3.81E-03 | 2.73E-03 | 1.71E-03 |
| Pb | 2.53E-03 | 1.65E-03 | 2.08E-03 |
| Sb | 4.52E-04 | 8.42E-04 | 3.11E-04 |
| Sn | 3.75E-06 | 1.37E-06 | 8.42E-07 |
| Tl | 5.33E-02 | 2.09E-02 | 1.17E-02 |
| V | 7.10E-03 | 3.78E-03 | 1.90E-03 |