Human exposure to trace elements and PCDD/Fs around a hazardous waste landfill in Catalonia (Spain)

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ABSTRACT

Since 2007, the concentrations of various trace elements (As, Cd, Cr, Hg, Ni, and Pb) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been periodically analysed in air and soil samples collected inside and near a hazardous waste landfill (HWL) located in Castellolí (Catalonia, Spain). In the current survey, as expected, once again the levels of the analysed trace elements were higher inside the HWL than in the surrounding areas. However, no relevant differences between zones under the potential influence of the HWL and non-affected areas were found. With respect to PCDD/Fs, a decrease in their concentrations has been observed over the years. The human health risks associated with the assessed contaminants were within acceptable ranges according to national and international legislations.

Keywords: Hazardous waste landfill; PCDD/Fs; trace elements; human exposure; risk assessment.

1. Introduction

In 2016, a total of 2,533 million tonnes of waste were generated in Europe, including all economic activities and households ("Waste statistics - Statistics Explained," 2016.). Up to 4% of this waste was classified as hazardous waste. Although the best way to manage wastes is to minimize their production, if this is not possible, the EU proposes other options that allow to reduce its adverse environmental effects through the Directive 2018/850/EC: to recycle, to reuse and to improve the final disposal (European Union Parliament and Council, 2018). In this sense, waste incinerators and landfills are just considered as the last option for waste disposal. In addition, their locations have usually generated, and still generate, a notable concern on the population living nearby, even if these facilities work within high environmental standards.

Because of the industrial combustion, bottom and fly ashes are produced. These are characterized by their high content of heavy metals, such as cadmium (Cd) and mercury (Hg), as well as metalloids, such as arsenic (As) (Li et al., 2018; Seniūnaitė et al., 2018), whose exposure is related with known adverse effects on the human health (Sun et al., 2017). On the other hand, they also contain a wide variety of organic compounds, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), which are persistent, toxic and bioaccumulative compounds (Hsieh et al., 2018). This kind of chemicals can be present in the surroundings of landfills and incinerators. In a number of epidemiological studies, it has been concluded that living near hazardous waste landfills can have serious effects on health, such as cancers, non-Hodgkin lymphoma, asthma, congenital anomalies, low birth weight and pre-term birth (Vrijheid et al., 2000;

69 Fazzo et al., 2017). Therefore, it is important to conduct periodical surveillance studies
70 near hazardous waste management facilities in order to guarantee the safety of the
71 population living in the neighborhood.

72 In 1984, a hazardous waste landfill (HWL), initially built to receive chromium (Cr)
73 residues, started to operate in Castellolí (Catalonia, Spain). When in 1998 the activity
74 that generated this type of waste finished, the landfill began to receive wastes
75 compatible with those already deposited, such as bottom ash from municipal solid
76 waste incinerators, asbestos and other non-recyclable materials. Nowadays, the HWL
77 remains very active. In 2007, our research group started a surveillance program aimed
78 at analyzing the levels of certain pollutants around the HWL of Castellolí , as well as the
79 potential health risks for the population living in the neighbourhood. In that program,
80 and taking into consideration the kind of managed waste, the concentrations of
81 PCDD/Fs, As, Cd, Cr, Hg, nickel (Ni) and lead (Pb) were initially determined in air and soil
82 samples (Mari et al., 2009). From 2007 to 2014, several campaigns have been conducted
83 to measure the levels of PCDD/Fs, As and the remaining trace elements in samples of air
84 and soil, with the main goal of detecting any possible changes in the health risks for the
85 population living near the HWL (Nadal et al., 2016; Rovira et al., 2012).

86 The objective of the present study, which has been carried out more than ten years
87 after the surveillance program was initiated, has been to update the information
88 regarding the environmental impact and the human health risks of the HWL of Castellolí
89 due to the presence of PCDD/Fs, As, and 5 heavy metals (Cd, Cr, Hg, Pb and Ni). To the
90 best of our knowledge, this study is part of –until now- the longest (12 years)
91 environmental surveillance program conducted around a HWL.

2. Materials and methods

2.1. Sampling

The HWL of Castellolí (41°35'22"N; 1°40'32"E) is located in a rural region of Catalonia (NE Spain), with three nearby towns: Castellolí, Òdena and Igualada. In the same area, there is also a highway with a mean traffic intensity higher than 40,000 vehicles per day, including 18% of heavy vehicles (Ministerio de Fomento, 2017).

Between 2015 and 2018, four environmental sampling campaigns were conducted around the landfill of Castellolí (Table 1). Samples were collected annually, being all the studies conducted in July to assure the comparability of data. Sampling points were located as previously reported (Nadal et al., 2016): two inside the HWL, and four outside the facility. The latter were located in the nearby towns of Castellolí (at 2.5 km) and Òdena (at 3 km), both under the HWL influence, as well as in the villages of Jorba (at 11 km) and Copons (at 14 km from the landfill), which were considered as background/control area. In Copons, a town unaffected by the traffic of the main highway, only soil samples were collected. During the four sampling campaigns whose results are here presented (2015-2018), no rainfall was recorded for the previous week or during the sampling. The mean temperature was between 22.4 and 26.9 °C, with minimum and maximum values ranging 1.2-14.7 °C and 33.3-40.1 °C. Prevailing winds in the area typically blow from south-east.

Sampling characteristics were previously described (Rovira et al., 2012). In brief, soil samples were taken from the upper 5 cm of ground. Each sample (500 g, approximately)

consisted of four subsamples collected in an area of 10 m^2. Once in the laboratory, the samples were dried at room temperature. Then, they went through a sieve of 2 mm of diameter in order to homogenize the size of the particles. Air samples were collected using high-volume active samplers (TE-1000 PUF for PCDD/Fs and TE-6070DV for PM_{10}, both from Tisch Environmental, Cleveland, OH, USA). Sampled volumes of air were 600 m^3 for PCDD/Fs and 1600 m^3 for PM_{10}, which were obtained after sampling for 48 h, for PCDD/Fs, and for 24 h, for trace elements. Samples were properly stored in a cold dry place, or in amber bottles, at -20ºC until trace elements or PCDD/Fs analysis, respectively, were carried out.

2.2. Analytical methods

The analytical methods were previously reported (Nadal et al., 2016). Briefly, the levels of As, Cd, Cr, Hg, Ni and Pb were determined in air and soil samples by inductively coupled plasma spectrometry (ICP-MS). Previously, soil samples were digested with HNO_3 (65 % Suprapur, E. Merck, Darmstadt, Germany) in a hot block at 103ºC. Regarding air samples, four replicates of an eighth part (6.3 cm^2) of each filter were digested with HNO_3 in a hot block at 103ºC. For the analysis of both matrices, soil and air, blank and control samples, as well as reference materials, were used to check the accuracy of the instrumental methods. Recovery rates were between 92% and 105% for soils, and between 88% and 107% for air samples.

PCDD/F concentrations in the environmental samples were determined by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS),

following the German VDI 3499 method (Mari et al., 2018). Prior to extraction, $^{13}C_{12}$-PCDD/F congeners were spiked as recovery internal standards to detect any potential loss during the process. Samples were extracted with toluene by accelerated solvent extraction (ASE). The extract was subsequently subjected to an acid/base clean-up procedure on micro columns of silica gel and alumina. The final extract was again spiked with isotopic labelled internal standards, being then analysed by HRGC-HRMS. Recoveries needed Toxic equivalency factors from the World Health Organization (WHO-TEFs) were used to calculate the total concentrations in toxic equivalents (WHO-TEQ) for PCDD/Fs (Van den Berg et al., 2006).

2.3. Human health risks

The concentrations of PCDD/Fs and trace elements in soils and air were used to estimate human exposure and health risks at the different sampling points inside/around the HWL. Three routes of exposure were taken into account: dust and soil ingestion, dermal contact with soil and dust, and air inhalation. Calculation methods have been previously described (Nadal et al., 2016).

2.4. Data analysis

Concentrations below the detection limit (DL) were assumed to be one-half of that DL (ND = ½ DL). Statistical analysis of the data was performed using the statistical software package SPSS Statistics v.25.0. To evaluate significant differences between groups, the

Levene's test was applied to verify the equality of variances. Furthermore, ANOVA or Kruskal–Wallis tests were executed for normally or non-normally distributed data, respectively.

3. Results and discussion

3.1. Metal concentrations in air and soil

The concentrations of trace elements and PCDD/Fs in soil samples collected in 2016 and 2018 inside and around the HWL of Castellolí, are summarized in Table 2. In agreement with previous findings (Mari et al., 2009; Nadal et al., 2016; Rovira et al., 2012), the elements with the highest concentrations were Cr and Pb. In 2016, Cr showed the highest concentration, ranging between 5.00 and 18.4 mg/kg, followed by Pb, whose values ranged between 2.93 and 17.3 mg/kg. However, in 2018, the element showing the highest levels was Pb (range: 5.99-64.4 mg/kg), which was followed by Cr (range: 5.39-15.3 mg/kg). In contrast, Hg levels could be only detected (DL: 0.01 mg/kg) inside the HWL, with levels of 0.03 and 0.07 mg/kg in 2016 and 2018, respectively. Arsenic ranged from 1.49 to 5.66 mg/kg in 2016, and from 0.43 to 5.97 mg/kg in 2018, while Cd levels were between 0.04 and 0.26 mg/kg in 2016, and between 0.04 and 0.24 mg/kg in 2018. Finally, Ni levels were between 2.80 and 12.0 mg/kg in 2016, and between 3.04 and 10.6 mg/kg in 2018. In general terms, the highest trace elements levels were found inside the HWL. Statistically significant differences ($p<0.05$) were noticed in the levels of Cd, Cr, Hg and Ni, when comparing the values inside the HWL and those from the rest of

184 sampling points (Castellolí, Òdena, Jorba and Copons). According to their proximity to
185 the HWL, the sampling points were classified into 2 groups: those within the potentially
186 affected area (Castellolí and Òdena) and those located in an unaffected area (Jorba and
187 Copons). In the period 2015-2018, significant differences ($p<0.05$) were observed for Cd,
188 Cr, Hg, and Pb levels between the samples collected in the HWL and those in the rest of
189 sampling points, either affected or not by the HWL emissions. No significant differences
190 ($p>0.05$) were noticed between affected and unaffected zones. However, taking into
191 account our previous sampling campaigns (between 2007 and 2018) around the HWL of
192 Castellolí (Table 1S, Fig. 1S), significant differences ($p<0.01$) were found between the
193 samples collected inside the HWL and those form the outskirts for most elements (As,
194 Cd, Cr, Ni and Pb). These results clearly point out a low long-term impact of the facility
195 on the surrounding areas. No significant ($p>0.05$) temporal trend between 2007 and
196 2018 was observed, with levels fluctuating through time. Considering all the sampling
197 campaigns (2007-2018), significant positive correlations were found for samples
198 collected inside the HWL, for the following pairs of elements: As-Cd (0.824; $p<0.01$), As-
199 Ni (0.898; $p<0.01$) and As-Pb (0.719; $p<0.05$); Cd-Ni (0.915; $p<0.01$) and Cd-Pb (0.790;
200 $p<0.05$); Cr-Hg (0.907; $p<0.01$); and finally Ni-Pb (0.814; $p<0.05$). In contrast, no
201 significant Pearson correlations in the concentrations of trace elements in soils were
202 found, irrespective of the closeness to the HWL, with the only exception of Cd and Cr
203 (0.756; $p<0.05$) in the unaffected area.

204 In Catalonia, the Catalan Waste Agency has established generic levels of reference
205 for soils in order to protect human health (Agència de residus de Catalunya, 2009). The
206 most restrictive category, which corresponds to soils not intended for urban or industrial

purposes, sets these thresholds: 30 mg/kg for As, 2.5 mg/kg for Cd, 400 mg/kg for Cr(III), 1 mg/kg for Cr (IV), 2 mg/kg for Hg, 45 mg/kg for Ni, and 60 mg/kg for Pb. Comparing these limits with the concentrations found in the last two campaigns (2016 and 2018), none of the analysed trace elements exceeded the most restrictive level, excepting Pb inside the HWL in 2018. Notwithstanding, it must be noted that Pb did not exceed the limit value established for industrial soils (550 mg/kg), which is the corresponding category to which values inside the HWL should be compared. The concentrations in air samples during the four campaigns, from 2015 to 2018, of the trace elements associated to PM_{10} are summarized in Table 3. Lead and Ni showed the highest levels in each sampling campaign, followed by Cr, As and Cd. Traces of Hg were found in soils inside the HWL in all the sampling campaigns, while only in the first survey (2015) this element was detected in samples collected outside the plant. In general, the highest levels of As, Cd, Hg, and Pb were usually found inside the HWL, in all the campaigns (2015-2018).

Significant differences ($p<0.05$) were noted for the air levels of Cd, Hg and Pb, when comparing the levels in samples collected inside and outside the HWL, and independently on the closeness to the facility. In turn, significant differences in the levels of Cr ($p<0.05$) were noticed between the samples within the HWL and those in affected sites, being the trend very similar to that observed in soils. Considering only sampling points outside the HWL, no differences of metal concentrations were observed ($p>0.05$) between affected (Castellolí and Òdena) and unaffected (Jorba) sites. When assessing the whole period (2007-2018), (Table 2S, Fig. 2S), the levels of Cd and Pb were significantly ($p<0.01$) higher inside the HWL than outside the facility, either close to or far away the facility. In turn, the mean level of Cr in the air of the affected area (0.043

ng/m^3) was lower ($p<0.05$) than that in the unaffected area (0.037 ng/m^3). As above commented for soils, the current results indicate that, despite relatively higher levels of trace elements were detected in air within the HWL, no impact was registered in nearby areas. Moreover, similar air levels were observed between the theoretically affected zones and the control/unaffected areas. The European legislation (2008/50/EC and 2004/107/EC) has set annual average limits of 6, 5, 20 and 500 ng/m^3 for As, Cd, Ni and Pb, respectively (European Union Parliament and Council, 2008, 2005). The daily values obtained in the present study are well below the threshold values. However, it must be reminded that current results are not given as annual average means, but as daily values. In any case, no statistically significant ($p>0.05$) correlations were found in the concentrations of trace elements when comparing data regarding air and soil, for any sampling area (HWL, affected or unaffected zones).

3.2. PCDD/F concentrations in air and soil

The concentrations of PCDD/Fs in soils in the two campaigns conducted between 2015 and 2018 inside and around the HWL of Castellolí are shown in Table 2. Total PCDD/F levels in soils were similar in both campaigns: between 0.08 and 0.80 ng WHO-TEQ/kg in 2016, and between 0.08 and 0.54 ng WHO-TEQ/kg in 2018. As for trace elements in soils, the maximum PCDD/F concentration was found in soils within the HWL. In turn, PCDD/F values outside the facility were similar irrespective of the distance to the HWL and notably lower than those collected inside (ranges: 0.08-0.12 ng WHO-TEQ/kg in 2016, and 0.08-0.13 ng WHO-TEQ/kg in 2018). Nowadays, at Catalan, Spanish

253 or European Union level, there are not soil guidance levels for PCDD/Fs. However, some
254 specific European countries, such as Austria and Finland, have assumed a maximum
255 acceptable concentration of 10 ng I-TEQ/kg for all uses of soils (US Environmental
256 Protection Agency, 2009). In Sweden, a limit for industrial soil has been set at 200 ng
257 TEQ/kg (US Environmental Protection Agency, 2009). Based on these limit values, levels
258 inside and around the HWL in both sampling campaigns are clearly under these limits.
259 According to the PCDD/F congener profile (Fig. 1), OCDD showed the highest
260 contribution to the total concentration, followed by 1,2,3,4,6,7,8-HpCDD, in the villages
261 of Jorba, Òdena and in Castellolí (in 2018), but followed by OCDF in Castellolí (in 2016)
262 and Copons. Regarding the samples collected inside HWL, the highest PCDD/F levels
263 corresponded to OCDF followed by the OCDD. No significant ($p<0.05$) differences were
264 observed between the 2016 and 2018 campaigns for any PCDD/F congener, except for
265 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,7,8,9-HpCDF. Significant differences
266 ($p<0.05$) between samples inside the HWL and those collected outside were only
267 detected for 1,2,3,7,8,9-HxCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-
268 HxCDF. Thus, congeners showed different profiles between samples from the HWL and
269 the remaining sampling points, which presented a similar profile between them, with
270 the exception of Copons (Fig. 1). However, considering all sampling campaigns (2007-
271 2018), significantly ($p<0.01$) higher total PCDD/F levels were found in soils collected
272 inside the HWL (5.03 ng WHO-TEQ/kg) than outside, either from affected or unaffected
273 areas (0.23 and 0.18 ng WHO-TEQ/kg, respectively).
274 Inside the HWL, the levels of PCDD/Fs in soils have been decreasing since 2007,
275 excepting only those registered in 2013 (Table 3S). Actually, PCDD/F soil concentrations

276 in the last two campaigns (2016 and 2018) were significantly lower ($p<0.05$) than those
277 found in the baseline survey (2007). Significant positive Pearson correlations were
278 observed in the campaigns conducted between 2007 and 2018 for the following pairs of
279 chemicals: PCDD/Fs-Cd (0.999; $p<0.01$), PCDD/Fs-Cr (0.904; $p<0.05$), PCDD/Fs-Hg (0.990;
280 $p<0.01$), and PCDD/Fs-Pb (0.993; $p<0.01$) inside the HWL, and PCDD/Fs-Pb (0.848;
281 $p<0.01$) in the affected area (Fig. 3S).

282 Table 3 summarizes the total PCDD/Fs air levels collected in the four campaigns
283 between 2015 and 2018. Total PCDD/Fs ranged from 2.50 to 3.73 fg WHO-TEQ/m^3 in
284 2015, from 1.30 to 8.00 fg WHO-TEQ/m^3 in 2016, from 1.40 to 6.70 fg WHO-TEQ/m^3 in
285 2017, and from 2.10 to 4.90 fg WHO-TEQ/m^3 in 2018. The concentrations of PCDD/Fs in
286 air showed a great temporal and spatial variability. However, no significant ($p>0.05$)
287 differences were observed between sampling campaigns (from 2015 to 2018), or
288 between samples collected inside and outside the HWL. This clearly points out that there
289 may exist other emission sources of PCDD/Fs (i.e., traffic or biomass combustion) in the
290 area under evaluation and/or the HWL has a low influence on the surrounding areas,
291 considering the levels of PCDD/Fs in air.

292 The PCDD/F congener profiles in air samples collected in the four sampling point
293 between 2015 and 2018 are depicted in Fig. 2. In general, two different profiles were
294 observed: one with high contributions of OCDF (55-80%), in samples collected inside
295 the HWL, and another one, with contributions of OCDF (30%), and 1,2,3,4,7,8,9-HpCDF
296 (5%) and OCDD (25-35%), corresponding to samples collected outside the facility.

297 Considering the air levels of PCDD/Fs obtained in all the campaigns carried out to
298 date (Table 4S and Fig. 4S), a decreasing trend can be observed. However, in some

sampling points (inside HWL or Castellolí), such as those collected in 2018, PCDD/F concentrations were slightly higher than those found in the previous campaign (2017). PCDD/Fs air levels ranged from 2.30 to 22.1 fg WHO-TEQ/m^3 inside the HWL (in 2014 and 2007, respectively), while in Castellolí a notable decreased was observed between the first and last studies (371 and 2 fg WHO-TEQ/m^3 in 2007 and 2018, respectively). In Òdena and Jorba, the concentrations were lower than those found in other sampling points in 2007, both around 4 fg WHO-TEQ/m^3, while in the last campaign the levels were reduced around 50% (around 2 fg WHO-TEQ/m^3). As above-mentioned, the fact that higher concentrations were detected outside the facility, even in sampling points unaffected by the HWL indicates: a) the presence of other emission sources, such as traffic or other combustion processes (biomass), and b) the comparatively very low impact of the HWL as a potential emission source of PCDD/Fs.

A high positive correlation was found between total PCDD/Fs levels in air and soil inside the HWL (0.895). The activity inside the landfill, including earth movements for opening and sealing sections, wind or truck transit, makes easier the resuspension from soils to air. However, a similar trend was not observed for any of the trace elements analyzed in this study.

3.3. Environmental monitoring around other HWLs and waste management facilities

In the scientific literature, there are some reports of studies carried out around landfills. The methodological approach may vary notably among the different studies, depending on their objectives or the respective hypotheses. In addition, various

chemicals and matrices have been considered. Thus, studies can focus on analysing only a single pollutant, such as the study performed by Han et al. (2017), who determined Hg was determined in air, leachates, effluent water and soil. In Italy, Finardi et al. (2017) investigated the emission of volatile organic compounds in a landfill, while in Japan, Yamamoto et al. (2001) analysed bisphenol A in leachates from ten waste landfill sites. Other studies have focused on chemical mixtures, being analysed different sets of compounds, including metals and isotopes in freshwater sediments near a landfill in Brazil (Barbieri et al., 2014), organo compounds of tin, Pb and Hg in gases and leachates from German municipal and hazardous waste landfills (Ilgen et al., 2008), or even BTEX, PCBs, PAHs, among others, in air and leachates of a German HWL (Gade et al., 1996).

Other studies published in the scientific literature own a similar design to that used in the current investigation. In the Czech Republic, a number of trace elements was analyzed in soil and vegetation samples collected around a former deposit of galvanic sludge (Száková et al., 2016). In turn, trace elements were analyzed in soils of a hazardous waste disposal site located in India (Tomar et al., 2011). In the current study, Cd, Ni and Pb levels in soil samples were similar to those reported in the Czech Republic landfill (0.18 mg/kg, 10.1 mg/kg and 17.5 mg/kg respectively). Contrastingly, Ni levels in India (65 mg/kg) were much higher than those found in Catalonia (5.60 mg/kg) and the Czech Republic (10.1 mg/kg). In turn, the concentrations of Cr were notably higher in soils near the HWL of Castellolí than those reported in the Czech Republic (0.09 mg/kg) and India (5 mg/kg). It would be probably related to the fact that the facility was previously used as a landfill of Cr-derivative products, or even to the natural occurrence of Cr found in Catalan soils (Bech et al., 2008).

345 Table 4 shows the concentrations of metals and PCDD/Fs around various cements
346 plants and waste incinerators located in Catalonia (Spain). The concentrations of metals
347 and PCDD/Fs in air and soils found around the HWL of Castellolí fell in the low part of
348 the range, compared to data from other waste management facilities (waste
349 incinerators and cement plants). In general, similar values were found around facilities
350 located in rural areas (Rovira et al., 2018), while higher concentrations than those of the
351 current study were observed in studies performed in urban and industrial zones
352 (Domingo et al., 2015, 2017).
353
354 *3.4. Human health risks*
355
356 The human exposure to various trace elements and PCDD/Fs through air inhalation,
357 dust and soil ingestion, and dermal contact with soil and dust inside and around the HWL
358 is summarized in Table 5. For both groups of chemicals (trace elements and PCDD/Fs),
359 the highest exposure occurred inside the HWL. The main pathway for As was dermal
360 contact and ingestion with dust and soils, with mean contributions of 51% and 48%,
361 respectively. Air inhalation was a minor route, contributing with approximately 3% for
362 all elements, excepting Cd and Pb, for which it was the second route of exposure, with
363 contributions of 15% and 21%, respectively. Finally, for PCDD/Fs, the main routes were
364 dermal absorption (39%) and soil ingestion (36%) inside the HWL, which is due to their
365 high levels in soils, while air inhalation was the main route of exposure outside the HWL,
366 with contributions ranging from 59%, in Òdena, to 68%, in Jorba.

The Hazardous Quotient (HQ) is defined as the ratio between exposure and reference dose (US Environmental Protection Agency, 2001). HQs are used to assess non-carcinogenic risks. In all campaigns and sampling points of our surveillance program, HQs were below the threshold value, which is set at 1. The highest HQs (around 0.2) were found inside the HWL, because of the highest pollutant levels.

Carcinogenic risks were calculated for the three routes: soil ingestion, dermal contact and air inhalation for As, Cr (VI) and PCDD/Fs. However, for Cd and Ni, the carcinogenic risks were only calculated for air inhalation because a carcinogenicity potential for ingestion and dermal contact have not been established yet. The carcinogenic risks for As, Cd, Cr(VI), Ni and PCDD/Fs, for the adult population living near the HWL (2015-2018 campaigns) are depicted in Fig. 3. Only Cr(VI) inside the HWL exceeded the maximum acceptable risk, set at 10^{-5} according to the national legislation (Ministerio de Educación y Ciencia, 2007). However, international standards also consider as acceptable values ranging between 10^{-6} and 10^{-4} (US Environmental Protection Agency, 2016). It should take into account that for calculations, we assumed that Cr(VI) levels were a sixth part of total Cr, while all the As was exclusively in the inorganic form.

4. Conclusions

The concentrations of As, Cd, Cr, Ni and Pb, as well as those of PCDD/Fs, were determined in air and soil samples collected inside and around the HWL of Castellolí (Catalonia, NE Spain) during the period 2015-2018, in four different annual campaigns.

The concentrations were usually higher inside than outside the HWL. However, no differences were observed between areas potentially affected by the HWL and those considered as control areas. The results of the environmental monitoring campaigns here presented (2015-2018) were similar to those obtained in previous surveys (2007-2014). Although both trace elements and PCDD/Fs showed higher levels inside the HWL, based on the current results, it is obvious that the landfill is not an important source of emissions of trace elements and PCDD/Fs for the surrounding zones. Different PCDD/F congener profiles were observed between inside and outside HWL, in both, air and soil samples. Finally, the potential human health risks due to exposure to trace elements and PCDD/Fs for the population living near the HWL are acceptable, according to national and international standards.

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Table 1

Summary of the samples collected and chemicals analyzed in each campaigns of the monitoring program conducted around the HWL of Castellolí from 2007 to 2018.

Year[a]	Matrix		Reference
	Air	Soil	
2007	PCDDs/Fs and elements*	PCDD/Fs and elements*	Mari et al., 2009
2009	PCDDs/Fs and elements*	Trace Elements*	Rovira et al., 2012
2010	PCDDs/Fs and elements*	PCDD/Fs and elements*	
2011	PCDDs/Fs and elements*	Elements*	Nadal et al., 2016
2012	PCDDs/Fs and elements*	Elements*	
2013	-	PCDD/Fs and elements*	
2014	PCDDs/Fs and elements*	PCDD/Fs and elements*	
2015	PCDDs/Fs and elements*	-	Present study
2016	PCDDs/Fs and elements*	PCDD/Fs and elements*	
2017	PCDDs/Fs and elements*	-	
2018	PCDDs/Fs and elements*	PCDD/Fs and elements*	

* Elements include As, Cd, Cr, Hg, Ni and Pb. [a]All sampling campaigns were performed in June or July, excepting in 2007, when two seasonal campaigns (July and December) were carried out.

Table 2

Concentrations of trace elements (in mg/kg) and PCDD/Fs (in ng WHO-TEQ/kg) in samples of soils collected inside and around the HWL of Castellolí in 2016 and 2018.

Campaign		HWL[a]	Castellolí	Òdena	Jorba	Copons
2016	As	5.66	1.49	2.40	2.34	2.35
	Cd	0.26	0.12	0.18	0.04	0.07
	Cr	18.4	8.94	5.00	9.54	8.29
	Hg	0.03	<0.01	<0.01	<0.01	<0.01
	Ni	12.0	3.61	2.80	4.44	4.00
	Pb	17.3	6.79	2.93	8.36	6.60
	PCDD/Fs	0.80	0.12	0.09	0.11	0.08
2018	As	4.11	1.68	0.43	5.97	2.70
	Cd	0.24	0.10	0.04	0.07	0.07
	Cr	15.3	7.91	9.52	9.96	5.39
	Hg	0.07	<0.01	<0.01	<0.01	<0.01
	Ni	10.6	3.44	3.04	8.79	3.34
	Pb	64.4	9.91	6.13	7.92	5.99
	PCDD/Fs	0.54	0.11	0.13	0.09	0.08

[a] Mean values from 2 point samples collected inside the HWL.

Table 3

Concentrations of trace elements (in ng/m^3) and PCDD/Fs (fg WHO-TEQ/m^3) in air samples collected inside and around the HWL of Castellolí between 2015 and 2018.

Campaign		HWL[a]	Castellolí	Òdena	Jorba
2015	As	0.29	0.35	0.25	0.43
	Cd	0.15	0.07	0.07	0.09
	Cr	2.19	<0.10	<0.10	0.71
	Hg	0.04	0.03	0.02	0.02
	Ni	3.55	3.57	4.71	6.26
	Pb	5.80	3.11	2.20	3.92
	PCDD/Fs	3.62	2.50	3.72	3.73
2016	As	0.66	0.10	0.26	0.28
	Cd	0.49	0.06	0.10	0.04
	Cr	4.25	<0.10	0.62	4.69
	Hg	0.09	<0.05	<0.05	<0.05
	Ni	6.26	1.07	2.29	1.08
	Pb	14.2	1.59	4.18	1.32
	PCDD/Fs	1.30	4.60	2.40	8.00
2017	As	0.30	0.20	0.22	0.18
	Cd	0.17	<0.003	0.05	<0.003
	Cr	2.93	0.70	0.64	0.50
	Hg	0.06	<0.01	<0.01	<0.01
	Ni	3.23	2.91	7.13	1.76
	Pb	5.92	1.28	3.05	1.17
	PCDD/Fs	3.30	1.40	6.70	3.70
2018	As	0.55	0.18	0.19	0.28
	Cd	0.25	0.10	0.05	0.05
	Cr	5.83	1.09	1.13	2.45
	Hg	0.20	<0.06	<0.06	<0.06
	Ni	4.34	1.56	8.00	1.14
	Pb	8.16	1.40	2.39	1.85
	PCDD/Fs	4.90	2.20	2.10	3.50

[a] Mean values from 2 point samples collected inside the HWL.

Table 4. Concentrations of metals (mg/kg and ng/m^3) and PCDD/Fs (ng WHO-TEQ/kg and fg WHO-TEQ/m^3) in soils and in air in various studies carried out around industrial facilities in Catalonia, Spain.

	Soil Mean (min-max)	Air Mean (min-max)	Background-Studied facility	Reference
As	2.91 (0.43-5.97)	0.29 (0.10-0.66)	Rural-HWL	Present study
	13.5 (7.63-26.5)	0.71 (0.35-1.37)	Urban-cement plant	Mari et al., 2017
	7.70 (4.69-10.7)	0.80 (0.37-1.22)	Urban-cement plant	Rovira et al., 2014
	5.52 (5.14-5.90)	0.39 (0.36-0.42)	Industrial-Waste incinerator	Vilavert et al., 2015
	1.06 (0.65-1.85)	0.39 (0.24-0.78)	Urban-Waste incinerator	Rovira et al., 2015b
	5.13 (3.60-8.20)	0.78 (0.20-1.70)	Rural-cement plant	Rovira et al., 2015a
	8.10 (7.65-8.55)	0.22 (0.19-0.24)	Rural-cement plant	Mari et al., 2018
Cd	0.12 (0.04-0.26)	0.11 (0.04-0.49)	Rural-HWL	Present study
	0.25 (0.22-0.34)	0.19 (0.16-0.24)	Urban-cement plant	Mari et al., 2017
	0.22 (0.14-0.34)	0.34 (0.12-0.55)	Urban-cement plant	Rovira et al., 2014
	0.19 (0.18-0.19)	0.10 (0.08-0.11)	Industrial-Waste incinerator	Vilavert et al., 2015
	0.06 (ND-0.09)	0.19 (0.10-0.45)	Urban-Waste incinerator	Rovira et al., 2015b
	0.18 (0.10-0.20)	0.10 (ND-0.30)	Rural-cement plant	Rovira et al., 2015a
	0.24 (0.23-0.24)	0.03 (ND-0.05)	Rural-cement plant	Mari et al., 2018
Cr	9.83 (5.0-18.4)	1.74 (0.50-5.83)	Rural-HWL	Present study
	21.9 (16.8-27.3)	1.76 (0.97-4.20)	Urban-cement plant	Mari et al., 2017
	18.6 (15.9-21.2)	2.03 (0.36-3.69)	Urban-cement plant	Rovira et al., 2014
	16.7 (15.5-17.8)	2.83 (ND-2.83)	Industrial-Waste incinerator	Vilavert et al., 2015
	7.16 (2.62-10.3)	6.75 (ND-9.56)	Urban-Waste incinerator	Rovira et al., 2015b
	10.9 (7.70-13.9)	5.22 (ND-9.90)	Rural-cement plant	Rovira et al., 2015a
	19.3 (17.9-20.7)	1.79 (0.76-2.82)	Rural-cement plant	Mari et al., 2018
Ni	5.61 (2.80-12.0)	3.72 (1.07-8.00)	Rural-HWL	Present study
	24.9 (11.3-55.9)	2.86 (2.09-3.86)	Urban-cement plant	Mari et al., 2017
	11.7 (8.97-25.7)	3.20 (3.10-3.29)	Urban-cement plant	Rovira et al., 2014
	8.28 (7.39-9.16)	3.83 (3.51-4.14)	Industrial-Waste incinerator	Vilavert et al., 2015
	2.42 (1.15-3.43)	1.53 (1.08-2.43)	Urban-Waste incinerator	Rovira et al., 2015b
	9.80 (7.60-13.9)	2.42 (ND-4.30)	Rural-cement plant	Rovira et al., 2015a
	13.4 (11.5-15.2)	2.35 (1.23-3.47)	Rural-cement plant	Mari et al., 2018
Pb	13.6 (2.93-64.4)	3.85 (1.17-14.2)	Rural-HWL	Present study
	27.9 (16.1-37.5)	7.82 (5.70-10.8)	Urban-cement plant	Mari et al., 2017
	20.1 (15.0-25.1)	19.1 (5.79-32.3)	Urban-cement plant	Rovira et al., 2014
	37.0 (34.2-39.5)	4.89 (4.40-5.38)	Industrial-Waste incinerator	Vilavert et al., 2015
	9.74 (3.18-20.4)	5.38 (3.84-5.20)	Urban-Waste incinerator	Rovira et al., 2015b
	11.5 (7.50-16.4)	5.40 (0.70-7.0)	Rural-cement plant	Rovira et al., 2015a
	28.9 (27.9-29.8)	2.72 (1.86-3.57)	Rural-cement plant	Mari et al., 2018
PCDD/Fs	0.21 (0.08-0.80)	3.95 (1.30-8.0)	Rural-HWL	Present study
	1.14 (0.29-2.66)	7.75 (5.0-10.0)	Urban-cement plant	Mari et al., 2017
	0.39 (0.37-0.41)	37.5 (18.0-57.0)	Urban-cement plant	Rovira et al., 2014
	0.61 (0.58-0.63)	6.83 (3.56-10.1)	Industrial-Waste incinerator	Vilavert et al., 2015
	0.27 (0.13-0.43)	14.5 (6.0-18.0)	Urban-Waste incinerator	Rovira et al., 2015b
	0.22 (0.20-0.30)	8.05 (4.70-8.6)	Rural-cement plant	Rovira et al., 2015a
	0.54 (0.36-0.72)	6.0 (4.0-8.0)	Rural-cement plant	Mari et al., 2018

Table 5. Exposure to trace elements (As, Cd, Cr, Hg, Ni and Pb) (mg/(kg·day)) and PCDD/Fs (ng WHO-TEQ/(kg·day)) inside and around the HWL of Castellolí from 2015 to 2018.

	Pathway	HWL	Castellolí	Òdena	Jorba	Copons
As	Soil ingestion	$7.92 \cdot 10^{-6}$	$1.99 \cdot 10^{-6}$	$2.78 \cdot 10^{-6}$	$4.55 \cdot 10^{-6}$	$2.53 \cdot 10^{-6}$
	Dermal contact	$8.44 \cdot 10^{-6}$	$2.12 \cdot 10^{-6}$	$2.97 \cdot 10^{-6}$	$4.85 \cdot 10^{-6}$	$2.69 \cdot 10^{-6}$
	Inhalation	$1.03 \cdot 10^{-7}$	$4.31 \cdot 10^{-8}$	$4.80 \cdot 10^{-8}$	$6.81 \cdot 10^{-8}$	NC
	TOTAL	$1.65 \cdot 10^{-5}$	$4.15 \cdot 10^{-6}$	$5.80 \cdot 10^{-6}$	$9.47 \cdot 10^{-6}$	$5.22 \cdot 10^{-6}$
Cd	Soil ingestion	$8.15 \cdot 10^{-7}$	$1.66 \cdot 10^{-7}$	$1.89 \cdot 10^{-7}$	$8.06 \cdot 10^{-8}$	$9.85 \cdot 10^{-8}$
	Dermal contact	$2.89 \cdot 10^{-8}$	$5.89 \cdot 10^{-9}$	$6.73 \cdot 10^{-9}$	$2.86 \cdot 10^{-9}$	$3.49 \cdot 10^{-9}$
	Inhalation	$6.09 \cdot 10^{-8}$	$1.59 \cdot 10^{-8}$	$1.53 \cdot 10^{-8}$	$1.23 \cdot 10^{-8}$	NC
	TOTAL	$9.05 \cdot 10^{-7}$	$1.88 \cdot 10^{-7}$	$2.11 \cdot 10^{-7}$	$9.58 \cdot 10^{-8}$	$1.02 \cdot 10^{-7}$
Cr	Soil ingestion	$3.43 \cdot 10^{-5}$	$1.31 \cdot 10^{-5}$	$1.23 \cdot 10^{-5}$	$1.63 \cdot 10^{-5}$	$1.38 \cdot 10^{-5}$
	Dermal contact	$5.42 \cdot 10^{-6}$	$2.57 \cdot 10^{-6}$	$2.25 \cdot 10^{-6}$	$3.01 \cdot 10^{-6}$	$4.89 \cdot 10^{-7}$
	Inhalation	$7.33 \cdot 10^{-7}$	$1.04 \cdot 10^{-7}$	$1.23 \cdot 10^{-7}$	$5.38 \cdot 10^{-7}$	NC
	TOTAL	$4.04 \cdot 10^{-5}$	$1.58 \cdot 10^{-5}$	$1.47 \cdot 10^{-5}$	$1.99 \cdot 10^{-5}$	$1.43 \cdot 10^{-5}$
Hg	Soil ingestion	$8.42 \cdot 10^{-8}$	NA	NA	NA	NA
	Dermal contact	$1.65 \cdot 10^{-8}$	NA	NA	NA	NA
	Inhalation	$7.76 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$	NC
	TOTAL	$1.78 \cdot 10^{-7}$	$1.10 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$	$1.10 \cdot 10^{-8}$	NA
Pb	Soil ingestion	$3.86 \cdot 10^{-5}$	$6.07 \cdot 10^{-6}$	$6.70 \cdot 10^{-6}$	$1.07 \cdot 10^{-5}$	$1.20 \cdot 10^{-5}$
	Dermal contact	$1.93 \cdot 10^{-6}$	$3.60 \cdot 10^{-7}$	$9.65 \cdot 10^{-7}$	$4.55 \cdot 10^{-7}$	$4.25 \cdot 10^{-7}$
	Inhalation	$1.68 \cdot 10^{-5}$	$5.93 \cdot 10^{-6}$	$4.35 \cdot 10^{-6}$	$9.59 \cdot 10^{-6}$	NC
	TOTAL	$5.74 \cdot 10^{-5}$	$1.24 \cdot 10^{-5}$	$1.20 \cdot 10^{-5}$	$2.08 \cdot 10^{-5}$	$1.24 \cdot 10^{-5}$
Ni	Soil ingestion	$1.91 \cdot 10^{-5}$	$3.32 \cdot 10^{-6}$	$4.08 \cdot 10^{-6}$	$5.21 \cdot 10^{-6}$	$5.47 \cdot 10^{-6}$
	Dermal contact	$9.45 \cdot 10^{-6}$	$1.63 \cdot 10^{-6}$	$1.44 \cdot 10^{-6}$	$1.34 \cdot 10^{-6}$	$1.95 \cdot 10^{-7}$
	Inhalation	$5.02 \cdot 10^{-5}$	$9.05 \cdot 10^{-6}$	$6.54 \cdot 10^{-6}$	$8.30 \cdot 10^{-6}$	NC
	TOTAL	$7.87 \cdot 10^{-5}$	$1.40 \cdot 10^{-5}$	$1.21 \cdot 10^{-5}$	$1.49 \cdot 10^{-5}$	$5.67 \cdot 10^{-6}$
PCDD/Fs	Soil ingestion	$1.44 \cdot 10^{-6}$	$1.43 \cdot 10^{-7}$	$1.02 \cdot 10^{-7}$	$1.66 \cdot 10^{-7}$	$2.68 \cdot 10^{-7}$
	Dermal contact	$1.54 \cdot 10^{-6}$	$1.53 \cdot 10^{-7}$	$1.08 \cdot 10^{-7}$	$1.76 \cdot 10^{-7}$	$2.86 \cdot 10^{-7}$
	Inhalation	$1.01 \cdot 10^{-6}$	$4.92 \cdot 10^{-7}$	$3.07 \cdot 10^{-7}$	$7.34 \cdot 10^{-7}$	NC
	TOTAL	$3.99 \cdot 10^{-6}$	$7.88 \cdot 10^{-7}$	$5.17 \cdot 10^{-7}$	$1.08 \cdot 10^{-6}$	$5.54 \cdot 10^{-7}$

NC: Not calculated because air samples were not collected.

NA: Not assessed because the levels of Hg were below the detection limits in all the campaigns

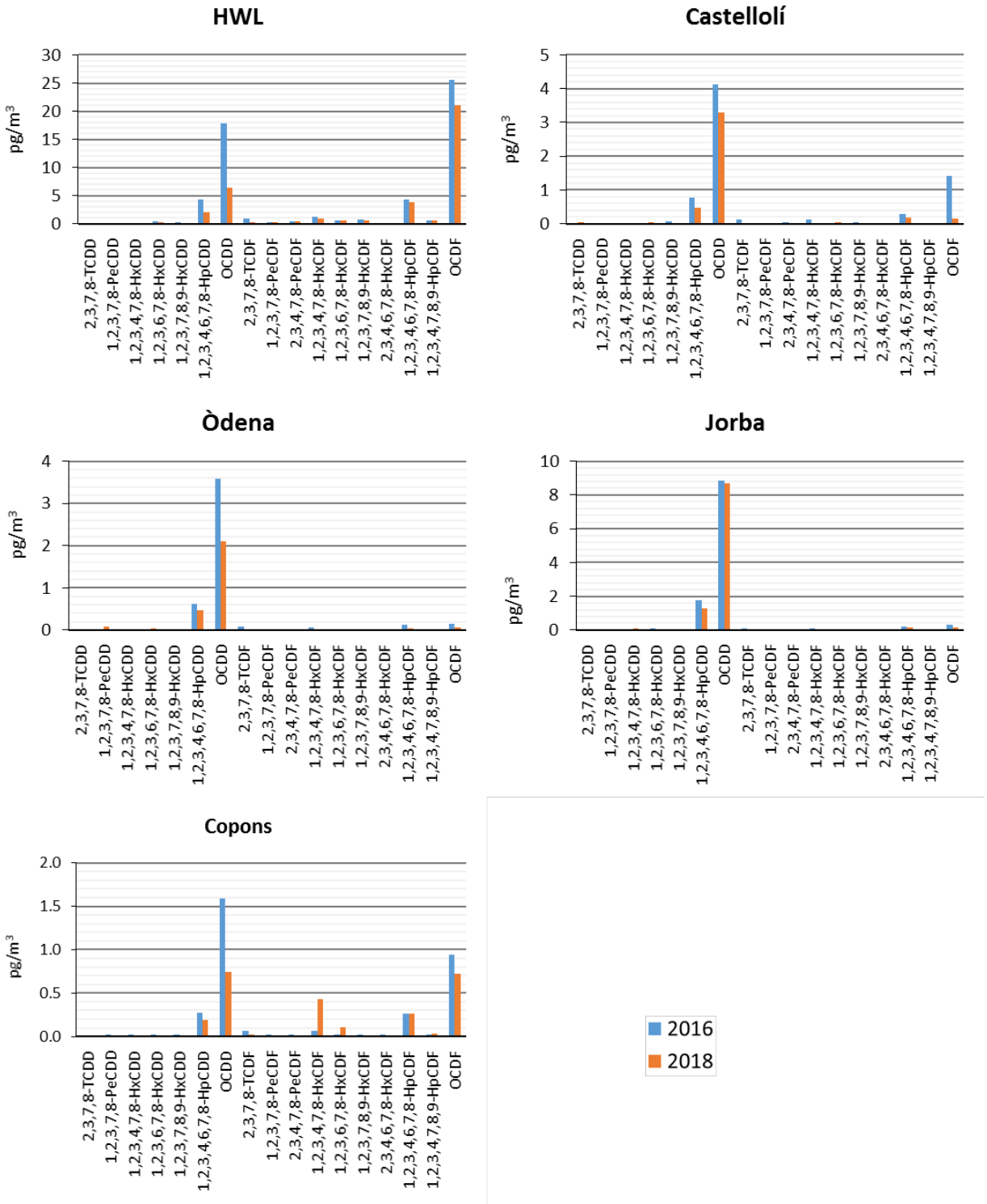

Fig. 1. PCDD/F congener profiles in soil samples collected in 2016 and 2018 inside and around the HWL of Castellolí.

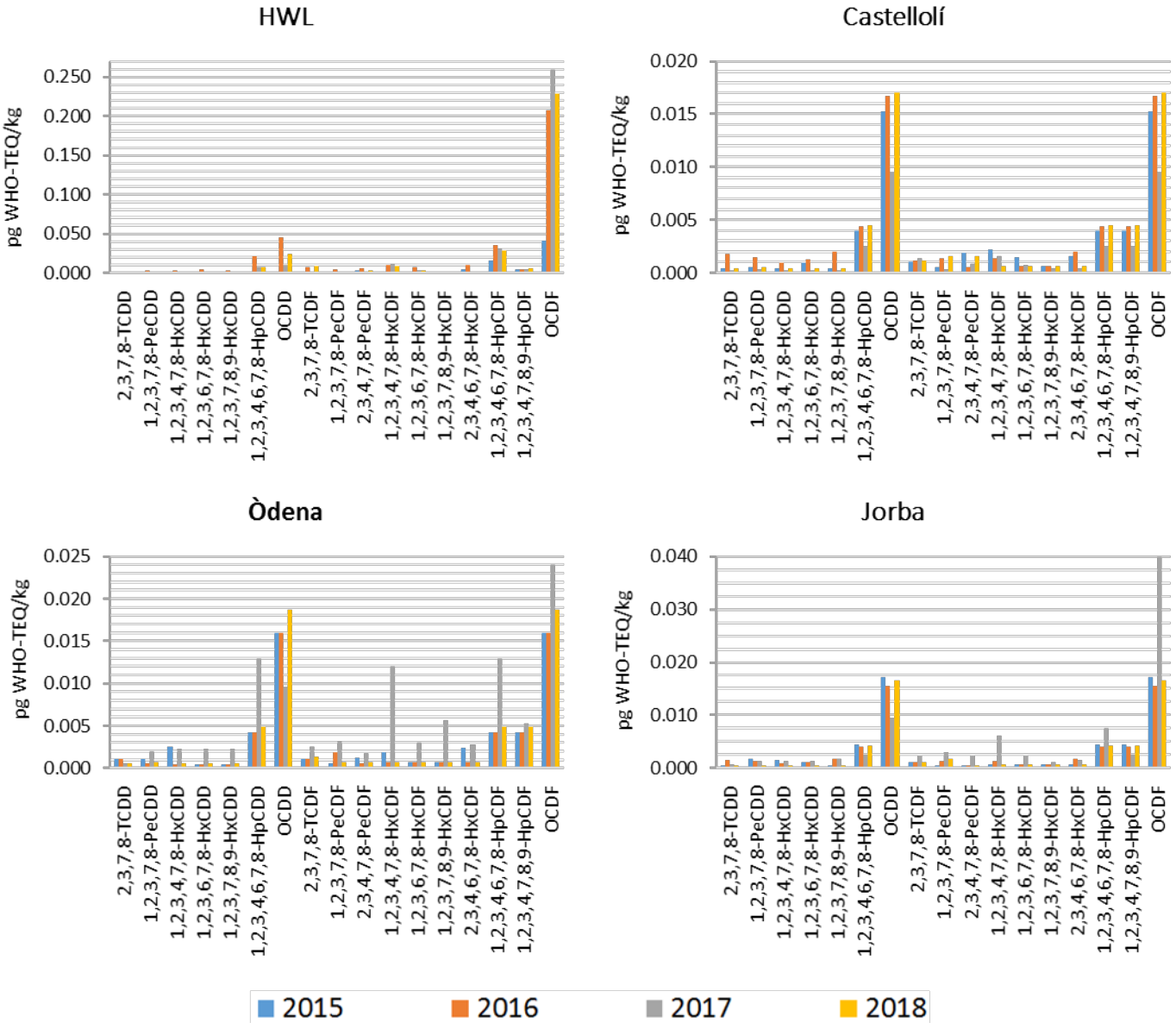

Fig. 2. PCDD/F congener profiles in air samples collected in 2015, 2016, 2017 and 2018 inside and around the HWL of Castellolí.

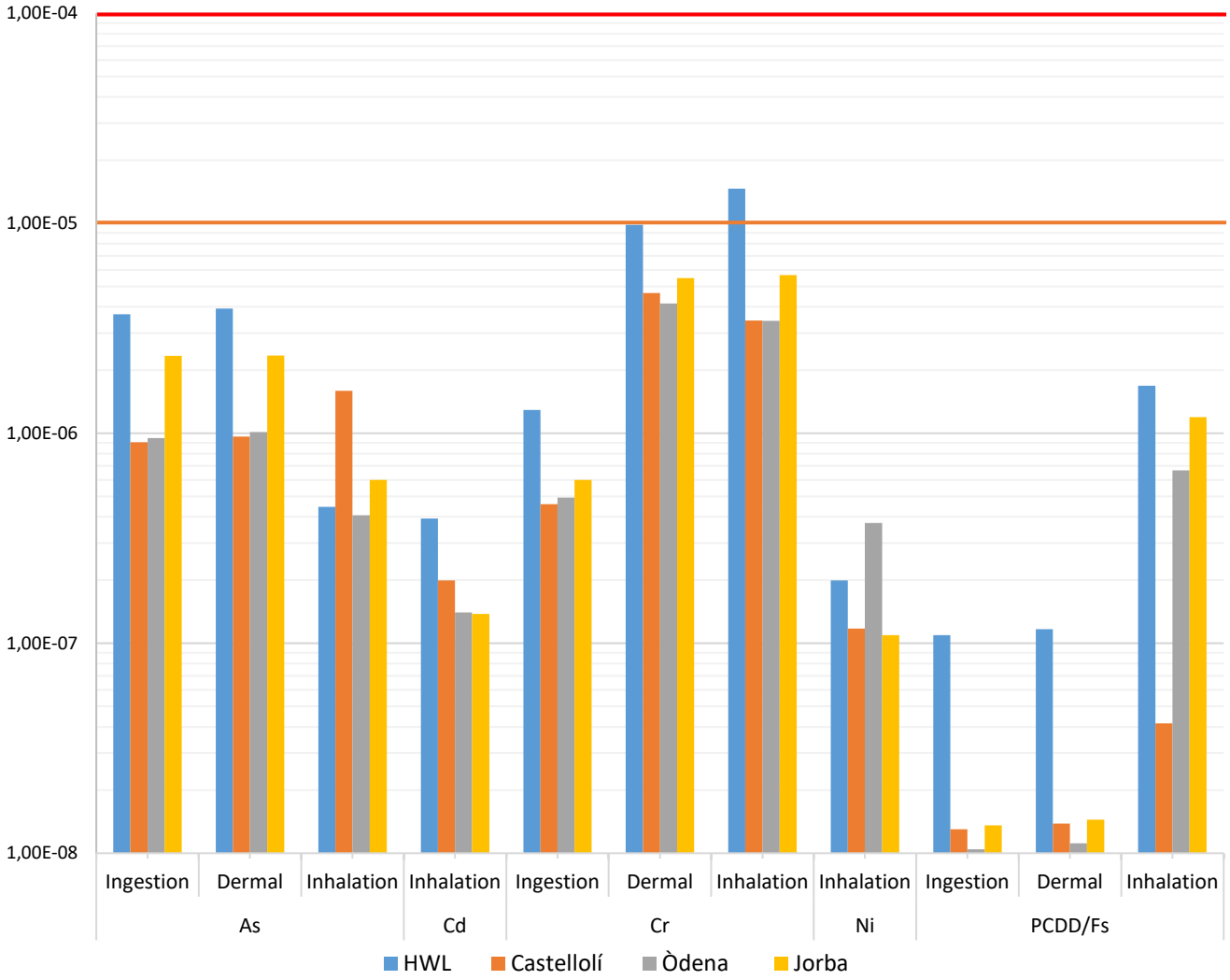

Fig. 3. Carcinogenic risks associated to exposure to As, Cd, Cr (VI), Ni and PCDD/Fs inside and around the HWL of Castellolí in the period 2015-2018.