Organochlorine pesticides air monitoring near a historical lindane production site in Spain

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HIGHLIGHTS

- High levels of HCHs and PeCB were detected at former HCH production and disposal site.
- The highest HCH levels were detected in Sardas landfill and INQUINOSA Factory sites.
- HCH levels correlated positively with temperature in all sampling points.
- Higher PeCB values were detected in Sardas landfill than in Sabiñánigo urban core.
- HCB concentrations were comparable to background levels from other locations.

GRAPHICAL ABSTRACT
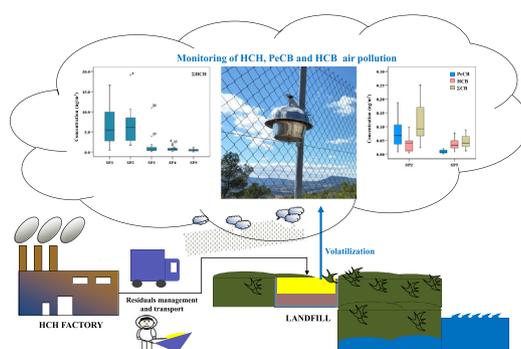
ARTICLE INFO

ABSTRACT

The landfilling and dumping of persistent organic pollutants (POPs) and other persistent hazardous chemicals, such as hexachlorocyclohexane (HCH) isomers can have significantly adverse environmental consequences and cause contamination in soil, water, and atmosphere systems. Approximately 115,000 t of HCH wastes were generated by INQUINOSA Factory located in Sabiñánigo (Aragón, Spain) from 1975 to 1992, and were mainly dumped at Bailín and Sardas landfills. Under the frame of the project plan approved by the Government of Aragón, remediation and containment measures were implemented at the derelict production facility and landfill sites. To protect and assess the local environment, the concentrations of HCH isomers, pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) in air were periodically monitored in the Sardas landfills and surroundings by passive sampling devices. The influence of meteorological parameters was evaluated, showing positive correlations between temperature and HCH and HCB concentrations. The highest HCH levels were detected in Sardas landfill and INQUINOSA Factory sites. PeCB values were statistically higher in Sardas landfill than in Sabiñánigo urban core, nevertheless, HCB concentrations were similar in both sampling points. Statistically positive correlations were found among HCH isomers in all sampling points, showing a major common source. The chlorobenzenes also correlated positively with each other. The α-/γ-HCH ratios were calculated (1.46 ± 1.25; mean ± S.D.), corroborating that concentrations detected were mainly originated from the historical production, storage and waste disposal of technical HCH.

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1. Introduction

Hexachlorocyclohexane isomers (α-, β-, γ-, δ-, ε-HCH), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) are pollutants of great concern because of their persistence, toxicity and widespread distribution in the environment (Barber et al., 2005; Bailey et al., 2009; Vijgen et al., 2011; Saadati et al., 2012). Therefore, α-HCH, β-HCH and γ-HCH (lindane), have been listed under Annex A of the Stockholm Convention, with specific use exemptions in the case of γ-HCH (human health pharmaceutical for control of head lice and scabies) and PeCB and HCB under the Annex A and C (POP, 2001; UNEP, 2009). PeCB was used in polychlorinated biphenyl (PCB) products, in dyestuff carriers, as a fungicide, a flame retardant and as a chemical intermediate. It is also produced unintentionally during combustion, thermal and industrial processes and it is present as impurities in products such as solvents or pesticides (UNEP, 2007). HCB has been used in the past for a variety of applications from which it could potentially enter the environment (fungicide, military pyrotechnic smokes, synthetic rubber peptizing and degassing, wood preservation, etc.) (Bailey, 2001). Among HCH isomers, only γ-HCH has a specific pesticide activity and its purification resulted in the production of other waste residues, so-called "HCH muck", which were mostly dumped near the production site (Jit et al., 2011; Torres et al., 2013; Wycisk et al., 2013; Liu et al., 2017). For the production of 1 t of lindane, approximately 8–12 t of HCH waste isomers (α-HCH, 55–80%; β-HCH, 5–14%; δ-HCH, 2–16%, ε-HCH, 3–5%) were generated (Bodenstein, 1972; Vijgen et al., 2011; Weber et al., 2011). The landfilling and dumping of persistent organic pollutants (POPs) and other persistent hazardous compounds can have significantly adverse environmental consequences. The widespread application of lindane and a large amount of the other HCH isomers as by-products and chlorobenzenes (CBs) have caused contamination in soil, water, and atmosphere systems (Bailey, 2001; Prakash et al., 2004; Barber et al., 2005; Bailey et al., 2009; Saadati et al., 2012; Berger et al., 2016; Fang et al., 2017; De la Torre et al., 2018a).

In Spain the manufacture of lindane has been associated with four production sites that generated nearly 200,000 t of HCH wastes (Vega et al., 2016). Nevertheless, approximately 65% of these wastes (115,000 t) was generated by the INQUINOSA Factory located in Sabiñánigo (Aragón, Spain) (Vijgen, 2006). The company manufactured lindane from 1975 to 1988 in this production site, and continued formulating lindane products until 1992 (Fernández et al., 2013). The HCH wastes (including solid waste and dense non aqueous phase liquid - DNAPL - waste from the distillation process) were mainly dumped at two unlined landfills, Bailín and Sardas, located in the surroundings of the production site (Fig. 1). These landfills represent hazardous POPs contaminated sites which becomes a threat to the environment (De Miguel et al., 2015). POPs have adverse effects on human health. Therefore, POP contaminated sites need to be properly managed or remediated. In the studied area, considerable investment has been done in activities focused on the remediation and containment at the production site as well as to secure landfills, framed in a project plan approved by the Government of Aragón. Besides, further pollution control activities are still ongoing to assess the potential impact on the local environment.

In a previous work, the α-, β-, γ-, δ-, ε-HCH air levels were determined in the Bailín area to evaluate the influence of the dismantling works performed for the remediation of Bailín landfill (De la Torre et al., 2018a). Now, the present study takes a step forward monitoring α-, β-, γ-, δ-, ε-HCH but also PeCB and HCB concentrations in air in the Sabiñánigo area, and Sardas landfill and surroundings to assess the current status and evaluate the existence of other pollution sources, in which it may be necessary to carry out remediation works in the future.

2. Material and methods

2.1. Sample collection

The present study includes 145 samples collected in 29 consecutive sampling campaigns conducted from winter 2016 to autumn 2018 (Table S1). Samples were collected from five sampling points (SP) located at INQUINOSA Factory (SP1: 42° 31′ 3″N, 0° 21′ 17″W), Sardas landfill (SP2: 42° 31′ 52″N, 0° 20′ 30″W), and the urban core of Sardas (SP3: 42° 30′ 25″N, 0° 20′ 8″W) and Sabiñánigo (SP4: 42° 31′ 6″N, 0° 21′ 55″W and SP5: 42° 31′ 39″N, 0° 21′ 51″W; Figs. 1 and S1). The sampling points SP1 and SP2 were selected as possible source of pollution and the rest locations (SP3, SP4 and SP5) were chosen as residential areas located at the influence area. HCH isomers were monitored in all sampling points and campaigns while CBs were determined in SP2 and SP5 from the 8th campaign. Meteorological data in each sampling campaign were considered in the data analysis (Table S1). During the sampling campaigns, the mean temperature, relative humidity and solar radiation were 4 ± 1 °C, $74 \pm 5\%$, 107 ± 25 W/m², respectively, in winter, 13 ± 3 °C, $63 \pm 5\%$, 217 ± 34 W/m² in spring, 21 ± 1 °C, $54 \pm 7\%$, 239 ± 27 W/m² in summer and 10 ± 5 °C, $70 \pm 7\%$, 124 ± 38 W/m² in autumn.

Passive air samplers with polyurethane foam (PUF) disks were used for passive sampling as described elsewhere (Shoeib and Harner, 2002; De la Torre et al., 2018b). PUF disks (TechnoSpec, Spain) were precleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, then wrapped in aluminum foil and stored in polyethylene bags at −20 °C until deployment. At each sampling point, one sampler with a PUF disk was deployed for a month. Compound-specific sample air volumes were calculated following the Tom Harner Template (Harner, 2017), where PUF characteristics, analyte physico-chemical characteristics and temperature and sampling duration of the campaigns were considered.

2.2. Chemical analysis

The sample treatment for HCH and CB analysis was based on methodology reported previously (De la Torre et al., 2018a, 2018b). Briefly, samples spiked with ^{13}C-labeled surrogate standards (^{13}C$_6$-α-, β-, γ- and δ-HCH, ES-5344-50×; ^{13}C$_6$-PeCB and ^{13}C$_6$-HCB, ES-5465-5×; purchased from Cambridge Isotope Laboratories Inc.) were Soxhlet extracted in toluene for 24 h. The extracts were solvent exchanged into hexane and purified by florisil column (1 g anhydrous sodium sulphate, 6 g florisil activated at 450 °C, 1 g anhydrous sodium sulphate). The elution was carried out with 25 mL of n-hexane and 60 mL of n-hexane:dichloromethane (50:50, v/v). The final extracts were concentrated under a gentle nitrogen stream, redissolved in nonane and spiked with the ^{13}C injection standards solutions (^{13}C$_{12}$-PCB 15 and ^{13}C$_{12}$-PCB 70; EC-5350-L from Cambridge Isotope Laboratories Inc.) prior to instrumental analysis. Target analytes (α-, β-, γ-, δ- and ε-HCH isomers, PeCB and HCB) were analyzed on a Varian CP-3800 gas chromatograph connected to a 320 MS-TQ mass spectrometer.

2.3. Quality assurance and statistical evaluation

Quantification was carried out using isotopic dilution method. Mean recoveries of ^{13}C-labeled surrogate standards were 78 ± 7 (^{13}C$_6$-α-HCH), 83 ± 8 (^{13}C$_6$-β-HCH), 79 ± 7 (^{13}C$_6$-γ-HCH), $84 \pm 9\%$ (^{13}C$_6$-δ-HCH), 83 ± 4 (^{13}C$_6$-PeCB) and 97 ± 9 (^{13}C$_6$-HCB). Limits of detection (LODs), defined as the concentration giving a signal to noise ratio >3 were 0.34 (α-HCH), 0.03 (β-HCH), 0.69 (γ-HCH), 0.64 (δ-HCH), 0.43 (ε-HCH), 0.52 (PeCB) and 0.19 pg/m³ (HCB). Isomer concentrations were higher than LODs in all cases. Instrumental blanks consisting of nonane were run before each sample injection to check instrumental contamination. Field blanks (precleaned PUF disks) were taken to each sampling sites at each sampling campaign and analyzed as samples. Data were blank corrected.

Sampling points	Latitude °N	Longitude °W
SP1	42° 31' 3"	0° 21' 17"
SP2	42° 31' 52"	0° 20' 30"
SP3	42° 30' 25"	0° 20' 8"
SP4	42° 31' 6"	0° 21' 55"
SP5	42° 31' 39"	0° 21' 51"

Fig. 1. Geographical distribution of sampling sites.

Statistical analyses were conducted with the software SPSS 14.0 for Windows. Since data deviate from normality, Kruskal-Wallis Test ($p < 0.01$) was performed to evaluate differences between sampling points and sampling campaigns. Spearman Rho correlations were explored to assess relationships between compounds and meteorological parameters.

3. Results and discussion

3.1. Levels of HCH, PeCB and HCB in air

The concentrations of the target analytes were shown in Fig. 2 (HCH isomers) and Fig. 3 (PeCB and HCB). Complete details were listed in Table S2.

Sum of α-, β-, γ-, δ- and ϵ-HCH (ΣHCH) concentration in the area evaluated ranged between 0.07 and 19.2 ng/m^3. Spearman rank correlations were examined on the premise that significant positive associations are indicative of the existence of a common source. Interestingly,

positive relationships were obtained among HCH isomers in all sampling points ($r > 0.413$, $p < 0.05$; Table S3), which evidences a major source in the area easily associated to the historical manufacture of lindane and the uncontrolled dumping of wastes in Bailín and Sardas landfills. However, ΣHCH air concentrations obtained at INQUINOSA Factory (SP1; 5.48 ng/m^3 median Table S2) and Sardas landfill (SP2; 6.12 ng/m^3, median) showed statistically higher ($p < 0.01$, Kruskal-Wallis Test) values than the other locations (0.61, 0.65 and 0.51 ng/m^3 for SP3, SP4 and SP5, respectively). This result clearly highlights these facilities as currently HCH air pollution sources. Interestingly, samples obtained from SP1, SP2, SP3 and SP5 showed a similar isomer profile with a higher contribution of α-HCH (46 ± 8%, 39 ± 7%, 51 ± 10% and 45 ± 8%; mean ± SD at SP1, SP2, SP3 and SP5, respectively) followed by γ-HCH (31 ± 6%, 34 ± 6%, 27 ± 7% and 30 ± 7%), δ-HCH (16 ± 5%, 18 ± 5%, 14 ± 5% and 17 ± 5%), β-HCH (5 ± 3%, 7 ± 4%, 7 ± 4% and 6 ± 4%) and ϵ-HCH (1 ± 1%, 2 ± 1%, 1 ± 1% and 1 ± 1%). However, in SP4 case, the main isomer was γ-HCH (54 ± 11%) followed by α-HCH
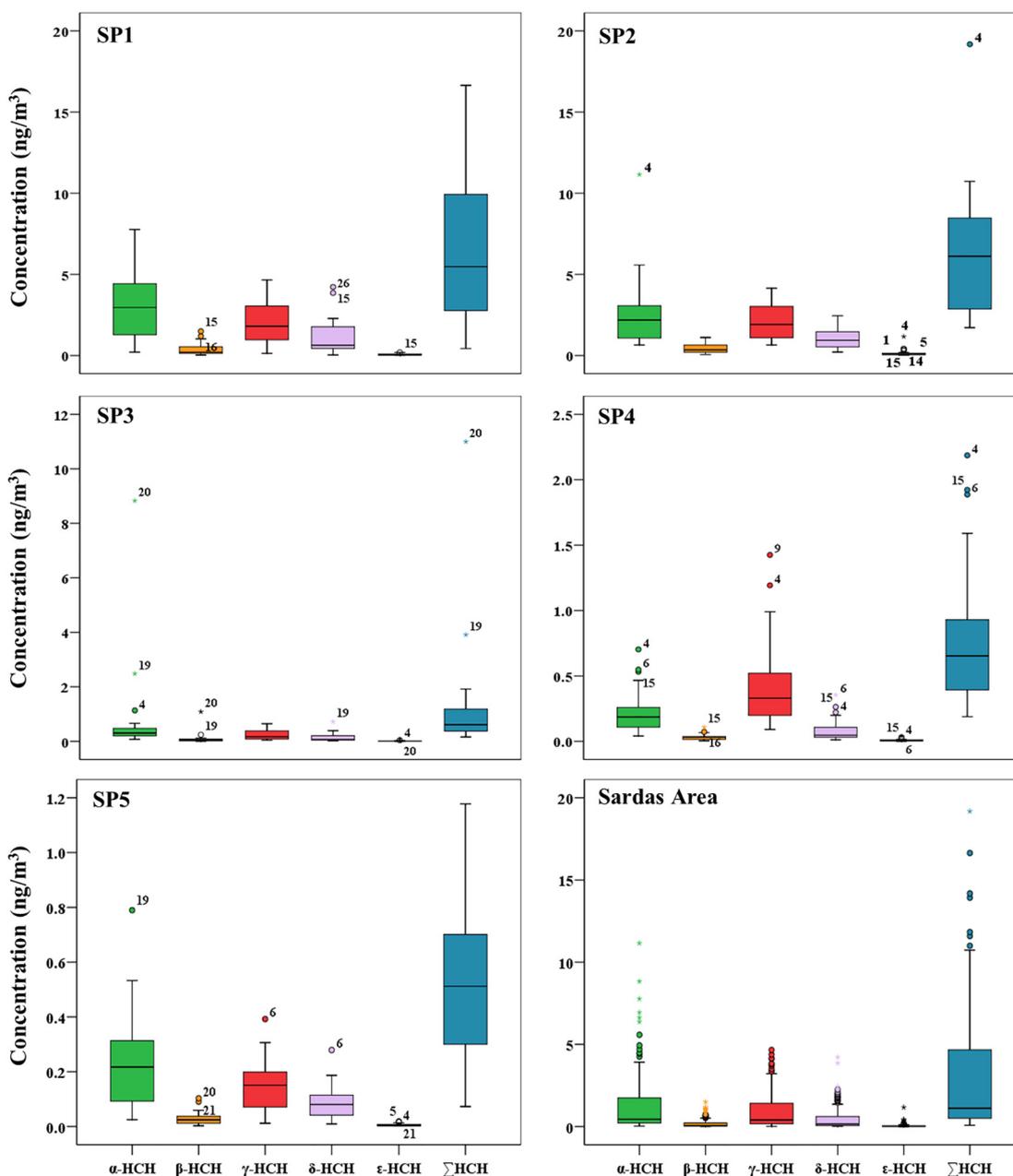
Fig. 2. Box and whisker plots of hexachlorocyclohexane (HCH) air concentration (ng/m³) obtained in each sampling point (SP1, SP2, SP3, SP4 and SP5). Upper edge of the box, line within the box and lower edge of the box, represents the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value, excluding outliers (circles) and extreme (asterisks) values which were labeled with sampling campaign code.

(29 ± 7%). Although the isomers α- and β-HCH are the main isomers in HCH wastes (Vijgen et al., 2011), the concentrations of β-HCH in air are low compared to the more volatile α- and γ-HCH (Li et al., 2003). Then, the evaluation of α-/γ-HCH ratios in air is used to locate HCH sources and to identify the possible origin with lindane or technical HCH air transport. The α-/γ-HCH ratios obtained in each location were detailed in Fig. 4. Data calculated (1.46 ± 1.25; mean ± S.D.; Table S2) were below the α-/γ-HCH ratios in technical HCH (4.64–5.83; Iwata et al., 1995) corroborating that air HCH concentrations quantified in the study areas were mainly originated from the historical production, storage and waste disposal of technical HCH. Nevertheless, it is worth to mention that α-/γ-HCH ratio obtained in SP4 (0.59; median) was statistically lower (p < 0.01, Kruskal-Wallis Test) than those calculated for the rest of sampling sites (1.45, 1.13, 1.77 and 1.49 for SP1, SP2, SP3 and SP5, respectively). This result suggests the presence

of a lindane source hitherto unknown with significant influence at SP4.

HCH air concentrations in the present study were higher than others reported for urban and background location from Spain (0.13–154 pg/m³, De la Torre et al., 2016), North America (5–370 pg/m³, sum of α-, β-, and γ-HCH, Venier and Hites, 2014), Canada (3.7–75 pg/m³, sum of α- and γ-HCH, Shunthirasingham et al., 2016), India (33–207 pg/m³, sum of α- and γ-HCH; Pozo et al., 2017) or Kuwait (0.2–383 pg/m³, Gevao et al., 2018), in accordance with air levels reported for surroundings of contaminated sites or historical production facilities from Pakistan (1.5–9.3 ng/m³, Alamdar et al., 2014), China (1.30–13.8 ng/m³, Fang et al., 2017) and India (0.9–17.0 ng/m³, Chakraborty et al., 2010), but lower than other highly contaminated locations or hot spots from Spain (0.2–6561 ng/m³, De la Torre et al., 2018a), United States (3500 ng/m³, sum of α-, β-, and δ-HCH, NYSDOH, 1981) or China
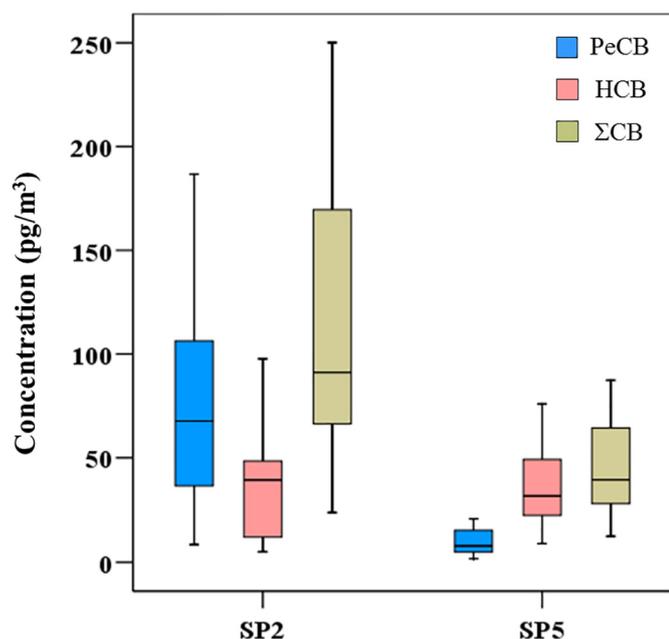
Fig. 3. Box and whisker plots of chlorobenzenes (CB) air concentration (pg/m³) obtained in each sampling point (SP2 and SP5). Upper edge of the box, line within the box and lower edge of the box, represents the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value.

maximum levels were also below the inhalation reference concentration (RfC) established for α-HCH (250 ng/m³, based on a NOAEL of 0.025 mg/m³ for liver and kidney toxicity observed in a subchronic inhalation study in rats, EPA, 2006) and the chronic inhalation reference exposure level calculated by California Environmental Protection Agency (CalEPA) for γ-HCH (300 ng/m³, based on kidney effects in rats, EPA, 2000).

Measured PeCB and HCB air concentrations (from 1.7 to 187 pg/m³ and from 4.7 to 98 pg/m³ for PeCB and HCB, respectively; Table S2) were comparable to values observed in other studies carried out in different locations (Tables S5 and S6). Levels obtained for HCB in the studied area (36 ± 22 pg/m³; mean ± SD Table S2) did not present significant differences between sampling sites (39 and 32 pg/m³, median, in SP2 and SP5) and closely resembled those reported in our previous study conducted at both urban and remote locations from Spain (51 and 61 pg/m³, median, respectively; De la Torre et al., 2016), which suggest that HCB levels could reflect background concentrations. Regarding PeCB, to the best of our knowledge, air concentrations reported here are first data available in Spain. Therefore, level comparison can only be performed between locations of studied area. The PeCB concentrations found in Sardas landfill (68 pg/m³; median SP2 Table S2) were statistically higher (p < 0.01, Kruskal-Wallis Test) than those obtained at the urban core of Sabiñánigo (7.4 pg/m³ SP5). It is important to mention that statistically positive associations between HCB and PeCB were observed at both sampling sites. However, the less impacted location (SP5: r = 0.744; p < 0.01; Table S7) presented statistically stronger correlations compared to the landfill (SP2: r = 0.527; p < 0.05). These results suggest a major common origin for both chlorobenzenes at SP5 that can be attributable to background air concentrations, but also point out the HCH waste dumpsite at SP2 as a PeCB air source. Wenzel et al. (2006) determined the levels of several compounds, as HCH and CBs, in air at 10 locations in Germany. They noticed that higher concentrations of CBs (PeCB: 5.7–7.5 pg/m³ and HCB: 55–83.6 pg/m³) occurred at sites where direct inputs of HCH isomers took place, as hazardous waste dump with lindane and another pesticides, where levels detected in air ranged from 6.2 to 3900 pg/m³. Nevertheless, no positive correlations between HCHs and PeCB or HCB were found in the present study (Table S7).
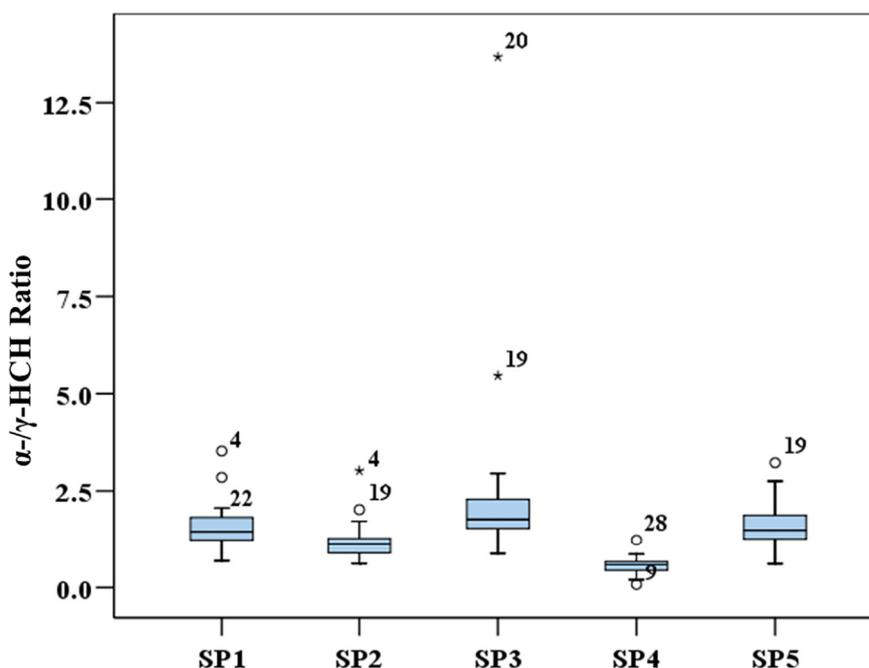
(14.3–133 ng/m³, Fang et al., 2017) (Table S4). At this point, it is important to note that maximum γ-HCH concentrations quantified at INQUINOSA Factory (4.66 ng/m³; SP1) and Sardas (4.15 ng/m³; SP2) restricted areas, where only workers and authorized staff can access, were below the occupational exposure limit (0.5 mg/m³) established for lindane by the Spanish National Institute for Safety, Health and Welfare at Work (INSSBT, 2018). In the case of sampling points located in residential areas, both α-HCH (8.83, 0.70 and 0.79 ng/m³; SP3, SP4 and SP5) and γ-HCH (0.65, 1.43, 0.39 ng/m³)

Fig. 4. α-/γ-Hexachlorocyclohexane (HCH) air profile at the different locations.

3.2. Influence of the meteorological parameters

The influence of meteorological parameters (temperature, solar radiation and relative humidity) on targeted analytes was evaluated. PeCB levels did not correlate with any meteorological values and HCB moderately did with temperature (r = 0.493; p < 0.05, SP2 Table S7) and with relative humidity (r = −0.425; p < 0.05, SP5 Table S7). Regarding HCH, air concentrations positively correlated with temperature and solar radiation and negatively with relative humidity (Table S3). Therefore, it is not strange that the highest concentrations for all HCH isomers were obtained in the warmest months (Fig. S2). Nevertheless, the relationship between HCH concentrations and temperature statistically decreased as locations move away from INQUINOSA Factory and Sardas landfill (SP1 r > 0.530, p < 0.01 for all isomers; SP2 r > 0.475, p < 0.01, except for β-HCH; SP4 r > 0.372, p < 0.05, except for γ-HCH; SP3 r > 0.392, p < 0.05 only observed for γ-, δ- and ε-HCH; and finally SP5 r > 0.475 p < 0.01 for γ- and δ-HCH; Table S3). The temperature dependence of atmospheric concentrations of semivolatile organic compounds can be expressed as linear regressions of the logarithm of the partial pressure in air versus reciprocal temperature: Ln P_a = m (1/T) + b (Hillery et al., 1997). The slope m reflects thermodynamics of air-surface partitioning, then, steeper slopes (high temperature dependence) involve high surface concentration in the vicinity of sampling location while shallow slopes (low temperature dependence) suggest that the long-rate transport controls the atmospheric levels. Then, the relationship between the logarithm of the partial pressure (Ln P_a) for HCH isomers, PeCB and HCB in air and the temperature (1/T) was evaluated (Table S8 and Figs. S3 and S4). Interestingly, inclination absolute median values obtained for HCH isomers ranked as follows: SP1 (7324 ± 1781, mean ± SD; p < 0.001) followed by SP4 (5484 ± 2057; p < 0.101), SP2 (4560 ± 910; p < 0.076), SP5 (4066 ± 1328; p < 0.379) and finally SP3 (3800 ± 2057; p < 0.072). Again, HCH steeper slopes obtained at INQUINOSA Factory revealed the historical HCH production facilities as pollution sources that must be conveniently managed. Considering chlorobenzenes, while similar slopes were calculated for HCB, the one obtained for PeCB at Sardas landfill (−3857; SP2) was four times higher than the one found at the urban core (−991; SP5), which could be attributable to higher concentrations in the vicinity of this dumpsite.

4. Conclusions

The concentrations of HCH isomers, PeCB and HCB in air have been periodically monitored at locations in the Sardas landfill and surroundings. The HCH values detected were higher than those reported for background and urban locations from Spain. The HCH concentrations obtained at INQUINOSA Factory (SP1) and Sardas landfill (SP2) were statistically higher than the rest of the sampling sites, pointing out the production of HCH and unlined landfill where HCH production residues were dumped as current sources of HCH pollution. The γ-HCH levels found in SP4 (urban core of Sabiñánigo) also reflected a possible lindane pollution source hitherto unknown. The α-/γ-HCH ratios calculated (1.46 ± 1.25) corroborated that the HCH air concentrations detected in the area were mainly originated from the historical production, storage and waste disposal of technical HCH.

HCB concentrations obtained were in accordance with values detected in other locations worldwide, which suggests that HCB levels could reflect background concentrations. Neverthelss, in PeCB case, levels found at Sardas landfill (SP2) were statistically higher than the values detected in urban core of Sabiñánigo (SP5), suggesting the former facility as a possible PeCB source, although contribution of long-range transport cannot be ruled out. Among the meteorological parameters studied, the temperature showed positive correlations with HCH concentrations in all sampling points. To date, passive air samplers have been mainly used to monitor background concentrations at remote locations. However, in light of results obtained here they also revealed as a reliable method to monitor polluted environments. Results highlight that despite of remediation and containment measures implemented, further pollution control activities should be carried out to protect the environmental compartments and the human health.

Conflict of interest

The authors declare that there is no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.03.313.

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