

Persistent Pesticides in Air from a Former HCH Production Site in Spain

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1 Introduction

The landfilling of persistent organic pollutants (POPs) and other hazardous compounds can have significantly adverse environmental consequences. More concretely, the widespread dumping of γ -HCH (lindane) and a large amount of α -, β -, δ - and ϵ -HCH isomers as by-products and chlorobenzenes (CBs) have caused contamination in soil, water, and atmosphere systems^{1,2}.

Among HCH isomers, only γ -HCH has a specific pesticide activity and its purification resulted in the production of other waste residues. In Spain the manufacture of lindane has been associated with four production sites that generated nearly 200,000 t of HCH wastes³ and approximately 65% of these wastes (115,000 t) was generated by the INQUINOSA Factory located in Sabiñánigo (Aragón, Spain)⁴. The company manufactured lindane from 1975 to 1988 in this production site, and continued formulating lindane products until 1992⁵. The HCH wastes were mainly dumped at two unlined landfills, Bailín and Sardas, located in the surroundings of the production site, becoming a threat to the environment. Since 2007, a 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 landfill⁶. Now, the present study takes a step forward monitoring α -, β -, γ -, δ -, ϵ -HCH but also PeCB (pentachlorobenzene) and HCB (hexachlorobenzene) concentrations in the air of 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 Materials and Methods

The present study includes 200 air samples collected in 40 consecutive sampling campaigns conducted from winter 2016 to autumn 2019. Five sampling points were selected: P1 and P2 (possible sources of pollution) and P3, P4 and P5 (residential areas located at the influence area). While HCH isomers were monitored in all locations and campaigns, CBs were determined in P2 and P5 from the 8th campaign. At each sampling point, one passive air sampler with polyurethane foam (PUF) disk was deployed for a month. PUF disks (TechnoSpec, Spain) were pre-cleaned 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. Compound-specific sample air volumes were calculated following the Tom Harner Template⁷.

Samples spiked with ¹³C-labeled surrogate standards (¹³C₆- α -, β -, γ - and δ -HCH, ES-5344-50X; ¹³C₆-PeCB and ¹³C₆-HCB, ES-5465-5X; 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. The elution was carried out with n-hexane and n-hexane:dichloromethane (50:50, v/v). The final extracts were concentrated under a nitrogen stream, redissolved in nonane and spiked with the ¹³C injection standards solutions (¹³C₁₂-PCB 15 and ¹³C₁₂-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.

Quantification was carried out using isotopic dilution method. Mean recoveries of ¹³C-labeled surrogate standards were 83 ± 13 (¹³C₆- α -HCH), 85 ± 9 (¹³C₆- β -HCH), 81 ± 8 (¹³C₆- γ -HCH), 87 ± 12% (¹³C₆- δ -HCH), 84 ± 5 (¹³C₆-PeCB) and 96 ± 9 (¹³C₆-HCB). Limits of detection (LODs), defined as the concentration giving a signal to noise ratio >3 were 0.32 (α -HCH), 0.10 (β -HCH), 0.66 (γ -HCH), 0.62 (δ -HCH), 0.43 (ϵ -HCH), 0.43 (PeCB) and 0.14 pg/m³ (HCB). Isomer concentrations were higher than LODs in all cases. Instrumental blanks (nonane) were run before each sample injection to check instrumental contamination.

Field blanks were taken to each sampling sites at each sampling campaign and analyzed as samples. Data were blank corrected.

3 Results

Hexachlorocyclohexanes (HCHs)

The concentrations of the HCH isomers are shown in Figure 1 and Table 1. Sum of α -, β -, γ -, δ - and ϵ -HCH (Σ HCH) concentration in the area evaluated was ranging between 0.07 and 19.2 ng/m³. Positive relationships ($r > 0.331$, $p < 0.05$, Spearman test) were obtained among HCH isomer levels in all sampling points, which evidences a major source in the area easily associated to the historical manufacture of lindane and the uncontrolled dumping of wastes in Sardas landfill. However, Σ HCH air concentrations obtained at INQUINOSA Factory (P1; 4.21 ng/m³, median) and Sardas landfill (P2; 5.11 ng/m³, median) showed statistically higher ($p < 0.01$, Kruskal-Wallis Test) values than the other locations (0.50, 0.58 and 0.30 ng/m³ for P3, P4 and P5, respectively), pointing out these facilities as currently HCH air pollution sources.

Samples obtained from P1, P2, P3 and P5 showed a similar isomer profile with a higher contribution of α -HCH (46 \pm 11%, 39 \pm 7%, 50 \pm 9% and 45 \pm 8%; mean \pm SD at P1, P2, P3 and P5, respectively) followed by γ -HCH (30 \pm 7%, 35 \pm 7%, 28 \pm 7% and 31 \pm 8%), δ -HCH (17 \pm 8%, 18 \pm 5%, 14 \pm 5% and 16 \pm 5%), β -HCH (6 \pm 3%, 6 \pm 4%, 7 \pm 4% and 7 \pm 4%) and ϵ -HCH (1 \pm 2%, 2 \pm 1%, 2 \pm 1% and 2 \pm 2%). However, in P4 case, the main isomer was γ -HCH (54 \pm 10%) followed by α -HCH (27 \pm 8%), see Table 1.

The evaluation of α -/ γ -HCH ratios in air is commonly used to locate HCH sources and to identify the possible origin with lindane or technical HCH air transport. The α -/ γ -HCH ratios obtained (1.42 \pm 0.54; mean \pm S.D.) were below the α -/ γ -HCH ratios in technical HCH (4.64–5.83)⁸ 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 P4 (0.57; median) was statistically lower ($p < 0.01$, Kruskal-Wallis Test) than those calculated for the rest of sampling sites (1.45, 1.12, 1.67 and 1.49 for P1, P2, P3 and P5, respectively), this result suggests the presence of a lindane source hitherto unknown with significant influence at P4.

The influence of meteorological parameters (temperature, solar radiation and relative humidity) on the HCH content was evaluated. A good positive correlation was found between the HCH concentrations and temperature (P1: $r > 0.437$, $p < 0.01$; P2: $r > 0.370$, $p < 0.01$; P3: $r > 0.336$, $p < 0.05$; P4: $r > 0.445$, $p < 0.01$; P5: $r > 0.423$, $p < 0.01$), pointing out the highest levels during the warmest months. Besides, a good negative correlation with relative humidity was found, mainly in P1 ($r > -0.326$; $p < 0.05$), P2 ($r > -0.316$; $p < 0.05$) and P4 ($r > -0.372$; $p < 0.05$) and, additionally, an increase in HCH concentration with the solar radiation (P1: $r > 0.319$, $p < 0.05$; P2: $r > 0.318$, $p < 0.05$; P3: $r > 0.324$, $p < 0.05$; P4: $r > 0.403$, $p < 0.01$).

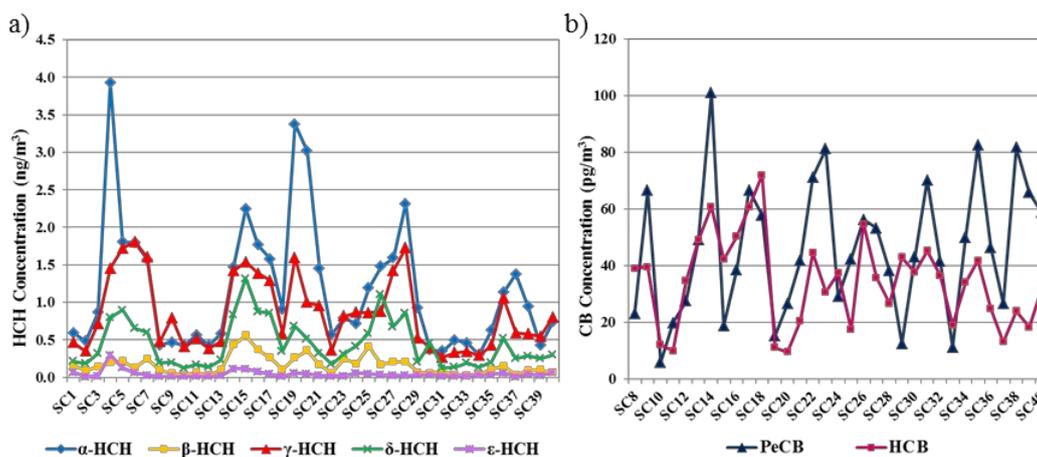


Figure 1: Mean a) α -, β -, γ -, δ - and ϵ -HCH (ng/m³) and b) PeCB and HCB (pg/m³) air concentrations obtained during the different sampling campaigns (SC1 =winter 2016 to SC40 = autumn 2019).

Table 1: Mean concentration (ng/m³) and contribution (%) of HCH isomers obtained in air samples.

	Concentration (ng/m ³)					Contribution (%)				
	α -HCH	β -HCH	γ -HCH	δ -HCH	ϵ -HCH	α -HCH	β -HCH	γ -HCH	δ -HCH	ϵ -HCH
P1	2.67	0.33	1.72	1.03	0.07	46	6	30	17	1
P2	2.20	0.34	1.81	0.93	0.13	39	6	35	18	2
P3	0.56	0.07	0.20	0.11	0.01	50	7	28	14	2
P4	0.20	0.04	0.39	0.08	0.01	27	6	54	11	2
P5	0.20	0.03	0.13	0.07	0.01	45	7	31	16	2

Clorobenzenes (CBs)

The mean concentrations of the CBs are detailed in Figure 1 and Table 2. CB air concentrations ranged from 0.6 to 187 pg/m³ for PeCB and from 1.0 to 98 pg/m³ for HCB. Positive correlations were found between PeCB and HCB at

the two sampling points evaluated (P2: $r > 0.446$, $p < 0.01$; P5: $r > 0.671$; $p < 0.01$), suggesting a major common origin for both chlorobenzenes. PeCB concentrations were statistically higher ($p < 0.01$, Kruskal-Wallis Test) in P2 (80 pg/m^3 , median) than P5 (7.9 pg/m^3). The concentrations of these compounds have not shown significant time trends ($p > 0.05$, Kruskal-Wallis Test) during 33 sampling campaigns, which could reflect background concentrations.

The samples obtained from P2 and P5 showed important differences. The main compound in P2 was PeCB ($70 \pm 16\%$; mean \pm SD) while HCB ($79 \pm 9\%$; mean \pm SD) predominated in P5 (Table 2). This fact could reflect a possible pollution source of PeCB in the HCH waste dumpsite.

The influence of meteorological parameters was also evaluated for CB compounds, but no significant correlations were observed ($p > 0.05$).

Table 2: Mean concentration (pg/m^3) and contribution (%) of CB compounds obtained in air samples.

	Concentration (pg/m^3)			Contribution (%)	
	PeCB	HCB	Σ CB	PeCB	HCB
P2	83	35	118	70	30
P5	8.9	33	42	21	79

4 Discussion

The HCH values detected in the area of study were higher than those reported for background and urban locations from Spain⁹, North America¹⁰, Canada¹¹ or Kuwait¹², in accordance with air levels reported for surroundings of contaminated sites or historical production facilities from Pakistan¹³, China² and India¹⁴, but lower than other highly contaminated locations or hot spots from Spain⁶ or China².

At this point, it is important to note that maximum γ -HCH concentrations quantified at INQUINOSA Factory (4.66 ng/m^3 ; P1) and Sardas (4.15 ng/m^3 ; P2) restricted areas, where only workers and authorized staff can access, were below the occupational exposure limit (0.5 mg/m^3) established for lindane by the Spanish National Institute for Safety, Health and Welfare at Work¹⁵. In the case of sampling points located in residential areas, both α -HCH (8.83, 0.70 and 0.79 ng/m^3 ; P3, P4 and P5) and γ -HCH (0.65, 1.43, 0.39 ng/m^3) maximum levels were also below the inhalation reference concentration (RfC) established for α -HCH (250 ng/m^3 , based on a NOAEL of 0.025 mg/m^3 for liver and kidney toxicity observed in a subchronic inhalation study in rats¹⁶) and the chronic inhalation reference exposure level calculated by California Environmental Protection Agency (CalEPA) for γ -HCH (300 ng/m^3 , based on kidney effects in rats¹⁷).

Measured PeCB and HCB air concentrations were comparable to values observed in other studies carried out in different locations worldwide^{9,12,18}. Regarding HCB levels, results were closely resembled those reported in our previous study conducted at both urban and remote locations from Spain⁹, which suggest that HCB levels could reflect background concentrations.

5 Conclusions

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 in Sabiñánigo, further pollution control activities should be carried out to protect the environmental compartments and the human health.

Besides, this research reveals the necessity of suitable air monitoring plans in those mega-sites where obsolete pesticides were improperly dumped.

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7 References

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