

Dumpsite dismantling influence on HCH air levels: Sabiñánigo case

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Introduction

Lindane has been used as a broad-spectrum insecticide for seed and soil treatment, foliar applications, tree and wood treatment and against ectoparasites in both veterinary and human applications. However, the legacy of lindane production with the associated large HCH waste deposits has become recognized as an issue of global concern. Each tonne of lindane generated between 8 and 12 t of other HCH waste isomers (α -HCH, 55–80 %; β -HCH, 5–14 %; δ -HCH, 2–16 %; and ϵ -HCH, 3–5 %) ¹. Remaining largely unknown to the public and indeed to the scientific community until relatively recently, this has generated the globe's largest POP stockpile—estimated at between four and seven million t of wastes ^{2,3}. These wastes, together with those generated from recycling of HCH residues, were generally dumped, usually in an uncontrolled manner, in the vicinity of the production facilities.

This is the case of Sabiñánigo, a small industrial city located in the Aragonian Pyrenees, in the northeast of Spain, where INQUINOSA Company produced lindane from 1975 to 1992. HCH production resulted in the generation of approximately 115,000 t of waste isomers which were mainly dumped in two unlined landfills. These two dumpsites (Bailín and Sardas), together with the former production site, are recognized sources of environmental pollution. It is estimated that the two landfills were found to be the major legacies of lindane production with aggregated waste quantities estimated at between 30,000 and 80,000 t of HCH solid waste and 2,000 t in liquid form of Dense Non-Aqueous Phase Liquid (DNAPL; waste from the inefficient production process of lindane distillation) for the respective dumpsites. In addition, about 100 t of HCH still remains in the abandoned and derelict production site ⁴. In 2007, a project plan was approved by the Government of Aragon for excavation of Bailín dumpsite and transfer the waste to a new cell. A total of 65,000 t of HCH solid waste and 342,000 t of polluted soil were transferred and 25 t of DNAPL were removed.

The present work evaluated the influence of dismantling works performed in Bailín landfill, the transfer of waste to the new cell and the state once the works finished, in the α -, β -, γ -, δ - and ϵ - HCH air levels of Bailín area.

Materials and methods

Passive air samplers (PASs) with polyurethane foam (PUF) disks as sorbent media were used. PASs are cheaper than active samplers, easier to deploy and, thus, better-suited for remote air sampling or for developing a large monitoring network. Five sampling points were selected. Four of them were located in the vicinity of the Bailín landfill (P1 to P4), and the fifth one within the town of Sabiñánigo (P5; 1800 m from Bailín). At each sampling point, one PAS, with a PUF disk, was deployed for a month obtaining a total of 112 samples in twenty three consecutive sampling campaigns (S1-S23) from summer 2014 to autumn 2016.

Prior to deployment, PUF disks (14 cm diameter; 1.2 cm thickness, and 0.03 g cm⁻³ density; TechnoSpec, Spain) were precleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, wrapped in aluminum foil and stored in polyethylene bags at -20°C until deployment. Isomer-specific sample air volumes were calculated according to the Tom Harner Template ⁵.

Samples were spiked with a known amount of ¹³C-labeled surrogate standards (¹³C₆- α -, β -, γ - and δ -HCH; ES-5465-5X Cambridge Isotope Laboratories Inc.), before Soxhlet extraction in toluene for 24 h. Extracts obtained

were solvent exchanged into hexane prior to a subsequent clean-up step performed by open column chromatography. Columns were packed with 6 g of florisil activated at 450°C. Elution was carried out with 25 mL of n-hexane. The first 7 mL were discarded and the following 18 mL were collected in a flask together with 60 mL of n-hexane:dichloromethane (50:50, v/v). Final extracts were rotary evaporated until 1 mL, transferred to vials, and dried under a gentle nitrogen stream. Samples were reconstituted in nonane containing PCB 15 and PCB 70 as recovery standards prior to instrumental analysis. α -, β -, γ -, δ - and ϵ -HCH isomers were analyzed on a Varian CP-3800 gas chromatograph, connected to a 320 MS-TQ mass spectrometer. GC column was a 30 m x 0.25 mm x 0.25 μ m film thickness (VF-5ms from Varian).

Blank levels were assessed from the field blanks consisted of the pre-extracted PUF disks that were taken to each sampling site at each sampling period. They were extracted and analyzed in the same conditions as the samples. Data were blank corrected.

Results and discussion:

In general, HCH levels reported worldwide for locations where the use of the chemical is the recognized main source, are in the range of pg m^{-3} (from 0.13 to 154 pg m^{-3} for background and urban sites in Spain; sum of α -, β - and γ -HCH)⁶. However, concentrations obtained in Bailín area (195 ± 658 (35.9), 0.24 – 6561 ng m^{-3} ; average \pm SD, (median), min – max) were in accordance to those associated to historical production sites. Fang et al⁷ reported HCH air concentrations (52.3, 14.2 - 133 ng m^{-3} ; average, min –max for the sum of α -, β -, γ - and δ -HCH) in an organochlorine pesticide factory that produced 220,000 t of HCH powder from 1952 to 1983 in China. Besides, Zhao et al⁸ and Abhilash and Singh⁹ described soil HCH concentrations up to 42.8 and 99 mg kg^{-1} (sum of α -, β -, γ - and δ -HCH) in HCH production plants from China and India. These result showed that historical HCH production facilities are top pollution sources. Nevertheless, at this point it should be addressed that all concentrations obtained at Bailín landfill (P1 to P4), that is a restricted area, were below daily occupational exposure limit (0.5 mg m^{-3}) established for lindane by the Spanish National Institute for Safety and Hygiene in the Work¹⁰. In addition, data from P5 were below inhalation reference concentration (RfC = 0.00025 mg m^{-3} based on a no-observed-adverse-effect level (NOAEL) of 0.025 mg m^{-3}) considered for relevance for nonoccupational exposure for α -HCH¹¹ even when dismantling works were performed.

Statistical significant differences (Kruskal-Wallis Test; $p < 0.01$) were found between sampling point (geographic distribution) and sampling campaign (temporal trend). HCH concentrations obtained during first two sampling campaigns presented statistically higher concentrations for the sum of isomers (THCH) compared to those obtained afterwards. Considering that the first two sampling campaigns covered the dismantling of the old landfill and the subsequent sealing of the new cell, this result indicates that: i) the existence of the old landfill and/or ii) the work performed during its dismantling have been a source of HCH contamination.

In accordance with HCH levels, sampling locations were grouped in three zones: Zone 1 (Z1 including P1 and P2; fitting the landfill dismantled), Zone 2 (Z2 including P3 and P4; vicinity of landfill dismantled) and P5 (Sabiñánigo town). Sum of α -, β -, γ -, δ - and ϵ -HCH levels (THCH) in these zones ranked ($p < 0.01$) as follows Z1 (198 ng m^{-3}) > Z2 (12.2 ng m^{-3}) > P5 (1.22 ng m^{-3}). Even after dismantling works of Bailín dumpsite had been finished, THCH concentrations obtained in old landfill area (187 and 11.8 ng m^{-3} ; median for Z1 and Z2) were higher than those found in P5 (1.16 ng m^{-3}), and these even higher than levels reported (from 0.13 to 154 pg m^{-3} ; min- max for the sum of α -, β - and γ -HCH) during a five-year study carried out in urban and remote sites in Spain⁶. This latter comparison indicates a heavier contamination caused by the production, storage, and waste disposal than the corresponding to application of lindane and/or technical HCH in Spain. It is important to point out that soil of Zone 1 are currently generating leachates arriving to the bare surface of the dismantled landfill.

Isomer profile evidences during Bailín dismantling works (S1-S2) lower decline rates of β -HCH with source distance than that of the other isomers (12, 18, 34, 46 and 67% β -HCH to THCH contribution). This isomer has all six chlorine atoms in the equatorial position, a configuration which greatly reduces the susceptibility to chemical and biological transformation. This result might be also expected for the most volatile isomer (α -HCH) that maintained relative high contribution in Bailín landfill sampling points (P1 to P4) during this period. A similar isomer profile was obtained in all sites, α -HCH ($46 \pm 7\%$, mean \pm SD) followed by γ -HCH ($22 \pm 7\%$)

and δ -HCH ($22 \pm 5\%$), and to a lesser extent by β -HCH ($7 \pm 3\%$, mean \pm SD) and ϵ -HCH ($3 \pm 1\%$), once dismantling works finished, reflecting a background or equilibrium state.

Influence of meteorological parameters (temperature, solar radiation and relative humidity) in HCH air concentrations and their temporal trends (sampling campaign) was evaluated: i) for all sampling locations grouped and ii) for each one of the established zones (Z1, Z2 and P5). In all cases, only data collected after dismantling works had finished (from S3 to S23) were considered. As expected, positive correlations ($r_s > 0.794$, $p < 0.01$) were obtained among all HCH isomers, underlining a common origin in all geographic points evaluated. HCH levels from Z1 and P5 did not reflect any temporal trend ($p > 0.05$), however negative correlations were obtained for Z2 ($r_s = -0.606$, $p < 0.01$ for THCH). This result seemed to indicate: i) a decrease in HCH levels in Z2 with time, proving that the emissions from the depleted cell (Z1) were decreasing, and ii) that as P5 concentrations remained constant, an equilibrium or background level would have been reached. In Zone 1, the one that fits the landfill dismantled, a weak increase in THCH concentrations with temperature ($r_s = 0.346$; $p < 0.05$), mainly due δ -HCH isomer ($r_s = 0.474$; $p < 0.01$) was obtained. Nevertheless, this relationship could not be assessed in the other two areas further away from the source or in the total of the samples.

Evaluation of α - and γ -HCH ratios in air has been proposed to associate their origin with lindane or Technical HCH air transport, but also to pinpoint HCH sources¹². Results showed an increase in the quotient α -/ γ -HCH as sampling points move away from the dismantled old cell (P1 < P2 < P3 < P4), which could be associated to photochemical transformation of the γ -HCH isomer into α -HCH that has been demonstrated under laboratory conditions¹³. However, no correlation ($p > 0.05$) between the content of these isomers and solar radiation was obtained to support this hypothesis. Proximity of sampling points to the source obliged to consider the different volatility rates of both isomers, being the α -isomer more volatile. Results obtained in P5 seem to indicate the existence of a different scenario. This location, even being the farthest from the dismantled landfill, presented lower α -/ γ -HCH ratios than P3 and P4, which would be in agreement with the existence of other γ -HCH sources, like Sardas dumpsite or INQUINOSA production site, with higher influence in P5 than in the other sampling locations.

Results from the present study revealed that Bailín dumpsite and/or works performed during its dismantling were clearly identified as a HCH source in Sabiñánigo area. Thus, this research detaches the need of suitable air monitoring plans in those mega-sites where obsolete pesticides were improperly dumped.

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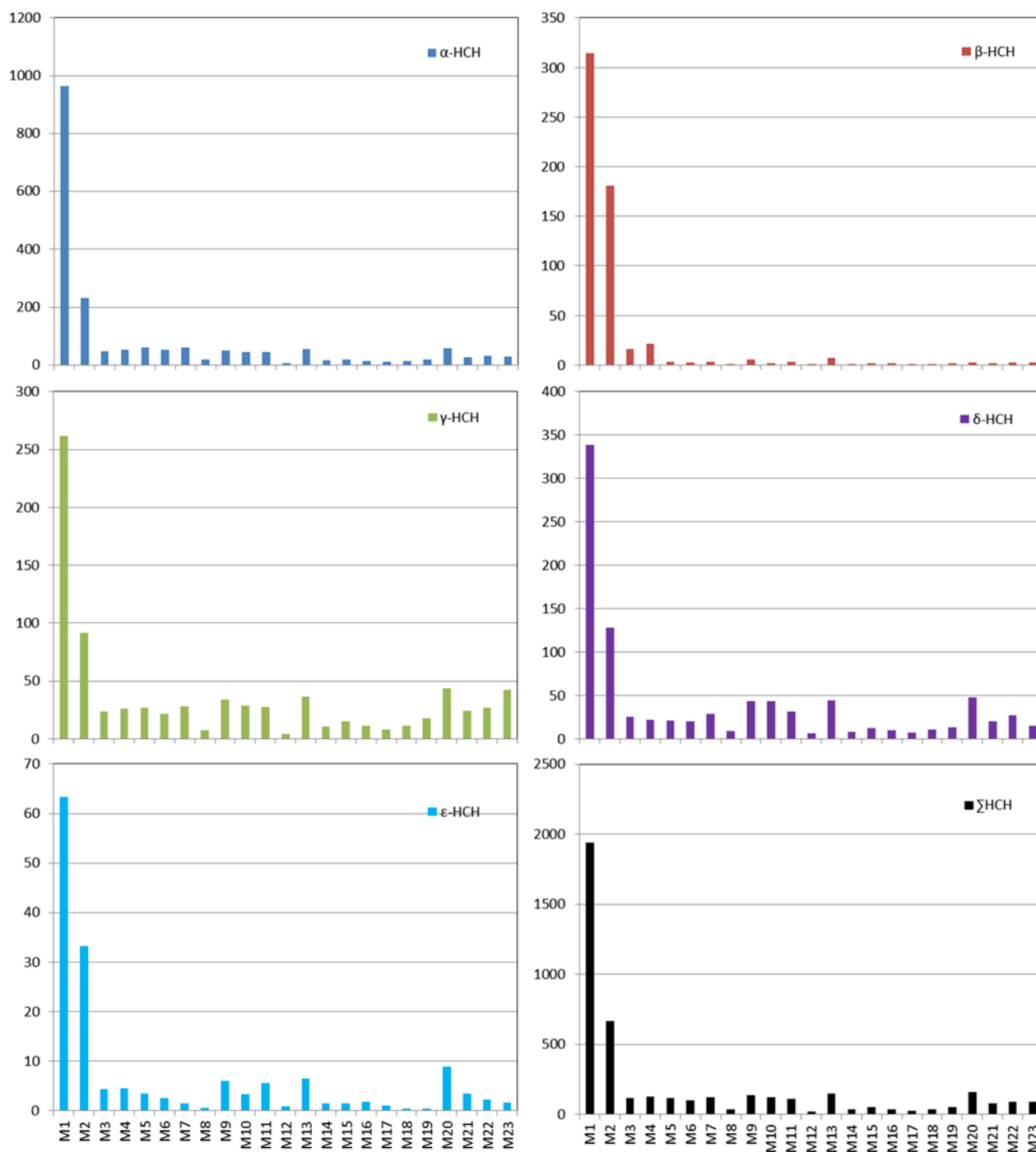


Figure 1. Mean HCH air concentrations (ng m⁻³) obtained in 23 sampling campaigns (from summer 2014 to autumn 2016).