Cod: 8.10005

EFFECT OF THE BAILÍN LANDFILL DISMANTLING (SABIÑÁNIGO, SPAIN) ON THE HCH AIR CONCENTRATION

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INTRODUCTION

Hexachlorocyclohexane isomers (α- HCH, β-HCH, and γ-HCH [lindane]) were added to the persistent organic pollutants (POP) list of the Stockholm Convention in May 2009. Accordingly, the legacy of HCH/lindane production with the associated large HCH waste deposits has become recognized as an issue of global concern and is addressed in the implementation of the Convention.

This is the case of the HCH Bailín landfill, located approximately 3 km south of Sabiñánigo (Spain) and 800 m from the Gállego river. From the mid 80s until early 90s, this landfill was used for the storage of by-products generated in the production of lindane, DNAPL (Dense Non-Aqueous Phase Liquid) as well as others types of industrial and urban waste. DNAPL is the liquid waste from the inefficient production process of lindane: distillation. Each tonne of lindane generated between 8 and 12 tonnes of other HCH waste isomers (α-HCH, 55–80 %; β-HCH, 5–14 %; δ-HCH, 2–16 %; and ε-HCH, 3–5 %)[1], which were largely deposited in the past around lindane production facilities[2]. This landfill did not present safe conditions to ensure the isolation of the waste, enabling both the input of groundwater and the infiltration of contaminated fluxes. So it became the main source of active pollution for the soil, groundwater and surface water in the area.

During a period of seven years, the pollution status of the area was assessed by the Regional environmental authorities. In 2007 a Plan was approved by the Government of Aragon for dismantling the dumpsite and moving and relocating the waste to a new safety cell, very close to old one[3]. The activities started in 2009 with the construction of a new cell and the previous infrastructure required. Dismantling works began in May 2014, coinciding with the historical lowest rainfall period. Additional health and safety measures were implemented to ensure that workers and the nearby Sabiñánigo population were not affected by the dispersion of POPs. In addition, an environmental monitoring plan was also developed in order to minimize impacts to the environment during the dismantling works. 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.

This work is focused on the HCH air monitoring in Bailín Landfill and surroundings, from the beginning of the dismantling up to date, by using passive air samplers (PASs) with polyurethene foam disks (PUF disks) as the sorbent media.

MATERIAL AND METHODS

Sampling: A total of five sampling points were monitored (Figure 1). 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; 3 Km from dismantled landfill). At each sampling point, one PAS, with a PUF disk, was deployed for a month, and then, collected after exposure. A field blank was also deployed at each point and at each sampling period. Data shown in the present study correspond to the first sixteen sampling campaigns, from August 2014 to February 2016, including 80 samples and their corresponding field blanks.

Prior to deployment, PUF disks (14 cm diameter, 1.2 cm thickness, and 0.03 g/cm^3 density) were precleaned by Soxhlet extraction with acetone and diethyl ether, wrapped in aluminum foil and stored in polyethylene bags at -20ºC until deployment[4].

Chemical analysis:

Samples were spiked with $^{13}C_6$- α-, β-, γ- and δ-HCH isomers internal standards before Soxhlet extraction in toluene for 24 h. A subsequent clean-up procedure was performed by open column chromatography. Columns were packed with 6 g of florisil activated at 450ºC. 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 µm film thickness (VF-5ms from Varian). Identification and quantification were carried out using isotopic dilution. All data are blank corrected. Statistical analyses were performed with IBM SPSS 23.0 software, using Mann-Whitney U test ($p<0.01$) to find differences between sampling points and sampling campaigns and Pearson correlation to find relationships between HCH isomers and temperature.

RESULTS AND DISCUSSION

Total HCH concentration (ng/m^3) and the average temperature for each sampling point (P1 to P5) at each sampling period are represented in Figure 2. As can be seen, during the first two sampling campaigns, corresponding to the landfill dismantling process, HCH concentrations were higher in P1 and P2 which are very close to the old landfill, than those related to the other sampling locations (P3, P4 and P5). HCH levels in P1 and P2 decreased very significantly from the third campaign, although their values remains always higher than the ones obtained in the other sampling points. As expected, P5 presented the lowest concentration for all isomers analysed in all sampling campaigns.
Despite of the high temperature variation (from 1 to 22 ºC) during sampling period, temperature does not appear to be affecting greatly the total-HCH air levels. Results from Pearson correlation showed that α-HCH (major isomer) and the total concentration (mainly affected by α-HCH levels), were not correlated with temperature while a positive correlation was observed for the minor isomers (ß-, γ- and δ-HCH $p<0.05$; ε-HCH $p<0.01$). Concentration pattern: α-HCH (44%) > γ-HCH (19%) ~ δ-HCH (20%) > ß-HCH (12%) > ε-HCH (4%).
Figure 2 shows that HCH levels measured in summer (June to September 2015) did not present an increase in comparison to the ones related to other campaigns. As mentioned before, the highest levels obtained between August and October 2014 corresponded to the dismantling period.
Regarding to the evolution of the concentration versus time, three different periods were observed:
• Period 1: From the waste movement (old cell dismantling) up to the new HCH cell closure.
As distance to the old HCH cell increases, the HCH-isomer concentrations decreases, except for ß-HCH, because of its high persistence.
• Period 2: Two months after new HCH cell closure.
A clear decrease in the HCH air content is observed in comparison to the former period (~ one order of magnitude). However, P1 and P2 locations (the nearest to the old HCH cell) still presented the highest levels of all HCH isomers.
• Period 3: One year after the old cell dismantling.
The decrease in pollution levels continues respect to Period 2 (~ one order of magnitude), but it is slowed within the period analyzed. In this period, P1 and P2 present, again, the highest HCH concentrations, thus indicating the old HCH cell is still behaving as a pollution source. This fact could be due to P1 and P2 are placed in the Bailín valley wind directional axis, and, currently, influenced by emissions coming from the bare and polluted surface of the old HCH cell.
In order to reach definitive conclusions, including spatial and temporal trends, the maintenance of this HCH monitoring plan, involving periodic air samplings is estimated mandatory. Only in this way, it will be possible a proper evaluation of the measures taken to reduce the HCH levels in Bailín landfill and surroundings.

ACKNOWLEDGEMENTS

This work has been supported by the Goverment of Aragon, through the public company SARGA under the contracts nº 5505003-11, 5505003-20 and 5506079-16.

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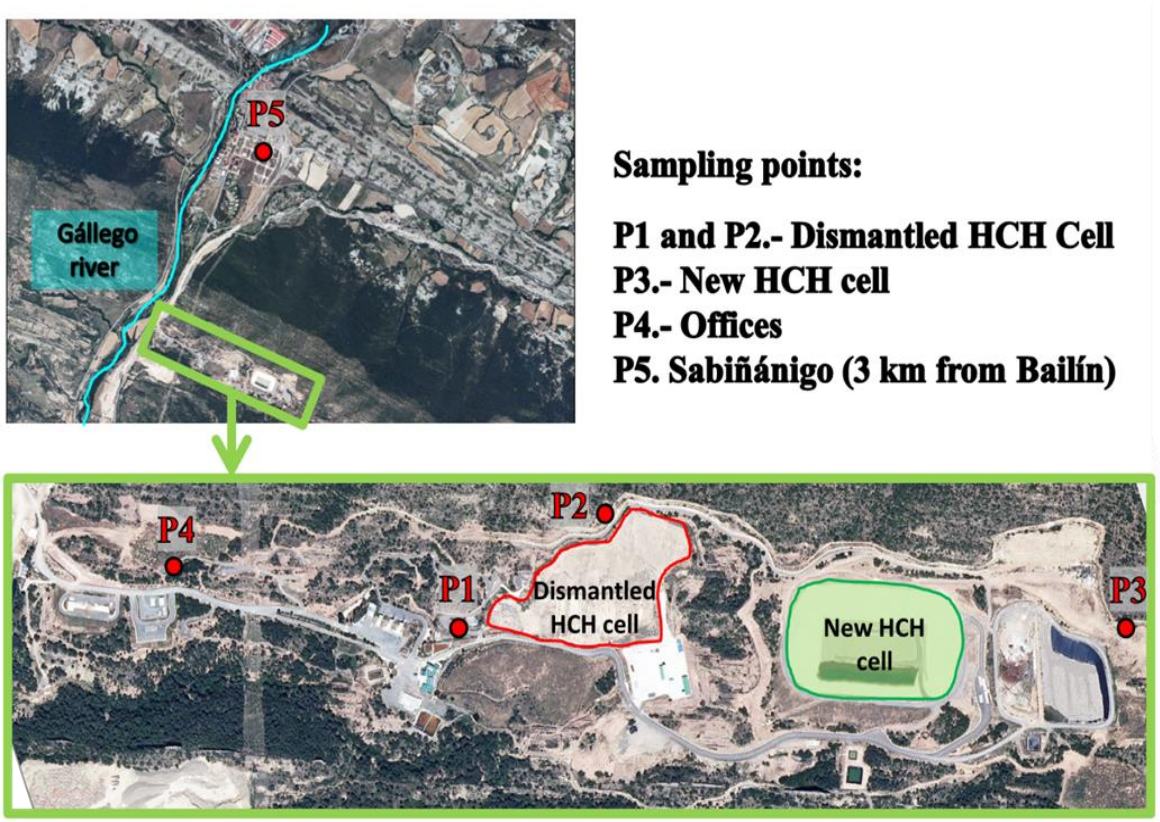

Figure 1. Location of the passive air sampling points selected in the Bailín landfill and surroundings.

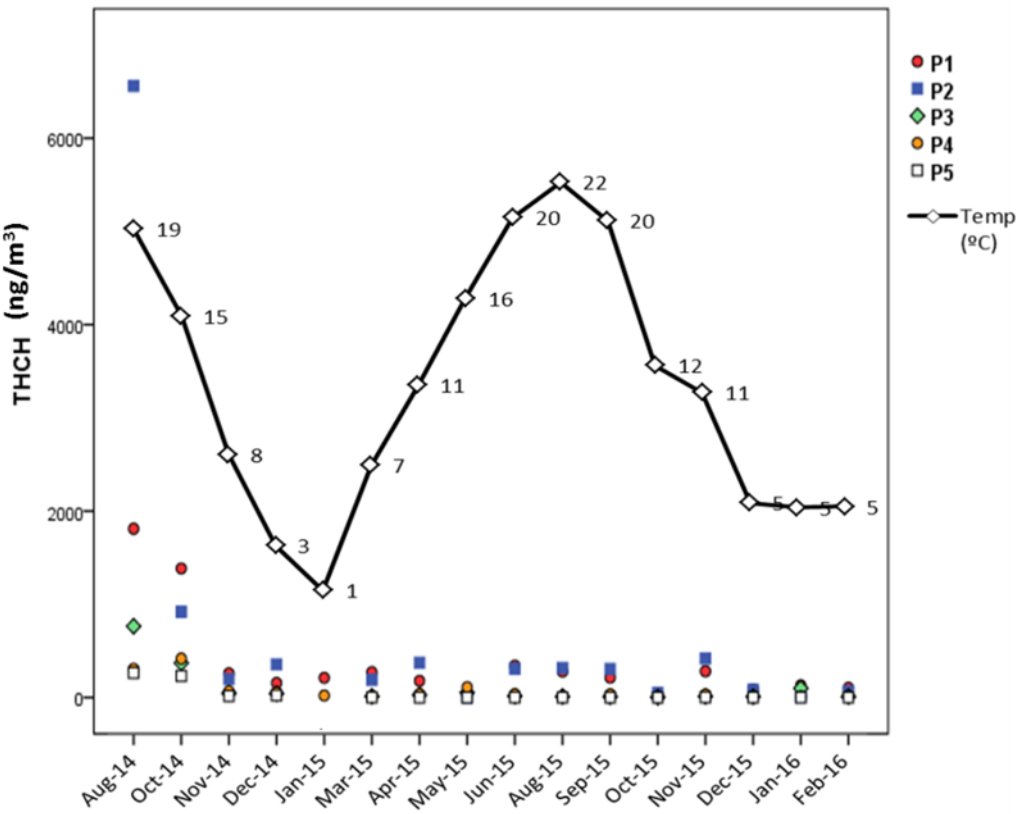

Figure 2. HCH total concentration, expressed in ng/m^3, and average temperature for each sampling point (P1 to P5) at each sampling period (August 2014 - February 2016).