HCH isomers change in Pyrenean freshwater ecosystems triggered by the transfer operation of Bailín landfill: the case of Sabocos tarn

Understanding the airborne transport pathways of organic semi-volatile pollutants is crucial to prevent their dissemination and minimize or even avoid their environmental hazards. For decades, technical hexachlorocyclohexane (HCH) mixtures (55–80 % α-HCH, 5–14 % β-HCH, 8–15 % γ-HCH, and 2–16 % δ-HCH; from 1940 to 1970), as well as purified lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane, γ-HCH; since 1970) were extensively used as insecticides. HCH isomers are synthetic molecules that do not exist in nature. The inefficient techniques used for years in the production of γ-HCH, the well-known pesticide lindane (a paradigmatic non Green chemical process), generated between 8 and 12 tonnes (t) of by-products and residues (mostly HCH waste isomers α-HCH, 55–80 %; β-HCH, 5–14 %; δ-HCH, 2–16 %; and ε-HCH, 3–5 %), per tonne of usable lindane (Bodenstein, 1972; Vega, Romano and Uotila, 2016; Santos et al., 2018). These by-products persist in the environment causing bioaccumulative toxic effects. HCH isomers can be spread through the food chain and transported by wind and water, affecting both wildlife and human population far away from the spots where they were originally produced and released. This is the origin of a global-scale problem, which triggers extensive contamination of soils, water and groundwater (Vega et al., 2016; Vijgen et al., 2019).

Lindane production and use made a significant contribution to global contamination, generating the world's largest persistent organic pollutants (POPs) stockpile (Breivik et al., 1999; Li, 1999; Vijgen, 2006; Vijgen et al., 2011; Santos et al., 2018; Vijgen et al., 2019). As a result, lindane, along with the organochlorine isomers abundantly generated as residues in its manufacture, were added to the list of POPs of the Stockholm Convention on 26th August 2009 (Vijgen et al., 2011). Today, both its industrial production and use is severely restricted. Nevertheless, from 1940 until reaching modern manufacturing standards, producers usually stockpiled their HCH residues in open landfills, causing concomitant air, soil and water pollution. Due to their persistence and recalcitrance, HCHs residues and lindane persist in water, soil and sediments, for a long time (Kumar and Pannu, 2018). Beyer and Matthies (2001) reported half-life periods for lindane in soil and water 708 and 2292 days, respectively.

Lindane was produced in numerous countries worldwide, such as Argentina, Azerbaijan, Brazil, China, Ghana, India, Japan, Russia and the United States (Vijgen, 2006). In Europe, no less than 47 lindane production facilities were located in various countries, such as the Czech Republic, France, Germany, the United Kingdom, the Netherlands, Italy, Slovakia, Romania, Poland and Spain, mainly from the 1950 decade to the 1990 decade (Vega et al., 2016).

Just in European territory, around 400,000 t of technical HCH and 81,000 t of lindane were used from 1970 to 1996 (Breivik, Pacyna and Munch, 1999). In Europe, the top 10 countries with the largest lindane usage between 1950 and 2000 were: Czechoslovakia, Germany, Italy, France, Hungary, Spain, Russia, Ukraine, Yugoslavia and Greece, representing 96 % of the total usage in Europe (Vijgen, 2006).

Although different attempts were made to develop methods to re-use waste HCH isomers synthesized during the manufacture of lindane, most of these procedures were rejected over time and, consequently, most of the waste products have been dumped during the last 50 years (Vijgen, 2006). As a consequence, in some European countries that previously manufactured lindane and technical-HCH (e.g., France, Germany and Spain), the amount of HCH-waste is estimated to be hundreds of thousands of tonnes (Vijgen, 2006).

Spain hosts some of the largest HCH waste deposits worldwide (Fernández, Arjol and Cacho, 2013; Vijgen, 2006; Vijgen et al., 2011; Vijgen et al., 2019). Lindane was industrially synthesized in Spain at four production facilities, though all of them came to an end several years ago. Two manufacturing units were located in the Basque Country, generating approximately 82,000 t of wastes. A smaller factory located in Galicia produced several thousand tonnes of HCH waste together with several hundred thousand tonnes of contaminated soil, as a result of the dumping process.

Spain's last and, undoubtedly, largest single lindane production plant, INQUINOSA (Industrias Químicas del Noroeste S.A.), was located in Sabiñánigo (Huesca province, Spain, located at 750 m.a.s.l.) and was operating until 1988 (Vijgen et al., 2011). Purified lindane was obtained in a two-step process. Firstly, the reaction of benzene with free chlorine, triggered by ultraviolet rays produced what is known as technical HCH. Secondly, the technical HCH was distilled with methanol to isolate the gamma isomer (Gobierno de Aragón, 2014). From 1975 to 1988, INQUINOSA produced lindane in Sabiñánigo, with a resulting by-product of approximately 115,000 to 160,000 t of waste isomers, that were dumped in two unlined landfills located in Sardas (close to Sabiñánigo's ring road) and Bailín (Fernández, Arjol and Cacho, 2013; Vijgen, 2006; Gómez-Lavín et al., 2018; Santos et al., 2018; Navarro et al., 2019). These two landfill sites, together with the INQUINOSA former production facility, nowadays a derelict full of raw materials and chemical waste, are documented as one of the largest HCH waste deposits worldwide (Fernández, Arjol and Cacho, 2013; Vijgen, 2006; Vijgen et al., 2011). In the last 25 years, the Government of Aragón has invested some 54 M€ in a number of remediation measures with the purpose of minimizing environmental pollution caused by lindane residues in the Sabiñánigo area, and presuming a total investment of 550 M€ during the next 25 years (Gobierno de Aragón, 2017), along with the construction of an analysis laboratory in Sabiñánigo (Chic, 2018). In addition, the Government of Aragón is elaborating a first version of Strategic Action Plan against the lindane waste contamination in Aragón, aided by LINDANET, a project that joins European regions to work towards the improvement of the HCH (lindane) contaminated sites (LINDANET, 2021).

Environmental pollution generated by HCH waste isomers in the Sabiñánigo area affects soils, ground and surface freshwater masses. Over the years, the Aragón Regional Government and the Spanish Environmental Ministry have evaluated and carried out various remediation works with unequal success. As a result, groundwater plumes, adding up approximately 4,000 t, of the so-called dense non-aqueous phase liquids (DNAPLs) composed by HCH isomers, benzene, chlorobenzenes and chlorophenols (Fernández, Arjol and Cacho, 2013), have been discovered at both dumpsites and also at the former INQUINOSA factory. Remarkably, additional extremely hazardous pollutants as polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/PCDFs), have been found in the Sabiñánigo affected area (Gómez-Lavín et al., 2018). Having an extraordinary migration and pollution potential, DNAPL plumes constitute a severe environmental hazard downstream the Gállego River aquatic environment and, therefore, to nearby soils and land ecosystems.

HCH isomers waste at Sardas landfill, is estimated between 30,000 and 80,000 t of solid HCH waste isomers and 2,000 t in its liquid phase (DNAPL; Fernández, Arjol and Cacho, 2013) soaking some 350,000 m3 of waste. Nonetheless, Sardas hazardous waste dump lacks a liner system or other standard safety measures in place. Yet, the high amount of toxic residues contained in Sardas and its extremely difficult management and transport close to Sabiñanigo's urban area, ruled out its excavation and transfer to the new secure cell in Bailín.

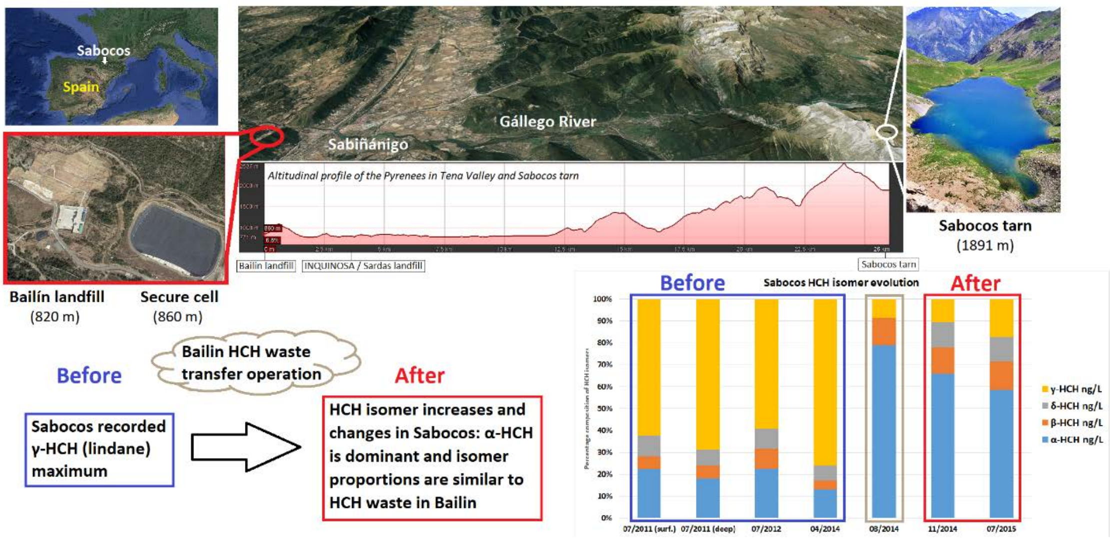
The unlined Bailín dumpsite (Lat.:42°29'12.9"N – Long.:0°21'39.6"W; 820 m.a.s.l.) was used from 1984 to 1992. It is located on top of an interbedded vertical sequence of sandstone and fine-grained limolite layers and stores approximately the same amount of residues of HCH isomers as the Sardas landfill, adding up 180,000 m3 of waste. Over the years, its underground DNAPL plume has reached the Gállego River stream repeatedly, causing pollution episodes and serious health risks for human population downstream. Thus, to prevent future pollution episodes, the transfer of the bulk waste from their original unlined dumpsite to a new security cell was planned in 2007. Finally, the transfer operation was carried out during the 2014 summer. Due to the inadequate geological structures and lithology of the area, the new cell (Lat.:42°29'07.5"N – Long.:0°21'24.5"W; 860 m.a.s.l.) was designed and built with supplementary isolating measures (Fernández, Arjol and Cacho, 2013; De la Torre et al., 2018).

De la Torre et al. (2018) evaluated the influence of Bailín dumpsite dismantling using passive air samplers, ranging the period from summer 2014 to autumn 2016. The recorded amounts of α, β, γ, δ and ε HCH isomers analyzed by De la Torre et al. (2018) in 112 air samples suggested that the actions performed during and even after the transfer operation were a main source of HCH air pollution. However, the study of De la Torre et al. (2018) was limited to the work area at the Bailín landfill and a single sampling point located in Sabiñanigo. Our study, on the other hand, highlights the relevance of the transfer operation as the main source of HCH isomers air pollution in mountainous ecosystems located at distances of tens of kilometers from the contamination focus.

High mountain lakes and tarns are excellent proxies for assessing the impact of atmospheric anthropic pollutants in freshwater ecosystems (Battarbee et al., 1997; Catalan et al., 2006; Arruebo, 2014; Santolaria et al., 2015a, b; Moser et al., 2019). They are seldom affected by direct human activities, thus receiving their pollutant inputs mainly airborne (Catalan et al., 2013; Santolaria et al., 2015a,b; Kang et al., 2019; Moser et al., 2019). Moreover, due to their exceptional environmental features, tarns allow high-resolution studies of both local direct airborne transport and global environmental processes (e.g., global distillation effect or grasshopper effect and particulate airborne transport). This is due to their high sensitivity to airborne inputs and also by the very dynamics of the POPs, prone to condense in cold climates (i.e., high latitude or altitude environments; Santolaria et al., 2015a,b).

The 2014 HCH waste transfer works at Bailín landfill provided a unique and historic opportunity in the Pyrenees mountain range to assess the effect of local airborne transport in a high mountain environment such as Sabocos tarn. We did so by testing its effects in the water mass of Sabocos tarn, one of the region's largest glacial lakes, located NNE from Bailín, in a non-prevalent winds direction. The mountain cirque around Sabocos tarn most likely prevents a direct wind corridor to Balin. Thus, thermally sourced hillside breezes are the most probable vector for the HCH isomer airborne transport from Bailin to Sabocos.

Since local airborne HCH isomers pollution was barely studied and assessed in the Bailín area prior to the 2014 remediation work, our research team accomplished a preliminary study at the Sabocos tarn (Santolaria et al., 2015a). The initial results showed a concentration peak of HCH isomers recorded in summer 2014 that might be related with the transfer operations that was being carried out.



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PARDO, A., RODRÍGUEZ-CASALS, C., ANTOLARIA, Z., ARRUEBO, T.; URIETA, J. S.; LANAJA, J. (2021). *HCH isomers change in Pyrenean freshwater ecosystems triggered by the transfer operation of Bailín landfill: the case of Sabocos tarn. Science of the Total Environment.* 787, 147655.