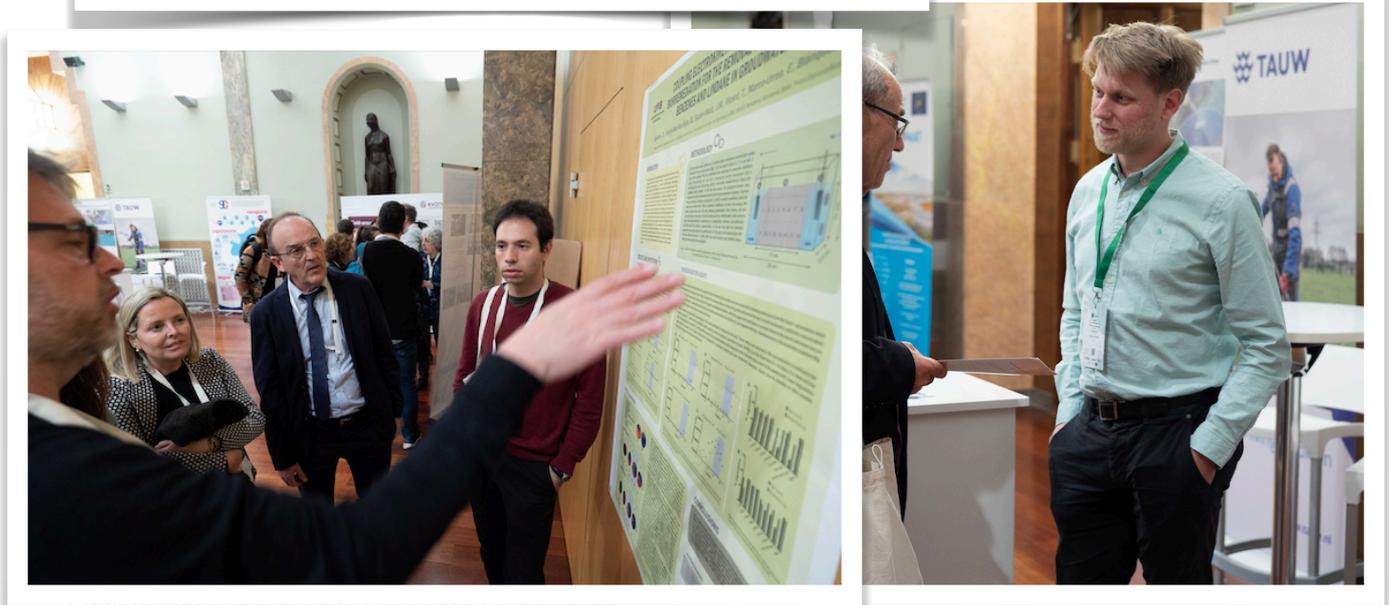
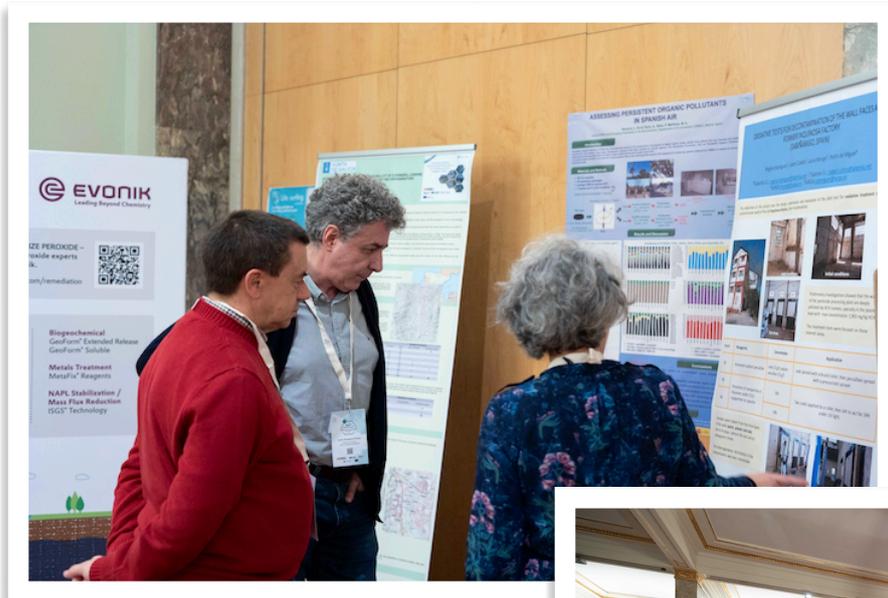


## Block 15

# POSTERS AND SUBMITTED PAPERS



# REMEDIATION OF GROUNDWATER POLLUTED WITH HCHS USING SOLAR LIGHT IRRADIATION

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## **Summary**

Nowadays, pesticides in groundwater are a major concern to scientists because of the serious problems these compounds can cause for human health. Pesticides are commonly used in agricultural activities to prevent weeds in crops and are spread on the soil. One of the most used pesticides until the 90s was lindane ( $\gamma$ -hexachlorocyclohexane,  $C_6H_6Cl_6$ ), an organochlorine compound with high toxicity and bioaccumulative. Several companies produced this pesticide for many years until its use was banned. In the particular case of Spain, the INQUINOSA company operated in the north of the country, producing this compound. However, different isomers of hexachlorocyclohexane ( $\alpha$ -,  $\beta$ -,  $\delta$ - and  $\epsilon$ -hexachlorocyclohexane, HCHs) were also produced as wastes. These compounds, together with lindane, were uncontrolled dumped in Sardas and Bailin landfills, promoting the occurrence of HCHs in groundwater. Currently, a physical-chemical process is carried out to treat the extracted effluents or rainwater runoff. This process separates these pollutants from water but does not degrade them. Hence, subsequent treatment is necessary to destroy HCHs completely.

In this context, Advanced Oxidation Processes (AOPs) can be considered an excellent alternative for removing HCHs from groundwater. These processes are based on producing large amounts of free radicals that significantly contribute to eliminating organic pollutants. Hydroxyl radical is the most common species generated in these processes due to their high oxidation potential (2.8 V). However, it is demonstrated that the ability of these radicals to degrade aliphatics can be limited, and the total mineralization of HCHs could be incomplete. With this background, this work proposes the use of solar light irradiation for the degradation of HCHs from groundwater in the presence of persulfate (oxidant) and ferrioxalate (catalyst). To do this, actual effluents from Sardas and Bailin landfills polluted with different HCHs were treated using a solar simulator and different dosages of oxidant and catalyst. Furthermore, a compound parabolic collectors (CPC) solar reactor was also used under direct sunlight to evaluate the technical viability of the technology at a large scale. During the process, free sulfate radicals are expected to be generated from the activation of persulfate by iron. These radicals can contribute to the degradation and mineralization of HCHs contained in groundwater. The use of ferrioxalate as a catalyst allows working under circumneutral pH conditions. Results show that it is possible to attain a total HCHs conversion up to 75 % in 600 min with the solar simulator ( $q_w$ :  $1.12 \cdot 10^{-7} \text{ E cm}^{-2}\text{s}^{-1}$ ) using  $250 \text{ mg dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8$  and  $3.5 \text{ mg dm}^{-3} \text{ Fe}$ . This value is slightly reduced when using the CPC reactor, suggesting that different amounts of oxidant and catalyst could be required to increase the process efficiency at large scale.

## **Keywords**

Lindane, groundwater, solar light, HCHs, CPC reactor

## **Introduction**

During the 20<sup>th</sup> century, lindane ( $\gamma$ -hexachlorocyclohexane, HCH,  $C_6H_6Cl_6$ ) was a pesticide produced and marketed worldwide. The synthesis of this compound was carried out with benzene and chlorine under UV irradiation [1]. In 2008, the European Union forbade the production of lindane because it was classified as a cancerogenic compound by the International Agency for Research on Cancer [2]. Despite this, uncontrolled industrial landfills still exist where chemical companies dumped tonnes of lindane and other isomers of HCH over the years, causing soil and groundwater pollution by leaching [3, 4]. In Spain, two landfills in the Aragón region (northeast of Spain) are highly contaminated by lindane production wastes (Bailín and Sardas). For this reason, it is necessary to develop clean and efficient

technologies that allow the removal of HCH isomers (HCHs) from water bodies.

Biological processes can be suitable for removing HCHs in aqueous phases because they are low-cost and environmentally friendly technologies [5, 6]. However, the ability of these technologies to achieve the complete dechlorination or mineralization of these compounds can be limited, favouring the production of toxic organochlorine intermediates. Furthermore, the operation times required for the biodegradation of HCHs are expected to be very long. On the other hand, traditional physical-chemical treatments could be considered adequate for removing HCHs from water [7, 8]. These technologies are mainly based on adsorption or coagulation processes. However, they allow moving the pollutants from the aqueous to the solid phase but not degrading them. Hence, it

is necessary to carry out additional steps to eliminate the pollutants from the adsorbents or retained in the coagulants.

To avoid this situation, Advanced Oxidation Processes (AOPs) emerge as an efficient and environmentally friendly alternative to biological and physicochemical processes for degrading organic pollutants in water bodies [9]. These processes are based on producing large amounts of free radicals that can attack the pollutants, favouring their degradation and even their complete mineralization. For this reason, it is expected that these technologies will allow the degradation of HCHs from water and groundwater without the need for additional treatments. AOPs can be classified into photochemical and non-photochemical processes. The use of light irradiation under specific operating conditions can promote the production of large amounts of free radicals to eliminate organic pollutants. However, the energy requirements can compromise the implementation of the technology. To overcome this limitation, the application of direct sunlight has been proposed in recent years as a cost-free and renewable light source. With this background, the main aim of the present work is to evaluate the degradation of HCHs in the aqueous phase using sunlight-activated persulfate in the presence of ferrioxalate as the catalyst. The use of a chelating agent allows operating under circumneutral pH conditions.

### **Materials and Methods**

Sigma Aldrich (Spain) purchased all chemicals (HCHs, oxidant, catalyst and reagents for analysis). Solutions were prepared using high-purity water from a Millipore Direct-Q system (resistivity >18 M $\Omega$  cm at 25°C). The pH of the solutions was adjusted using sulfuric acid or sodium hydroxide. Experiments were performed in a cylindrical glass reactor equipped with a quartz window to allow the total transmittance of the simulated solar radiation. Synthetic water saturated in HCHs was continuously recirculated in the system (discontinuous operating mode). HCHs were extracted from the aqueous samples with hexane, and the concentration of HCHs in the organic phase was determined by gas chromatography (GD/FID/ECD). Spectrophotometric measurements were used to monitor the concentration of the oxidant (persulfate) and the catalyst (iron). Ion chromatography was employed to measure the concentration of different ions and oxalate in the aqueous samples. Further details about the experimental setup and the analytical techniques have been reported elsewhere [10].

### **Results and Discussion**

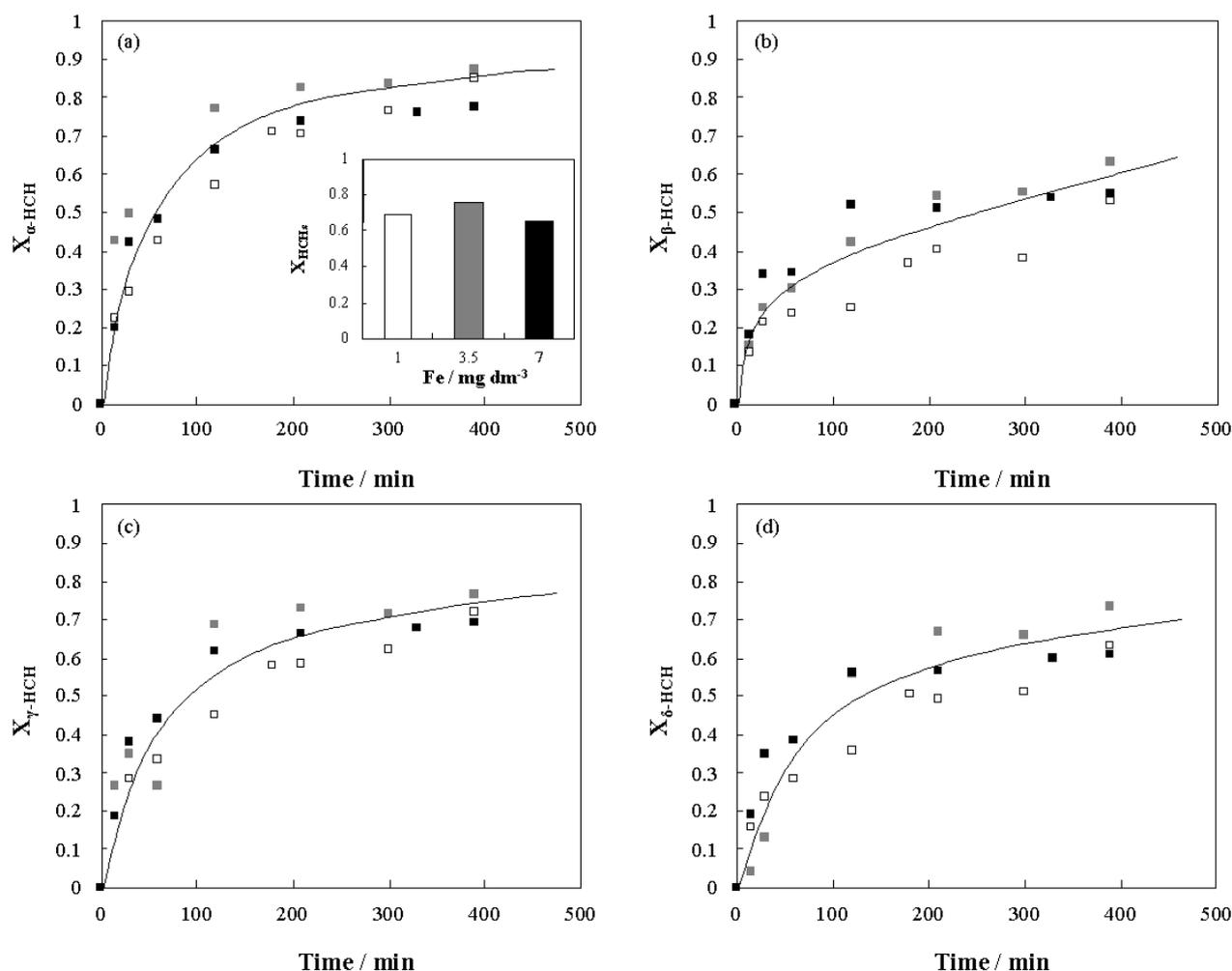
Figure 1 shows the effect of catalyst concentration on the oxidation of HCHs with persulfate under

simulated solar irradiation. The concentration of oxidant used was 100 mg·dm<sup>-3</sup> persulfate, and the concentration of iron (catalyst) ranged from 1 to 7 mg·dm<sup>-3</sup>.

As can be observed, the maximum HCHs conversion is achieved when using 3.5 mg dm<sup>-3</sup> Fe. The use of low catalyst dosages could limit the activation of persulfate and the subsequent production of free sulfate radicals. These species are the main ones responsible for HCHs removal; hence, the amount of catalyst directly influences the removal efficiency. High catalyst dosages are expected to increase the process performance, promoting a large amount of sulfate radicals in the solution and the rapid oxidation of HCHs. However, the conversion of total HCHs reaches 66 % under these conditions, being lower than the values achieved when using 1 and 3.5 mg·dm<sup>-3</sup> Fe (70 and 76 %, respectively). This behaviour can be related to the occurrence of competitive oxidation reactions during the process. In this context, it is important to highlight that the chelating agent (oxalate) is an organic compound susceptible to oxidation by sulfate radicals. The degradation of oxalate promotes the release of iron to the effluent by leaching, decreasing the amount of soluble catalyst available to activate persulfate. Likewise, sulfate radicals produced at the highest catalyst dosage can be wasted in the oxidation of the intermediate organic compounds formed during the oxidation of the parent pollutants. Therefore, an excess of the catalyst does not increase the process performance because of parallel side reactions.

On the other hand, the conversion achieved in each HCH isomer is different, being highest in  $\alpha$ -HCH (~82%) followed by  $\gamma$ -HCH (~73%),  $\delta$ -HCH (~66%) and, finally,  $\beta$ -HCH (~58 %). This can be related to a different initial concentration of each isomer in the effluent or the position of chlorine atoms in the HCH molecule since it has been reported in the literature that the attack of sulfate radicals to HCHs can be different depending on the chlorine atoms positions [11].

Finally, a CPC reactor was used to increase the TRL of the developed technology. This system allows testing the removal of HCHs under direct sunlight, increasing the treated volume and using actual effluents. Results (data not shown) show that high amounts of catalyst and oxidant are required to achieve the conversion obtained during the lab tests since the composition of real effluents is more complex than synthetic matrixes. Nonetheless, the conversions attained are enough to affirm that the photo-oxidation of groundwater polluted with HCHs using persulfate and ferrioxalate under direct solar irradiation is an efficient and very promising technology.



**FIGURE 1. CONVERSION OF HCHS AS FUNCTION OF THE OPERATION TIME DURING THE PHOTO-OXIDATION OF SYNTHETIC WATER SATURATED WITH HCHS.**

(a)  $\alpha$ -HCH; (b)  $\beta$ -HCH; (c)  $\gamma$ -HCH; (d)  $\delta$ -HCH; ( $\square$ )  $[\text{Fe}]_0$ :  $1 \text{ mg} \cdot \text{dm}^{-3}$ ; ( $\blacksquare$ )  $[\text{Fe}]_0$ :  $3.5 \text{ mg} \cdot \text{dm}^{-3}$ ; ( $\bullet$ )  $[\text{Fe}]_0$ :  $7 \text{ mg} \cdot \text{dm}^{-3}$ ;  $[\text{Na}_2\text{S}_2\text{O}_8]_0$ :  $100 \text{ mg} \cdot \text{dm}^{-3}$ ;  $q_w$ :  $1.12 \cdot 10^{-7} \text{ E} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ . Onset: total conversion of HCHs as function of the catalyst dosage.

### Conclusions

Using persulfate and ferrioxalate under solar irradiation promotes the degradation of the HCHs in aqueous phases. Specifically, it is possible to attain a total HCHs conversion up to 75% in 600 min with the solar simulator ( $q_w$ :  $1.12 \cdot 10^{-7} \text{ E} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) using  $100 \text{ mg} \cdot \text{dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_8$  and  $3.5 \text{ mg} \cdot \text{dm}^{-3} \text{ Fe}$ . This value is slightly reduced when using the CPC reactor, suggesting that different amounts of oxidant and catalyst could be required to increase the process efficiency at a large scale.

### Acknowledgements

This research is part of the project PID2019-105934RB-I00 funded by MCIN/AEI/10.13039/501100011033 and project S2018/EMT-4317 (CARESOIL CM) funded by the Community of Madrid. Leandro O. Conte gratefully acknowledges the Marie Skłodowska-Curie Grant Agreement N° 844209.

### References

1. Santos, A., et al., Chlorinated organic compounds in liquid wastes (DNAPL) from lindane

production dumped in landfills in Sabiñanigo (Spain). *Environmental Pollution*, 2018. 242: p. 1616-1624.

2. Romano, D., et al., Lindane (persistent Organic Pollutant) in the EU: Study. 2016: European Parliament.

3. Vijgen, J., et al., European cooperation to tackle the legacies of hexachlorocyclohexane (HCH) and lindane. *Emerging Contaminants*, 2022. 8: p. 97-112.

4. Biosca, B., et al., Detection of chlorinated contaminants coming from the manufacture of lindane in a surface detritic aquifer by electrical resistivity tomography. *Journal of Applied Geophysics*, 2021. 191.

5. Kumari, M., et al., Development of artificial consortia of microalgae and bacteria for efficient biodegradation and detoxification of lindane. *Bioresource Technology Reports*, 2020. 10: p. 100415.

6. Salam, J.A. and N. Das, Degradation of lindane by a novel embedded bio-nano hybrid system in aqueous environment. *Applied Microbiology and Biotechnology*, 2015. 99(5): p. 2351-2360.

7. Patil, I.D., Y.S. Patil, and B.L. Pangarkar, Removal of lindane from wastewater using liquid-liquid extraction process. *Polish Journal of Chemical Technology*, 2013. 15(3): p. 81-84.
  8. Tor, A., et al., Removal of lindane from an aqueous solution by using aminopropyl silica gel-immobilized calix[6]arene. *Journal of Hazardous Materials*, 2013. 262: p. 656-663.
  9. Oturan, M.A. and J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. *Critical Reviews in Environmental Science and Technology*, 2014. 44(23): p. 2577-2641.
  10. Conte, L.O., et al., Degradation of Lindane by persulfate/ferrioxalate/solar light process: Influential operating parameters, kinetic model and by-products. *Applied Catalysis B: Environmental*, 2023. 324: p. 122288.
  11. Conte, L.O., et al., LED visible light assisted photochemical oxidation of HCHs in aqueous phases polluted with DNAPL. *Process Safety and Environmental Protection*, 2022. 168: p. 434-442.
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# COUPLING ELECTROKINETIC SOIL FLUSHING WITH BIOREMEDIATION FOR THE REMOVAL OF CHLORINATED BENZENES AND LINDANE IN GROUNDWATER

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Bioremediation is coupled with electrokinetic soil flushing technology to check the proper performance in the degradation of chlorinated benzenes and lindane in the soil and groundwater from Sardas (Sabiñánigo, Spain). Biological barriers using microbial consortia from the site are used, and aerobic and anaerobic conditions were tested. The electric field (17 V) does not hamper biological activity and promotes a water flow that allows the pollutants to reach the biological barrier, where the pollutants can be removed.

## Keywords

Chlorinated benzenes, lindane, bioremediation, electrokinetic soil flushing, biological barrier, groundwater.

## Introduction

Chlorinated benzenes and hexachlorocyclohexanes (HCHs or lindane) are toxic compounds that can be frequently found in natural environments due to negligence or improper disposal during their industrial use in the production of pesticides and other chemicals (Field & Sierra-Alvarez, 2008; Kumar & Pannu, 2018). These compounds have been seen to be persistent and harmful to health and they are listed in the ATSDR's Priority List (ATSDR, 2019). Sarda's landfill, located in Sabiñánigo (Aragón, Spain), near the Gállego river, received many industrial wastes from pesticides manufacture. Although now it is closed, it has polluted the soil and groundwater from the site mainly with HCHs and chlorinated benzenes. Bioremediation is a suitable technology to remove pollutants *in situ* given the low cost and acceptability (Li et al., 2016). Previous studies point out that the lower chlorinated compounds are more easily degraded in aerobic conditions, while higher chlorinated compounds have to be treated in anaerobic conditions (Field & Sierra-Alvarez, 2008; Trueba-Santiso et al., 2022). However, the application of bioremediation in soils may be limited by the access of microorganisms to nutrients and pollutants. To overcome it, bioremediation can be coupled with different techniques, such as the electrokinetic soil flushing (Li et al., 2016; Ramírez et al., 2015). It consists of the application of an electric field to make nutrients and pollutants available to microorganisms using a flushing solution. This electric field promotes extreme pH values in soil, as well as soil heating in some soil types. For this reason, a good strategy to protect the microorganisms is to confine them in a biological barrier (Ramírez et al., 2015). Thus, we evaluate the combination of both electrokinetic and bioremediation technologies at bench scale to efficiently remove HCHs and chlorinated benzenes from a silt soil coming from Sardas. The tests operated with a biological barrier inoculated with

microbial communities from Sarda's groundwater, and both aerobic and anaerobic conditions were assessed.

## Methodology

All the assays were carried out in methacrylate containers of 26 cm × 3.5 cm × 16 cm hermetically sealed divided in three compartments separated by a 0.5 mm nylon mesh (Figure 1) (Ramírez et al., 2015). The middle compartment was divided in 16 portions according to Figure 1. An electric field of 17 V in all tests (1 V/cm) was applied.

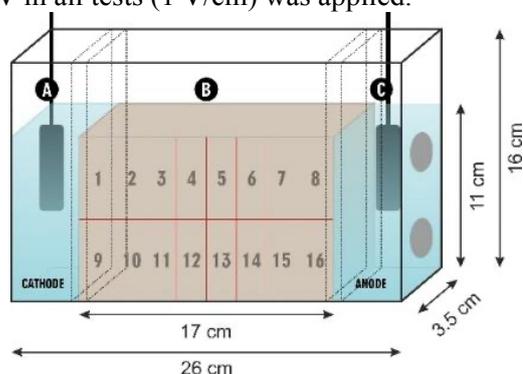


FIGURE 1. SCHEME OF CONTAINERS USED IN THE EXPERIMENTS. A: CATHODIC WELL; B: SOIL; C: ANODIC WELL

The first experiment lasted 12 days and was developed in anaerobic conditions using non-polluted silt soil with a biological barrier inoculated with a *Dehalogenimonas*-containing culture (anaerobic bacteria) and the electrode compartments were filled with synthetic saline solution (30.36 mg/L KNO<sub>3</sub>, 70 mg/L NaHCO<sub>3</sub>, 88.75 mg/L Na<sub>2</sub>SO<sub>4</sub>). In the two next assays (14 days of operation), the biological barriers were inoculated using two microbial consortia from the groundwater in Sardas. One had been previously enriched by spiking with 1,4-dichlorobenzene (1,4-DCB) as sole carbon source in aerobic conditions, while the other was enriched with  $\gamma$ -HCH in anaerobic conditions. In these two assays, the

anode compartment was fed with polluted groundwater from Sardas and saline solution was placed in the cathode compartment. In each experiment, the biological barriers were prepared using 70% (w/w) soil and 30% (v/v) active microbial culture.

Liquid samples from the anodic and the cathodic wells were taken to measure pH, conductivity, and pollutants concentration during the experiment. Solid samples were taken *post-mortem* to determine pH, conductivity, moisture, and pollutants concentration. In the two last tests the microbial population was also analysed. Temperature was measured in the biological barrier during the first test. Analysis of pollutants from both liquid and solid samples were determined by GC-MS with ISTD patrons. To determine pH and conductivity from solid samples, 10 g of soil were mixed and stirred with 25 mL deionized water. When sedimented, pH and conductivity were measured in the liquid phase (EPA 9045C). Moisture was determined measuring wet and dry weight (after 24 h at 100 °C). Microbial population was determined by amplifying the 16S gene and sequencing using an Illumina MiSeq Run Nano 2 × 250. DNA from soil samples was isolated using a DNeasy® PowerSoil® Kit from QIAGEN.

### Results and discussion

In the first assay, temperature values ranged between 22 °C and 26 °C in the biological barrier (Figure 2A), so the soil heating due to the electric field was negligible and was not a hindrance for the microorganisms. The moisture of the soil was enough to allow the biological activity (Figure 2B). However, the pH values were extreme in the electrolytic wells, as well as in the soil in zones close to the cathodic well (Figure 2C, D). The extreme pH could be a limiting factor to the microbial activity, for this reason, and because the electroosmotic flux is from anode to cathode, the following two assays were performed moving the biological barrier near to the anodic well, to the 6, 7, 14 and 15 portions (Figure 1).

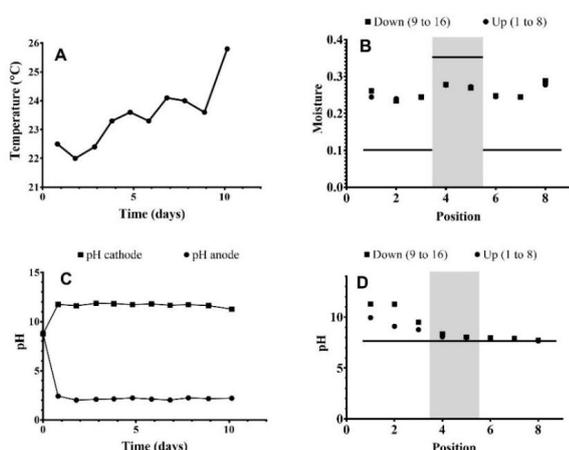


FIGURE 2. PARAMETERS ANALYSED DURING THE FIRST

ASSAY: A) TIME COURSE OF THE TEMPERATURE IN THE BIOLOGICAL BARRIER; B) MOISTURE PROFILE IN SOLID SAMPLES ANALYSED *POST-MORTEM*; C) TIME COURSE OF THE PH IN BOTH ANODIC AND CATHODIC WELLS; D) PH PROFILES IN SOLID SAMPLES ANALYSED *POST-MORTEM*. GREY ZONES INDICATE THE LOCATION OF THE BIOLOGICAL BARRIER. SOLID HORIZONTAL LINES ARE INITIAL VALUES.

These two assays aimed to prove the capacity of two consortia (one aerobic and one anaerobic) to remove pollutants from the Sardas's groundwater which flow through the biological barrier. Figure 3 shows the degradation percentage of the main pollutants analysed in the soil. These values are referred to the concentration of pollutants that remain in portions 1 and 9 of the soil (Figure 1) with respect to that analysed in portions 8 and 16 (Figure 1) at the final time ( $t = 14$  days). It is observed that most of the pollutants reach the 1 and 9 portions at very low concentrations with respect to the concentration near to the anodic well. Lower degradation percentages for some of the higher chlorinated compounds in aerobic treatments are observed. However, losses due to volatility or other possible physical processes have not been addressed. The molecular biology analysis in the two last experiments will provide valorous information about the possible responsible for the degradation.

The next step in this work was to evaluate the capability of the biological barrier to bioremediate polluted soil while polluted groundwater was fed to the anodic well. An aerobic test with a biological barrier using an inoculum from the site is proposed, using a polluted silt soil. An abiotic control was also carried out to assess volatility losses.

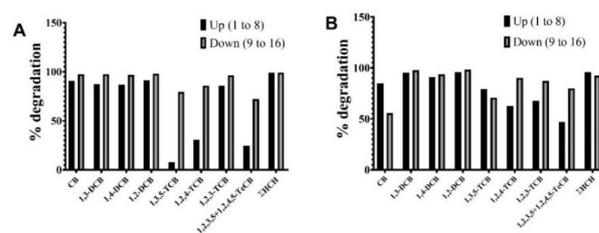


FIGURE 3. DEGRADATION PERCENTAGE OF THE MAIN POLLUTANTS DETECTED IN THE SOIL. A) AEROBIC TREATMENT. B) ANAEROBIC TREATMENT

### Conclusions

By coupling both technologies, bioremediation and electrokinetic soil flushing, pollutants contained in the groundwater can be efficiently removed when pass through the biological barrier. The biological barrier must be located slightly closer to the anodic well, in order to avoid extreme pHs achieved near the cathodic well. Both, the aerobic and anaerobic autochthonous inoculum could adapt to the bioremediation and electrokinetic soil flushing experimental conditions.

### **Acknowledgements**

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### **References**

- Field, J. A., & Sierra-Alvarez, R. (2008). Microbial degradation of chlorinated benzenes. *Biodegradation*, *19*(4), 463–480. <https://doi.org/10.1007/s10532-007-9155-1>
- Kumar, D., & Pannu, R. (2018). Perspectives of lindane ( $\gamma$ -hexachlorocyclohexane) biodegradation from the environment: A review. *Bioresources and Bioprocessing*, *5*(1), 29. <https://doi.org/10.1186/s40643-018-0213-9>
- Li, T., Wang, Y., Guo, S., Li, X., Xu, Y., Wang, Y., & Li, X. (2016). Effect of polarity-reversal on electrokinetic enhanced bioremediation of Pyrene contaminated soil. *Electrochimica Acta*, *187*, 567–575. <https://doi.org/10.1016/j.electacta.2015.11.097>
- Ramírez, E. M., Camacho, J. V., Rodrigo, M. A., & Cañizares, P. (2015). Combination of bioremediation and electrokinetics for the in-situ treatment of diesel polluted soil: A comparison of strategies. *Science of The Total Environment*, *533*, 307–316. <https://doi.org/10.1016/j.scitotenv.2015.06.127>
- Trueba-Santiso, A., Palau, J., Soder-Walz, J. M., Vicent, T., & Marco-Urrea, E. (2022). Assessment of aerobic biodegradation of lower-chlorinated benzenes in contaminated groundwater using field-derived microcosms and compound-specific carbon isotope fractionation. *Journal of Environmental Sciences*, *118*, 204–213. <https://doi.org/10.1016/j.jes.2021.12.025>
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# SNI SACCO RIVER VALLEY – CENTRAL ITALY: CHARACTERIZATION OF AGRICULTURAL AREAS

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## **Summary**

The Sacco River Valley is included by the Italian Ministry of the Environment among the sites of national interest (SNI), for which the reclamation process is a priority for the Italian State (National Decree 152/2006). The perimeter of the area includes 19 municipalities, 4 of which in the province of Rome and 15 in the province of Frosinone. Among the numerous environmental problems, the greatest is the contamination of soil and river sediments by  $\beta$ -HCH, which has caused since 2005 the prohibition of all agricultural activities in riparian areas up to 100 m from the riverbanks, and in the floodable zones. In 2019, the regional authority signed a framework agreement with various competent public bodies, in order to finance interventions for the promotion of citizen health and for environmental characterization, preparatory to the reclamation of the area.

In this context, the Istituto Zooprofilattico Sperimentale (IZSLT), together with the Istituto Superiore di Sanità (ISS), have been charged with planning, organizing and coordinating the "Characterization of Riparian Agricultural Areas". The main objectives of the Plan are: i. determine soil contamination levels at a very detailed scale; ii. remove the ban on agricultural activities for non-contaminated areas; iii. contribute to the assessment of the exposure risk for soils, plants, animals and humans.

For this purpose, an executive project was approved. The three main pillars of the plan are: 1. soil sampling and analysis; 2. sampling and analysis of wild plants; 3. sampling and analysis of bulk milk from livestock farms. Dedicated and trained personnel will work on a total of approximately 700 “land-plots” covering an area of 1,700 hectares. In each “land-plot”, a variable number of soil and plant samples representative of the land surface will be collected. A single pooled sample of soils and one of plants will then be created for each land-plot. Two samples of bulk milk will be taken during the year in each of the landplot, if there is at least a dairy farm.

The analyses of soil will detect the presence and concentration of an extended spectrum of contaminants; POPs, metals and PAHs will be searched for in plants; bulk-milk will be examined only for  $\beta$ -HCH, unless other critical issues emerge from the other matrices. This is the very first experience in Italy of a such extended characterization plan, foreseen by the recent Italian legislation (DM 1 marzo 2019 n. 46).

## **Keywords**

Italy, Sacco River Valley, soil pollution, Lindane, hexachlorocyclohexane (HCH), characterization.

## **Introduction**

The Sacco River Valley is a territory in Italy affected by hexachlorocyclohexane pollution. It was declared Site of National Interest (SNI) in 2005. Sites of national interest are large contaminated areas classified as hazardous by the Italian state and in need of remediation of soil, subsoil and/or surface and groundwater to prevent environmental diffusion and health consequences on exposed population. In Italy, the responsibility of the SIN remediation procedure is attributed to the competence of the Ministry of the Environment and Energy Security (MITE). The primary source of HCH contamination was an industrial area on the right side of the Sacco River in the municipality of Colleferro (60 km south from Rome) that produced lindane between 1950 and 1980 and

buried waste in different landfills inside its borders. Among the numerous environmental problems, the greatest is the contamination of soil and river sediments by  $\beta$ -HCH, which has caused since 2005 the prohibition of all agricultural activities in riparian areas up to 100 m from the riverbanks, and in the floodable zones.

This contribution describes the "Characterization of Riparian Agricultural Areas" Plan, one of several initiatives resulting from the agreement between the regional authority and various competent public bodies, including the Istituto Zooprofilattico Sperimentale (IZSLT). The plan will start in the coming months, by mid-2023, with the final general objective of providing an updated characterization of the entire area, never systematically carried out since 2005. The specific objectives of the plan can be summarized as

follows: i. determine soil contamination levels at a very detailed scale; ii. remove the ban on agricultural activities for non-contaminated areas; iii. contribute to the assessment of the exposure risk for soils, plants, animals and humans. The characterization plan is based on a process of monitoring-surveillance and on an integrated analysis of results obtained within a conceptual model of risk evaluation involving soils, plants & animal productions (bulk milk).

This approach derives from the evidence produced during the emergency phase of 2005-2006 where it was demonstrated that  $\beta$ -HCH contamination reached animals and food chain through surface waters and fodders cultivated near the river. Since then a milk monitoring plan was adopted (PNR) to ensure compliance with the restrictive requirements imposed on the area (prohibition of using local forage) and food safety. Since 2009 the Lazio Region, started a program of "Health and epidemiological surveillance of the resident population near the river Sacco" and a periodic human biomonitoring.  $\beta$ -HCH has stronger lipophilic properties. It can be absorbed by humans through assumption of contaminated food and it is bioaccumulated in body fat. In 2012, the human biomonitoring showed that the beta-HCH blood concentration in the interested area was on average 99.05 ng/g fat in urban areas and 150 ng/g along the river, higher than those found in general population of European countries (about 50 ng/g fat - period 1996-2006). The blood contamination resulted associated with attitude to consumption of locally produced food.

### Methodology

The process of monitoring-surveillance will include soils for characterization of riparian agricultural areas, plants biomonitoring and animal monitoring through bulk milk. The work will be done following these steps: sampling; chemical laboratory analysis and data analysis. Field activity will be accomplished by 2 teams operating simultaneously 5 days/week, each with 2 land plot per team/die. Therefore sampling will be carried out in 80 land plot/ month. Complete soil analysis are expected in approximately 13 months from the start of the operational phase of the characterisation plan, barring unforeseen events.

The perimeter of the intervention area involves 3 municipalities in Rome province and 13 in Frosinone Province. Length is approximately 54 km downstream the Sacco river from Colferro up to the confluence with the Liri river. It is included the area prohibited for agricultural use in 2006 within 100 meters from the riverbanks and the area corresponding to the floodable zones with return periods 30-50 years. There are approximately 1,730 hectares with the exclusion of areas already involved in land reclamation. The perimeter has

been divided into further subdivision (land plots), which are homogeneous polygons (*unit of land*) with a known surface, respecting the homogeneity of land use (satellite orthophoto), when possible.

TABLE 1. CONTAMINANTS SOUGHT IN SOILS

Inorganic compounds	Hydrocarbons	Pesticides
Antimony	Hydrocarbons C10-C40(1)	Aldrin
Arsenic		$\alpha$ -hexachlorocyclohexane
Beryllium	<b>Aromatic polycyclic hydrocarbons</b>	$\beta$ -hexachlorocyclohexane
Cadmium	Benzo(a)anthracene	$\gamma$ -hexachlorocyclohexane
Cobalt	Benzo(a)pyrene	Chlordane
Total Chromium	Benzo(b)fluoranthene	DDD
Chromium VI	Benzo(k)fluoranthene	DDT
Nickel	Benzo(g,h,i)perylene	DDE
Lead	Chrisene	Dieldrin
Copper	Dibenzo(a,h)anthracene	Endrin
Selenium	Indenopirene	Dioxins and furans
Tallies		PCDD, PCDF + dioxin-like (PCD-DL)** summation (t.e conversion)
Vanadium		
Zinc		PCB NON DL***

TABLE 2. CONTAMINANTS SOUGHT IN PLANTS

Organochlorines
Aldrine
$\alpha$ -hexachlorocyclohexane
$\beta$ -hexachlorocyclohexane
$\gamma$ -hexachlorocyclohexane
Chlordane
DDD
DDT
DDE
Dieldrin
Endrin
Dioxins and furans

The soils characterization will be ensured by accredited laboratory chosen by a regional tender. Milk is one of the food most sensitive to beta-HCH contamination and for this reason used for biomonitoring. Sampling on bulk milk (performed by official Vets of cattle and sheep) is done twice in a year. The milk samples will be analysed only for  $\beta$ -HCH by IZSLT. If soils and/or plants will result

contaminated by other molecules, these will be also searched in milk or organs of animals at the end of their career.

Plants biomonitoring is in charge of IZSLT. In a symmetrical way and at the same time and in the same collection points where the soil sampling is carried out, plant essences will be sampled. This will ensure the exact correspondence of the survey on the two matrices and test possible correlations. Sampling will be carried out by IZSLT staff working within the sampling teams in a coordinated manner with the corresponding soil sampling. Plant matrices will be systematically tested for organochlorine contaminants on all the samples collected.

**TABLE 3. COMPOUNDS SOUGHT IN PLANTS, IF PRESENCE DETECTED IN THE CORRESPONDING SOILS**

Inorganic compounds	Aromatic polycyclic hydrocarbons (IPA)
Antimony	Benzo(a)anthracene
Arsenic	Benzo(a)pyrene
Beryllium	Benzo(b)fluoranthene
Cadmium	Chrysene
Cobalt	
Total Chromium	
Nickel	
Lead	
Selenium	
Tellurium	
Vanadium	
Zinc	

In the event of evidence of a match on the corresponding soils, Polycyclic Aromatic Hydrocarbons (PAHs) and Inorganic Compounds will also be searched for on plants.

At the conclusion of the field activity a dedicated risk evaluation will be carried out in order to take

decisions about the use of the soil and to adopt any measures needed to protect animals and humans from exposure and prevent contamination along the food chain

**TABLE 4. RISK EVALUATION**

Removal of ban for agricultural uses	soils and plants < CSC or legal limit
Ban maintenance and in-depth analysis	soils < CSC and plants < legal limit
Ban maintenance and targeted sampling: 1) repetition of sampling in	soils > CSC and/or plants > legal limit

### References

1. Accordo di programma tra il Ministero dell'Ambiente della Tutela del Territorio e del Mare e la Regione Lazio per la realizzazione degli interventi di messa in sicurezza e bonifica del Sito di Interesse Nazionale Bacino del Fiume Sacco 12/03/2019
2. Council Directive 29/04/1996, 96/22/EC
3. Decreto del Segretario Generale Piano operativo ambiente (FSC 2014-2020) 01/08/2022 n. 232
4. Decreto del presidente del consiglio dei ministri 19/05/2005
5. Decreto legislativo 03/04/2006 n. 152
6. Decreto legislativo 23/02/2010 n. 49
7. Decreto ministeriale 01/03/2019 n. 46
8. Decreto ministeriale 22/11/2016
9. Determinazione Dirigenziale n. B0244/2009
10. Fantini F, Porta D, Fano V, De Felip E, Senofonte O, Abballe A, D'Ilio S, Ingelido AM, Mataloni F, Narduzzi S, Blasetti F, Forastiere F. [Epidemiologic studies on the health status of the population living in the Sacco River Valley]. *Epidemiol Prev.* 2012
11. Ordinanza del presidente del consiglio dei ministri 10/06/2005 n. 3441
12. Pro S, Studio di Sorveglianza Sanitaria ed Epidemiologica della popolazione residente in prossimità del fiume Sacco dopo esposizione al beta-esaclorocicloesano ( $\beta$ -HCH) – Rapporto tecnico attività 2010-2013; Dipartimento di Epidemiologia del Servizio Sanitario Regionale Lazio. 2015

# INTEGRAL INVESTIGATION ON THE COUNCIL OF O PORRIÑO, LOOKING FOR SOLUTIONS TO THE GREAT DISPERSION OF THE CONTAMINATION

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## **Summary**

We have been working for many years with the problem of lindane contamination in the area of O Porriño. We have carried out actions such as the removal of contaminated soils and their management in hazardous waste landfill, a safety cell was built in the area of Torneiros and several phytoremediation studies were carried out throughout all these years.

But the reality is that even today uncontrolled sources of contamination continue to appear as occurred in 2017 in the area of O Contrasto in which, during the performance of sanitation works a continuous layer of lindane was found under the pavement of the road, which had previously been used to smooth the surface of the road.

This last episode showed the need to investigate the existence of other potential sources distributed throughout the territory, so an investigation was commissioned to cover the entire municipality of O Porriño. Now with this work, we want to present you the results of the integral investigation of the city council of O Porriño, what were the results, conclusions and recommendations of this study.

## **Keywords**

Lindane, O Porriño, dispersion, integral investigation, public administrations, coordination.

## **Introduction**

The use of the neighbours of the Lindane waste uncontrolled deposited by Zeltia during the 50's in the municipality of O Porriño (Pontevedra), made that the contamination is nowadays, distributed throughout the territory without knowledge.

The first episode of Lindane contamination found was in 1.992 when a new highway was built. Subsequently, in 1.998, Xunta de Galicia carried out an investigation in Torneiros Industrial area to find out if these lands had lindane residues. In this area blocks of apartments and a park were constructed. The solution to this problem was the construction of a security cell which contaminated soil with concentrations bellow 5mg/kg of lindane was taken. The rest of the contaminated soils were taken to the hazardous waste landfill (SOGARISA). This security cell continued been monitoring but 20 later it needs a definitive solution to decontaminate the area.

A new episode of pollution was discovery in 2.017 in the O Contrasto area, when the town council carried out sanitation works, where a continued layer of lindane was found under a public road.

At that time, the regional authorities decided to carry out an investigation throughout the territory of the municipality of O Porriño with the aim to finding other possible sources of contamination until now unknown, in order to be able to carry out decontamination and control actions.

This work also showed the need to establish coordination mechanisms between the different administrations involved due to the ownership of the land affected by the contamination.

## **Location**

The study area is located in Galicia in the northwest of the Spain, occupying a research surface of 74.035.105 m<sup>2</sup> (Figure.1).

Is located in the valley of the Louro river, a tributary of the Miño, which crosses the area from north to south, where numerous small urban centers are located, the largest being Porriño and Sanguñeda and industrial areas such as the industrial estates of A Granxa, As Gándaras, As Gándaras Granxa, As Gándaras, Torneiros, A Relva and the granite quarries.

The rest of the surface area is occupied by large extensions of forests of timber exploitation especially in the higher areas of the valley.

## **Data mining**

The database of groundwater and surficial water was constructed up samplers and analyses carried out during October and November 2020. A total of 91 control points, 21 piezometers, 15 wells, 23 spring and 32 springs/surface watercourses were inspected.

Soil sampling was conducted from January to the end of May 2021, dividing the entire area into 9 zones. A total of 239 sampling points had been

executed. Collecting a total of 472 soil samples (Table 1).

The analytical results showed the presence of soil and surface water contamination in two areas, one of which was not delimited. The results were evaluated with the project's technical managers, it was agreed to present a second proposal to expand the investigation to delimit the soil in that area.

New characterization was performed in the area with the aim to delimit the contaminated area.

The characterization extension was carried out in two phases (Table 2).

Finally, a total of 716 soil samples were collected during the comprehensive investigation, and 141 water samples.

### Results

Of the 35 groundwater sampling points, the presence of HCH was detected in 7 of them, all of them located at the industrial sites where lindane waste had historically been deposited. None of the analysed HCH isomers were detected in the 27 liquid samples from watercourses and springs.

The following table shows the data of the samples in which the presence of HCH has been detected (Table 3):

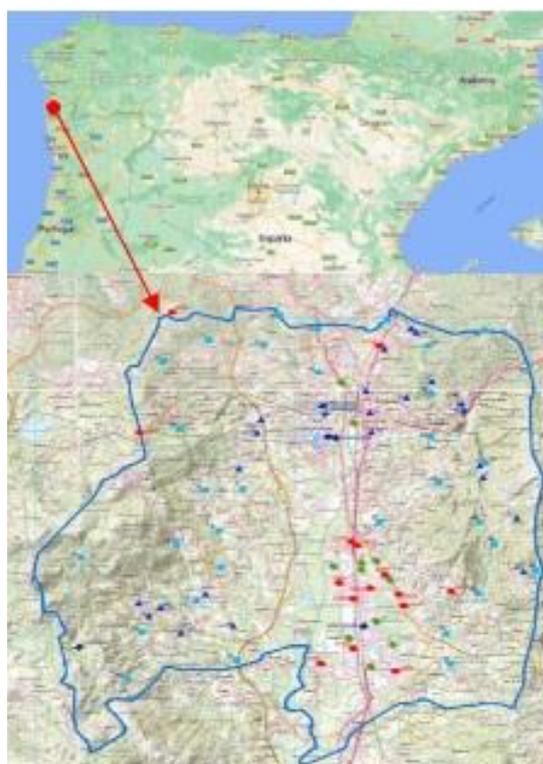


FIGURE 1. LOCATION OF THE INVESTIGATED AREA

TABLE1. SAMPLING POINTS AND NUMBER OF SAMPLES

Zones	Sampling points				Number of samples		
	Manual boring	Short boring	Long boring/ piezometer	Calicata	Soils	Groundwater	Surficial water
ZEC Gándaras	39				48		15
Monte Risca				15	34		
Alvarín	2			10	23		
Atín	3			15	35		
Roads N120-N550	1	10	2	2	29	2	
PV-5	7	10	3	14	68	4	
Regato das Laxes	3			47	117		5
PI As Gándas-A Granxa	7	3	3	28	89	4	
Sanguiñeda	2			12	29		
<b>Total</b>	<b>64</b>	<b>23</b>	<b>8</b>	<b>143</b>	<b>472</b>	<b>10</b>	<b>20</b>

TABLE 2. ADDITIONAL SAMPLING POINTS

Zones	Sampling points				Number of samples		
	Manual boring	Short boring	Long boring/ piezometer	Calicata	Soils	Groundwater	Surficial water
Regato das Laxes	15			37	97		17
As Laxes-AP2401	73				147		3
<b>Total</b>	<b>88</b>			<b>37</b>	<b>244</b>		<b>20</b>

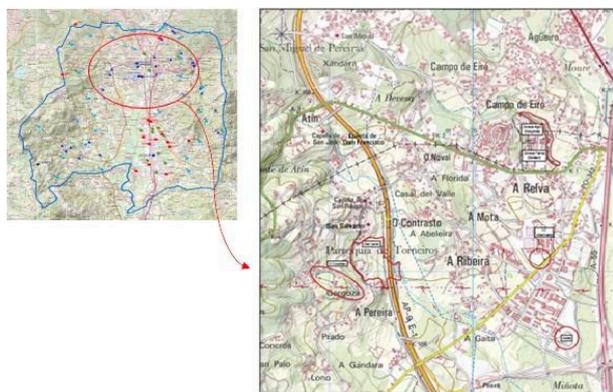
**TABLE 3. GROUNDWATER AND SURFICIAL WATER**

Parameter	alfa-HCH	beta-HCH	gamma-HCH	delta-HCH	suma HCH
<i>Legal limit</i>	0,1	0,1	0,1	0,1	0,5
MS045	0,054	0,77	<0,01	0,94	1,764
MS047	<1	13	<1	<2	13
MS048	0,037	0,86	0,086	0,13	1,113
MS057	<0,01	0,25	<0,01	0,023	0,273
DM1-A	2	4,5	1,3	2,8	10,6
S-25	<0,01	0,18	<0,01	<0,02	0,18
Pz-1	0,062	4,7	<0,05	<0,1	4,762

\* In blue the values above the target.

Within the scope of the study, the following contaminated areas by HCH were identified (Figure 2):

- Area enclosed between Laxes creek and EP-2402 road.
- Neighbourhood of O Contrasto.
- SYNGENTA and BIOFABRI site
- CZ Veterinaria site
- Security cell of Torneiros



**FIGURE 2.. LOCATION OF THE CONTAMINATED AREAS IDENTIFIED**

The areas with the presence of lindane identified in this study are located to the north of the town hall

and in the surroundings of the industrial sites in which the activity had been carried out by Zeltia during the 1940s (Figure 2).

The results obtained are summarized in the following table (Table 4).

**Conclusions and Recommendations**

New contaminated areas have been identified and further action is needed.

- Extend the investigation to the EP-2402 road and agricultural use land located to the west of that road
- Carry out a characterization of EP-2401 road.
- Restriction on agricultural use of the contaminated areas.
- Conducting a biodegradation studies as a protection measure for the Laxes creek.

**TABLE 4. SOIL TEST RESULTS (HIGHEST VALUES)**

Parameter	alfa-HCH	beta-HCH	gamma-HCH	delta-HCH
<i>Legal limit (RD9/2005)</i>	0.01	0.01	0.01	
Rego das Laxes_C-22/1.3	0.088	0.54	0.0027	0.003
Rego das Laxes_C-2003/1.1	0.17	22	<0.10	0.1
Rego das Laxes_C-2012/1.7	0.066	1.5	0.0088	0.017
Rego das Laxes_C-2016/0.9	0.051	1.4	0.0061	0.01
Rego das Laxes_C-2017/0.4	0.044	3.9	0.023	0.03
Rego das Laxes_SM-29/0.4	16	71	0.36	0.66
Rego das Laxes_SM-44/0.8	110	62	1.4	0.97
Rego das Laxes_SM-69/0.6	0.84	9.6	0.04	0.062
Rego das Laxes_SM-73/1.2	6.9	4.2	0.14	0.072

**References**

Geocisa, July 2021. Plan de investigación integral de las zonas afectadas por la contaminación por Lindano. Expte 26/2018 CA Lote 2. Informe final. Xunta de Galicia. Consellería de Medio Ambiente e Cambio Climático.

# DISPOSAL OF PRODUCTION WASTE FROM LINDANE MANUFACTURING: COLLABORATION BETWEEN UNIVERSIDAD DE ZARAGOZA AND GOBIERNO DE ARAGÓN

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## **Summary**

Collaboration between the University of Zaragoza (UZ) and the Regional Government of Aragon since 2017 has been devoted to bibliographic search, sample analysis, and research on the chemical or physical transformation of different stereoisomers of HCH and waste from lindane manufacturing into harmless and industrial-valuable compounds. Benzene, biphenyl, and other non-chlorinated compounds have been obtained, either directly or involving intermediate isolation of a mixture of chlorinated products, which could be used as platform molecules in industrial synthesis. High yields were obtained by modifying reaction conditions at a laboratory scale, which allow scaling these results up in the next future. Non-conventional techniques such as laser irradiation for HCH transformation are also currently under study.

## **Keywords**

Benzene, Bibliographical Search, Dehydrochlorination, HCH Analysis, Hydrodechlorination, Hydrogen, Laser.

Lindane ( $\gamma$ -HCH stereoisomer), used as a pesticide in the 20th century, was manufactured by benzene photochlorination reaction producing a mixture of eight stereoisomers of HCH and many other chlorinated hydrocarbons (1 kg of lindane production involved 10 kg of HCH waste), which were placed in uncontrolled landfills. It is estimated that between 4 and 7 million tons of toxic, carcinogenic, bioaccumulative, and persistent waste were produced and disposed around the world for 60 years of lindane manufacturing. The legacy of lindane constitutes a serious problem for the European Union,<sup>1</sup> and specifically for the Spanish Region of Aragon due to the Inquinosa plant located in Sabiñánigo (Huesca), which was in production from 1975 to 1992 and accumulating ca. 150,000 tons of chlorinated waste in Sardas and Bailín landfills provoking the contamination of soils, water, groundwater, and air.<sup>2</sup> Now we must address the transformation of these harmful products into valuable and useful compounds, or at least, into inert materials.

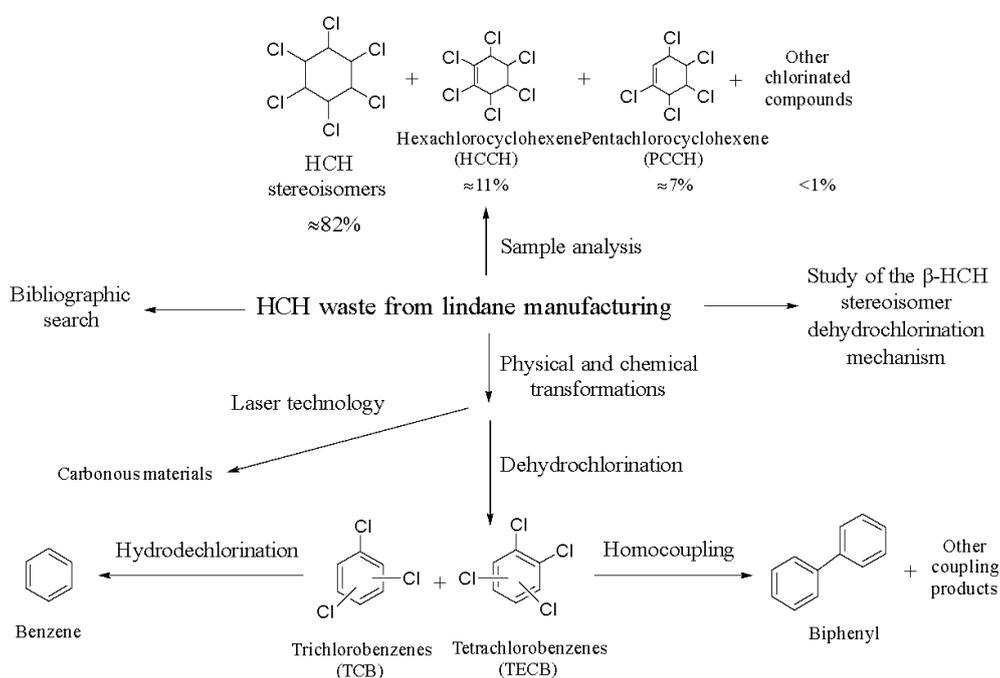
A bibliographic search of scientific reports, patents, and online-webs focused on HCH treatment allowed us to obtain a general current description of this topic. The remediation of solid HCH waste and HCH-contaminated soils using thermal, physicochemical, biological, and inertisation methods have been envisaged during the last decades. In the case of having mixtures of chlorinated compounds with other chlorinated or non-chlorinated chemicals, separation methodologies,<sup>3</sup> including excavation, thermal desorption, and extraction using solvents, supercritical CO<sub>2</sub>, surfactants, and adsorbents could

be necessary. The transformation of solid HCH waste can be achieved by a large series of chemical technologies<sup>4</sup> which involves different reactions such as dehydrochlorination, incineration, pyrolysis, oxidation, and reduction. Besides these conventional technologies, advanced methods,<sup>5</sup> such as electroremediation, photoremediation, sonoremediation, plasma and laser technologies, radiolysis, and inertisation, as well as the bioremediation strategies,<sup>6</sup> using bacteria, plants, enzymes, fungi, algae or earthworms, are available. Considering this information, different studies were carried out (Scheme 1). As a first step, in order to characterize this highly concentrated waste, HCH extraction with conventional and neoteric solvents has been addressed, proving acetone as the most efficient solvent for these chlorinated compounds. On the one hand, the transformation of HCH to trichlorobenzenes can be subsequently carried out through a basic dehydrochlorination reaction<sup>7</sup> by using either soluble (NaOH, different carbonates, triethylamine) or insoluble bases in different solvents (ethanol, isopropanol, tetrahydrofuran or glycerol). The combination of NaOH as a base and ethanol as a solvent allows obtaining high yields of trichlorobenzenes in short reaction times. The mixture of trichlorobenzenes can be considered a raw material for its transformation into useful products. In a simple approximation, trichlorobenzenes can be converted into benzene,<sup>8</sup> a major oil component (sale price in 2011: 933 \$/t) used as a precursor of many chemical products.<sup>9</sup> Different hydrogen donors (hydrodechlorination reaction) as hydrogen gas, isopropanol, glycerol, and other alcohols, using Pd catalysts in presence

of base and solvent were employed to obtain benzene starting from trichlorobenzenes as well as from HCH waste in a one-pot two-steps process without isolating or purifying intermediate products. High yields of benzene are obtained when hydrogen gas is used as a hydrogen donor, NaOH as a base, Pd/C as a catalyst in EtOH (99% benzene in one hour).

On the other hand, the synthesis of high added value compounds can also be considered. For example, polyphenylene derivatives, showing very interesting properties in electronic devices, lead to stable complexes with transition metals that can be used as catalysts and are nanocarriers for drug delivery.<sup>10</sup> Biphenyl, terphenyls, and even quaterphenyls, have been obtained through a

homocoupling reaction of trichlorobenzenes from HCH waste. Chlorinated biphenyls and terphenyls (showing interesting properties)<sup>11</sup> have been observed as intermediates in a reaction using water as a solvent, with a phase-transfer agent and a palladium catalyst. Although great yields of coupling compounds are obtained (around 80% of biphenyl + terphenyls + quaterphenyls), high temperatures and an excess of base are required for this homocoupling reaction which makes necessary a comprehensive study of the reaction parameters. Laser irradiation techniques for the transformation of HCH into carbonous materials<sup>12</sup> are also currently under study, though, up to now, HCH-derived products with a lower number of chlorine atoms are obtained.



**SCHEME 1. RESEARCH ON DIFFERENT STRATEGIES FOR HCH WASTE REMEDIATION BETWEEN UNIVERSIDAD DE ZARAGOZA AND GOBIERNO DE ARAGÓN**

In summary, the combination of bibliographic, theoretical and experimental studies allow obtaining non-chlorinated products from highly concentrated waste from lindane production. Further studies in the obtention of industrial and synthetical-valuable compounds can let higher yields after optimization of the reaction conditions. In a near future, these results, obtained at a laboratory scale, will be scaled up, together with the separation and purification of products. Non-conventional techniques, such as laser irradiation, will also be explored.

### References

1. Vijgen, J.; Abhilash, P. C.; Li, Y. F.; Lai, R.; Forter, M.; Torres, J.; Singh, N.; Yunus, M.; Tian, C. G.; Schäffer, A.; Weber, R. *Environ. Sci. Pollut.*

*Res.* **2011**, *18*, 152–162. <https://doi.org/10.1007/s11356-010-0417-9>

2. Gobierno de Aragón. Plan estratégico de lucha integral contra la contaminación por lindano y otros isómeros del HCH en Aragón [on-line, accessed in December 2022]. <http://www.stoplindano.es/>

3. Scott, W. C.; Dean, J. R. *J. Environ. Monitor.* **2003**, *5*(5), 724–731. <https://doi.org/10.1039/b305309a>

4. Caliman, F. A.; Brindusa, M. R.; Camelia, S.; Vasile, L. P.; Gavrilescu, M. *Clean Technol. Environ. Policy.* **2011**, *13*(2), 241–268. <https://doi.org/10.1007/s10098-010-0319-z>

5. Babak, J.; Nasrollahzadeh, M.; Mohazzab, B. F.; Eslamipanah, M.; Sajjadi, M.; Ghafari, H. *Ceram. Int.* **2021**, *47*(8), 10389–10425. <https://doi.org/10.1016/j.ceramint.2020.12.197>

6. Tripathi, V.; Edrisi, S.A.; Chaurasia, R.; Pandey, K. K.; Dinesh, D.; Srivastava, R.; Srivastava, P.; Abhilash, P. C. *Sci. Total Environ.* **2019**, *689*, 1304–1315. <https://doi.org/10.1016/j.scitotenv.2019.06.444>
7. Ukisu, Y.; Miyadera, T. *J. Hazard. Mater.* **2005**, *122*, 1–6. <https://doi.org/10.1016/j.jhazmat.2005.02.016>
8. Wu, B. Z.; Chen, H. Y.; Wang, S. J.; Wai, C. M.; Liao, W.; Chiu, K. *Chemosphere* **2012**, *88*, 757–768. <https://doi.org/10.1016/j.chemosphere.2012.03.056>
9. Folkins, H. O. Benzene. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley. [https://doi.org/10.1002/14356007.a03\\_475](https://doi.org/10.1002/14356007.a03_475)
10. a) Bauer, R. E.; Grimsdale, A. C.; Müllen, K.; *Top. Curr. Chem.* **2005**, *245*, 253–286. <https://doi.org/10.1007/b98171>. b) Hammer, B. A. G.; Moritz, R.; Stangenberg, R.; Baumgarten, M.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44*, 4072–4090. <https://doi.org/10.1039/C4CS00245H>
11. Jain, Z. J.; Gide, P. S.; Kankate, R. S. *Arabian J. Chem.* **2013**, *10*(2), 2051–2066. <https://doi.org/10.1016/j.arabjc.2013.07.035>
12. Schmaltz, B.; Weil, T.; Müllen, K. *Adv. Mater.* **2009**, *21*, 1067–1078. <https://doi.org/10.1002/adma.200802016>
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# ASSESSMENT OF IN-SITE DIOXIN DEGRADATION IN WASTE, 1995-2021

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## **Summary**

The period of maximum contamination of the industrial zone of the city of Ufa - soil, sewage, and sludge with toxic waste containing PCDD/Fs is the 70s of the 20th century. In 1964-67 "Ufakhimprom" organized a pilot production of 2,4,5-T butyl ether, 2,4-D herbicide, and operated an organochlorine waste incinerator. It is these industries that make the main contribution to dioxin pollution of "hot spots"<sup>1</sup>. There are no analytical data on the content of dioxins in products and the environment during this period of time. After the cessation of production of the most dioxin-hazardous products, the level of pollution of the territory did not increase significantly, and now we are dealing with the consequences of pollution 60 years ago<sup>2</sup>. The main depot of dioxins is sludge reservoirs, territory and industrial buildings. Some of the previously completely filled sludge reservoirs were not exposed to any impact, and the results of monitoring dioxins in sludge can serve as field studies of dioxin degradation in "natural" conditions. It is believed that the half-life of dioxins in soil depends on soil type, mineral content and climatic conditions. Estimates vary widely from 1-3 years at the surface and to tens of years at depth<sup>3</sup>. Under in-situ conditions in a contaminated area, based on information for 1992-2021, we estimated the half-life of dioxins in the mass of sludge reservoirs as 10-14 years, in the soil of the plant - 8-10 years.

## **Keywords**

*Dioxins, half-life, sludge, soil, accumulated damage*

The plant was shut down in 2004, however, it is difficult to call it the mode of conservation of the dioxin contamination zone, since the production of Bisphenol-A (BPA) and periodically a medical waste incinerator functioned on the territory. In 2008–2010 eight large industrial buildings, which previously produced chlorophenol products, were destroyed to the foundations. The dismantling of buildings was carried out without observing the necessary safety measures, which contributed to the transfer of toxicants into a more accessible form for transfer. The construction scrap was stockpiled on the territory of the plant without any protective measures. The equipment of the workshops was dismantled and taken out for disposal without dioxin control, the cleaning technology is unknown to us.

The volume of analytical studies carried out at the facility is significant. Analysis of the contamination of the territory of the former "Ufakhimprom" was carried out by various organizations with the participation of dioxin laboratories and a number of foreign laboratories, starting from 1995 to 2021<sup>4,5</sup>. In addition, studies have been performed to evaluate the half-life of dioxins in exposed workers, as well as work to change the sex ratio of the offspring of workers<sup>6</sup>.

The primary data were obtained in 1992-1995 and most often contained an analysis of only 2378-TCDD. At present, there are data on the content of dioxins in soil, sludge and sludge from sludge collectors, wastewater, construction waste for 1995-2021. The main studies were carried out by four labs (Lab 1,2,3 and 4) in Russia. All of them have national accreditation and experience in international comparative studies and intercalibrations.

The most interesting data were obtained during this time on the change in the content of dioxins in the sludge reservoirs on the territory. Some of them have not been affected for 40 years. This makes it possible to evaluate the dynamics of changes and estimate the half-life of dioxins in the sludge in-situ. The dioxin monitoring results are shown in Table 1.

The filled storages No. 1-3, 5 and 6 were practically not affected. In storages No. 4, 7 and 8 in 2008-2010, materials from the destruction of workshops, incineration furnaces, etc. were placed. The typical composition of the sludge is 74% SiO<sub>2</sub>, 14% CaO, 5% H<sub>2</sub>O, 3.5% Al<sub>2</sub>O<sub>3</sub>, 3.5% (K, Na, Mg, Fe oxides), 0.003% organics including PCDD/Fs and PCBs. The effect of the matrix on the degradation of PCDD/F is diverse (7,8).

**TABLE 1. SAMPLING LOCATION AND DIOXIN CONTENT IN SLUDGE, I-TEQ PCDD/FS, NG/KG**

Sludge tanks	Lab 1 (2021)	Lab 2 (2019)	Lab 3 (2014-2015)	Lab 3 (2008-2013)	Lab 4 (2008)	Lab 3 (1995-2003)	Lab 1,2 et al. (1992-1995)
No 1	115	40	39.8-54.7	86.35			

No 2		388	780			
No 3	2404.8		4783			
No 4	20010.8		10240.5		4815.6	8150 2378-TXДД
No 5	586.1	2100			0.2-1.2	3825.3 6700 2378 TXДД
No 6	3870.2	1059	2084.1		6068.4	11277 16333 2378 TXДД
No 7	7034.2	1266		1432.6	2201.5	
No 8	13070.9	29.0	4721.2		112.8	

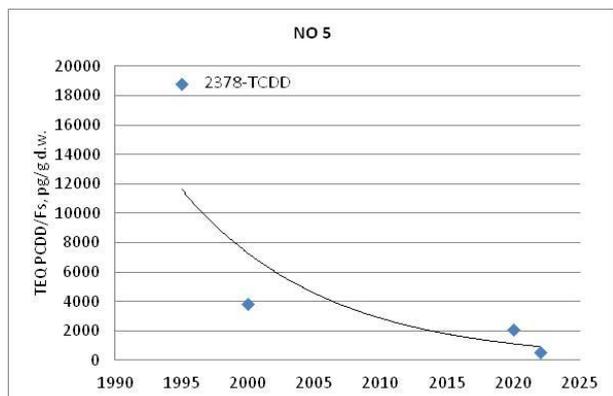


FIGURE 1. THE CONTENT OF DIOXINS IN THE SLUDGE STORAGE NO.5

From Table 1 and Figures 1 and 2 it follows that the half-life of dioxins in the mineral-organic composition of the sludge in the conditions of the Urals is 10-14 years.

Figure 3 shows the impact of contaminated material on the spike in sludge tank 7. Similar changes occurred in 3 4 and 8 for the same reasons.

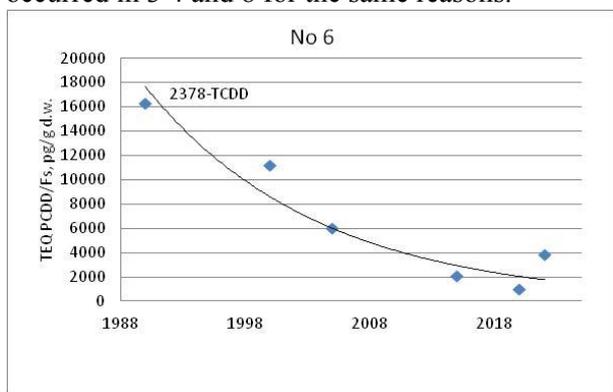


FIGURE 2. THE CONTENT OF DIOXINS IN THE SLUDGE STORAGE NO.6

The destruction of workshops in 2008-2010 and the movement of masses affected the contamination of the soil of the plant (Figure 4). Increased values were noted in the period 2008-2012. Before 2005, the half-life of dioxins in the topsoil can be estimated as 8-10 years.

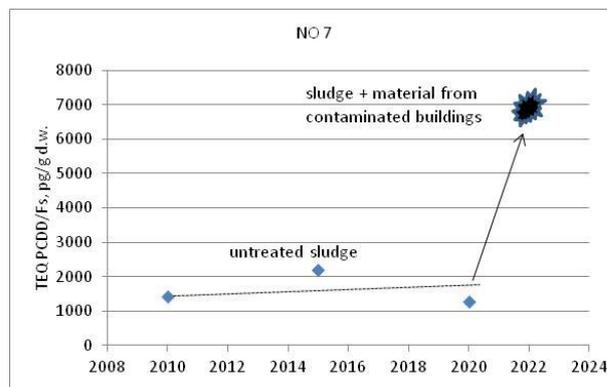


FIGURE 3. THE CONTENT OF DIOXINS IN THE STORAGE NO.7

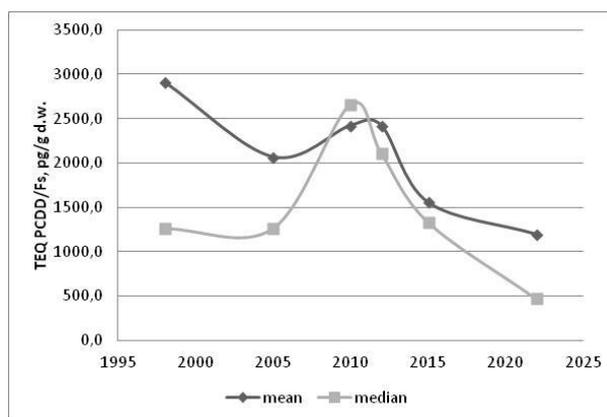


FIGURE 4. THE CONTENT OF DIOXINS IN THE SOIL

### References

1. Weber, R., Gaus, C., Tysklind, M. et al. Dioxin- and POP-contaminated sites—contemporary and future relevance and challenges. *Environ Sci Pollut Res* 15, 363–393 (2008). <https://doi.org/10.1007/s11356-008-0024-1>
2. Amirova, Z., Weber, R. Massive PCDD/F contamination at the Khimprom organochlorine plant in Ufa—a review and recommendations for future management. *Environ Sci Pollut Res* 22(19) 14416–14430 (2015), doi:10.1007/s11356-015-5048-8
3. N. Nhung, X. Nguyen, V. Long, Y. Wei, T. Fujita. A Review of Soil Contaminated with Dioxins and Biodegradation Technologies: Current Status and Future Prospects. *Toxics*. (2022). Jun; 10(6): 278. doi: 10.3390/toxics10060278

4. Amirova Z., Kruglov E. Russian dioxin “hot spot” – Ufa. Comparison with Seveso. *Organohal. Comp.* 67, 2094–2098 (2005).
  5. Amirova Z., Kruglov E., Maystrenko V., Khizbullin F. PCDD/Fs Contamination from Defoliants and Chlorinated Pesticides Production: Steps for Remediation of Stockpiles, Soil and Utilization of Contaminated Buildings. *Organohal. Comp.* 68, 2225–2228 (2006).
  6. Ryan, J., Amirova, Z., Carrier, C.. Sex ratios of children of Russian pesticide producers exposed to dioxin. *Env.Health*,110, n.11, 699-701 (2002).
  7. Weber, R., Nagai, K., Nishino, J., Shiraishi, H., Ishida, M., Takasuga, T., Konndo, K., Hiraoka, M.,. Effects of selected metal oxides on the dechlorination and destruction of PCDD and PCDF. *Chemosphere* 46, 1247–1253, (2002).
  8. Lundin, L., Molty, J., Fullana, A. Low temperature thermal degradation of PCDD/Fs in soil using nanosized particles of zerovalent iron and CaO. *Chemosphere*, 91,740–744, (2013).
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# ASSESSING PERSISTENT ORGANIC POLLUTANTS IN SPANISH AIR

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## Summary

The present study is framed in the Spanish Implementation Plan (SIP) of the Stockholm Convention, managed by the Ministry of the Agriculture, Food and Environment (currently named Ministry for the Ecological Transition and the Demographic Challenge) since 2007 to date. This work has been focused on investigating POP levels in Spanish air, to elucidate background concentrations and their potential sources. Target analytes were polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides such as DDT and their metabolites, pentachlorobenzene (PeCB), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs) and endosulfan.

Samples collected in remote areas presented the following pattern of concentration: HCB >  $\Sigma$ PCBs >  $\Sigma$ DDTs  $\approx$   $\Sigma$ HCHs >  $\Sigma$ Endo > PeCB >  $\Sigma$ PBDEs >  $\Sigma$ PCDD/Fs. However, this pattern varied for urban areas:  $\Sigma$ PCBs > HCB >  $\Sigma$ DDTs >  $\Sigma$ HCHs >  $\Sigma$ PBDEs >  $\Sigma$ Endo > PeCB >  $\Sigma$ PCDD/Fs. Urban sites presented statistically higher concentrations for  $\Sigma$ PBDEs,  $\Sigma$ PCBs,  $\Sigma$ DDTs and  $\Sigma$ HCHs than remote locations. This result revealed anthropogenic activities as potential sources for these chemicals.

Data obtained in this study are necessary to evaluate properly the effectiveness of practices adopted to reduce POP emissions.

## Keywords

POPs, air monitoring network, passive air samplers, remote locations, urban areas.

## Introduction

Persistent Organic Pollutants (POPs) are chemicals that persist in the environment, biomagnify at higher trophic levels, exhibit toxic effects that may threaten the health of the environment and undergo long-range atmospheric transport from their sources to remote regions. The Stockholm Convention on Persistent Organic Pollutants is an international environmental treaty to protect human health and the environment from POPs [1].

The present study is framed in the SIP and shows the results of the Spanish air monitoring network obtained by CIEMAT in relation to mostly inner sampling points.

## Materials and methods

Data shown in the present study included 387 samples obtained during 38 sampling campaigns from summer 2008 to autumn 2017. Samples were collected from seven remote and four urban locations using European Monitoring and Evaluation Program (EMEP)/Global Atmospheric Watch (GAW)/Control Atmospheric Monitoring Program (CAMP) and State Meteorological Agency (AEMET) locations (Figure 1,a).

Passive air samplers with polyurethane foam (PUF) disks as the sorbent media were used. PUF disks were precleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, wrapped in aluminium foil and stored in polyethylene bags at -20 °C until deployment. At each sampling point, four PUFs were deployed for 3 months, corresponding with each season: three of them were used for PCDD/F, PCB and PBDE determinations, and the fourth one

was used for the analysis of organochlorine pesticides (OCPs: DDTs and their metabolites,  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCHs, PeCB, HCB and  $\alpha$ - and  $\beta$ -endosulfan). A field blank at each station and each sampling period was also deployed.

Samples were spiked with  $^{13}\text{C}$ -labeled surrogate standards before Soxhlet extraction. Purification was achieved by florisil column in the case of OCPs and a multi-layer silica column followed by activated carbon SPE cartridges for the rest of the compounds. The final extracts were concentrated under a nitrogen stream, redissolved in nonane and spiked with the  $^{13}\text{C}$  injection standards solutions prior to instrumental analysis. PCDD/Fs, PCBs, HCB, HCHs and DDTs were analyzed on a high resolution mass chromatograph, connected to a high resolution mass spectrometer while PBDEs were determined with a low resolution mass spectrometer. Identification and quantification were carried out using isotopic dilution. All data were blank corrected. Final results are expressed as concentration, considering 4 m<sup>3</sup>/day as the volume sampled by each PUF disk [2,3].

## Results and discussion

Concentration levels for all families considered, according to remote and urban locations are shown in Table 1. Samples collected in remote areas presented the following pattern of concentration (median; pg/m<sup>3</sup>): HCB (32.11) >  $\Sigma$ PCBs (15.57) >  $\Sigma$ DDTs (12.87)  $\approx$   $\Sigma$ HCHs (12.68) >  $\Sigma$ Endo (2.37) > PeCB (1.55) >  $\Sigma$ PBDEs (0.78) >  $\Sigma$ PCDD/Fs (0.028). However, this pattern varied for urban areas (median; pg/m<sup>3</sup>):  $\Sigma$ PCBs (32.9) > HCB

(30.81) > ΣDDTs (27.53) > ΣHCHs (21.74) > ΣPBDEs (8.47) > ΣEndo (2.29) > PeCB (1.94) > ΣPCDD/Fs (0.045). In both cases PCDD/Fs were the minor pollutants. Urban sites presented statistically higher concentrations ( $p < 0.05$ ; Mann-Whitney U test) for ΣPBDEs, ΣPCBs, ΣDDTs and ΣHCHs than remote locations. This result revealed anthropogenic activities as potential sources for these chemicals.

Average congener and isomer patterns for each group of compounds were also established for each sampling point. In all cases, a common pattern was identified: OCDD/F > HpCDD/F > HxCDD/F, ΣmPCBs > Σmono ortho-PCBs >> Σno-ortho-PCBs, BDE 209 >> BDE 47 > BDE 99, γ-HCH > α-HCH >> β-HCH, DDE > DDT >> DDD and α-endosulfan > β-endosulfan. As an example, the HCH isomer profile found for remote areas -γ-HCH (64%), α-HCH (30 %), β-HCH (5%)- was similar to that for urban areas -γ-HCH (71%), α-HCH (24 %), β-HCH (5 %)- (Figure 1).

POP levels reported in this study have been compared with those from the Global Atmospheric Passive Sampling Network (GAPS)4. Thus, levels of ΣPBDEs (sum of BDE 47, 99 and 100), ΣHCHs (sum of α- and γ- HCH) and ΣDDE/Ts (sum of pp'-DDE and pp'-DDT) evaluated in this study are in the same order of magnitude as those obtained in the GAPS Network.

In order to reach reliable conclusions, including spatial and temporal trends, the maintenance of this POP monitoring plan, involving periodic air samplings throughout the Spanish territory, is

consider essential for a proper evaluation of the measures taken to reduce POPs levels.

### Acknowledgements

This work has been supported by the Spanish Ministry for the Ecological Transition and the Demographic Challenge under the project "POP monitoring in some matrices and areas of interest". The authors thank The State Meteorological Agency (AEMET) for allowing the use of their sampling stations and AFC Ingenieros, S.A. and Ingenieros Asesores, S.A. for the diligence and willingness to establish the sampling dates.

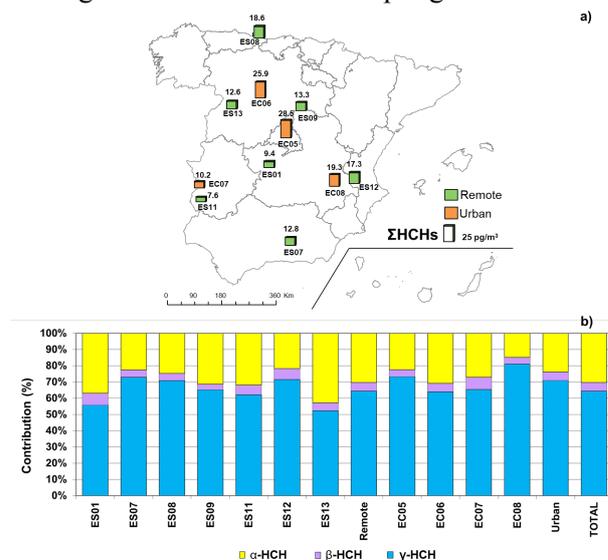


FIGURE 1. GEOGRAPHICAL LOCATION OF SAMPLING POINTS EVALUATED SHOWING HCH CONCENTRATION (MEDIAN, PG/M<sup>3</sup>) (A). AVERAGE CONCENTRATION PROFILE FOR HCHs (B).

	IPCCDD/Fs	IPCBs	IPBDEs	ΣHCHs	ΣDDTs	PeCB	HCB	ΣEndo
ES01	0.037 ± 0.056 (0.021)	18.97 ± 16.38 (14.88)	1.74 ± 4.14 (0.17)	11.85 ± 8.33 (9.36)	8.46 ± 4.63 (7.89)	1.89 ± 1.35 (1.36)	39.85 ± 32.11 (30.29)	2.04 ± 0.88 (1.99)
ES07	0.006 - 0.27 (0.036)	1.43 - 69.51 (14.13)	0 - 17.56 (0.68)	0.16 - 45.19 (12.81)	0.35 - 19.31 (13.61)	0.47 - 3.59 (1.28)	0.003 - 169.17 (28.66)	0.94 - 3.66 (6.74)
ES08	0.007 - 0.51 (0.054)	0.64 - 51.65 (21.84)	0.02 - 5.72 (1.81)	3.31 - 93.16 (18.63)	6.91 - 26.46 (3.79)	0.36 - 3.68 (2.81)	7.88 - 87.5 (43.62)	0.63 - 8.86 (1.33)
ES09	0.011 - 0.26 (0.024)	5.29 - 340.63 (16.44)	0.13 - 25.32 (1.15)	0.13 - 87.35 (13.26)	0.35 - 31.78 (10.12)	0.99 - 3.83 (1.96)	2.52 - 200.11 (45.16)	0.52 - 1.95 (3)
ES11	0.007 - 1.77 (0.03)	3.42 - 386.48 (13.73)	0.082 - 16.38 (0.6)	0.94 - 99.95 (7.57)	2.16 - 43.69 (17.99)	0.69 - 5.66 (1.37)	0.41 - 244.5 (26.26)	1.34 - 3.78 (2.09)
ES12	0.009 - 1.02 (0.028)	2.08 - 359.26 (16.01)	0.018 - 10.75 (1.41)	0.23 - 40.4 (17.31)	0.4 - 87.78 (29.34)	0.41 - 3.39 (1.1)	0.76 - 174.21 (31.32)	1.14 - 5.47 (3.55)
ES13	0.006 - 0.32 (0.024)	0.12 - 92.41 (10.99)	0.12 - 21.41 (1.01)	1.18 - 100.3 (12.64)	4.15 - 88.06 (20.6)	0.37 - 3.7 (2.07)	3.58 - 135.05 (31.45)	0.9 - 5.68 (2.18)
Remote	0.006 - 0.55 (0.028)	0.44 - 347.67 (15.57)	0.032 - 23.95 (0.78)	1.81 - 39.9 (12.68)	3.07 - 109.62 (12.87)	0.74 - 5.54 (1.55)	0.36 - 148.4 (32.11)	0.51 - 3.11 (2.37)
EC05	0.054 ± 0.041 (0.048)	110.59 ± 71.99 (84.56)	31.23 ± 34.72 (22.35)	37.82 ± 26.83 (28.48)	68.73 ± 88.16 (53.14)	2.96 ± 1.79 (3.52)	41.37 ± 29.66 (32.1)	2.55 ± 1.03 (2.33)
EC06	0.018 - 0.23 (0.049)	41.86 - 325.03 (31.18)	5.9 - 201.97 (6.84)	8.52 - 154.19 (25.86)	13.99 - 560.6 (8.38)	0.6 - 4.99 (1.95)	5.54 - 151.76 (41.57)	0.67 - 3.92 (2.18)
EC07	0.027 - 0.23 (0.038)	13.48 - 160.08 (17.24)	0.9 - 22.3 (2.91)	7.72 - 102.41 (10.16)	2.74 - 28.24 (54.67)	0.87 - 6.32 (1.31)	12.03 - 122.77 (27.47)	1.21 - 5.68 (2.75)
EC08	0.011 - 0.27 (0.047)	3.89 - 608.77 (18.17)	0 - 23.55 (8.38)	5.04 - 34.86 (19.3)	15.24 - 158.15 (18.38)	0.58 - 3.62 (1.49)	5.56 - 94.63 (30.72)	1.74 - 3 (2.18)
Urban	0.054 ± 0.045 (0.045)	41.63 ± 60.47 (32.9)	11.32 ± 10.89 (8.47)	24.94 ± 19.68 (14.59)	22.85 ± 14.16 (27.53)	2.26 ± 1.47 (1.94)	35.01 ± 19.05 (30.81)	2.42 ± 0.86 (2.29)
TOTAL	0.057 ± 0.12 (0.034)	38.49 ± 62.99 (18.17)	6.65 ± 14.28 (2.16)	20.81 ± 19.08 (14.59)	25.58 ± 36.55 (16.73)	2.26 ± 1.54 (1.94)	41.72 ± 33.18 (31.49)	2.72 ± 1.71 (2.3)

TABLE 1. DESCRIPTIVE STATISTICS (MEAN ± SD; (MEDIAN); MIN-MAX; PG/M<sup>3</sup>) OF PCDD/FS, PCBs, PBDES, HCHs, DDTs, PECB, HCB, ENDOSULFAN IN AIR AT REMOTE AND URBAN AREAS.

### ***References***

1. Stockholm Convention on Persistent Organic Pollutants; United Nations Environment Programme. <http://chm.pops.int>.  
2. Shoeib M, Harner T. (2002) Environ. Sci. Technol. 36, 4142-51.

3. Pozo K, Harner T, Wania F, Muir DCG, Jones KC, Barrie LA. (2006) Environ. Sci. Technol. 40, 4867-4873.  
4. Global Monitoring Plan for Persistent Organic Pollutants. (2009) First Regional Monitoring Report. Western Europe and other States Group (WEOG) Region. Annex I: Air.

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# IMPACT OF ORGANIC MATERIALS ON HEXACHLOROCYCLOHEXANE VOLATILIZATION FROM CONTAMINATED SOILS

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## ***Abstract***

Addition of organic materials such as compost is a common practice for the remediation of contaminated soils. Numerous studies have shown that this practice improved soil quality and reduced the leaching of contaminants into groundwater. However, studies of its effect on the transfer of pollutants to the atmosphere are not available. The objective of this work was to evaluate the impact of organic materials, used as soil amendments, on the volatilization of hexachlorocyclohexane isomers ( $\alpha$ ,  $\beta$ ,  $\delta$  and  $\gamma$ -HCH) from contaminated soils. For this, a laboratory test was carried out using a soil sample contaminated with residues obtained from an old lindane factory. The amendments tested were derived from organic residues of different nature (compost and biochar) and were applied at different doses. An active sampling system and solid phase microextraction (SPME) were used for monitoring HCH isomers in air. Results were different depending on both the characteristics of the specific soil amendment and dose, but volatilization was reduced by up to 85%. The application of soil amendments may be a promising practice to mitigate the transfer of HCH isomers to the atmosphere and the risk of long-distance transport in areas contaminated with lindane residues.

## ***Keywords***

Hexachlorocyclohexane, Lindane, Volatilization, Organic soil amendments.

# PESTICIDE EXPOSURE AND PREMATURE IDIOPATHIC THELARCHE IN GIRLS: RESIDUE LEVELS IN URINE AND IN FOOD WITHIN THE PEACH PROJECT

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## Summary

Several pesticides are recognized as endocrine disruptors (EDs) since they can interfere with the dysregulation of sexual, thyroid and neuro-endocrine hormones contributing to earlier pubertal onset. Exposure to pesticides can be considered an important factor associated with precocious puberty and premature thelarche in girls. Children are particularly vulnerable to the effects of EDs due to their developmental stage, peculiar lifestyle and dietary habits.

The main objective of the PEACH project is to evaluate the association between exposure to pesticides and idiopathic premature thelarche in girls, through the measurement of pesticides in urine and the dietary intake, by analysing locally produced foods.

Girls living in an agricultural area of Marche region (Centre of Italy) with idiopathic premature thelarche (2-7 years old), matched to healthy subjects (controls), were enrolled (N=60+60). They were asked to fill in the food frequency questionnaire (FFQ) and to deliver urine samples. Furthermore, sampling of locally produced foods was performed. Food and urine were analysed by LC or GC-MS/MS to detect the pesticide levels.

All the urine samples analysed (N=60 premature thelarche and N=60 controls) showed pesticide levels below the quantification limit of the method. Otherwise, several pesticides were detected in fruits and vegetables (N= 12 samples consumed by cases and N=12 by controls) sampled in the local farms. Small fruits and berries, in particular grape and strawberry, and stone fruits (apricots, peaches, cherries, and plums) reported the highest number of pesticides including carbamates, pyridinylethylbenzamide, benzamide, phenylpyrrole and triazole fungicides and also insecticides as neonicotinoids and carbohydrazide. The pome fruit and cucurbits (melon and watermelon) reported only the presence of neonicotinoids. Leafy vegetables reported the presence of a systemic fungicide, the metalaxyl.

Differently, all vegetables and fruit from private gardens reported pesticide levels below the quantification limit except for kiwi that resulted contaminated by boscalid.

Olive oil from private garden resulted contaminated by several pesticides including fenazaquin, phosmet and deltamethrin, while no pesticide was detected in all other commodity categories as meats (red and white), eggs and honey sampled in local and private gardens.

The project PEACH (RF-2016-02364628) is funded by the Italian Ministry of Health.

## Keywords

Pesticides; endocrine disruptors; dietary exposure; idiopathic premature thelarche

## Introduction

In agriculture, pesticides, including acaricides, insecticides, herbicides and fungicides, are used to control insects, weeds, fungi and rodents that can damage crops. Despite the beneficial effects on plant production, pesticides can represent a risk for non-target organisms, including humans [1]. Several pesticides are recognized as endocrine disruptors (EDs) since they can interfere with the dysregulation of sexual, thyroid and neuro-endocrine hormones. General population is exposed

to pesticides mainly via food intake, considering the presence of residues in food. By a systematic evaluation of epidemiological studies concerning the association between pesticide exposure and health outcome, the European Food Safety Authority (EFSA) highlighted that human exposure to pesticides is linked to a large number of health implications, including cancer, neurological diseases and mental development, respiratory and cardiovascular diseases, diabetes reproductive diseases and endocrine disorders. Children are

particularly vulnerable to the adverse effects of EDs due to their developmental stage, such as in puberty, peculiar lifestyle and dietary habits. In the last decades, a progressive shortening of the time of puberty in girls and a consequent increased incidence of precocious puberty (i.e., the development of pubertal changes before the age of 8 years) and premature thelarche (i.e., early breast development before the age of 8 years) were observed worldwide [2]. Evidence carried out in an area of intense agricultural activity in the Central of Italy (Marche Region) showed an increase in the incidence of idiopathic premature thelarche (IPT) in girls. In this frame, the project “Integrated approach to evaluate children agricultural pesticide exposure and health outcome” (PEACH project, funded by the Italian Ministry of Health, RF-2016-02364628) fully described in Coppola et al., 2020 [3] included the following implementation actions (a) a case-control study on IPT in selected areas of Marche Region central Italy; (b) the analytical determination of selected pesticides and their metabolites in urine samples of enrolled girls, as well as a number of selected pesticides in food commodities locally produced and consumed by the enrolled girls; (c) the assessment of the dietary exposure of girls to the selected pesticides; (d) the evaluation of the potential adverse effects of widely used pesticides (i.e., chlorpyrifos, glyphosate and imidacloprid) by an in vitro model of the main target organ of disease, i.e., human breast cell line, at real exposure concentrations occurring in children [4]. In this paper, we showed the results on pesticide residues levels in girls’ urine samples and in food commodities, sampled in local farms and in private gardens according to data collected by questionnaires.

### **Materials and method**

The project was evaluated and approved by ethics committees of the Italian National Health Institute and Marche Region. It started at the end of 2018 and it will be concluded at the end of March 2023. Fermo and Macerata Districts, Marche Region, were the two specific areas considered in the study, both characterized by agriculture practice in farms and in private vegetable gardens. The case-control study was conducted on girls with idiopathic premature thelarche matched for age with healthy girls as controls (n = 60 + 60), living in the selected areas. Idiopathic premature thelarche girls were enrolled at the Fermo and Civitanova Marche Hospitals by the pediatric endocrinologist, verifying the following conditions, including the differential diagnosis of true early puberty and premature thelarche, for their inclusion of patients in the study: age: 2–7 years, breast development (Tanner stage II), absence of other signs of puberty, normal stature, normal growth rate, age bone corresponding to chronological age or advanced of

no more than 1 year, pelvic ultrasound consistent with pre-puberty, prepuberal Gonadotropin-releasing Hormone Stimulation Test. Moreover,  $10 < \text{BMI (Body Mass Index)} > 75$  and no concomitant therapy were applied as criteria for the enrolment of both cases and controls. The enrolment of controls was carried out by the family pediatricians of the Italian National Health System in the same areas.

Each enrolled subject was asked to sign the consent, to collect a first morning urine sample and fill in the Food Frequency Questionnaire (FFQ) and the food diary during the day before the urine sampling. The FFQ was structured to collect personal information, residential area data and food consumption information indicating the frequency of consumption (daily, weekly, monthly), the usual portion consumed (small, medium, large) and the place of purchase/production (supermarket, farm or private garden). On the basis of data elaborated from the FFQ, a consistent number of commodities were collected for all categories, including vegetables and fruits, meat, honey, eggs and oil. Samples came from private garden or local farms as indicated by the enrolled girls and the commodities were divided in several groups following the SANTE/12682/2019 [5]. Furthermore the samples coming from controls and cases were collected and analyzed independently.

A multiresidue method was used to detect 450 pesticides in foods after the extraction performed by QuEChERS extraction technique. In the urine samples were determined 21 pesticides and their metabolites.

### **Results and discussions**

The results obtained in the urines (N=60 premature thelarche and N=60 controls) showed pesticide levels (parents and metabolites) below the quantification limit (LOQ = 0.002 mg/L) of the method. Concerning food categories, several pesticides were detected in fruits and vegetables (N= 12 samples consumed by cases and N=12 by controls) sampled in the local farms (Table 1). Small fruits and berries, in particular grape and strawberry, and stone fruits (apricots, peaches, cherries, and plums) reported the highest number of pesticides including carbamates, pyridinylethylbenzamide, benzamide, phenylpyrrole and triazole fungicides and also insecticides as neonicotinoids and carbonylhydrazide. The pome fruit and cucurbits (melon and watermelon) reported only the presence of neonicotinoids. Leafy vegetables reported the presence of a systemic fungicide, the metalaxyl, probably because is the most widespread fungicide in Italia agriculture. The great number of vegetables and fruit from private gardens (N=8 samples consumed by cases and N=5 by controls) reported the pesticides levels below the LOQ, except for one sample of kiwi where boscalid was detected at the

concentration of 0.005 mg/L. The two samples of oil, coming from private garden and consumed by cases and controls, reported the presence of fenazaquin (0.015 and 0.024 mg/L respectively), deltamethrin (0.043 and 0.11 mg/L) and phosmet at 0.020 mg/L. All samples of meat, eggs and honey showed pesticides levels below the LOQ.

Among all detected compounds, the triazole and pyrimidine fungicides were the most representative in a large majority of the samples. Considering the food commodities, the small fruit and berries category (strawberry and grapes in particular)

confirmed the highest number of co-occurring fungicides typically ranging from 2 to 9.

Interestingly, the results of this study highlighted the presence of pesticides mixtures in several commodities groups, especially fruits and vegetables, confirming the importance to gather co-occurrence data to evaluate the human exposure to multiple pesticides and the associated risk for human health [6, 7]. All pesticides found in the several food categories were below the maximum residue levels (MRLs).

**TABLE 1. PESTICIDES CONCENTRATIONS, EXPRESSED AS MG/KG, DETECTED IN VEGETABLE AND FRUITS COMING FROM LOCAL FARMS. LOQ=0.005 MG/KG**

	Categories	Acari cides	Carbama tes	Acylala nine	Pyridinyl ethyl benzamide	Strobi lurin	Triazolic and pyrimidine	Insecti- cides	Neonicotinoid s
C O N T R O L S	Pome fruit						0.081(Flu)		0.031(A)
	Stone fruit								0.009(A)
	Watermelon /melon								0.045(I)
	Kiwi				0.008(F)		0.038(Flu)		
	Small fruit and berries	0.098(Hx)	0.034(I)			0.01(Py)	0.26(Bup) 0.25(Cyp) 0.12(Dim) 0.47(Fen) 0.56(Flu) 0.038(Met) 0.030(Pen) 0.027(Spi) 0.042(Zox)		0.071(A)
	Leafy vegetables			0.007(M)	0.022(F)		0.044(Bit)		
C A S E S	Kiwi	0.079(Spi)							
	Pome fruit								0.007(A)
	Small fruit and berries	0.006(Hx)	0.005(P)			0.026(Az) 0.038(Py)		0.18(T)	0.067(Spi)
	Stone fruit					0.009(Py)	0.43(Bos) 0.16(Cyp) 0.006(Dif) 0.096(Flu) 0.098(Myc)		0.011(A) 0.023(Spi)
	Stem vegetables					0.006(Py)	0.14(Bos) 0.012(Flu) 0.020(Tb)		

Abbreviation: Hexitiazox(Hx), Spirodiclofen(Spi), Indoxacarb(I), Pirimicarb(P), Metalaxil(M), Fluopyram, (F), Pyraclostrobin(Py), Azoxystrobin(Az), Fludioxonil(Flu), Bupirimate(Bup), Cyprodinil(Cyp), Dimethomorph(Dim), Fenexamide(Fen), Metrafenone(Mt), Penconazole(Pen), Spiroxamine(Spi), Zoxamide(Zox), Bitertanol(Bit), Boscalid(Bos), Difeconazole(Dif), Myclobutanil(Myc), Tebuconazole(Tb), Tebufenozide(T), Acetamiprid(A), Imidacloprid(I), Spinosad(Spi).

### Conclusions

This project evidence as the general population can be exposed to multiple pesticide residues, especially via food consumption. The monitoring of pesticide residues in food by multiresidue analysis procedures is nowadays a primary objective in pesticide detection in order to extensively evaluate food quality and dietary human exposure [8]. As

the multiple residue exposure may pose a risk to human health, data on dietary exposure, internal exposure levels and toxicological effects and interactions of pesticide mixtures can contribute to a more complete cumulative risk evaluation, according to EFSA criteria and methodology [9-11]. The strength of the project is the ability to combine different approaches, namely a case-control study, dietary exposure and in vitro studies,

to provide scientific information to support risk assessment of multiple pesticides exposure in children, as a possible hazard linked to increasing cases of the dysregulation of puberty onset.

### *References*

1. Aktar M.W., Sengupta D., Chowdhury A. Impact of Pesticides use in Agriculture: Their Benefits and Hazards. *Interdiscip Toxicol* 2009; 2, 1–12. <https://doi.org/10.2478%2Fv10102-009-0001-7>
2. Farello G., Altieri C., Cutini M., Pozzobon G., Verrotti A. Review of the Literature on Current Changes in the Timing of Pubertal Development and the Incomplete Forms of Early Puberty. *Front Pediatrics* 2019; 7, 147. <https://doi.org/10.3389/fped.2019.00147>
3. Coppola L., Tait S., Ciferri L., Frustagli G., Perugini M., Fabbri E., La Rocca C. Integrated Approach to Evaluate the Association between Exposure to Pesticides and Idiopathic Premature Thelarche in Girls: The PEACH Project. *Int J Mol Sci* 2020; 21, 3282. doi:10.3390/ijms21093282]
4. Coppola L, Tait S, Fabbri E, Perugini M, La Rocca C. Comparison of the Toxicological Effects of Pesticides in Non-Tumorigenic MCF-12A and Tumorigenic MCF-7 Human Breast Cells. *Int J Environ Res Public Health*. 2022; 19(8):4453. doi: 10.3390/ijerph19084453.
5. European Commission. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed (SANTE/12682/2019). 2020, pp. 1–49. [https://www.eurl-pesticides.eu/docs/public/tmpl\\_article.asp?CntID=727](https://www.eurl-pesticides.eu/docs/public/tmpl_article.asp?CntID=727) (accessed on 22/12/2022).
6. European Commission, 2020 Progress Report on the Assessment and Management of Combined Exposure to Multiple Chemicals (Chemical Mixtures) and Associated Risks (Staff Working Document SWD 250 Final) (2020) [https://ec.europa.eu/environment/pdf/chemicals/2020/10/SWD\\_mixtures.pdf](https://ec.europa.eu/environment/pdf/chemicals/2020/10/SWD_mixtures.pdf)
7. Socianu SK, Bopp E, Govarts L, Gilles J, Buekers M, Kolossa-Gehring T, Backhaus A. Franco Chemical mixtures in the EU population: composition and potential risks. *Int J Environ Res Publ Health*. 2022; 19 (10) p. 612. doi:10.3390/ijerph19106121
8. French Agency for Food, Environmental and Occupational Health & Safety (ANSES); Chatzidimitriou E, Mienne A, Pierlot S, Noel L, Sarda X. Assessment of Combined Risk to Pesticide Residues through Dietary Exposure. *EFSA J*. 2019; 17, e170910. <https://doi.org/10.2903%2Fj.efsa.2019.e170910>
9. EFSA Panel on Plant Protection Products and their Residues(PPR). Scientific Opinion on the Relevance of Dissimilar Mode of Action and its Appropriate Application for Cumulative Risk Assessment of Pesticides Residues in Food. *EFSA J*. 2013; 11(12): 3472.
10. EFSA Scientific Committee. Guidance on Harmonised Methodologies for Human Health, Animal Health and Ecological Risk Assessment of Combined Exposure to Multiple Chemicals. *EFSA J*. 2019; 17(3):5634
11. Hernández AF, Tsatsakis AM. Human Exposure to Chemical Mixtures: Challenges for the Integration of Toxicology with Epidemiology Data in Risk Assessment. *Food Chem Toxicol*. 2017; 103, 188–193. <https://doi.org/10.1016/j.fct.2017.03.012>

# DESIGN AND EVALUATION OF TEST BY OXIDATIVE METHOD FOR DECONTAMINATION OF THE WALLS OF THE OLD INQUINOSA FACTORY

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## Summary

TALANTIA carried out a study of lindane ( $\gamma$ -HCH) decontamination in the walls of an old factory by applying oxidative techniques. The study was promoted by SARGA-Gobierno de Aragón and was part of a larger project focused on testing different cleaning methods of the building prior to its demolition.

Three methods were chosen to check their effectiveness in a pilot test. First of them consisted of spraying activated persulfate after alkalizing the wall with soda. The other two consisted of spreading a photocatalytic suspension of photosensitive titanium oxide ( $\text{TiO}_2$ ) in two concentrations: 10% and 20%. The results show that the persulfate treatment reduced the concentration of HCH in the coat of paint more than 80% and by 70% in the plaster underneath. Regarding the  $\text{TiO}_2$  treatment, it was concluded that the 10% concentration was too low, while the solution at 20% concentration reduced the concentration of HCH in the wall paint by more than 80% and by more than 90% in the underlying plaster.

## Keywords

HCH, lindane, decontamination, wall, oxidation.

## Introduction

The old Inquinosa factory, located in “La Fosforera” industrial estate in Sabinánigo (Huesca, Spain), produced and storage lindane( $\gamma$ -HCH) from 1974 to 1992. After its closure, the factory was left in a state of abandonment, with the abundant waste throughout the facility. Pilot tests for oxidative decontamination of buildings are part of the preliminary actions prior to the demolition of the factory.

Sociedad Aragonesa de Gestión Agroambiental (SARGA) promoted several projects to test decontamination methods on the buildings’ walls and TALANTIA was involved in the “Design and evaluation of the oxidative pathway test for the decontamination the walls of Inquinosa” project.

The objective of the project was the design, supervision and evaluation of the pilot test for oxidative treatment of the contaminated walls.

## Technology design

As basic information for design this test program, analytical data from 20 sampling points on various locations of the site were available. The maximum lindane content in the walls (1965-775 mg/kg) were detected in the former pesticide production area, so the pilot tests were conducted there. However, complete analysis were not available and the content of the rest of HCH isomers and their photochemical degradation products (chlorobenzenes and chlorophenols) was unknown. In the design of the pilot test, the choice of reagents and the application method played a crucial role. Two reagents were finally tested: activated sodium persulfate and nanoparticles of titanium oxide

( $\text{TiO}_2$ ) supported on micro-sized particles. Easy-to-implement application methodologies were also chosen.

The following alternatives were made:

1. **Activated persulfate:** its application requires a first phase of alkalization of the surface, followed by the application of the persulfate. The soda could be easily spread with a brush/roller, and the persulfate was spread immediately after with a pressurized spray.

2. **Photocatalytic titanium oxide suspension:** two tests were carried out, at concentrations of 10% and 20% of  $\text{TiO}_2$  photosensitive emulsion, applied by a roller. After the application of a first coat, preserving the humidity with a water sprayer, if necessary, a second coat was applied after 3 hours (final coat thickness >1mm). Then, the oxidant was left to act for 24 hours, with UV light on the surface. After 24 hours, a new coat was sprayed in the same way as on the first day, and after three hours, the final sampling was carried out.

## Field work

First, three framed areas of 1 m<sup>2</sup>, named V1, V2 and V3, were selected on the wall where the highest concentrations were detected. Prior to the beginning of the test, an initial sample was taken from each framed area (T0). In all the framed areas, the following layers were detected in the wall: a topcoat of paint, with a high phenol and benzene content and a very high HCH content; a medium layer of plaster, without phenol, with little benzene and a high HCH content, chlorobenzenes and chlorophenols; and the deep slab material, with very low or no contamination..

V1 was treated by soda-activated sodium persulfate. V2 and V3 were treated by 10 and 20% photosensitive suspensions respectively, of micro-sized titanium oxide nanoparticles supported on sepiolite to optimized coverage. The soda (15 g/l) and sodium persulfate (25 g/l) solutions were prepared the day before use by the SARGA laboratory, while the TiO<sub>2</sub> suspensions were provided by a company supplying special products for construction.

All these works were performed by SARGA technicians following the instructions of Talantia supervisors.

### Pilot test plan

#### V1. Activated persulfate

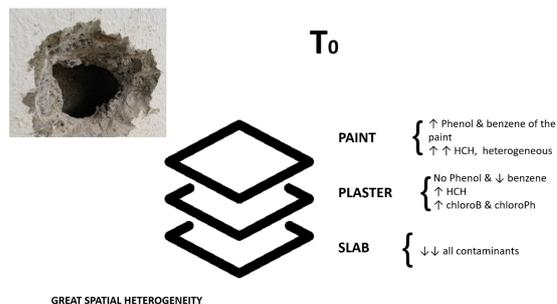
Characterization T0		21/08/2018
A1	1 <sup>st</sup> Application of soda with a roller + persulfate with a sprayer	
A2	2 <sup>nd</sup> Application of soda with a roller + persulfate with a sprayer	+1,5 h A1
A3	3 <sup>rd</sup> Application of soda with a roller + persulfate with a sprayer	+1,5 h A2
T1	23/08/2018	+0,5 h A3
T2	28/08/2018, before applications.	
A4	4 <sup>th</sup> Application of soda with a roller + persulfate with a sprayer	
A5	5 <sup>th</sup> Application of soda with a roller + persulfate with a sprayer	+1,5 h A4
A6	6 <sup>th</sup> Application of soda with a roller + persulfate with a sprayer	+1,5 h A5
T3	24/08 2018	+0,5 h A6

#### V2 and V3. TiO<sub>2</sub> emulsions at 10 and 20%

Characterization T0		21/08/2018
A1	1 <sup>st</sup> Application with a roller	
A2	2 <sup>nd</sup> Application with a roller	+ 3h A1
T1	23/08/2018	+ 3h A2
T2	24/08/2018, before applications.	
A3	3 <sup>rd</sup> Application with a roller	
A4	4 <sup>th</sup> Application with a roller	+3h A3
T3	24/08/ 2018	+3h A4

## Results

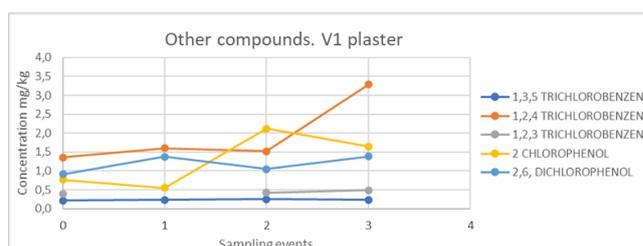
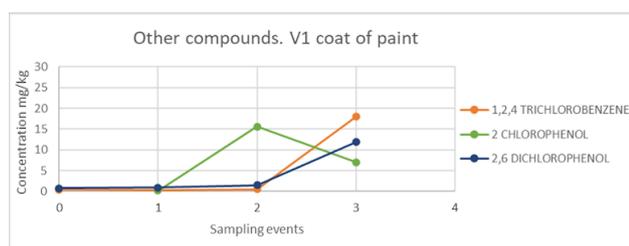
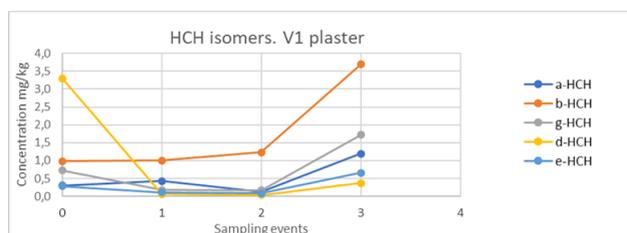
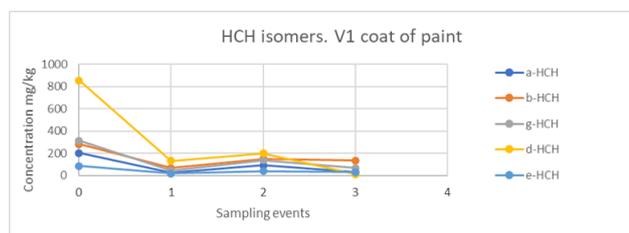
#### V1. Activated persulfate



Background levels of initial samples at T<sub>0</sub>

Below, it is shown a summary of the principal features of the different layers of the walls, before the treatments.

The following graphs show the evolution of the different contaminants in the paint layer and in the plaster underneath.



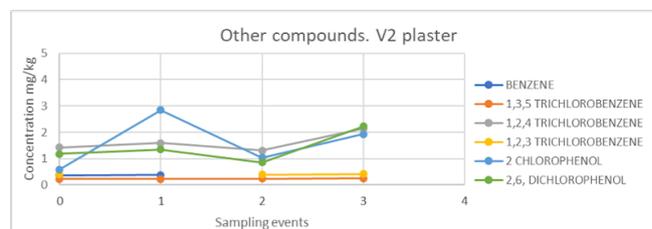
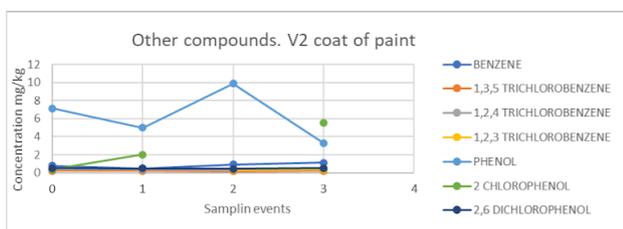
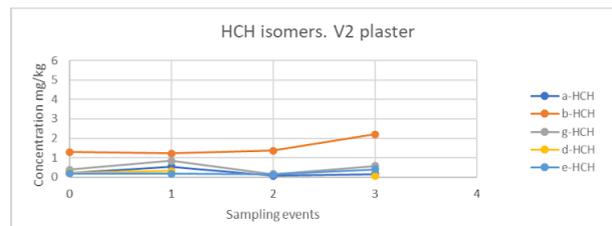
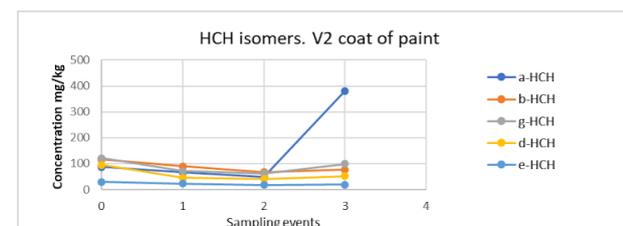
Below is a summary of these results.

PERSULFATE TREATMENT. ALKALINE ACTIVATION. RESULTS



- PAINT** { ↓ 84% HCH  
↑ (1,2,4 TCB & 2,6 DCF)  
Final concentrations in tens of mg/kg
- PLASTER** { ↓ 70% HCH  
Light ↑ (1,2,4 TCB and 2,6 DCF)  
Final concentrations in a few mg/kg
- SLAB** { No significant changes

**V1** Alkaline hydrolysis of HCH. Oxidation not finished.



Below is a global summary of these results.

TREATMENT WITH nanoTiO2 in sepiolite EMULSION AT 10% RESULTS



- PAINT** { ↓ 40-45 % HCH  
No clearly increase/decrease of (1,2,4 TCB y 2,6 DCF)
- PLASTER** { No significant changes
- SLAB** { No significant changes

**V2** Poor treatment results, insufficient dose.

**V3 TiO2 emulsions at 20%**

The following graphs show the evolution of the different contaminants treated with TiO<sub>2</sub> emulsion

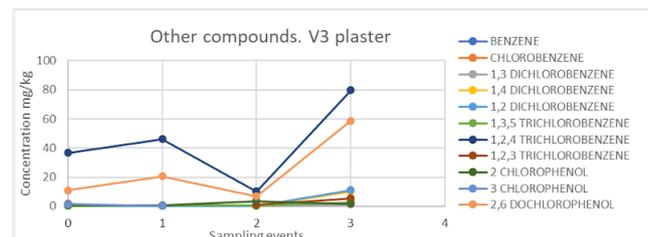
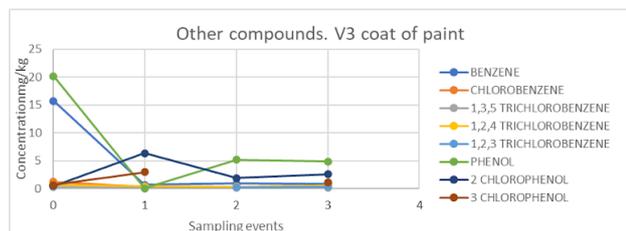
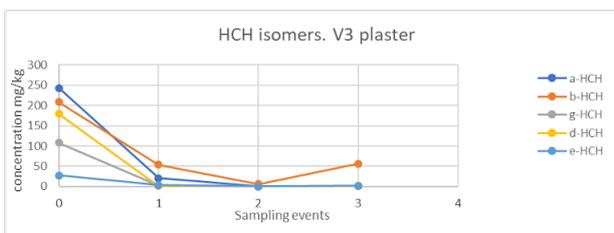
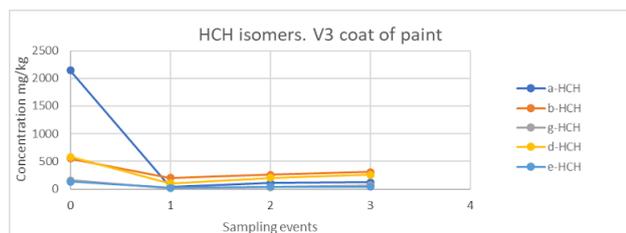
at higher concentration, 20%, in the paint layer and in the plaster underneath

TREATMENT WITH nanoTiO2 in sepiolite EMULSION AT 20% RESULTS



- PAINT** { ↓ 78 % HCH
- PLASTER** { ↓ ↓ >90 % HCH
- SLAB** { No significant changes

**V3** Good results in HCH, with complete mineralization.



Below is a global summary of these results.

### Summary and Conclusions

From the operational point of view:

- The application of oxidizing agents is simple (roller, brush, spray), safe (it does not generate vapors or splashes) and fast (reaction in 24-48 hours).
- Persulfate treatment generates a small amount of leachate, that must be treated.
- TiO<sub>2</sub> emulsion treatment requires UV-A activation. This activation occurs naturally by solar action outdoors, but UV lamps are required indoors.

The initial characterization of the material indicates:

- A very heterogeneous contamination on the walls.
- A coat of paint highly affected by HCH mixed with compounds from the paint (as phenol or benzene).
- An underneath layer of plaster that shows concentrations of contaminants between one or two orders of magnitude lower than the paint. However, the percentage of "daughter" compounds, derived from the hydrolysis of HCH, is quite striking.
- In the deep slab the contaminant content has a very low environmental relevance.

Two treatments have been tested; persulfate activated with soda and emulsion with TiO<sub>2</sub> at concentrations of 10 and 20%.

- The persulfate treatment achieved HCH reductions of more than 80% in the paint layer and 70% in the plaster, mainly due to the initial hydrolysis caused by the alkaline medium with soda. In parallel, increases in daughter product concentrations were observed, indicating that the oxidation was incomplete.
- Regarding the treatment with TiO<sub>2</sub>, it can be concluded that the concentration of 10% was insufficient.

- Meanwhile the TiO<sub>2</sub> emulsion at 20% concentration achieved interesting results:
- reduction in HCH isomers close to 80% in the coat of paint and >90% in the underneath plaster.
- Complete reduction of other major contaminants, benzene and phenol.
- Complete mineralization, without significant increases in daughter compounds.

In view of the results obtained, the option of using TiO<sub>2</sub> nanoparticle emulsion supported on micro-sized sepiolite with a concentration of 20% or higher seems to be the best option for the oxidative treatment of the contaminated walls of the factory.

### References

- Gupta, S.M. and Tripathi, M. (2011). "A review of TiO<sub>2</sub> nanoparticles". Chinese Science Bulletin. June 2011 Vol.56 No.16: 1639–1657. doi: 10.1007/s11434-011-4476-1
- Oudejans, L.; Wyrzykowska-Ceradini, B. (2017). "Assessment of Solution Application Methods for Decontamination of Surfaces Contaminated with Pesticides" EPA/600/R-17/394 | www.epa.gov/homeland-security-research.
- UK Government decontamination service (2017) "The decontamination of buildings, infrastructure and open environment exposed to chemical, biological, radiological substances or nuclear (CBRN) materials" Strategic National Guidance. [www.gov.uk/government/publications/strategic-national-guidance-the-decontamination-of-buildings-infrastructure-and-open-environment-exposed-to-chemical-biological-radiological-or-nuclear-materials](http://www.gov.uk/government/publications/strategic-national-guidance-the-decontamination-of-buildings-infrastructure-and-open-environment-exposed-to-chemical-biological-radiological-or-nuclear-materials)
- Volchek, K; Thouin, G.; Kuang, W.; Li, K.; Tezel, H.; Brown; C.E. (2014) "The release of lindane from contaminated building materials". Environ Sci Pollut Res (2014) 21:11844–11855. doi: 10.1007/s11356-014-2742-x