## Block 2

# STRATEGY-INFRASTRUCTURE-MONITORING SABINANIGO MEGASITE


MULTIDISCIPLINARY TEAM
CAJA RURAL


GOBIERNO DE ARAGON
14th International
HCH and Pestic
CAJA RURAL
DE ARAGÓN


GOBIERNO DE ARAGON
14th International
HCH and Pesticides
Forum
21-24 February 2023
Zaragoza, Spain


SAMPLE ANALYSIS
SOLID
MATRIX
LIQUID
GAS
AIR QUALITY


Funded by
the European Union
h International
H and Pesticides
rum
4 February 2023
goza, Spain


GOBIERNO DE ARAGON
14th International
HCH and Pesticides
Forum
21-24 February 2023
Zaragoza, Spain
CAJA RURAL
DE ARAGÓN


Funded by
the European Union
national
Pesticides
2023

# CASE STUDY OF THE INFLUENCE OF GEOLOGY AND THE PRESENCE OF DIFFERENT MATRICES ON THE APPLICABILITY OF HCH REMEDIATION TECHNOLOGIES

***Cano, E.[1], Fernández, J.[1], Net, J.[1], Velilla, S.M.[1], L. Monge[2], Arjol, M.A.[2]***

*[1]Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*
*[2]Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain*

***Summary***

Inquinosa factory (Sabiñánigo, Huesca) produced lindane (γ-HCH) from 1975 to 1989. Per each ton of lindane, 8 to 10 tons of other HCH isomers were produced and sent for disposal to two landfills: Sardas landfill, operating from 1975 to 1983 and Bailín landfill, operating from 1984 to 1989. As well as solid waste, the factory dumped liquid waste that has been found in form of DNAPL. None of the sites had proper isolation measures. Thus, the solid and liquid wastes leaked into the ground causing soil and water pollution.

The Government of Aragon is working in the control, containment and remediation of these orphaned polluted sites since 1992.

The three sites (Inquinosa, Sardas and Bailin) are close to each other, distributed around the axis of the Basa anticlinal. Whereas Inquinosa and Sardas bedrocks, separated 400 m by the Sabiñanigo reservoir, are composed of tertiary fractured marls of the fold axis, Bailin, 2 km south from Sardas, is composed by an alternancy of siltstones and fractured sandstones in vertical layers. In spite of their proximity, Sardas and Inquinosa present also geological differences, due to the diversity of the quaternary deposits present at each margin of the river. As a consequence of these variety, each of the three sites has its own groundwater behaviour. Such is the case that there is a free detrital aquifer in Inquinosa, a semi-confined detrital aquifer in Sardas influenced by the tidal effect of the reservoir, and a fractured aquifer in Bailín.

But apart of the natural geological materials, sediments and sludge are generated within the control and remediation activities.

The diversity of materials, aquifers and matrixes together with the existence of DNAPL and solid HCH, makes it impossible to solve the problem with an only one remediation technology, nor to replicate the same methodology in all sites. A site-specific train of techniques is needed to remediate all matrixes. Dedicated studies and pilot tests are currently undergoing to progress on its implementation.

***Keywords***

Lindane, hexaclorocyclohexane (HCH), DNAPL, fractured aquifer, detrital aquifer

## *Introduction*

Lindane, the gamma isomer of hexachlorocyclohexane or γ-HCH, was produced in Sabiñanigo (Huesca, Spain) from 1975 to 1989 in a factory owned by the company Inquinosa. Lindane production was highly inefficient so that per each ton of lindane, 8 to 10 tons of other HCH isomers were produced with not commercial value, thus constituting waste. Liquid waste was also generated from the failed reactions and the distillation tails.

During the production time, there was a lack of dangerous waste management regulation in Spain. The first provisions on toxic and dangerous waste take place after the adhesion of Spain to the European Economic Community in 1.986, with the transposition of certain directives to the Spanish regulation.

Inquinosa disposed the production waste, in two landfills: Sardas landfill from 1975 to 1983 and Bailín landfill from 1984 to 1989.

- Sardas landfill was the landfill for the municipal and industrial waste of Sabiñánigo town. Placed in an old marly gully, it is a multicompound landfill containing urban waste, construction and demolition waste and a variety of waste from the Sabiñanigo chemical industries. It holds 30,000 to 80,000 tons of solid HCH and 20 to 25 tons of HCH liquid waste [6]. From 1985 to 1987, the national road N-330 was constructed, whose alignment run across the footing of the landfill body. Around 50.000 m$^3$ of waste were moved from the footing and extended in the plot placed at the opposite side of the national road, splitting the landfill in two.
- In contrast, Bailin landfill was exclusive for the waste coming from Inquinosa factory. 65,000 tons of solid HCH [4] and 20 to 25 tons of liquid waste were dumped there.

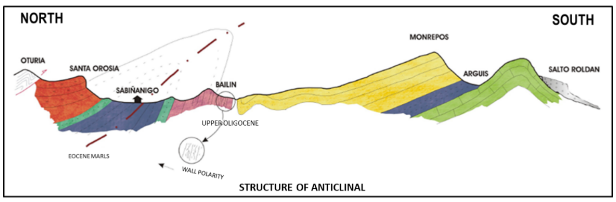
The solid and liquid wastes leaked into the ground causing soil and water pollution. The three sites (Inquinosa old factory, Sardas and Bailin) had been declared contaminated in the framework of the Spanish Law on Waste and Contaminated Soils.

Due to the disobedience of the responsible of the contamination related to the obligations to remediate the damage caused, the Government of

Aragon has assumed subsidiary the sites management and is working on the control, containment and remediation of these orphaned polluted sites since 1992. To enable the progress in remediation activities, in 2014, the Government of Aragon transferred Bailin waste to a security cell constructed 400 m far from the original landfill.
The geological characteristics of each site, together with the presence of pollution in different phases and matrixes makes remediation a primarily complex process that needs to be addressed through a wide combination of techniques applied in successive steps.

## *Geology*

The sites are located in the so-called turbiditic basin of Jaca-Pamplona, placed within the Southerpyrenean Zone, which constituted a foreland basin during the ulplift of the Pyrenean moutain chain (Upper Cretaceous – Paleogene). It is characterized by a continuity of the tertiary sediments and the southern vergence of the structures.
The Jaca-Pamplona Basin is an intermontane basin made up of syntectonic Paleogene materials, which form a synclinorium between the Internal Sierras (to the north) and the South Pyrenean front of the Exterior Sierras. The progressive deformation of the active margin produced the shifting of the sedimentary basin towards the foreland and the subsidence of the carbonate platforms of the passive margin, generating turbiditic facies. From the Bartonian to the Upper Oligocene, a structural uplift occurred due to the emergence of the thrusting of the Exterior Sierras, leading to the development of alluvial fans and a longitudinal filling of the platform with siliciclastic and alluvial plain facies. [1,2]




*Tertiary materials* [1,2]

Sardas and Inquinosa sites are located on the axis of the Basa overlying anticline (ESE direction and S vergence, with the southern flank inverted), on the Margas de Larrés formation, representative of the silting of the turbiditic basin (Upper Lucecian-Lower Bartonian). It is composed of massive grey marls with occasional levels of slump and fine-grained sandy turbidite intercalations. Lithologically, it is a calcareous silt with some sand, porosity around 10% and low to very low permeability. In Sardas, the dip of the layers varies from 35º to 75º SE, whereas in Inquinosa, bedding is predominantly subvertical. Two families of fractures have been identified.
Marls are weathered in the first 2 to 5 m. In the weathered area, permeability is higher than in the healthy marl by one order of magnitude (3.80E-4 to 6.70E-3 cm/s).
Bailín site is located on red siltsones, sandstones and conglomerates called "Bailín facies", dated on Upper Bartonian – Middle Priabonian. They correspond to alluvial fan deposits. They are present on both flanks of the Basa anticline, being thicker on the S flank, where the landfill is placed. The formation is made up of mudstones and red siltstones with abundant bioturbation in decametric layers and frequent intercalations of sandstones and conglomerates of metric scale. In Bailín area, bedding has ESE direction and subvertical dip, so that long sandstone and conglomerate ridges stand out from the relief due to differential erosion. In the landfill area, these conglomerates and sandstones are arranged in large-scale lenticular bodies, disappearing due to wedging in many cases. Two families of fractures perpendicular to the bedding can be also recognized. Fracturing is notably more developed in sandstones and conglomerates, which constitute fractured aquifers and preferential pathway of groundwater. Flow speed in fractures varies enormously depending on the opening, ranging between 1 and 200 cm/s. In some areas of the site, a shallow subhorizontal fracturing is detected affecting all materials, which is likely responding to decompression processes of the materials due to their erosion, and may be of importance with regard to the superficial hydrogeological behaviour.

*Quaternary materials* [1,2]:

Glacis and Terraces:
There are several generations of glacis-terraces that converge in the areas close to the course of the Gallego river.
The glacis have high amounts of material from the degradation of the terraces, as well as conglomeratic and terrigenous materials from the nearby Santa Orosia conglomerates. They can be recognized on the left bank of the Gállego River, in the upper area of the Sardas landfill, constituting a potential pathway for water entrances into the landfill body.
On the right bank of the Gállego River, around the Inquinosa site, deposits of fluvioglacial origin are identified. They constitute a free aquifer, with immediate response to rainfalls, being dry in lack of them.

*Lower valley alluvial deposits*

They are formed by the floodplain materials of the current course of the Gállego river and to the topographically lower terraces. Two levels of different lithology can be distinguished at Sardas site: a lower level of gravel and sand, with an average thickness of 5 m and high hydraulic conductivity, and an upper level of sandy silt with low permeability and variable thickness, between 5 and 10 m. The level of sand and gravel constitutes a semi-confined aquifer, being a preferential pathway of groundwater circulation between the landfill and the Sabiñanigo reservoir. The Sabiñanigo reservoir is used for regulation for hydroelectric purposes, being subject to continuous rises and falls of the water table level. These variations produce a tidal effect in the aquifer, acting the reservoir as a natural hydraulic barrier.

### *Phases and matrixes*

Inquinosa produced an estimate of approximately 6,800 t/year of solid waste and 300 to 1,500 t/year of liquid waste [6].

A mixture of five main isomers (α, β, γ, ε and δ HCH), called "technical-HCH" is manufactured by the photochlorination of benzene. Lindane (γ – HCH) is extracted and purified from this mixture of isomers using fractional crystallization to produce 99% pure lindane. At the end of this process 6 to 10 tons of HCH solid waste (non-commercial isomers) are obtained, that were sent for disposal to the landfills. [5,7]. For the mechanical stabilization of HCH waste inside the landfills, soil and straw were extended between the waste layers.

The solid waste is found at Sabiñanigo sites in different matrixes:

- Pure and mixed with soil in high concentration inside the landfill bodies.
- In the soils contiguous to the landfill bodies and at the old factory plots, all of them declared contaminated by Resolution of the Government of Aragon. This pollution is associated with solid waste dispersion, especially important in the early years of production.
- On the rocky surface of the old Bailin landfill. During the dismantling of the old Bailin landfill, more than 7,000 tons of surface rock were broken with hammer, excavated and disposed in the new cell and more than 30,000 $m^2$ of old landfill surface were cleaned by hand [4]. In spite of that, solid waste can still be found on the surface, in the first meters (sub-surface) and in the sediments generated by runoff-waters erosion.

Liquid waste is present on the sites in form of a DNAPL. The DNAPL found in Bailin and Sardas has average density of 1,5 $g/cm^3$ and it is composed by HCH isomers, benzene and chlorobenzenes. Since it was the result of the liquid residues generated during the process for the enrichment of the γ-isomer and from the mixture of faulty production batches, any compound of the reaction route of photochlorination of benzene to HCH may be found [6,7]. DNAPL was first detected during the drilling of a borehole at Bailin landfill in 2004. After that, in 2009, it was also found in surface at Sardas landfill. From the moment of its detection, the priority in both landfills has been to stop its flow and to control the contamination levels in the aqueous phase [6]. A network of boreholes was drilled to pump the free liquid phase for that purpose. After extraction, the liquid phase is decanted and sent to incineration. At Bailín landfill, the free DNAPL is almost exhausted but remains in residual phase absorbed to the rock fractures. There is also residual phase in the pores of Sardas silts as well as inside Sardas landfill body. As long as residual DNAPL exists, it will constitute a pollution source. Its extraction must be enhanced using specific remediation techniques. Due to the variability of matrixes (fractured aquifer in Bailin, low porosity detrital materials, anthropic fill), methodologies to be applied may differ significantly.

On the other hand, both, solid HCH and DNAPL are subject to dissolution processes and the generation of leachates. Leachates pathway starts with the contact of runoff and groundwater with solid or liquid waste going afterwards through all the control and containment facilities. As a consequence, the following matrixes present HCH concentrations:

- Groundwater of the contamination plume
- Pumped groundwater prior to treatment
- Activated carbon
- Sludge from the waste pools
- Vadose area -fractured aquifer in Bailin, detrital sediments of different permeability in Sardas and Inquinosa
- Vegetal species growing in Bailin runoff waters collection pools and Sardas waste pools

### *Results and discussion*

The variety of materials, contaminant phases and matrixes existing in the mentioned HCH polluted sites involve the existence of a wide range of pollution scenarios, each one of which requires the implementation of a specific remediation technology. The individual technologies must at the same time be compatible and complementary to the others, so that they become part of a global remediation strategy that addresses the comprehensive decontamination of the sites. The Government of Aragon elaborated a Roadmap with the needed actions to achieve the full remediation of the polluted areas [3]. Actions to date have been oriented to accomplish this Roadmap, so that the following remediation technologies are under development and/or under implementation.

| Pollutant concen-tration | Phase | Site | Matrix | Geology | Technology |
|---|---|---|---|---|---|
| + | Solid HCH | Bailin-Sardas | Pure waste | Anthropic fill | Phase 1: isolation Phase 2: (elimination) To be determined |
| | Free DNAPL | Bailin | Saturated rock | Sandstones – fractured aquifer | Pump & Treat |
| | | Sardas | Saturated antropic fill | Landfill | |
| | Residual DNAPL | Bailin | Rock | Sandstones – fractured aquifer | SEAR, S-ISCO |
| | | Sardas | Soil | Silts | SEAR + Electroremediation |
| | | | | Sands-gravels | SEAR, S-ISCO |
| | | | Saturated anthropic fill | Landfill, road embankment | Pump and treat, SEAR |
| | Dissolved HCH | Sardas | Sludges | Storm pool sediments | Electroremediation, bioremediation |
| | | All sites | Leachates | Pumped water | Alkaline hydrolysis, activated carbon |
| | | Bailin | Groundwater | Sandstones – fractured aquifer | ISCO, areation, bioremediation |
| | | Sardas | Groundwater | Detrital aquifer | |
| - | Solid HCH | All sites | Vadose zone | Variable geology | To be determined |
| | | | Soil | Sediments | Bio-phytoremediation (technosoils) |

***Conclusions:***

HCH remediation at the orphan pollution sites constitutes complex technical challenge, due to the own nature of the pollutants, moreover when DNAPL is present. As it happens in any remediation project, technologies to be applied vary depending on the matrixes to be treated. In the specific case of study of Bailin and Sardas landfill and Inquinosa old factory site, it is additionally remarkable how the differences in geology may condition the whole remediation strategy. The combination of these three variables: pollutant phase, matrix and geology involves the implementation of a comprehensive remediation strategy that gathers a large number of technologies and application methodologies. These technologies and methodologies must be designed to be compatible and complementary among them, having in mind the specific time frame for the application of each one so that the efficiency of the whole process is maximized.

***References***


1. IGME. 2012. MAGNA 50 - Hoja 177 (SABIÑANIGO)
2. IGME. 2012. MAGNA 50 - Hoja 210 (YEBRA DE BASA)
3. Government of Aragon. 2016. Strategic Environmental Action Plan against lindane waste contamination in Aragon
4. Kaifer Brasero, MJ; Fernández Cascán, J.; Corujo Cristóbal, J.M.; Caleya Sánchez, J.M.; Revuelto Palau, D.; Mir Morales, A.; Sainz Gutiérrez, R. 2015. Dismantling of the old lindane waste landfill of BAILÍN (Sabiñánigo-HUESCA). Final book XIII HCH Forum
5. Peti Committee European Parliament. 2016. Lindane (Persistent Organic Pollutant) in EU
6. POP-contaminated sites from HCH production in Sabiñánigo, Spain. 2013. J. Fernández & M. A. Arjol & C. Cacho, 2013
7. Santos, A., Fernandez, J., Guadano, J., Lorenzo, D., Romero, A., 2018a. Chlorinated organic compounds in liquid wastes (DNAPL) from lindane production dumped in landfills in Sabinanigo (Spain). Environ. Pollut. 242, 1616–1624.
8. Vijgen J. (2006). The Legacy of Lindane HCH Isomer Production. Main Report. A Global Overview of Residue Management, Formulation and Disposal. International HCH & Pesticides Association.

# UNIQUE STRATEGIC PROJECTS IN THE SITES AFFECTED BY HCH IN ARAGON

***Velilla, S.M.[1], Cano. E.[1], Monge, L.[2], Visanzay, A.[2]***

[1]*Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*
[2]*Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain*

***Summary***

In October 2015, a Management Unit for the Comprehensive Decontamination of Lindane was created, agreed by the Governing Council, which was integrated into the Service of Contaminated Soils in accordance with Decree 25/2020, of February 26, of the Government of Aragon, which approves the organic structure of the Department of Agriculture, Livestock and the Environment (BOA No. 43 of March 3). In 2016, the "The Strategic Environmental Action Plan against the lindane waste in Aragon" was approved. The Plan include five priority actions, and organizes them in a Roadmap. Action I is the isolation of waste, which began with the transfer of waste from the old Bailin landfill to the new security cell. This action will be completed with the "DEFINITIVE CLOSURE OF THE BAILÍN SECURITY CELL", which to date and since 2014 has been provisionally sealed in anticipation of receiving the waste from the dismantling of the old Inquinosa factory and the waste at that time stored in those facilities.
Included in Action III of the Strategic Plan is the so-called "HYDROLOGICAL CORRECTION AND BIOREMEDIATION PROJECT OF NORTH ZONE OF THE OLD BAILÍN LANDFILL" (CORHIBA) whose aim is the decontamination and restoration of a relevant part of the surface of the north zone of the old Bailin landfill.
Action III refers to the decontamination and restoration of surface soils. This has led to the drafting of the "PROJECT FOR THE DISMANTLING AND DEMOLITION OF THE OLD LINDANE FACTORY, SABIÑANIGO (HUESCA)" which addresses the dismantling of the facilities and structures of the old Inquinosa factory as a prior step to enable the subsequent decontamination of the soil and its restoration.

***Keywords***

Strategic Plan, Security cell, Corhiba, dismantling, Inquinosa, Bailin

### *Introduction*

The Government of Aragon has been acting in a subsidiary way since the 1990s in the sites affected by HCH contamination whose origin was the old Inquinosa factory. As a result of these actions, the Government of Aragon accumulates more than 25 years of technical, administrative and political experience in the fight against lindane. The elaboration of "*The Strategic Environmental Action Plan against the lindane waste in Aragon*" for the comprehensive fight against contamination by lindane and other HCH isomers, is carried out in accordance with the mandate of the Courts of Aragon expressed in several motions. In the Strategic Plan a roadmap closely connected to the selection of alternatives is established, aiming for both, the minimization of environmental risks and the decontamination of the sites, as well as for the environmentally sound disposal of waste. It consists of 5 main actions, among them actions I. Isolation of waste and III. Decontamination of surface soils and restoration, on which we will focus.

### *Definitive closure of the Bailín security cell*

In accordance with Action I of the Strategic Plan, the isolation of waste is included in the proposed roadmap, whose 3rd and final stage at the Bailin landfill is the "*Definitive closure of the security cell*".

On March 1, 1995, the Department of the Environment formulated the Environmental Impact Declaration for the construction project, sealing, and control and monitoring plan for a security deposit for excavation waste from the Inquinosa landfill, located in Bailín.

Two stages were established for this process:

PHASE A: It consisted of a stage of hydro-geological confinement to minimize, control, capture and treat the leachate from the old Bailín landfill, once its exploitation was completed in 1994. It was superficially sealed and a control and monitoring of the underground pollution flows was carried out.

In 2004, as a result of monitoring, a dense phase (DNAPL) was detected inside the fractures of the rock mass, outside the location of the old landfill body. The detection of this dense phase in the aquifer led to an important determination: this was the focus of greatest risk for the river and therefore it was necessary to dismantle the old landfill to undertake the control and cleaning of the dense phase.

PHASE B: the construction of a security cell was carried out to eliminate the source of contamination existing in the basin and thus be able to act on the affected rock mass. These actions began in 2009, and in 2014 the dismantling of the old landfill was carried out thanks to the excavation, transfer and storage of the waste in the new Bailín security cell, encapsulated in safe conditions.

The Bailín security cell is a hazardous waste landfill that contains around 65,000 tons of hexachlorocyclohexane (HCH), a compound classified as toxic, dangerous and potentially carcinogenic, which is included in the list of Persistent Organic Pollutants of the Stockholm Convention, transposed to European regulations by Regulation (EU) 2019/1021 of the European Parliament and of the Council of June 20, 2019, on Persistent Organic Pollutants, and in application of which their elimination from the environment is mandatory. Additionally, it contains around 342,000 tons of soils contaminated with HCH.

The construction project also contemplated the deposit of waste from the interior of the old Inquinosa factory as well as the waste from its dismantling and demolition inside the security cell, as established in Action I of the Strategic plan. It was considered that this waste would be stored and prepared to be dumped at the time the transfer works from the Bailín landfill were carried out. However, during the transfer of the landfill, neither the waste of the inside of Inquinosa had been encapsulated (action carried out in 2017) nor a project for the dismantling of the factory was elaborated (drafted in 2020).

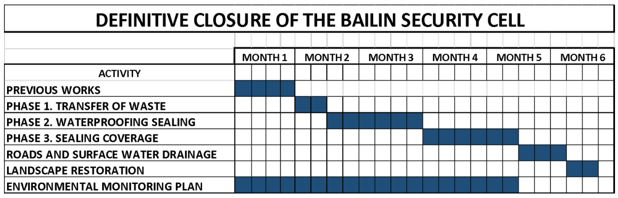
For this reason, the waste from the security cell was provisionally covered with a HDPE sheet for its subsequent opening once the encapsulated waste and rubble from the demolition of the old factory were available, leaving the final and subsequent filling and sealing revegetation pending. Taking into account that this type of sheets are designed to be buried in construction excavations, significantly reducing their durability if they are exposed to the elements and weather agents, in 2021 a check to verify the state of the sheet was made, resulting acceptable.

After carrying out an assessment of the risk that the reopening of the new cell would entail, and considering the technical progress in soil remediation, between 2017 and 2018 it was decided not to deposit the debris and waste from the old Inquinosa factory in the Bailín security cell. As a consequence of the decision not to open the Bailín security cell, during the years 2021 and 2022 the management of encapsulated waste inside Inquinosa has been carried out through external management.

The current provisional sealing with the installation of a HDPE sheet directly on the waste was not contemplated in the Project of works for phase B of the Bailín HCH landfill - Stage 3. This has caused a change in the starting situation of the sealing of the cover that requires the implementation of constructive solutions other than those included in the aforementioned project, requiring a new design. Additionally, and as commented in the previous section, the final volume of waste contained in the security cell is lower than initially expected, so the topography of the landfill cover differs notably from that initially considered in stage 3.

The temporary nature of the current sealing, together with the danger of the waste, make the closure of the landfill a priority, necessary to guarantee the correct functioning of the security cell from the near future and onwards, thus reducing environmental risks.

This facility has integrated environmental authorization, granted for specific conditions of encapsulation of the waste that currently, with the provisional sealing, would be outside the conditions provided in the authorization. Its final closure is necessary to adapt it to the mentioned conditions and to additionally comply with Royal Decree 646/2020, of July 7, which regulates the disposal of waste by depositing it in a landfill and therefore, the conditions these types of facilities must accomplish.




### *CORHIBA*

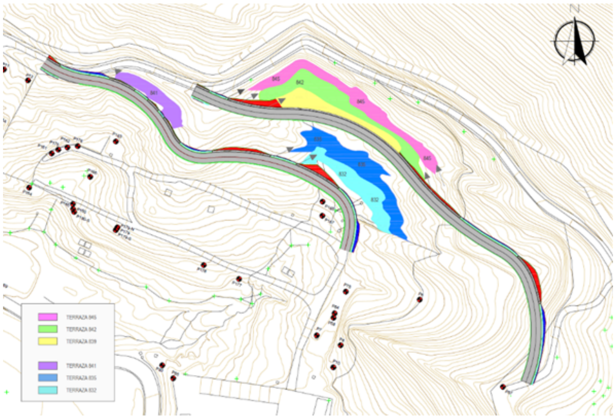
In accordance with Action III of the Strategic Plan, another singular project has been planned to be carried out on the old HCH landfill located in Bailín, which was used -between 1985 and 1992- as a location to host the waste generated by the old factory of the company Industrias Químicas del Noroeste, S.A. (INQUINOSA).

The landfill occupied an area of approximately 3 hectares and hosted a volume of waste close to 210,000 cubic meters, some 429,000 tons of waste, including 65,000 tons of solid HCH waste. The rest of the waste was, mainly, contaminated land (342,000 tons+ others).

Since the completion of the dismantling work of stage 2, a permanent monitoring of surface- and groundwater of the old Bailin landfill is carried out. As well as the monitoring of the quality of the soil and air.

Directly related to Phases A and B at the Bailin landfill, but not foreseen within them, the hydrological correction, phytobioremediation and environmental integration of the old Bailin landfill in its northern area will be carried out.

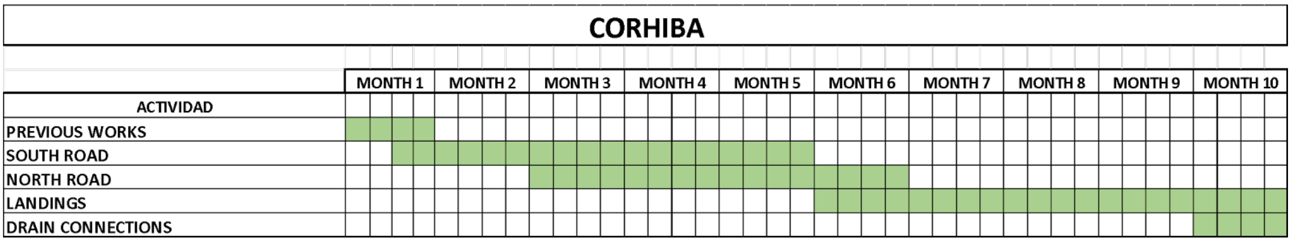
The area of action is part of the northern area of the dismantled landfill, outside the ISCO area where the injection and recirculation tests have been carried out inside the M layer in the old Bailín basin in the framework of the LIFE “SURFING TEST” project. ENGINEERING DESIGN LIFE SURFING: LIFE17 ENV/ES/000260”.



After the dismantling of the Bailín landfill in 2014, almost 3 hectares of steep slope without vegetation came to the surface formed by alternating limestones and sandstones in an approximate proportion of 9/1, with runoff coefficients close to one. The slope and the absence of soil and vegetation causes laminar erosion and rills with dragging of solids by runoff water that, together with the upwellings, involve that all the runoff water that comes into contact with the landfill surface has to be treated in the Bailin water treatment plant.

The construction project called "HYDROLOGICAL CORRECTION AND BIOREMEDIATION PROJECT OF THE OLD BAILÍN NORTH AREA LANDFILL. BAILÍN, HUESC" (CORHIBA) describes the construction of two roads, north and south, on the site of the old Bailin vase, already dismantled.

These roads will allow access to a series of terraces where artificial soil fillings (technosols) will be installed, which will serve as a base for the phytobiorremediation of the superficial zone of the vessel and at the shallower vadose zone. In addition, they will minimize the dragging produced by the runoff, currently in direct contact with the uncovered area. This hydrological correction will try to reduce the flows, to drain them and to lead them to treatment in the existing treatment plant at the Bailín facilities. With this action, flows in contact with the surface of the landfill will be minimized and, at the same time, the pollution load will be reduced. These terraces must be accessible for maintenance and for carrying out decontamination and control tests on the old vessel.




***Dismantling and demolition of the old Inquinosa factory***

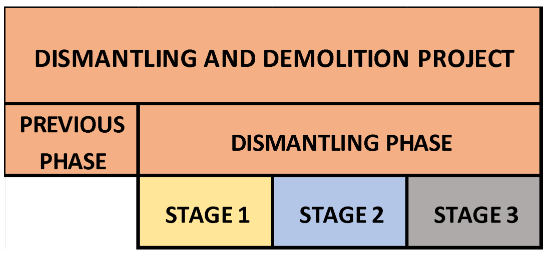
In accordance with Action III of the Strategic Plan, within the proposed roadmap, the affected surface soils at the site of the old INQUINOSA factory will be decontaminated and restored. For this, it is necessary to previously dismantle all existing facilities and structures.

To this end, several studies began to be carried out that allowed us to acquire a better knowledge of the location and of the decontamination techniques that could be applied in the old Inquinosa factory. In addition, a particle air dispersion model was designed given the characteristics of the action and the proximity of the factory to the population center of Sabiñánigo.

In a first step, a draft was made which concluded, among other aspects, the need to isolate the water flow of the area to be dismantled and where decontamination works would be carried out later, as well as a detailed characterization of the contamination of the walls of the buildings.

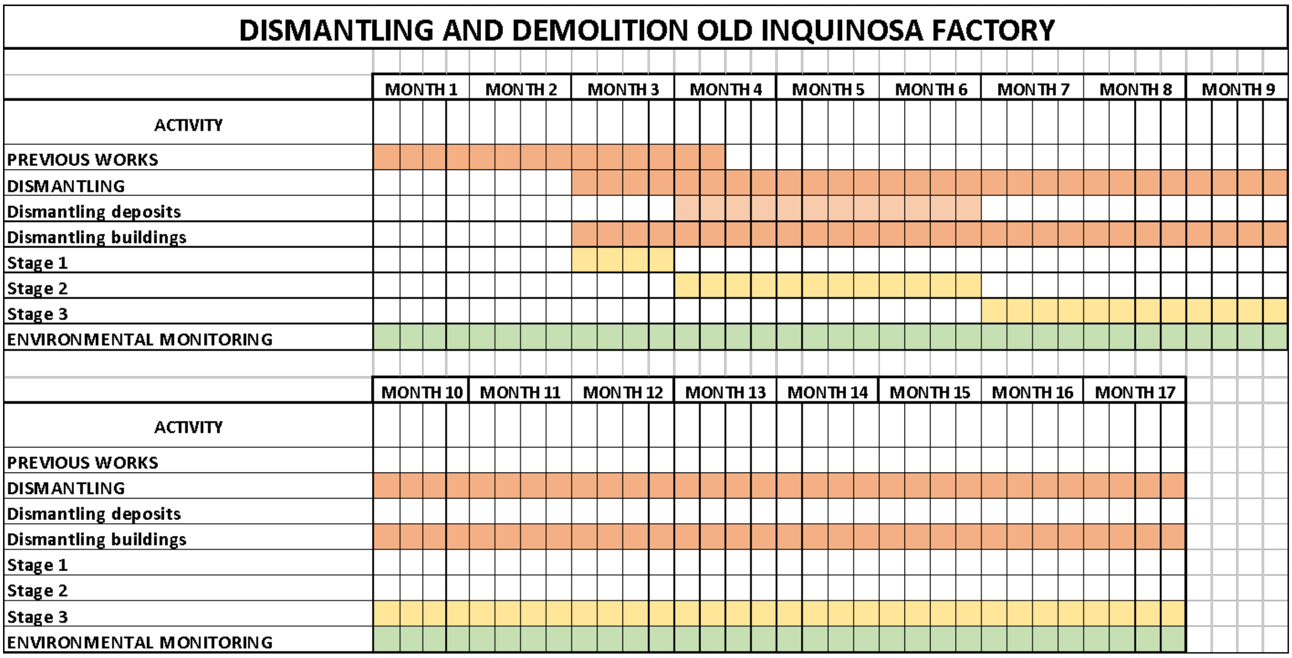
The dismantling project of the old INQUINOSA factory, whose facilities are affected by HCH derived from the productive activity, includes as a first action the recovery of the industrial ruin. As a second action not yet foreseen in the short-medium term, the concrete beds and the soil remediation will be addressed.

The demolition project does not contemplate the perimeter confinement of the groundwater flow, nor the treatment of contaminated soils, its objective is the demolition of structures and enclosures and the treatment of the waste generated by these actions, not including concrete beds or foundations.



For this reason, the project details the phases to be executed, the work method and the means to be used for the total dismantling of all the buildings. Additionally, it defines the necessary measures, aimed at protecting personal and environmental accidents that may occur during the execution of the work, the mandatory hygiene and well-being facilities for workers and the environment.

The project is currently under environmental processing, already exposed to public information and presented to possible interested parties. Said environmental processing has consisted of the request for a pronouncement on the submission to the simplified environmental impact assessment procedure provided for in Law 11/2014, of December 14. In a first request, additional documentation was required to complete the environmental annex of the project. After the incorporation of those documentation into the project, it went again under the same procedure, which is currently suspended pending of the reception of the mandatory reports.




### *Acknowledgements*

- Government of Aragón funding has made these projects possible
- EU whose financial support will make possible the execution of these projects.
- SARGA for the knowledge and effort in drafting the projects and support to decide the best solution to adopt.

### *References*

1. The Strategic Environmental Action Plan against the lindane waste in Aragon.
2. Definitive closure of the Bailín security cell
3. Hydrological correction and bioremediation project for the old Bailín landfill in the northern area (CORHIBA)
4. Project for the dismantling and demolition of the old lindane factory, Sabiñanigo

# MULTIDISCIPLINARY PERSPECTIVE OF THE ENVIRONMENTAL MANAGEMENT OF THE SARDAS SITE

***Joaquín Guadaño[1], Jorge Gómez[1], Elena Granados[1], Jesús Fernández[2]***

[1]*EMGRISA: Empresa para la Gestión de Residuos Industriales. Madrid, Spain*
[2]*Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*

***Summary***

For over two decades the Sardas landfill (Sabiñánigo, Spain) was used for the uncontrolled disposal of industrial waste as well as municipal and construction & demolition waste. In total, approximately 400,000 $m^3$ of waste have been deposited directly onto the ground, consisting of Eocene marls. As a consequence, the landfill had no base liner or any other waste mitigation systems installed. The industrial waste contained residues from chlorine production and in particular, approximately 70,000 tonnes of waste isomers from the hexachlorocyclohexane (HCH) production for the manufacture of lindane (γ-HCH). Lindane production was carried out by chlorination of benzene in a photochemical processes using ultraviolet radiation. For the production of one tonne of lindane approximately ten tonnes of HCH waste isomers were generated and were largely dumped in the past around the former lindane productions. These wastes are present in the Sardas landfill both in solid and in liquid form (as Dense Non Aqueous Phase Liquid, DNAPL).

The landfill site was assessed through a governmental project supported by joint funding from the European, National and Regional environmental authorities. Currently, the environmental monitoring of the site, the extraction of the DNAPL phase by pumping, the control and treatment of leachate and researches of different remediation techniques are ongoing.

Hydrogeology, chemistry, microbiology and mathematical modelling, are just some of the areas in which research is carried out on the site. In addition to the resources of the Government of Aragon, SARGA and EMGRISA, work is being done on the site with five university research groups.

This study will address the way to solve the environmental problem of the Sardas landfill from a multidisciplinary point of view in which different materials or soils, impacted to a different degree, require very different characterization and remediation techniques (Surfactant Enhanced Aquifer Remediation SEAR, In Situ Chemical Oxidation ISCO, pump & treat, electroremediation, bioremediation, phytoremediation), even in the same location.

***Keywords***

HCH, lindane, DNAPL, POPs, Sardas landfill, Sabiñánigo

### *Introduction and site conceptual model*

The Sardas site is complex in terms of hydrogeology, types and location of contaminants and also in terms of environmental risks. It has large volumes of contaminated materials with high concentrations of hazardous organochlorine compounds (OCs) for human health and the environment. In addition, the Gállego river is very close to the site, in fact the Public Hydraulic Domain (the Sabiñánigo Reservoir) borders the site.

The presence of DNAPL is a key factor in the site, Figure 1 shows a diagram of its distribution. Its historical underground migration has left an important trace of contamination in the subsoil. DNAPL has been located from fill materials to bedrock fractures at a depth of more than 40 m and constitutes a secondary focus of affection to the soils and groundwater and a priority in the remediation of the site.

On the other hand, contamination is found in various materials, highlighting the landfill fills (Initial source of contamination) as well the materials on which the DNAPL and leachates have flowed. In Figure 1, the presence of DNAPL shows a typical distribution pattern for a liquid dense pollutant.

The evolution of the site is shown in Figure 1 from before the construction of the Sabiñánigo reservoir in the 50s, until the sealing of the landfill in 1990. The construction of the Sabiñánigo reservoir in the 1960s stands out, which raised the levels of groundwater, confining the alluvial aquifer of the Gállego river, as well as the construction of the road that intersected the landfill, during which, the lower part of the site was filled with landfill contaminated wastes. Also noteworthy is the sealing of the landfill in 1995, which included a cement-bentonite slurry wall that retains the leachate inside.

The type of contamination and the fact that it is located in different lithologies and at highly variable depths makes it necessary to address the environmental problems of the site in general and remediation in particular from a multidisciplinary point of view. For this reason, the project has the collaboration of specialists in hydrogeology, chemistry, mathematical modelling, biology, geophysics, agriculture, and civil engineering, who are part of the project work team, including five university research groups, two public companies, and the Government of Aragón.

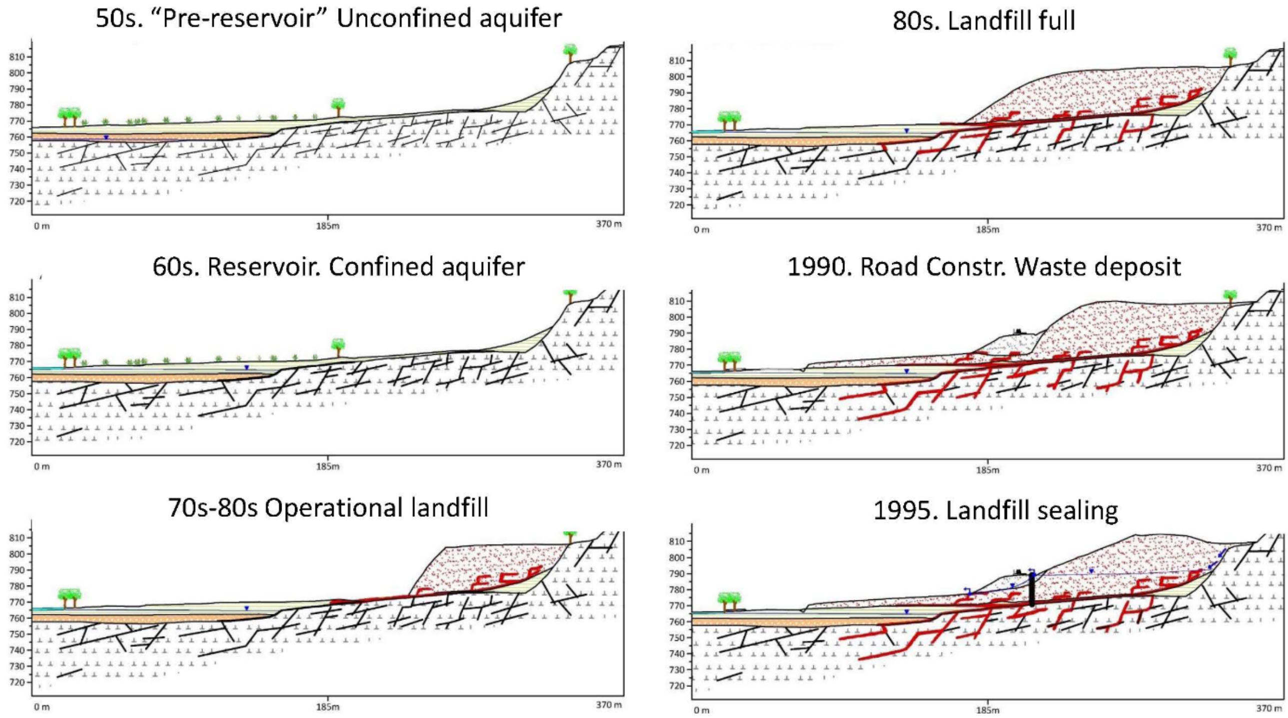



FIGURE 1. HISTORICAL EVOLUTION OF THE SARDAS LANDFILL. DNAPL IN RED

### *Characterization techniques*

The materials affected by contamination are varied and have very different hydrogeological characteristics, locations and degree of affection (anthropic fills, silts, gravels and marls). For this reason, many different methods have been used to characterize the site during the more than 10 years of work. Table 1 summarizes the characterization methods used at the Sardas site. Some techniques are used intensively and for years and continue to be used, such as borehole drilling, or the automatic monitoring of groundwater levels, electric conductivity and temp; Other techniques have been applied successfully, such as geophysical ones that have contributed to strengthening the conceptual model or predicting the location of boreholes.

The use of classical techniques for characterizing the hydraulic properties of the subsoil, such as pumping or tracer tests, have been an essential in strengthening the conceptual model of the site. On the other hand, the development and use of mathematical models of groundwater flow has become a very important tool, which also strengthens the conceptual model and gives important support to the design of remediation tests and trials.

A good example of this is shown in Figure 2, which represents the performance of a tracer test in the alluvial aquifer of the Gállego river to determine the actual velocity of groundwater, key aspect for remediation. The multidisciplinary of the project is clear, specialists in geology, hydrogeology, chemistry, and mathematical modelling have been involved in the design of this test.

TABLE 1. SUMMARY OF CHARACTERIZATION TECHNIQUES

| Characterization techniques | Objectives |
|---|---|
| Vertical borehole drilling | Soil and GW characterization |
| Inclined borehole drilling | Soil and GW characterization |
| Trial pits | Soil characterization |
| Electrical tomographies | Soil and GW characterization, boreholes location |
| Self-potential | GW flow characterization |
| Electromagnetic soundings | Deep soil and GW characterization |
| GW levels, temp and EC automatic monitoring | Hydraulic characterization, data mathematical modelling |
| Pumping tests | Hydraulic characterization |
| Tracer tests | Hydraulic characterization |
| Radon ($^{222}Rn$) manometry | DNAPL location |
| Aerophotogrammetric Digital Restitution | landfill volumetry |
| Mathematical GW flow and transport modelling | Support charact. and remedial decisions |
| Landfill hydraulic balances | Leachates outputs estimation |
| Genetic characterization of GW bacterial communities | Detection of degrading functional genes |
| Bacterial communities characterization | Bioaugmentation research |

The test results are very important for the design of biological and chemical remediation, in situ tests, as well as for the planning of new characterization, research, and remediation actions.

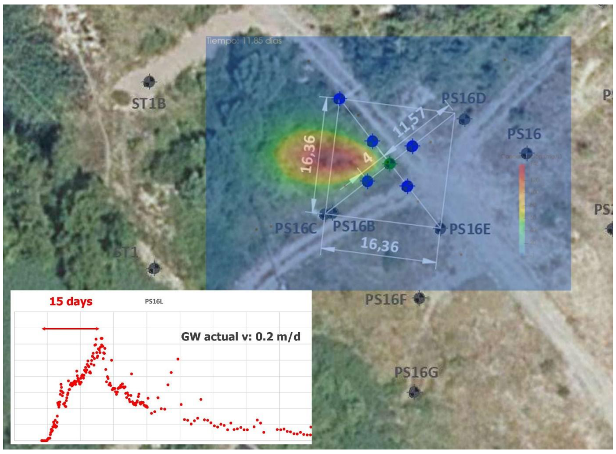



FIGURE 2. TRACER TEST MODELLING AND TRAVEL TIME

### *Site remediation techniques*

The various lithologies present and the location of soil and groundwater contamination, makes it necessary to address the environmental problems of the site in general, and remediation in particular, from a multidisciplinary point of view. For this reason, there is the collaboration of specialists in hydrogeology, chemistry, mathematical modelling, biology, geophysics, agriculture, and civil engineering, who are part of the project work team, including five university research groups, two public companies, and the Government of Aragón. Table 2 lists the main remediation techniques used at the site, some are in a higher degree of development than others. Some have been tried and discarded for different reasons, such as thermal desorption or nZVI. Other techniques are currently operational, such as the pumping of DNAPL or SEAR. Other techniques such as electrokinetics or bioremediation are being developed by the work team through various laboratory studies and on-site tests, ongoing or planned.

### *Future perspectives*

In recent years the efforts have mainly been directed at the characterization of environmental problem of Sardas Landfill, to ensure the environmental safety, and the investigation of treatment alternatives and technologies. Now, the main efforts are focused on remediation. Every year, the number of remediation techniques applied in the Sardas site increases and progress is made in the study of new treatment alternatives.

There have been promising advances in the investigation of various remediation techniques, highlighting bioremediation and SEAR. Although it is essential to continue working with proven and ongoing techniques, such as DNAPL pumping and SEAR, and to continue the open lines of research in techniques such as ISCO, biological, electrokinetic or phytoremediation.

TABLE 2. SUMMARY OF REMEDIATION TECHNIQUES

| Material | Technology | Objective | Development status |
|---|---|---|---|
| Fill material | Phytoremediation | Degrade soil OCs | Hothouse test ongoing |
| | Biopiles | Degrade soil OCs | 400 t treatment done |
| | Nanoscale zero-valent iron (nZVI) | Soil dechlorination | 50 t pilot test done |
| | Thermal desorption | Removal soil OCs | 43 t pilot test done |
| Silts | Electrokinetic techniques | Mobilize/ desorb OCs in $\downarrow$k soil | 2$^{nd}$ phase lab. test/in situ test |
| Gravels | SEAR | Residual DNAPL pumping | Ongoing |
| | ISCO | Residual DNAPL and dissolved OCs removal | In situ test |
| | Bioremediation | Degrade dissolved OCs | 2$^{nd}$ phase lab. test / In situ ORC test |
| | Pump & treat (alkaline hydrolysis and air stripping) | Removal dissolved OCs | Lab test/ treatment plant built |
| Marls, fill and gravels | DNAPL pumping | Extract DNAPL | Ongoing |
| Fill, silts and marls | Improve landfill drainage | Minimize leachate outputs | Ongoing |


### *Acknowledgments*

The authors thank the following research groups for their participation in the Sardas project, IMPROQUIMA, (Aurora Santos UCM), AQUATERRA (Javier Samper UDC), E3L (Manuel Rodrigro UCLM), DIQBA (Teresa Vicent UAB), IMIDRA Carmen Lobo and PROMEDIAM (Jesús Díaz UPM) and the field team, J. María Echevarría y M. Ángel Sesé, for their work in data collection, field tests and remediation.


### *References*


1. Fernández J., Arjol MA., Cacho C. (2013) POP-contaminated sites from HCH production in Sabiñánigo, Spain. Environ Sci Pollut Res Int. 20:1937-1950.

2. Fernández, J., Weber, R., Guadaño, J., 2014. Dioxin Contamination from Former Lindane (g-HCH) Production in Sardas Landfill and Surroundings, Sabiñánigo (Huesca, Spain). DIOXIN 2014, Madrid (Spain).

3. Fernández, J.R.A., Gonzalvo, P., Oria, I., 2015. General strategy for the HCH landfill pollution. The singular problem regarding the DNAPL presence. In: 13th International HCH and Pesticides Forum, Zaragoza, Spain 2015, Zaragoza (Spain), pp. 7e17.

4. Guadaño, J., Gómez, J., Pérez, J., and Fernández, J. (2011). Thermal desorption Feasibility study of

HCH treatment in a contaminated landfill, Sabiñánigo Spain. 11th International HCH & Pesticides Forum.
5. Guadaño J.,Fernádez J., Gómez J., Pérez J. Historical study of the Sardas landfill and site conceptual model. Sabiñanigo (Aragón, Spain) 13th International HCH & Pesticides Forum.
6. Pérez J.; Fernández, J.; Guadaño, J.; Gómez, J.; Amor, J. (2013) Sardas Landfill, HCH monitoring and remediation (Sabiñánigo, Aragón, Spain). 12th International HCH & Pesticides Forum.
7. Samper, J., Pisani, B.,Guadaño, J., Naves A., Sobral, B. Fernández, J. 2019 Modelo hidrogeológico de Balance del Vertedero de Sardas en Sabiñánigo (Huesca). Estudios en la Zona No Saturada. Vol XIV.
8. Samper, J, Sobral B, Mon A, Pisani B, Naves A, Guadaño J y Fernández J. (2019b) Modelo de flujo y transporte de solutos del emplazamiento de Sardas en Sabiñánigo (Huesca). Estudios de la Zona no Saturada Vol XIV.
9. Santos, A., Fernandez, J., Rodriguez, S., Dominguez, C.M., Lominchar, M.A., Lorenzo, D., Romero, A., 2018. Abatement of chlorinated compounds in groundwater contaminated by HCH wastes using ISCO with alkali activated persulfate. Sci. Total Environ. 615, 1070e1077.
10. Dirección General de Cambio Climático y Educación Ambiental, Gobierno de Aragón (2021) Monitoring and control service of Sardas landfill (Sabiñánigo, Huesca) Anual report. www.stoplindano.es

# PURIFICATION, ANALYSIS AND LABORATORY MANAGEMENT SERVICE, TECHNICAL ASSISTANCE TO THE FACULTY MANAGEMENT AND MONITORING FOR SPACES AFFECTED BY HCH CONTAMINATION

***Monge, L.*[1] *,Velilla, S.M.*[2] *, Cano, E.*[2]**

[1]*Aragonese Society for Agro-Environmental Management, SARGA, Zaragoza, Spain;*
[2]*Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*

### *Summary*

The public company SARGA as its own instrumental means of the Autonomous Community of Aragon, assists the Contaminated Soil Service of the General Directorate of Climate Change and Environmental Education to guarantee the control and monitoring of contamination by hexachlorocyclohexane, hereinafter, HCH, and other waste derived from the manufacture of lindane in Aragon, at the Bailín, Sardas and Inquinosa sites and other affected areas.
The purpose of this work is to avoid affecting the environment and the existing population in the environment, while guaranteeing the quality of the waters in the Gállego River after the possible incorporation of pollutants from the aforementioned locations.
This assistance includes the exploitation, management and maintenance services of the different existing facilities, as well as environmental monitoring which includes the analysis of the data offered by climatic parameters, the sampling and analysis of surface water and groundwater, the evolution of the quality of the soils in the affected environment, and monitoring of atmospheric dispersion and gases. An integral part of this monitoring are the surveillance services of the Gállego River and the ecological study of channels.
This assistance includes the drafting of projects and technical reports valued for the improvement of existing infrastructures, as well as the health and safety coordination service, coordination of business activities and occupational risk prevention.

### *Keywords*

HCH, Strategic Plan, surveillance of the Gállego River, air quality, SARGA

### *Introduction*

The residues from the production of lindane accumulated in the Sardas and Bailín landfills as well as the old INQUINOSA factory, constitute the biggest environmental problem in Aragon and one of the most important in Spain.
The continuous control of the quality of surface water, air, soil and flora and fauna in the area is included in the lines of action of the Government of Aragon to control and counteract the polluting effects of lindane. The public company SARGA assists the Contaminated Soil Service of the Climate Change Directorate in this work from the technical and executive point of view, supporting the multidisciplinary work necessary for the development of the work.
The minimization or elimination of environmental risks is a great technical challenge, due to the characteristics of both the contaminants and the affected sites, which requires a great effort demonstrating a high social and environmental commitment.

### *Environmental monitoring*

In order to assess the possible impacts on the different matrices (water, air and soil), environmental monitoring is carried out in the contaminated sites and environments, for which purpose fixed sampling facilities and analytical equipment are used to allow detailed monitoring of possible pathways. of contamination dispersion.

*1. Water quality*

Strategic plan for the comprehensive fight against pollution from the waste generated by the manufacture of lindane in Aragon, establishes as action 0 to guarantee the supply of drinking water and the quality of irrigation water. To this end, purification work is carried out to treat surface water that could be contaminated at the sites and leachate from pumping carried out at the Bailín and Sardas landfills. In addition, sampling and monitoring is carried out.

<u>Treatment of leachate and polluted runoff:</u>

There are 2 treatment plants at the Bailín site and one in Sardas that treat these leachates and affected runoff, ensuring the quality of the discharge in accordance with the parameters established by the basin authority.

<u>The emergency and early warning protocol</u>

It ensures the coordination of the affected Public Administrations, which responds to possible contaminations that affect the hydrological system. This protocol includes daily sampling and analysis of surface water from the Bailín ravine to Villanueva de Gállego, covering more than 150 km of the Gállego riverbed, as well as water from reservoirs and canals.

Sampling, analysis and interpretation of the results are carried out by SARGA personnel.

*2. Air quality*

There is an air quality Surveillance Network distributed in 11 positions close to the locations around the Sardas landfill, Bailín landfill and Inquinosa facilities. To this end, equipment is available to capture particles that can measure PM10 or PM2.5 sizes, sedimentable particle measurement equipment, gas collectors, and continuous particle measurement and counting equipment, the latter located in two positions.

Measured parameters:

- GASES: total sum and speciation in the laboratory of HCH isomers, Pentachlorobenzene, Hexachlorobenzene and sum of Chlorobenzenes
- SETTLEABLE PARTICLES : more than 10µm; gravimetric determination of total soluble and insoluble solids and subsequent speciation of HCH particles in the laboratory.
- PM10 (≤10 µm) and/or PM 2.5 (≤2.5 µm) PARTICLES in low-volume and high-volume sequential collectors: gravimetric determination of total solids and subsequent speciation of HCH particles in the laboratory and in measuring equipment in continuous counting of total particles without speciation.

Measurement campaigns and routines:

- The gas campaigns are carried out in periods of 35 days
- The sedimentable and non-sedimentable particle measurement campaigns are carried out on a monthly basis and last 24 hours.

The control routines, in general, are monthly at each point, although, depending on the contamination actions, routines with sequential sampling or extended to the duration of the works can be implemented.

*3. Soil quality*

In particular, the quality of the soils in terms of HCH content and its isomers is determined in those areas susceptible to study and monitoring of the quality of excavated land from cleanups at contaminated sites. There is a fixed sampling network associated with air quality points where monthly campaigns are carried out.

In the same way, studies and analyses are carried out in those areas where it is required by the Government of Aragon.

*4. Ecological status*

For more than 15 years, a study has been carried out on the ecological state of the Gállego river affected by the production of lindane from Inquinosa and its deposit in nearby landfills ( Bailín and Sardas).

At present, it incorporates the characterization through hydromorphological indicators (QBR and IHF), and biological indicators based on benthic macrophytes and macroinvertebrates, assesses the state of fish populations and determines the presence and concentration of lindane and other HCH isomers, metals and others. contaminants in water, sediments and fish.

In 2020, the study was expanded with an evaluation of the state of the populations of wild birds around the Bailín ravine, where a trend towards improvement in the state of the birds in the Bailín ravine was verified, with a progressive decrease in concentrations of HCH isomers and an improvement in population and reproductive parameters.

***Maintenance, operation and management of purification facilities, laboratories and auxiliary infrastructures in the sites affected by HCH***

The Government of Aragon has different facilities that help carry out environmental monitoring and minimize the adverse effects derived from HCH contamination. Among them we highlight the leachate and runoff water treatment plants at the Sardas and Bailín sites and the Bailín and Pirenarium laboratories, the latter a reference center for persistent organic compounds.

The operation of the treatment plants includes the maintenance of the treatment facilities and the correct management of waste and consumables.

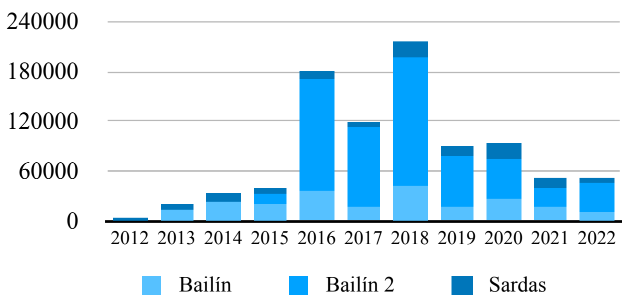



FIGURE 1. PURIFIED FLOW, M³

The operation of the laboratories includes all the tasks of the analysis derived from the activity as well as the actions that guarantee their functionality in order to carry out the analytical monitoring of the samples coming from:

- Environmental monitoring and Integrated Environmental Authorization of the Bailín landfill
- Control of purification plants
- Monitoring and control of the contamination plume in Bailín, Sardas and Inquinosa
- Control of the quality of surface waters around Sabiñanigo and surveillance protocol for the Gállego River
- Research and Microbiology Trials
- Air quality monitoring
- Macrophyte and microphyte organisms for the study of the ecological state

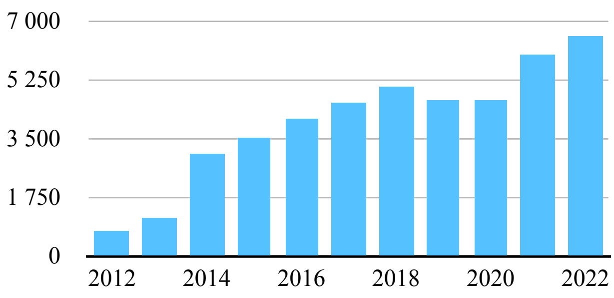



**FIGURE 2. ANALYSES PERFORMED**

As can be seen, (Figure 2) there is a constant increase in the performance of laboratory analyzes, mainly due to the evolution of research studies and tests of remediation techniques at the sites.

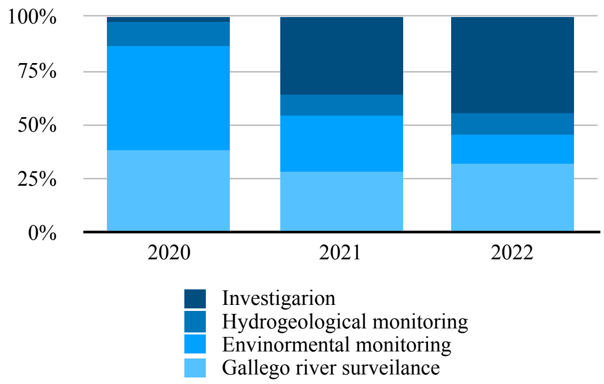



**FIGURE 3. PERCENTAGE OF TOTAL BY TYPE**

### *Technical assistance in the drafting of reports, projects and directions of works*

SARGA provides specialized technical advice that allows addressing all the problems by contamination in the municipality of Sabiñánigo, with a global vision, which brings together the history of actions carried out and the development of the different works.

In addition, it has a multidisciplinary team capable of addressing designs, projects and construction management, necessary for the improvement of the facilities and development of remediation works. The latest projects and works carried out are listed below:

- Project and construction management of the CECOPS Laboratory (Pirenarium)
- Project and construction management of the SARDAS Water Treatment Plant
- Project and construction management of the New SARDAS access road
- Project and construction management of the new INQUINOSA access road
- Project and construction management BAILÍN access road adaptation
- Project and construction management of the Power Line and Transformation Center in SARDAS
- BAILÍN ravine hydrological remediation project
- Small works aimed at maintenance and exploitation at the SARDAS, INQUINOSA and BAILÍN sites (tanks, pipelines, exploitation buildings, laboratories, manholes and auxiliary infrastructures)

*Trials and Research*

A fundamental support element is to maintain a line of research coherent with the planning established by the Government of Aragon, in this way, SARGA assists both in preparatory work and in execution of the different developments of physical-chemical tests and recently in the field of microbiology with the aim of designing the best techniques or trains of remediation techniques adapted to the different locations.

*Health and safety coordination*

For proper management of prevention in all work carried out on soils and/or sites contaminated by HCH and other compounds derived from production, it is essential to carry out protocols and assess the risks associated with the work carried out at the facilities and sites. affected. In addition to the risk assessment, a high percentage of the execution and exploitation is allocated to the purchase of individual protection equipment with the main objective of preserving the safety and health of the worker.

Due to the variety of companies or organizations that could work at the locations, business activities are coordinated in accordance with the criteria set out in RD 171/2004 and RD 1627/1997.

*Investment and financing*

The Government of Aragon allocates an average of 1.29 million euros per year to this service by commission to SARGA as its own instrumental means of the Autonomous Community of Aragon.

*Team 2022*

Currently, SARGA has a multidisciplinary team made up of 23 workers with the following distribution of personnel to provide the service:

- Technical assistance (5 people)
- SARGA personal support (4 people)
- Health and Safety Coordination (1 person)
- Laboratory (6 people)
- Essays and Research (2 people)
- Plant operation and facilities maintenance (5 people)

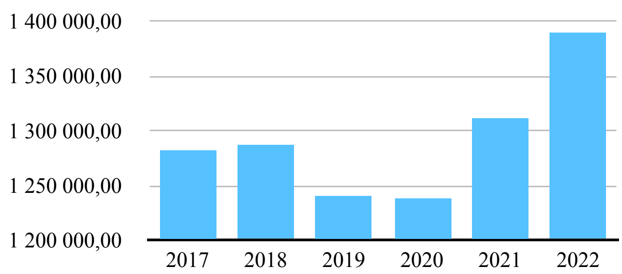



**FIGURE 4. INVESTMENT, EUR**

## *References*

1. Report on the Commission for the purification, analysis and laboratory management service, technical assistance to the facultative management and follow-up for spaces affected by HCH contamination, surveillance of the Gállego river, coordination of business activities
Annual report SARGA Year. 2014-2022

# ENVIRONMENTAL MONITORING IN THE SURROUNDINGS OF THE SPACES AFFECTED BY THE RESIDUE FROM THE MANUFACTURE OF THE HEXACHLOROCYCLOHEXANE PESTICIDE IN THE TOWN OF SABIÑANIGO

***Ruiz, A.[1], Arjol, M.A.[1], Monge, L.[1], Gonzalvo. P.[1], Cano, E.[2], Velilla, S.M.[2], Fernández, J.[2], Net, J.[2]***

*[1]Aragonese Society for Agro-environmental Management SARGA, Zaragoza, Spain*
*[2]Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*

## *Summary*

The Government of Aragon, from its public company SARGA SLU, carries out environmental monitoring of the surroundings of the spaces affected by the manufacture of γ- Hexachlorocyclohexane (Lindane), in Sabiñanigo. Environmental monitoring includes surveillance of surface water quality (rivers, reservoirs, canals, ravines, and lakes), groundwater quality (piezometers), soil quality (soils and sediments in rivers and reservoirs), quality of ichthyofauna, macroinvertebrates and birds, vegetation quality (trees, shrubs, riverside forest and macrophytes) and air quality (sedimentable particles and gases).
The Government of Aragon has a surveillance protocol on the Gállego river (early warning), which defines the actions to be carried out in case of contamination by lindane and which covers from the municipality of Sabiñanigo to the mouth of the Ebro river and coordinates the different organisms affected (General Directorate of Climate Change and Environmental Education, 112 Aragón, General Directorate of Public Health, Aragonese Water Institute).
The samples that involve both environmental monitoring and the surveillance protocol of the Gallego River are analyzed at the HCH laboratory in Sabiñanigo, a reference center for research on persistent organic compounds.

## *Keywords*

Lindane “ɣ- hexachlorocyclohexane ” (ɣ-HCH)

## *Introduction*

In the town of Sabiñanigo (Huesca), is the old factory of the company Northwest Chemical Industries, SA INQUINOSA, dedicated to the manufacture of γ - Hexachlorocyclohexane (Lindane), and three areas affected by the manufacture and dumping of waste are located: the Bailin landfill, the Sardas landfill and the Inquinosa factory itself.
The environmental monitoring, which the Government of Aragon, from its public company SARGA SLU carries out, covers the monitoring of surface and underground water quality, soil, plant and animal quality, and air quality, the latter in a separate document.

## *Environmental monitoring*

### *Surface water*

The municipal term is crossed by the river Gállego, being this river the transport vehicle of the possible surface contamination. The Gállego River Surveillance Protocol (early warning), which defines the actions to be taken in the event of lindane contamination.
The surveillance of the Gállego river is divided into 4 zones plus an additional control zone in the Bailín ravine, establishing control of the HCH concentration in the Gállego river bed with the placement of a sampler at the beginning of each one to be able to control the level of concentration dispersion by HCH throughout the basin:

- Zone 1 (MZ1): Between Sabiñánigo and La Peña Reservoir;
- Zone 2 (MZ2): Between the La Peña reservoir and the Ardisa dam;
- Zone 3 (MZ3): Gállego Channel - Monegros Channel (Between Ardisa and the Tardienta branch);
- Ontinar dam and the Ebro;
- MZ0, point of incorporation of any discharge from the area of the Bailin landfill, into the Gállego river.

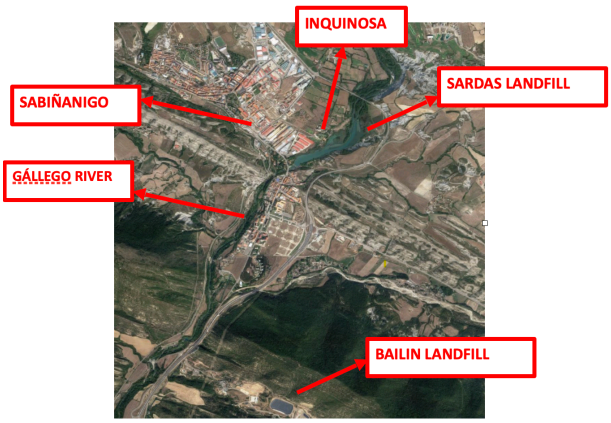



**FIGURE 1. LOCATION OF FOCI**

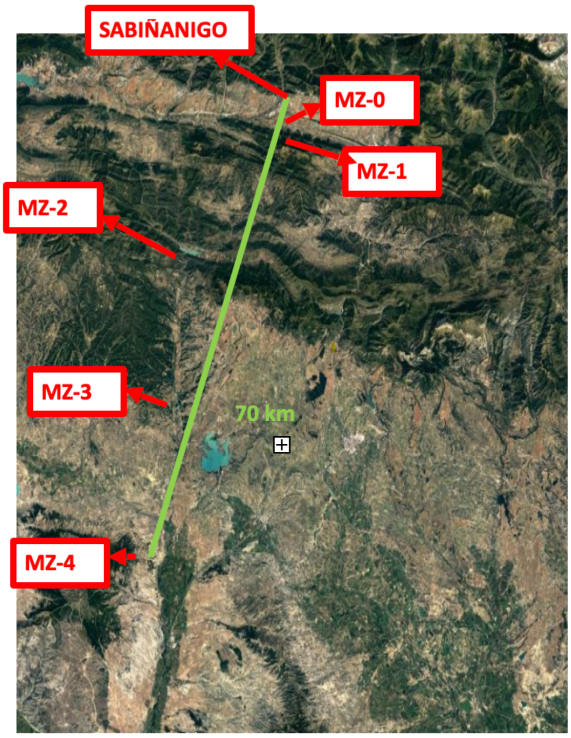



**FIGURE 2. LOCATION MZS**

Currently, it is sampled on a daily basis, in the proximity of the sources of contamination (MZ-0 and MZ-1). As we move away from the focus, the frequency decreases, being twice a week (MZ-2), once a week (MZ-3) and monthly (MZ-4). In the event of rain events greater than 30l m2 per day, the sampling is increased downstream of MZ1.

Samples are taken by integrated sampling 24 hours in daily samples and 48 hours in less frequent samples.

If certain threshold values are exceeded, the purification treatments with activated charcoal will be increased (> 0.5 ugr/l in any lindane isomer), or the supply cut-off (greater than 1 ugr/l in any lindane isomer) lindane).

Since the implementation of the Surveillance Protocol, it has never been necessary to cut off the supply of drinking water, only being necessary to verify the correct operation of the drinking water treatment facilities by the Aragonese Water Institute at specific moments (> 0.1 ugr/l of some isomer).

Bailin ravine was cleaned. At this point, the discharge from the Bailin treatment plant is incorporated , which provides the presence of all the isomers, always in a concentration of less than 50 ugr/l for the sum of isomers (maximum value allowed in the discharge authorization).

In addition to these points, other points in the Gállego river close to the sources of contamination are sampled with variable frequency, such as:

- RG before WWTP (daily) before leaving the urban treatment plant, which characterises the water before the Bailin spillway
- RG-04 in the feed channel to the hydroelectric power station (twice a week) that characterise the outlet of water from the Sabiñanigo reservoir.
- RG02 (quarterly) near the outlet of layer M of the Bailin landfill
- RG05 (daily) connection of water from the Bailin ravine and the water flowing through the Gállego riverbed.


**FIGURE 3. RGS LOCATION**

As can be seen in the diagram of the channel, from the Sabiñanigo reservoir to the MZ1 sampling point, the Gallego river has a series of contributions of flow such as the Basa river, the discharge from the urban treatment plant and the Tulibana ravines, Fundanito and Bailin and other flow reductions such as the bypass channel of the Javierrelatre hydroelectric plant (which in the case of turbination accounts for 95% of the flow) that masks the presence of some isomers from one point to another.

Estarrún River and quarterly of the channels that are incorporated upstream of Sabiñanigo are carried out, not detecting the presence of HCH in any of the channels.

To complete the monitoring of surface water, since 2019 sampling has been carried out at different depths (up to 20 meters) from the Urdiceto, Sabocos, Asnos and Cubilillas lakes to assess the possible impact by airborne pollution on the lakes upstream of the municipality.

The samples from Ibon de Urdiceto, outside the area of influence of the sources of contamination, are used as targets (55 km). Since 2019, the presence of any of the HCH isomers has not been detected.

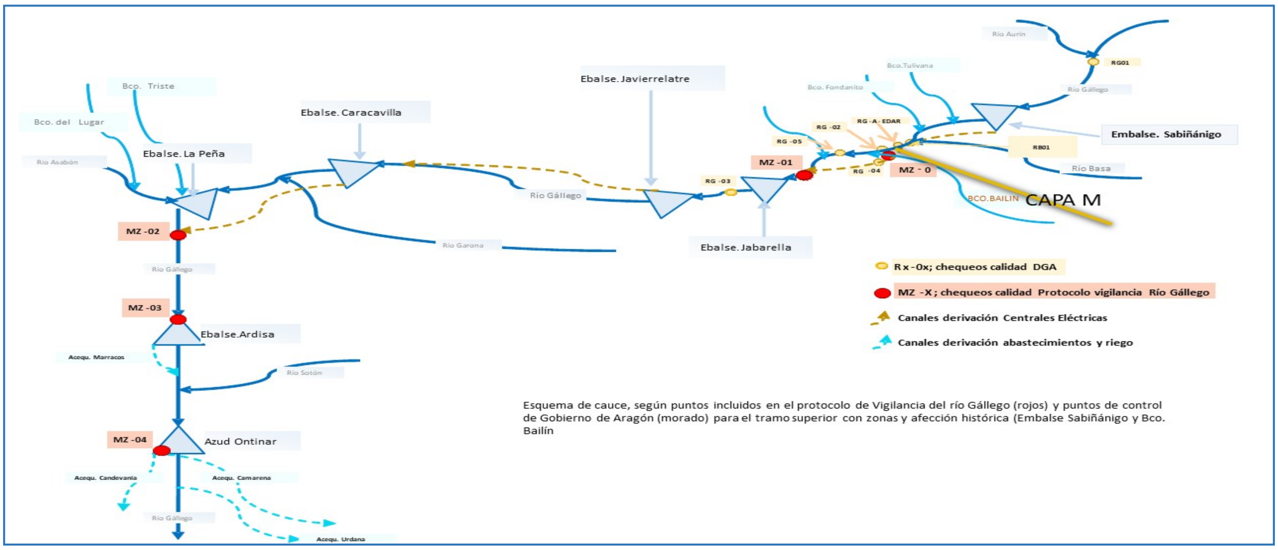



**FIGURE 4. SCHEME OF THE RIVERBED**

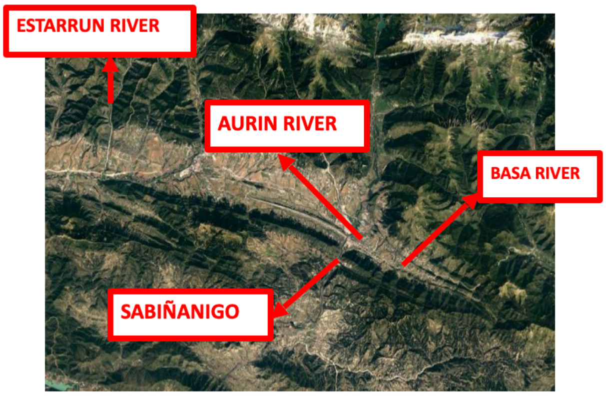



**FIGURE 5. LOCATION OF RIVER SAMPLING**

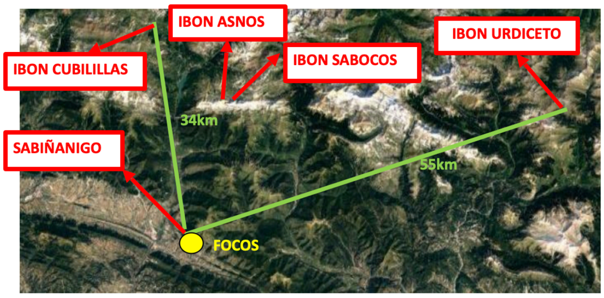



**FIGURE 6. LOCATION IBONES (GLARIAR LAKE)**

*Groundwater*

To monitor the quality of groundwater from the Bailin landfill and the surrounding area, there is a network of piezometers (172 units), of which 20 are equipped with pumping systems for automatic extraction of waste. Through this network of piezometers, contamination is monitored with monthly sampling in the vicinity of the incorporation of groundwater into the channel and two semi-annual campaigns for global evaluation of the contamination plume.

Similarly, to monitor the quality of groundwater from the Sardas landfill, there is a network of piezometers (180 units), of which 13 are equipped with pumping systems for automatic removal of waste. Through this network of piezometers, contamination is monitored with monthly sampling in the vicinity of the incorporation of groundwater into the Sabiñanigo reservoir and two semi-annual and two quarterly campaigns, for a global evaluation of the contamination plume.

In the old Inquinosa factory there are 40 piezometers to monitor contamination with monthly sampling in the vicinity of the incorporation of groundwater into the Sabiñanigo reservoir and four quarterly campaigns for global evaluation of the contamination plume.

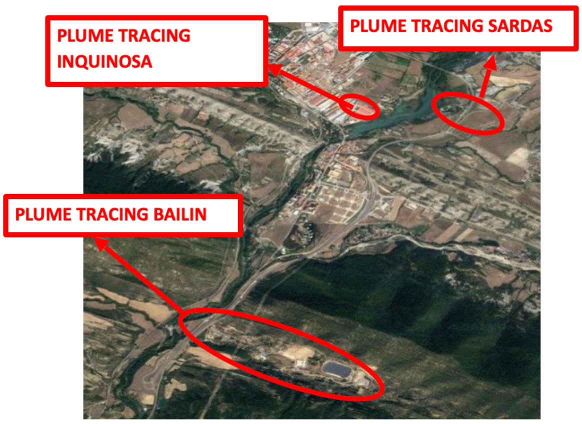



**FIGURE 7. LOCATION OF GROUNDWATER CONTAMINATION PLUMES**

*Study of the ecological state of the Gallego river*

In 2009, a study began on the ecological state of the Gállego River in the section affected by the Bailín landfill. As of the year 2010, the studies are completed with the analysis of samples of the quality of the waters, muds and sediments, fish, ichthyofauna, macrobenthos, emergents, diatoms and the determination of various quality indices in order to establish the possible condition by HCH and other contaminants, as well as determine the quality of the channels.

The 15 sampling points are:

- P1: Aurín River mouth
- P3: Río Gállego between the Sabiñanigo treatment plant and the mouth of Barranco Bailín
- P4: Río Gállego waters below the mouth of the Avena ravine
- P5: Río Gállego downstream of the medieval bridge (before Hostal de Ipiés)
- P7: Río Gállego upstream of the Javierrelatre hydroelectric plant , between the speed bump in the river and the tail of the reservoir of the Anzánigo plant , in the arm of the left bank
- P8: Rio Gállego upstream of Biescas
- Aurín River downstream of the Isín solids dam
- P10: Rio Basa upstream of the cattle sheds (2700m upstream of the mouth)
- EEC LIFE: Ontinar
- Mouth of the Bailin Ravine
- E1: Sabiñánigo reservoir, Inquinosa arm
- E2: Sabiñánigo Reservoir, Sardas area
- E3: Sabiñánigo reservoir gates
- Javarrella Reservoir
- E7: La Peña reservoir tail (Puente de la Peña station)

The parameters that are determined are:

- Hydromorphological indicators (QBR: riparian forest quality and IHF: fluvial habitat index), and biological indicators based on macrophytes (IM: Macrophyte Index and IVAM: Aquatic Vegetation Index) and benthic aquatic macroinvertebrates (ECR: Ecological Quality Ratio).
- Assessment of fish species, both in number of species, abundance, biomass, age distribution and health status.
- Determined the presence and concentration of lindane and other isomers of hexachloro-cyclohexane, metals and other contaminants in water, sediments and fish.

In general, at all points a trend of improvement or stabilization of the indices towards very good quality is detected, or the equalization of the parameters downstream of the sources with respect to upstream outside of contamination. Regarding fish, the P3 point most affected historically, has recovered the presence of some species since 2017.

*Bird tracking*

Since 2020, monitoring of the status of wild bird populations around the Bailín ravine and in a control area in El Boalar de Jaca has been carried out as a clean reference. Exposure to hexachlorocyclohexane (HCH) isomers and its effect on the abundance of forest bird populations and their reproductive parameters are evaluated. Infertile eggs and chicks from the natural mortality of birds are analyzed.

In the last three years there has been a trend towards improvement in the state of the birds in the Bailín ravine, with a progressive decrease in the concentrations of HCH isomers and an improvement in population and reproductive parameters. The presence of all the isomers was detected in the samples analyzed both in the Bailin ravine and in the Boalar ravine, the latter in less concentration.

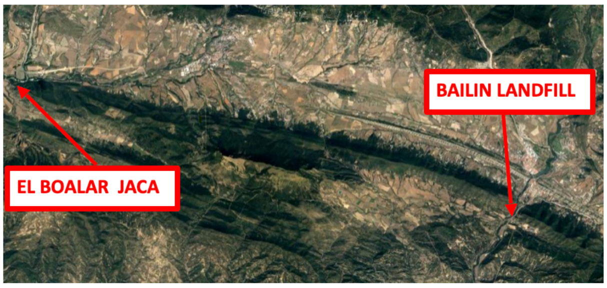



**FIGURE 8. LOCATION OF BIRD MONITORING POINTS**

*Air quality*

To monitor air quality, there is a Surveillance Network with 11 positions close to the locations around the Sardas landfill, Bailín landfill and Inquinosa facilities. To this end, equipment is available to capture particles that can measure PM10 or PM2.5 sizes, sedimentable particle measurement equipment, gas collectors, and continuous particle measurement and counting equipment, the latter located in two positions.

***References***

1. Report on the actions aimed at determining the ecological status of the channels in the Gallego river basin (Bailin -Sabiñanigo) Year 2022 (Sarga 2020/01) Ramon Antor Castellarnau;

2. Gállego River Surveillance Protocol, Government of Aragon.

# AIR QUALITY MEASUREMENT TASKS IN RELATION TO THE DECONTAMINATION WORKS OF MANUFACTURING WASTE OF THE HEXACHLOROCYCLOHEXANE PESTICIDE IN THE TOWN OF SABIÑÁNIGO


***Arjol, M.A.[1], Monge, L.[1], Cano, E.[2], Fernández, J.[2], Net, J.[2], Velilla, S.M.[2]***

*[1]Aragonese Society for Agro-environmental Management SARGA, Zaragoza, Spain*
*[2]Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*



## *Summary*

The Government of Aragon (GA) from its public company, Sarga SLU, monitors and assesses air quality in the surroundings of the sites affected by the manufacture of the pesticide γ-Hexachlorocyclohexane (Lindane), within the municipality of Sabiñánigo. Located on the Pyrenean axial and communication axis, which connects the autonomous communities of Aragon with Catalonia and Navarra. Here are shown the main works and equipment used, the results of the particulate matter and the updates that have been made since the beginning of the works for the remediation of the sites, adjusted to the regulatory requirements. The main evaluations and limitations regarding the limit thresholds and the campaigns executed are analyzed. The main objective is the design of a control and surveillance network, which allows for future remediation work (such as the dismantling of the Inquinosa Factory, the definitive sealing of the Bailín Landfill, etc.), coupling the experiences of the follow-ups carried out in Bailín and Sabiñánigo, according to historical data. However, there are still significant uncertainties that should be taken into account for future actions, without clear reference limit thresholds for some of the settleable particles, PM10 and/or PM2.5 in the case of Lindane. Only the data indicated for professional exposure is available. For this reason and taking into account the actions from 2009 to 2014 in the surroundings of the Bailín Landfill and the measurements between 2015 and 2022 in the surroundings of the sources of the Sardas Landfill, the Inquinosa Factory (abandoned), and the Bailín Valley, the Government of Aragon (from now on GA) wishes to consolidate a monitoring network for particulate matter to control dispersion in relation to the works in progress and to HCH isomers.



## *Keywords*

Lindane "ɣ-hexachlorocyclohexane" (ɣ-HCH), Particulate matter; surveillance network, settleable particles, PM10, spatial dispersion


## *Site*

The municipal term is crossed from North to South, by the main drainage route, the Gállego River, which leaves the city of Sabiñánigo on its right bank, at an altitude of 780 meters above sea level, located in the center of the axis of communication A-330 (Lérida-Sabiñánigo-Jaca-Pamplona). The plain on which the town of Sabiñánigo sits is sandwiched between two mountain ranges that run parallel following the WNW-ESE direction, with the Pyrenees to the north, finding heights above 3,000 meters above sea level. And the Pre-Pyrenees Mountain range to the south, cut by the Gállego river, of more moderate elevations. To the northwest, the most populated city is Jaca, 25 km away, and Biescas, 15 km away, to the northeast. Huesca, capital of the province, is about 50 km south of Sabiñánigo. The city and the sites under surveillance are therefore located in the center of a "Pot" surrounded by mountainous areas in almost all directions. Citing, as an exception, the corridors that leave the channels of the Tulivana river in the WNW (west-northwest) and the valleys of the Aurin and Basa rivers that extend respectively to the NNW (north-northwest) and ESE (east-southeast). With the Gállego River as the main North-South drainage channel, funnelling by the wind in summer.

In the municipality, three sites with historical activity for the manufacture of the pesticide Lindane (ɣ-Hexachlorocyclohexane) have been inventoried and studied. (1) Inquinosa Factory, (2) Sardas Landfill, (3) Bailín Landfill in Figure1.

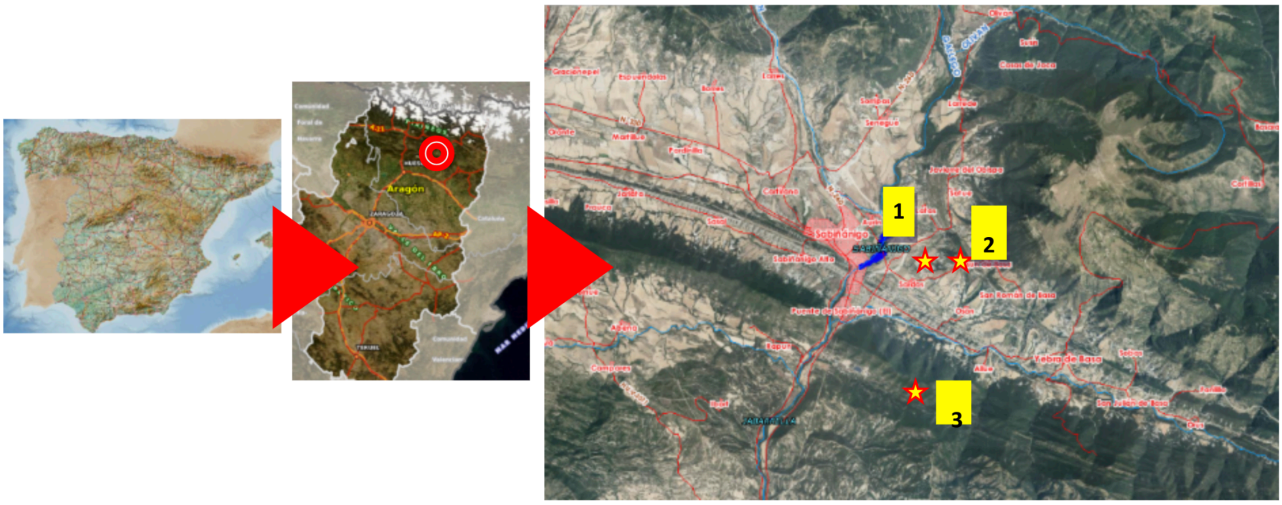



FIGURE 1. GEOGRAPHICAL LOCATION OF THE MUNICIPALITY AND AIR QUALITY MONITORING SITES

## *History of works and equipment*

*Background*

Prior to the start of the remediation work at these sites, similar experiences of measuring air quality with Hexachlorocyclohexane residues (and ɣ-HCH, Lindane) were only known in detail, in relation to the work for the management and sanitation of Lindane manufacturing waste, in the Basque Country, due to the exploitation, filling and closure of the Argalario Security Cell ("Sondica Airport" [1]). Without other more concrete and specific details on other sites in Europe, although the existence of some 299 sites contaminated with waste is known.

The measurement of air quality began due to the work to dismantle and relocate the waste generated by the Inquinosa company, at the Bailín landfill, in the municipality of Sabiñánigo (Huesca). The Environmental Impact Statement established two phases, a phase A for the initial isolation of waste and a second **"phase B",** in case of distinguishing impacts from phase A. Which involved the construction of a security deposit **(Phase 1)** on transfer of waste to the new security cell **(Stage 2)** and its final sealing **(Stage 3)**, pending.

With the "*Administrative resolution of June 26, 2009 of the Aragonese Institute of Environmental Management (INAGA), of the Environmental Impact Statement, (DIA)"*, Government of Aragon (GA) granted integrated environmental authorization (from now on AAI) for execution of the works. Among them, the control of Air Quality in different points (Figure *2* and location 3, of Figure 1).

In Stage 1, particulate matter, settleable dust and suspension, and gases were measured semi-continuously (according to AAI). In the works, the necessary infrastructures were built (2009-2010) to house the waste from the old Cell, excavating more than 110,000 $m^3$ of rocks and earth, which were relocated and placed for construction of the infrastructures (for 200 days). For Stage 2 (2014), the waste was transferred to a Security Cell (a total of 210,000 $m^3$, of which 63,000 $m^3$ were HCH waste), the rest was contaminated soil, liquid phase and other waste. In Stage 2, the AAI required monthly measurements at two singular and representative points of the preferred directions of the winds (study prior to modeling). In total, it was measured at least six points (Figure 2) both in Stage 1 and Stage 2.

Stage 3, the final sealing of the New Cell, still in drafting.

The applicable legislation was that of Directive 1999/30/CE and RD1073/2002 of air quality according to limits (50 µg/m3 day), a value that cannot be exceeded more than 35 times a year. Being the average of the calendar year of 40 $\mu g/m^3$. No observations regarding Lindane. In addition, in Stage 2, it was indicated with respect to the sedimentable particles, which should be below 60 $\mu g\ m^{2}$/day so as not to affect the soil, especially outside the work site, (RD 9/2005, with thresholds for HCH (alpha, gamma, delta) in industrial land of <1 mg/kg and <0.1 mg/kg in the case of urban land or <0.01 mg/kg (for other land uses).

State Decree 833/1975, which regulates the deposition of sedimentable particles, is repealed, and the legislation in force in the autonomous communities of Spain (Autonomous Community of Valencia and Andalusia) was adopted in both stages with a value of 300 $mg/m^2$ per day (within 24 hours), the same as indicated in the repealed Royal Decree. Being the threshold value for particles of Hexachlorocyclohexane and its isomers a value of 0.5 $mg/m^3$ (500 $\mu g/m^3$) used as an occupational exposure limit, in the working population.

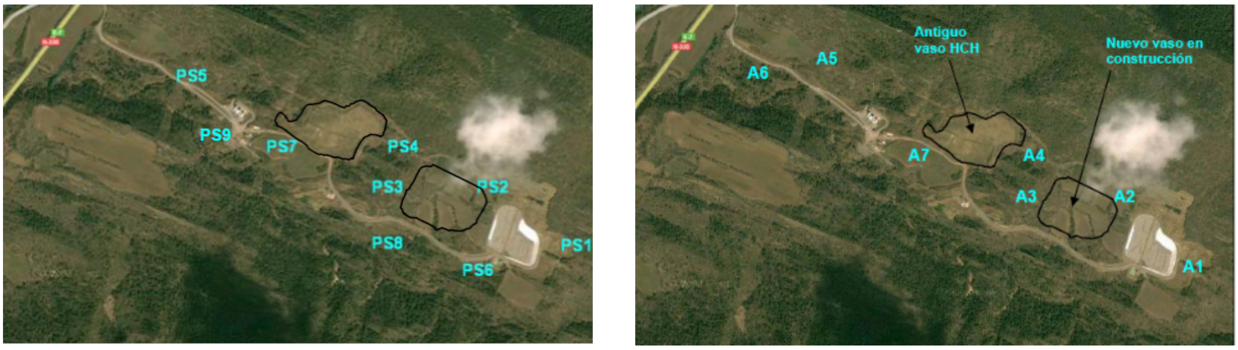



**FIGURE 2. MEASUREMENT POINTS OF SEDIMENTABLE PARTICLES (PSX) AND PM10 (AX) STAGE-1 AND STAGE-2 BAILÍN LANDFILL**

**FIGURE 3. AAI CONDITIONS, DUST AND PARTICLES. RESOLUTION OF 26.06.2009. DIA AND WORK AUTHORIZATION STAGE 1**

It is considered that the availability of limits facilitates the development of the works, the anticipation of occupational and environmental risk situations, as well as the assessment of the non-exposed population.

*Equipment used in the campaigns*

Settleable particles (>10µm), with the equipment proposed in State Decree 833/1975 (see Figure 3, right, in Stage-1 and 2.). For PM10, High Volume equipment was used (UNE-EN 12341:1999, Figure 3, center) with 150 mm filters for PM10 (UNE-EN 14097:2006) and coupled to heads with polyurethane sponges for the gaseous part (Stage 1 and Stage 2). Although measurements were also made in the stages with low-flow pumps coupled with activated carbon cartridges (Figure 3, Left). As of 2014, equipment has been updated to the new regulations (UNE-EN 12341:2015). Incorporating, a posteriori from 2022 programmable Sequential Collectors with PM10 and PM2.5 heads with 47 mm filters (Figures 4 left together with a continuous laser particle counter measurer) and new collectors (5 units) for sedimentable particles (see Figure 3, right), avoiding cross contamination due to duplication and use of equipment in various positions. Since 2014, an exclusive network for gas measurement has been operated. Therefore, the control points and areas have been increased.

***Particle work and measurements***

In Stage 1 and Stage 2, the campaigns were adjusted to work days and shifts, being 8 hours, 16 hours or 24-hour measurements (for better representativeness). On consecutive days in the first Stage and on single or complete days in the second Stage.

With the obtaining of an average value at least monthly, in different climatic conditions, of generic mass and of HCH isomers. Therefore, there is a population of data representative of the specific works executed during the period of 200 days in Stage 1 and 180 days in Stage 2. In addition, in both Stages campaigns were carried out before and after the works. Currently, since 2015 in Bailín and since 2016 in Sabiñánigo, 24-hour campaigns are carried out at least in different meteorological conditions on a monthly and consecutive basis in one location and another.

The average values according to the levels and thresholds established for Sedimentable Particles (SC), PM10 (High Volume Collectors, CAV) and gases (on passive polyurethane foam collectors), were within the specified ranges.

In Stage 2, in addition and prior to the start, a correlation of the winds, directions and points for adequate measurement was established, with the realization of a dispersive model.

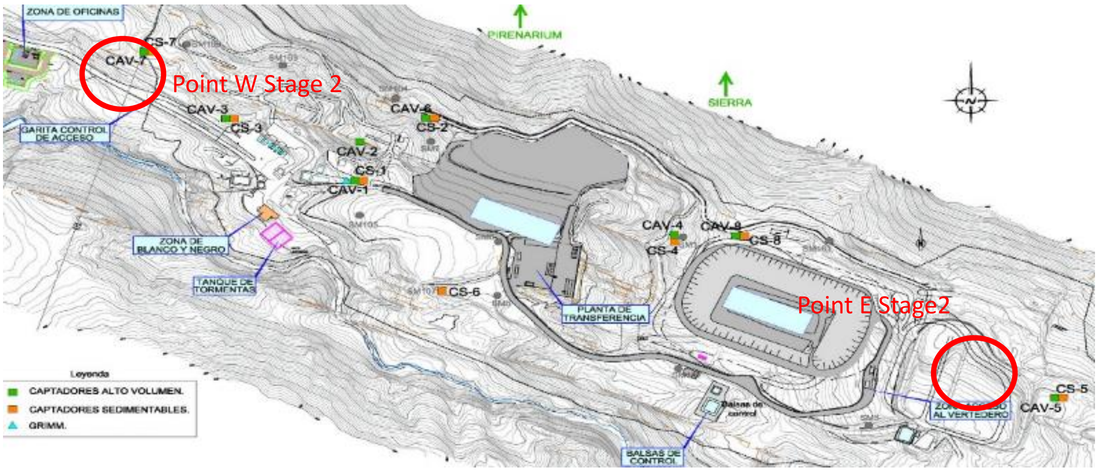



**FIGURE 4. SKETCH IMAGE OF DISTRIBUTION OF POINTS FOR DUST AND PARTICLE CONTROL. STAGE 2, MAY-OCTOBER-2014**

The object of the modeling was to establish the aerology and causality of the winds in the Bailín valley, ([3, unpublished]) identifying the ideal points for measurement (one to the West and one to the East). During the 180 days of operation, 34 campaigns were carried out. See dotted diagram Figure 4.

Depending on the model, the control revolved around the meter-counter in continuous (laser technology for counting PM10, PM2.5 and PM1), the location of two gravimetric meters in the preferred directions of the winds (required by the AAI), data from the Bailín Meteorological Station, and three-day forecast warnings. Not being able to use the model with its predictive potential, since there is no extensive history with campaigns in differentiated conditions with and without the presence of HCH prior to dismantling, a difficult aspect, given the novelty and exclusivity of the action.

Figure 5 shows the initial simulations of the model (Left) with expected average concentrations in the exclusion perimeter, the wind rose during the work (Center) and the average values obtained for PM10 according to campaigns, with average values in the West of 30 µg/m3 and in the East 42 µg/m³ (right image).

The gravimetry data were, comparatively, higher than those measured by the continuous laser counter-measurement, which recorded average values for the entire operation of 6.6 µg/m³ on average, with an average standard deviation of 4.9 µg/m³ (Figure 6). No speciation value exceeded 500 µg/m³ considered. And average values in the W meter of 0.0056 µg/m³ in 24 hours, a median of 0.0010 µg/m³ and a standard deviation of 0.0095 µg/m³. In position E, the average concentration was 0.0040 µg/m³ in 24 hours, the median was 0.0015 µg/m³ and the standard deviation was 0.0053 µg/m³.

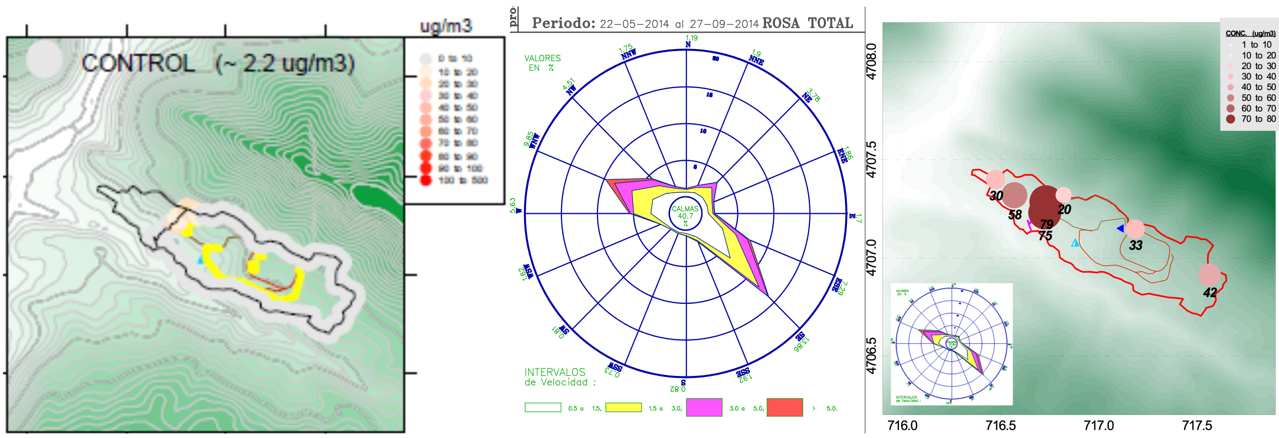



**FIGURE 5. TOTAL WIND ROSE IN THE WORK PERIOD AND ANALYSIS OF DISPERSION OCCURRED AAI, STAGE 2 WORKS**

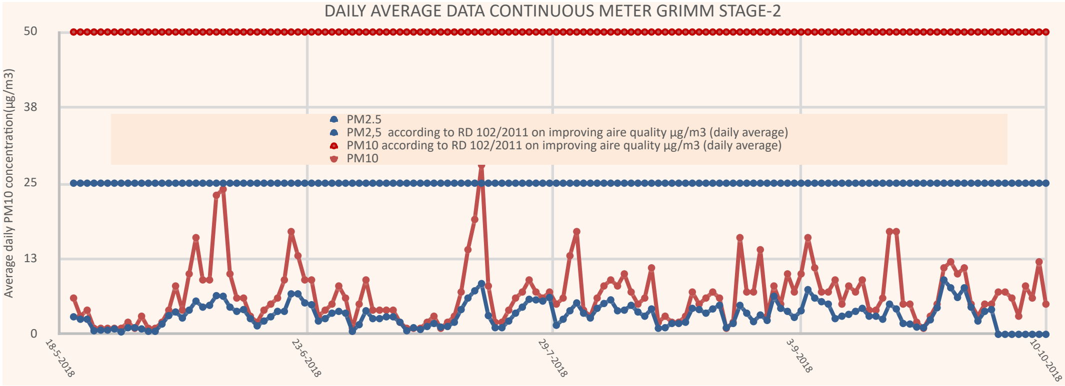



FIGURE 6. VALUES MEASURED FOR PM10-PM2.5, OUTSIDE THE PERIMETER FENCE OF THE EXCAVATION AREA AND EQUIPMENT USED FOR THE MEASUREMENT OF SEDIMENTABLE PARTICLES (IZ). AND PM10 (HIGH VOLUME, 30 M³/H)

The checks and samplings in the soils of the work environment and outside the site confirmed the condition of non-affected values with values below 60 µg/m² per day, with mean values in soils of less than 1 mg/kg and 0.1 mg/kg. The values for gases were lower than the limit considered 0.5 mg/m³ (500 µg/m³).

*Particle measurement work and campaigns 2015-2022*

The network was extended and the campaigns were increased with a monthly measurement per point, in at least ten points (5 Bailín + 5 Sabiñánigo). Elaborating a dispersive model of the Sabiñánigo area, with the main circulations. Having a large number (95 Campaigns with speciation included) in situations and with different climatological records [4,5, unpublished]. The result was the provision of a wide network (maximum buffer > 2 km from the sources) for the measurement of Sedimentable Particles, PM10 (recently expanded to PM2.5) and gases, with the execution of monthly campaigns lasting at least 24 hours, since 2015 in Bailín and since 2016 for Sabiñánigo (Figure 8).

With this, the modeling of flows of particulate and gaseous material is improved, adjusted and has predictive capacity, by joining predictive meteorological models of 3 to 5 days (Unpublished Bibliographic documents 7 to 9).

The monitoring was extended to points of singular ecosystems, such as "mountain lakes, Ibones" of the area (bibliography 2), with historical conditions and, among others, of origin in the particulate matter in dispersion. For this, and using the dispersive model, three points were selected as the most suitable; Culiblillas, Sabocos and Donkeys. With an ambient white, in the Ibón de Urdiceto. At distances greater than 30 km from the sources and an altitude of more than 1,600 m.a.s.l. [7,8].

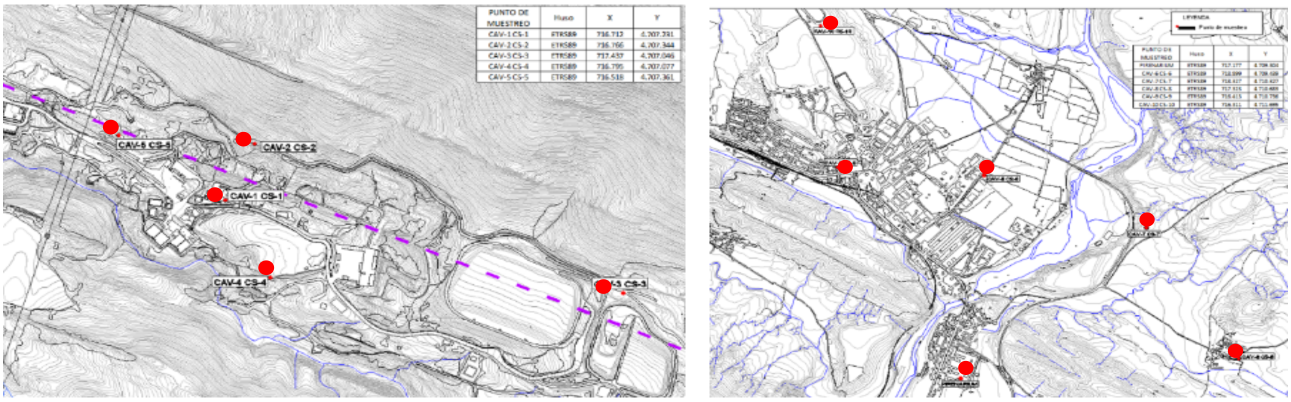


FIGURE 7. AIR QUALITY MONITORING AND CONTROL NETWORK IN RELATION TO HCH MANUFACTURING RESIDUES, PARTICLES AND GASES

The network is completed with specific gas measurement points in relation to HCH residues (campaigns every 35 days, from passive gas collectors in 10 positions. Figure 7.

The advantages and contribution of the "dispersive model" reinforce the monitoring tasks and allow, through the new equipment incorporated, to obtain: [4 and 5, unpublished]

1. Trajectories, the path that a certain pollutant emitted from a specific location will follow during the following hours. According to areas and impacts.
2. Retro-trajectories, which provide information on the origin of the air mass that affects a specific point. Identifies sources that cause pollution episodes.
3. Dispersals. Representing the dispersion of a certain element emitted into the atmosphere, knowing the quantity and duration in the emitter, sources and affected areas.

GA has (with the incorporation of computer tools):

- From a gravimetric network of points, permanently, with two "meter-counters" in real time (laser technology) with ease and remote access. With the possibility of projecting scenarios and dispersive plumes, according to the "surveillance network", and in relation to "buffers" concentric to the focus, and that if they are linked to weather forecast data for several days (24 hours, 48 hours, 72 hours ...), facilitates the drawing of future scenarios. Areas of interest can be assessed by drawing probable dispersive trajectories. The coupled meteorological model works with a 1km resolution and the dispersive model for environmental impact assessment at 100 meters horizontal resolution (WRF and CALPUFF models respectively).
- With the real-time monitoring of the concentrations observed and those foreseeable by areas and points, it is only necessary to set the thresholds and program alarms that anticipate risks ("predictive scenarios"), depending on the work and imposing, if necessary, the stops, in case of exceeding the "thresholds" or redesigning mitigation measures (Figure 8).

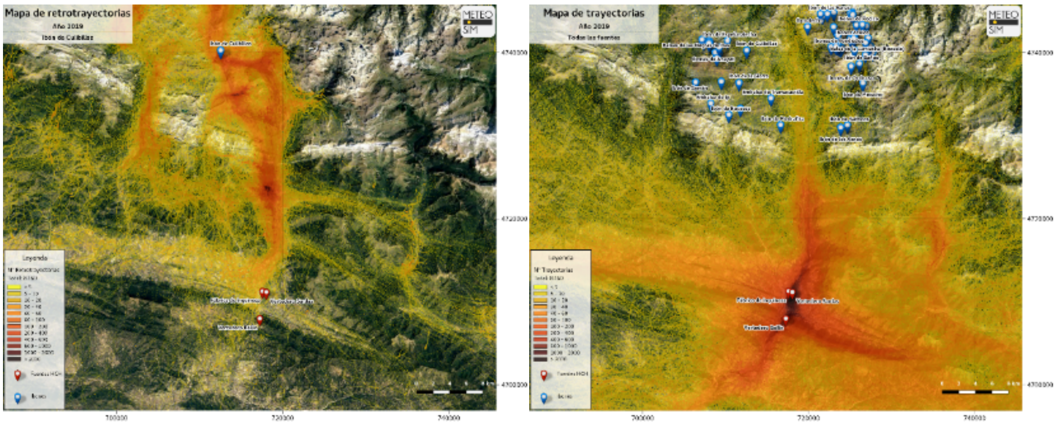



**FIGURE 8. MAPS OF TRAJECTORIES, RIGHT, AND RETRO-TRAJECTORIES, LEFT (FROM 8760 SIMULATIONS) 2019 [5]**

### *Results of the 2015-2022 Campaigns*

The non-availability of defined inmision limits or thresholds introduces uncertainties regarding air quality monitoring, and does not facilitate efficient and optimal project designs.

Below is a summary of the main statistical values obtained in the campaigns (Ca-1 to Ca-95) carried out in Sabiñánigo between 2016 and 2022, based on the "Surveillance Network". Showing the most basic statistics (means, 98th percentile and standard deviation), the values obtained below the determination limit in the equipment (<LD) have been taken into account in the sample space, with the consideration of "0" detected in Table 1.

From the measurement of PM10 (generic non-specified mass), the graph of Figure 9 is obtained, with a fairly uniform distribution between 7 µg/m³ and 20 µg/m³. Carrying out later speciation on the particle filter and determining the weight per HCH isomer.

The control and sampling allow to relate aspects of the works and the influence on the dispersed mass.

**TABLE 1. MAIN STATISTICAL VARIABLES BY POSITION ACCORDING TO CAMPAIGNS 2016-2022 SABIÑÁNIGO**

| Statistical Variables of ∑HCH | Statistical distributions by position of the campaigns from 2016 to 2022 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CS6 ug m²/ | CAV6 µg/m³ | CS7 ug m²/day | CAV7 µg/m³ | CS8 ug m²/day | CAV8 µg/m³ | CS9 ug m²/day | CAV9 µg/m³ | CS10 ug m²/day | CAV10 µg/m³ |
| Average value Ca1-Ca95 | 4.9E-01 | 2.8E-05 | 1.1E+00 | 3.3E-05 | 1.5E+00 | 2.7E-05 | 5.6E-01 | 4.3E-05 | 4.8E-01 | 3.7E-05 |
| 98th Percentile | 2.8E+00 | 3.8E-04 | 1.0E+01 | 8.0E-04 | 1,1E+01 | 4.8E-04 | 5.6E+00 | 6.9E-04 | 2.9E+00 | 6.4E-04 |
| Standard deviation | 7.1E-01 | 1.0E-04 | 2.3E+00 | 2.4E-04 | 2.9E+00 | 1.3E-04 | 1.3E+00 | 2.0E-04 | 7.0E-01 | 1.4E-04 |

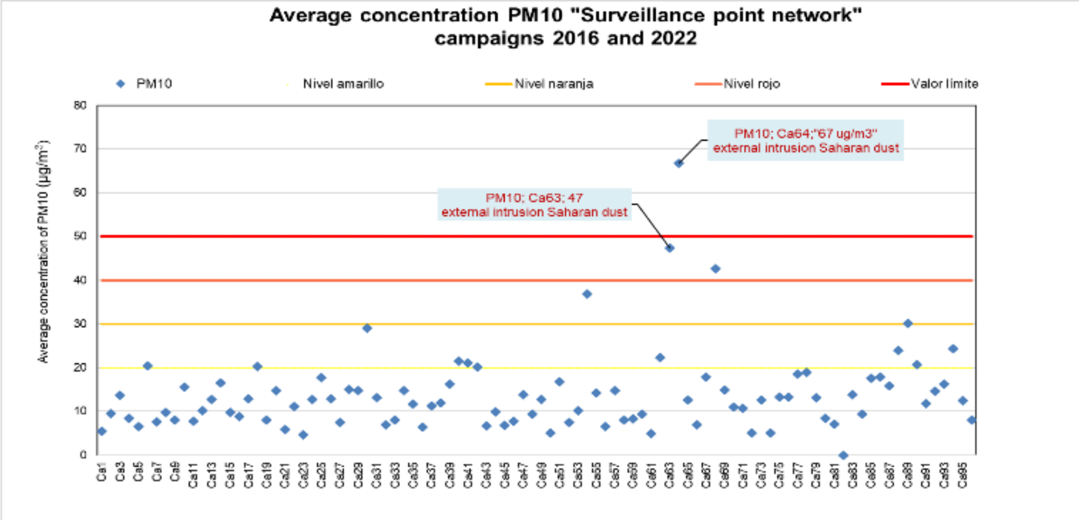



**FIGURE 9. GRAPH OF TOTAL PM10, CA1 TO CA95 (2016-2022) AVERAGE VALUES FROM THE "SURVEILLANCE NETWORK" METERS**

### *Conclusions*

- The measurement of the works and campaigns between 2009 and 2014, with the works of Phase B, remained on average according to the indicated values, without effects outside the work site. All the measurements were located inside the work areas and next to the stockpiles or excavation points.
- Currently there is a "Surveillance Network" with a wide area, around buffers of possible sources, with 11 total points, for the measurement of PM10, PM2.5, Gases, in which 2 particle counters-meters have been included. PM 10, PM 2.5 and PM1 (laser technology). Elaborating a dispersive model, which from the 95 available Gravimetry Campaigns and linked to continuous meters, improves the monitoring mode. If we can also include predictive meteorological models and the corresponding analysis applications, simulations can be obtained, and maps with dispersive trajectories and areas impacted by particulate matter. If alarms or threshold values for not exceeding are included, a powerful predictive tool is available, which reduces the uncertainty of waiting for the samples (gravimetric results are always delayed with respect to the events). Anticipating assessments, stops, incorporation of measures, or dispersive results on sensitive receptors (private ecosystems, population centers not professionally exposed, etc.)
- The non-availability of thresholds, or the application of limits for the population exposed at work. With the existing and consulted MAK-BAT, Germany, 0.1 ug/m$^3$ or 0.5 mg/m$^3$ in Spain, they are not enough to face the design, execution of projects, with total security for elimination of areas or sources with HGH residues. Other values consulted (EPA / CaLEPA 0.25 and/or 0.3 µg/m$^3$, only alpha or gamma) consider values for subchronic inhalation and damage in laboratory animals, transferred to humans according to safety factors, which are not sufficient to evaluate and carry out environmental monitoring on the unexposed population. With the consequent uncertainty, especially in places where this type of waste exists (another 229 locations in Europe are indicated) such as in Aragon. Where there are also limitation values in soils (RD 9/2005), already commented, and limit values in water with a maximum admissible concentration of 0.02 µg/L or 0.04 µg/L annual average (Royal Decree 817/2015, of September 11 in Spain). There is uncertainty and the taking of values adjusted to measurements and experiences must be discussed, especially outside the workplace, according to projects carried out, with scientific support and broad social consensus, to address projects that are otherwise unapproachable.
- GA has adopted the considerations contained in article 46 of decree D833/75, and which was developed by Law 38/1972 of December 22 on the protection of the atmospheric environment, and which indicates that "in the case of no specification for air pollutants Annex III (workplaces), the limit concentration will be such that the resulting inmision levels comply with the provisions of Annex I of the aforementioned legal text or, failing that, they must not exceed one thirty-fifth of the maximum concentrations allowed in the indoor environment."(considering professional exposure to Lindane of 500 µg/m$^3$), the limit would be 16.7 µg/m$^3$ for the sum of isomers and 3.33 µg/m$^3$ for each isomer. The evaluation for sedimentable particles of not exceeding 60 µg/m$^2$ per day outside the work areas continues, checking with sampling and normative values according to RD 9/2005 of the quality of the soils.

### *References*


1. Apraiz, MJ Villagrá, M. Novo, T. Laburu, I. Egiarte. Environmental Area, LABEIN -Technological Centre- 5th Int. HCH & Pesticides Forum, 1999. HCHs air quality control in the constructive project of Loiu safety cell

2. Pardo A., Arruebo T., Santolaria Z., Lanaja J., Urieta J., Rodríguez C., Betrán, J., Matesanz JM, Burgos J., Cruz JM, Del Valle, J. Origin, “Environmental characteristics and Ecological characteristics of the Aragonese lakes: effects of human activity on them. Boreas Foundation - University of Zaragoza - FARAS, National Environmental Congress, 2012.

3. Mantilla, E. “General considerations for carrying out experimental measurements to quantify the atmospheric impact of particulate matter due to loading and unloading operations of pulverulent material in the area of future Inquinosa dismantling actions, 2016”. Meteorology and Atmospheric Pollution Program. (Centre for Mediterranean Studies Foundation, CEAM) Unpublished, prepared for DGA-SARGA.

4. Manzanares, MA; Arasa, R. “Service for the characterization and simulation of the movement and dispersion of particles associated with the demolition work of the old Inquinosa factory, establishment of a control and warning network, TM Sabiñánigo (Huesca)”. 172 pg. METEOSIM SL Not published, prepared for DGA-SARGA.

5. Manzanares, MA; Arassa, R. "Analysis of the meteorological conditions and transport of pollutants associated with the environment of Sabiñánigo (Spain), March-2020". 70 pg. METEOSIM SL Not published, prepared for DGA-SARGA.

6. John Vijgen, Bram de Borst, Roland Weber, Tomasz Stobiecki, Martin Forter. HCH and lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue. Environmental Pollution 27 February 2019 Volume 248 (Cover date: May 2019) Pages 696-705.

7. European Commission, Directorate-General for Environment, Coterlet, G. 2019, Inventory of sites that are potentially impacted by HCH in EU Member States: summary report EU wide inventory (Task 1), Publications Office of the European Union, 2022, https://data.europa.eu/doi/10.2779/17080.

8. Toxicological Profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane (Update). Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane. Draft for Public Comment. US Public Health Service, US Department of Health and Human Services, Atlanta, GA. 1997.

9. UNEP 2001. United Nations Environment Programme. Stockholm Convention on Persistent Organic Pollutants (POPs). http://chm.pops.int/.

# LABORATORY HCH SABIÑÁNIGO-REFERENCE CENTER IN RESEARCH ON PERSISTENT ORGANIC COMPOUNDS

*Gonzalvo, P.[1], Ruiz, A.[1], Monge, L.[1], Velilla, S.M.[2], Cano, E.[2], Fernández, J.[2], Net, J.[2]*

[1]*Aragonese Society of Agro-environmental Management, Zaragoza, Spain*
[2]*Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*

**Summary**

Pirenarium laboratory in the municipality of Sabiñanigo, a reference center in the investigation of persistent organic compounds, to carry out the analytical monitoring of the samples taken in the surroundings of the spaces affected by the manufacture of γ-Hexachlorocyclohexane (Lindane), in Sabinanigo.
The number of samples analyzed annually is continuously growing, reaching seven thousand units in 2022. The complexity of the work carried out in the laboratory is the wide range of concentrations depending on the origin, being less than 0.02 ugr/l in clean samples of channel and reaching gr/l in DNAPL samples taken in piezometers inside the landfills. Various matrices are also analyzed, such as solids (sediments, plants and animals), gases (retained in active carbon) and liquids.
The laboratory has different equipment, the most relevant being gas chromatography equipment. The laboratory works with different work methods adapted to the compounds to be analysed, within the complexity of the matrices to be treated, and conditioning said methods to the precision and speed required.
The chromatography equipment undergoes periodic calibrations with standardized patterns, in addition to participating in intercomparison exercises with other accredited external laboratories.

**Keywords**

HCH ( Hexachlorocyclohexane ), Gas Chromatography (GC), FID Detector (Flame Ionization Detector), ECD Detector (Electronic Capture Detector), Extraction, Matrix.

## *Introduction*

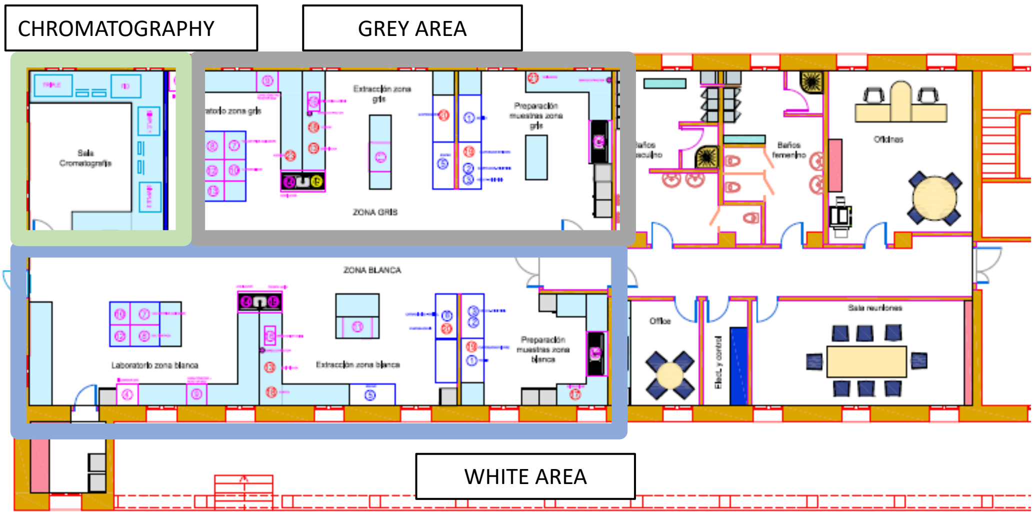
The INQUINOSA factory synthesized lindane from 1975 to May 1989 and definitively ceased its commercialization activity in 1992. During this period it is estimated that it produced more than 150,000 t of waste. Residues from the production of lindane, in powder and liquid form, were dumped in an uncontrolled manner at the Sardas landfill and subsequently at the Bailín landfill.
Since the end of 2009, a physical-chemical analysis service has been provided to monitor contamination in the sites affected by the manufacture of lindane in INQUINOSA and thus satisfy the analysis needs derived from the monitoring of the Sardas and Bailín landfills. After the approval of the surveillance protocol for the Gállego River in 2015, which increases the amount of sampling and daily analysis capacity, and the increase in monitoring, control and investigation tasks, the space and existing equipment in Bailín are insufficient to guarantee the service. For this reason, the Government of Aragon begins the processing and obtaining financing to carry out the works and obtain the appropriate equipment for the new laboratory in Pirenarium, now CECOP Reference Center for persistent organic pollutants. In 2019, the laboratory began to provide service, thus having better facilities and equipment to provide service guarantees.

### *Pirenarium laboratory*

The laboratory is attached to the Pirenarium building with an available area of 420 m2. The laboratory is divided into 3 rooms, a so-called clean laboratory, for less contaminated samples, a gray laboratory, for loaded samples, and the chromatography room. The administrative area has an office room, meeting room, changing rooms, office and control room and electricity.
The sanitation network is separative, with two: an administrative area network that goes to urban discharge and a laboratory sink network in which the discharge is filtered and regulated by means of a deposit before it is discharged into the municipal network.
With the incorporation of new equipment and the transfer to the Piranarium laboratory, progress has been made in a series of significant improvements from a qualitative and quantitative point of view:

- *Separation of two working lines*, gray line and white line, to avoid cross-contamination in samples with very different concentration ranges: a line to treat “clean” samples from riverbeds, with approximate concentrations of <0.02 to 10 ppb and a second line for “more contaminated” samples from: sewage treatment plants, contamination plumes, tests and investigations. This represents an increase in the space available for the arrangement of the equipment and improves the development of analysis work outside the affected spaces, thus eliminating possible interference in the analytical results due to existing conditions.


**Figure 1. Lines of work**




- Increase in the number of samples to be extracted and analysed: The number of samples that are analyzed has been increasing notably, in 2015, where some 3,500 were analyzed, reaching almost 7,000 in 2022, with an average of 550 samples per month.

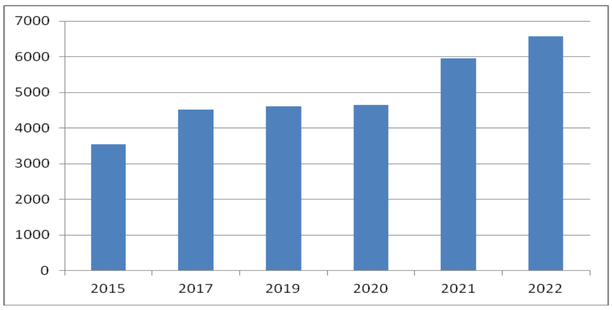



**FIGURE 1. EVOLUTION NUMBER OF SAMPLES**

- *Elimination of the risk of laboratory downtime due to the failure of a measurement equipment* due to the availability of additional equipment, as well as the elimination of analysis downtime periods due to maintenance needs or equipment breakdowns. The laboratory responds daily to the quality of the river water within the Gállego River Surveillance Protocol. A large investment has been made in chromatography.

Laboratory gas chromatographs are the equipment used for the analysis of organic compounds [Lindane (gamma- HexaChlorocycloHexane), other HCH isomers (alpha, beta, gamma, delta, epsilon), BTEX (Benzene-Toluene-Ethylbenzene-Xylenes), Chlorobenzenes, Phenol , Chlorophenols].
Currently the laboratory has 5 teams:

- 2 Gas-Mass-Simple Quadrupole chromatographs
- 1 Gas-Mass-Triple Quadrupole chromatograph, this detector has greater sensitivity, and is used to analyze samples of lower concentrations (<0.02 ppb)
- 2 Gas Chromatographs with Flame Ionization Detector (FID) and Electron Capture Detector (ECD), which are more robust detectors and are used for highly concentrated samples.

Chromatography equipment injection systems:

- Liquid injection, for analysis of semi volatile compounds
- Head Space (HS) injection, for analysis of volatile compounds
- SPME injection (adsorption of fiber analytes), for “chlorophenols”

FIGURE 2. CHROMATOGRAPHY ROOM

- Increase in worker safety with a work space according to the type of compounds that are handled, highlighting the increase in the number of extractor hoods and ambient air renewal. It has a gas extraction system to eliminate contaminants emitted inside using air outside the cabinet itself as a solvent. These gases and/or vapors are removed from the fume cupboard by forced extraction through pipes. The extracted air is conducted to the two-stage filtering system: dust particle pre-filters and activated carbon filters.

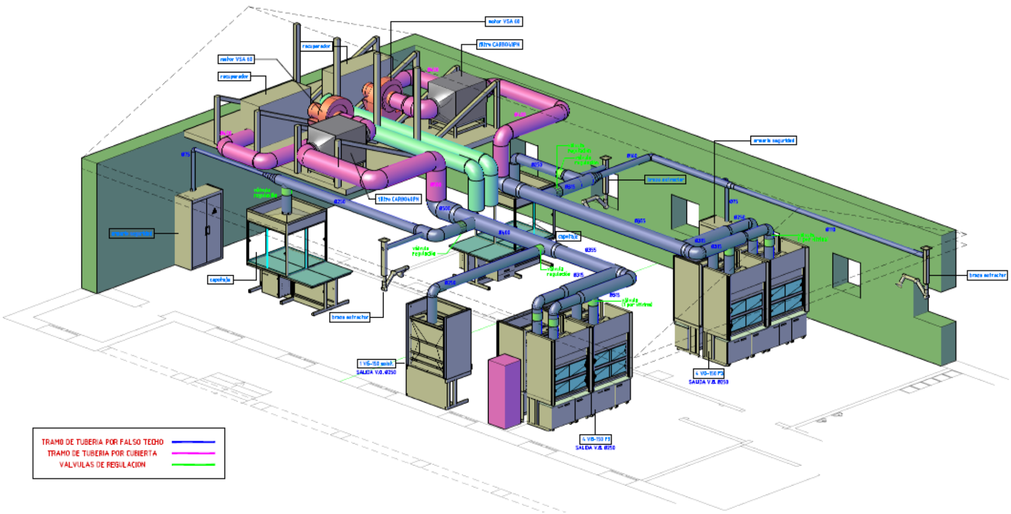



FIGURE 3. GAS EXTRACTION AND TREATMENT SYSTEM

### *Analytic program*

Within the tasks of control and monitoring of contamination, an analytical monitoring of surface and groundwater is carried out in the surroundings of both landfills derived from hydrogeological monitoring, operation of treatment plants, monitoring protocol of the Gállego river, research and air quality. As a consequence of the different activities, the following matrices are analyzed:

- *Liquid matrix:* surface water from riverbed monitoring, wastewater from purification lines, research work and remediation tests carried out by different entities with contaminated water and groundwater, from plume monitoring pollution, and remediation work.
- *Solid matrix* : muds and soils, from the bottoms of rivers and swamps, from ground surveys, from research works and remediation tests, plant samples, from studies of the channel, from contaminated sites and environments, from works and tests research and fish samples from the ecological studies of the channel.
- *Gases,* retained on a solid support (in fiberglass filters and in activated carbon cartridges), coming from air collectors from environmental control studies and monitoring, and from research tests.

Depending on the matrix and concentration of contaminants, different extraction methods are carried out.

- For liquid matrices:
  - Liquid-liquid extraction.
  - Liquid-solid extraction, with SPE cartridges (solid phase extraction), in the "Manifold" equipment.

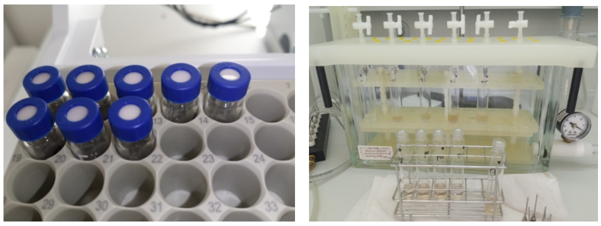


FIGURE 4. LIQUID SAMPLE EXTRACTION SYSTEMS

- For solid matrices:
- MERC extraction, by ultrasound.
- Microwave extraction.
- Extraction in SOXTEC, where organic solvent is recirculated through the solid sample placed in cellulose thimbles.
- Extraction with QuEChERS, extraction method with organic solvents and clean-ups of the extracts with salts, this method is mainly used for plant and animal matter.


FIGURE 5. SOLID SAMPLE EXTRACTION SYSTEMS

*Quality of the results*

Both the chromatography equipment and the rest of the equipment are subjected to periodic calibrations with standardized patterns. In addition, counter-analysis is carried out with accredited laboratories, as well as participation in intercomparison exercises with other external laboratories.

All contrast exercises with accredited laboratories confirm the reliability of the result obtained in the CECOP analyses.

***Conclusions***

The wide space of the laboratory and the equipment available to it, allows working with safety for the worker, safety for the environment, and safety and accuracy in the results of the samples.

The investment made in the construction of this space and the purchase of equipment is more than amortized, given that carrying out the analyzes in our own laboratory represents an annual saving of €950,000.

The speed of response is key in this laboratory to be able to comply with the requirements of the Gállego River surveillance protocol. Hours pass from taking the samples to obtaining the analytical result, while in an external laboratory the answer would be obtained several days later.

The samples delivered to the laboratory have a wide concentration spectrum, depending on their origin, so having several chromatography equipment and interdependent rooms helps to organize the work by concentration range of contaminants and eliminates the possibility of cross-contamination in the samples. equipment.

Daily maintenance, checks and calibrations are carried out, as well as counter-analysis with external laboratories.

There is a history of results by points, with which the treatment of the sample (dilutions, concentrations) is individualized.

Given the specialization of the laboratory in the analysis of persistent organic compounds, and the new lines of research imply a continuous improvement of the work methods and specific equipment for the type of compounds to be determined in order to increase sensitivity, accuracy, and speed. in response required.

# INTEGRAL MANAGEMENT OF OCCUPATIONAL RISK PREVENTION IN THE EXPLOITATION, EXECUTION OF WORKS AND SPECIAL ACTIONS, INVESTIGATION AND REMEDIATION OF SOILS AND/OR SITES CONTAMINATED BY HCH

*Ayala, C.[1], L. Monge[1], Cano, E.[2], Velilla, S.M.[2], Fernández, J.[2], Net, J.[2]*

*[1]Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain*
*[2]Department of Agriculture, Livestock and Environment, Government of Aragon, Spain*

**_Summary_**

The investigation and remediation of HCH contaminated soils and/or sites, as well as all the works associated with the control of the contamination plume, such as purification works, hydrogeological monitoring, construction works of essential infrastructures, execution of special actions, etc., often give rise to situations that may endanger the health and safety of people, material goods and the environmental resources involved or not in such works.

Uncertainty about the harmful substances present in soil, water or air, and, in many cases, their state and spatial distribution, are factors that condition the prevention measures to be established, as well as the actions to be taken, which differ from those normally implemented in usual working environments.

For a correct management of prevention in all works carried out on soil and/or sites contaminated by HCH, a document should be drawn up to serve as an effective prevention instrument, the Prevention Plan.

Subsequently, the preventive procedures must be detailed as well as some recommendations and examples of the contents of the Prevention Plan, which is available in the HCH contaminated sites in Sabiñanigo (Huesca). In addition, as an extension to the risk assessment method, the system of risk level indications implemented at the HCH contaminated sites in Sabiñanigo (Huesca) shall be described, which includes the risk assessment, the prevention measures for the established areas with contamination risks, the activities and/or operations and safe work protocols.

Specific aspects and own experiences related to industrial hygiene control, health surveillance and applicable regulations will be explained.

Likewise, the main characteristics of personal protective equipment, "black and white" installations, self-protection and emergency measures will also be detailed.

Finally, examples of processes where HAZOP (HAZard and OPeratibility study) analysis has been applied to analyse risks and identify potential hazards and operational problems will be explained.

**_Keywords_**

Prevention and Health Plan, HAZard and OPeratibility study, HCH

## *Introduction*

In the municipal area of Sabiñánigo, there are three sites currently affected by contamination by organochlorine compounds, mainly by HCH isomers from the activity of the former Inquinosa factory. The Government of Aragon has been carrying out remediation, control and monitoring actions. These actions are currently focused on the Inquinosa, Sardas and Bailín sites.

At these sites, the main contamination is linked to organochlorine compounds, mainly HCH isomers from the activity of the former Inquinosa factory, and this contamination includes persistent organic pollutants (POPs) and volatile organic compounds (VOCs), including benzene which is an extremely dangerous compound for health.

For an adequate management of prevention at these sites, a document must be drawn up to serve as an effective prevention instrument. This is a specific document in which the risks, preventive measures, emergency measures, protective equipment, etc. derived from the corresponding risk assessment are evaluated. We call this document the Prevention Plan.

It should be borne in mind that the entire preventive system in place at the sites is intended to ensure the protection of workers against risks related to exposure to carcinogens at work.

From the analytical determinations of the compounds present in the leachate water, groundwater and air at the sites, the presence in variable quantities of HCH and benzene should be highlighted. These two compounds are the ones that are of greatest concern, given their classification from the point of view of workers' health and safety. Lindane is an endocrine disrupting chemical agent and benzene is a chemical agent that has been shown to be carcinogenic in humans and can also produce hereditary mutations in human germ cells. In view of the above, preventive work on sites contaminated by HCH will fall within the regulatory scope of Royal Decree 665/1997 of 12 May 1997 on the protection of workers from the risks related to exposure to carcinogens at work, transposing Directive 90/394/EEC.

The main handicap in carrying out risk assessment for the presence of chemical pollutants is the variability and uncertainty of the concentrations to which workers may be exposed, with variables such as environmental conditions that may affect this exposure. Due to this uncertainty, preventive work is aimed at adopting protective measures always assuming the presence of pollutants, which means carrying out a correct zoning and determination of activities that may involve the presence of pollutants for the appropriate risk assessment.

### *Critical points for the prevention of occupational risks*

The following is an overview of the critical preventive phases that are being developed at the sites.

*1- Risk assessment*

One of the essential processes of risk prevention that must be implemented in the Safety Plan is the assessment of the risks associated with the execution of a given job.

**-Adoption of the risk level system**

As an extension to the risk assessment method, this section indicates the adoption of a system of risk level indications, which encompasses risk assessment, prevention measures for established areas at risk from contamination and safe work activities/operations and protocols.

Once implemented, the system of risk levels improves the determination of the means of protection for personnel involved in activities. It also favours the control, supervision and monitoring of the use of protective equipment, as well as the correct arrangement of the equipment by the personnel involved.

In order to establish the system of risk levels, the synthesis of the results of the risk assessment, hygiene measurements and water, soil and air analyses of the different areas/locations has to be taken into account. The following steps to be followed might be considered:

- Scrutiny of activities.
- Scrutiny of work areas.
- Scrutiny of safe working protocols.
- Scrutiny of protective measures and personal protective equipment.

Below is a part of the assessment by risk levels implemented at the sites.

| LEVEL 0 | LEVEL 1 | LEVEL 2 |
|---|---|---|
| Work clothes | Chemical protective clothing type 4-5-6 | Chemical protective clothing type 4-5-6. |
| Half-mask Respiratory protection A2P3 (purification process in operation) | Respiratory protection A2P3. | Powered breathing apparatus with A2P3 filters and head unit. |
| Protective goggles. Safety footwear | Protective goggles. Safety footwear | PVC boots with reinforced toecap and insole. |
| Double nitrile chemical protective glove EN 374 EN 388 | Double nitrile chemical protective glove EN 374 EN 388 | Double chemical protection glove made of nitrile EN 374 EN 388, outer glove with long cuff. |

| TASK TO BE PERFORMED | RISK LEVELS | | |
|---|---|---|---|
| | LEVEL 0 | LEVEL 1 | LEVEL 2 |
| **BAILIN TREATMENT PLANT** | | | |
| INPUT AND OUTPUT SAMPLING | | | |
| PEACHYMETRE CLEANING | | | |
| CLEANING OF PIPES AND SOLIDS PRE-FILTERS | | | |
| REPLENISHMENT OF REAGENTS (SULPHURIC ACID, FERRIC CHLORIDE, SODA | | | |
| REPLENISHMENT OF POLYELECTROLYTE | | | |
| REPLACEMENT AND MAINTENANCE OF ELECTRICAL AND PNEUMATIC EQUIPMENT | | | |
| DATA COLLECTION (READING OF FLOWMETERS, PH ETC.) | | | |
| CLEANING OF FACILITIES | | | |
| PHYSICO-CHEMICAL CLEANING | | | |

| TASK TO BE PERFORMED | RISK LEVELS | | |
|---|---|---|---|
| | LEVEL 0 | LEVEL 1 | LEVEL 2 |
| SLUDGE TRANSFER | | | |
| CHANGE OF ACTIVATED CARBON<br>*Working protocol areas with presence of free phase, high concentration of volatiles and/or lindane* | | | |
| SLUDGE PRESSING<br>*Working protocol areas with presence of free phase, high concentration of volatiles and/or lindane* | | | |

The assessment procedure with risk levels is dynamic and must be re-evaluated with the feedback of data obtained from hygiene measurement campaigns, measurements of pollutant concentrations in contaminated areas, environmental measurements, risk assessments of new activities etc.

*2-Carrying out hygiene measurement campaigns*

Three hygiene measurement campaigns are carried out annually at the sites, covering a complete spectrum of workstations and work areas.
Measurement campaigns are carried out in seven subdivided measurements covering all compounds that have been identified as potentially exposing workers.
The chemical compounds analysed in the hygiene measurement campaigns are listed below:

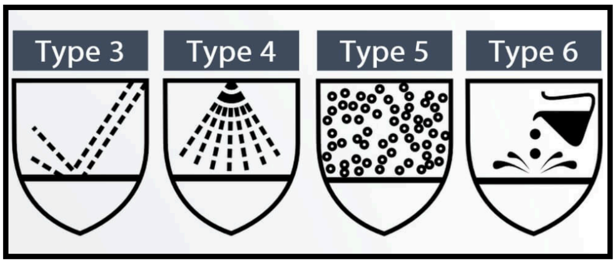
| STANDARD MEASUREMENT DAILY EXPOSURE ASSESSMENT LABORATORY | |
|---|---|
| 67-64-1 | ACETONE |
| 110-54-3 | n- HEXANE |
| 67-56-1 | METHANOL |
| STANDARD MEASUREMENTS DAILY EXPOSURE ASSESSMENT | |
| 95-50-1 | 1,2-DICHLOROBENZENE |
| 106-46-7 | 1,4 DICHLOROBENZENE |
| 87-61-6 | 1,2,3-TRICHLOROBENZENE |
| 120-82-1 | 1,2,4-TRICHLOROBENZENE |
| 108-70-3 | 1,3,5 TRICHLOROBENZENE |
| 118-74-1 | HEXACHLOROBENZENE |
| 108-90-7 | CHLOROBENZENE |
| 95-50-1 | 1,2-DICHLOROBENZENE |
| 106-46-7 | 1,4-DICHLOROBENZENE |
| 120-82-1 | 1,2,4-TRICHLOROBENZENE |
| 58-89-9 | LINDANE |
| 319-84-6 | HEXACHLOROCYCLOHEXANE |
| 319-85-7 | HEXACHLOROCYCLOHEXANE |
| 319-86-8 | HEXACHLOROCYCLOHEXANE |
| 71-43-2 | BENZENE |
| 108-90-7 | CHLOROBENZENE |
| 95-50-1 | 1,2-DICHLOROBENZENE |
| 106-46-7 | 1,4 DICHLOROBENZENE |
| 541-73-1 | 1,3 DICHLOROBENZENE |
| 79-01-6 | TRICHLOROETHYLENE |
| 127-18-4 | PERCHLOROETHYLENE |
| 107-06-2 | 1,2 DICHLOROETHANE |
| 75-09-2 | DICHLOROMETHANE (METHYLENE CHLORIDE) |
| 118-74-1 | HEXACHLOROBENZENE |
| 11097-69-1<br>53469-21-9 | POLYCHLORINATED BIPHENYLS (PCB's Aroclor 1242 and Aroclor 1254) |
| 87-61-6 | 1,2,3 TRICHLOROBENZENE* 1,2,3 TRICHLOROBENZENE* 1,2,3-TRICHLOROBENZENE |
| 120-82-1 | 1,2,4-TRICHLOROBENZENE |
| 108-70-3 | 1,3,5-TRICHLOROBENZENE* 1,3,5-TRICHLOROBENZENE* 1,3,5-TRICHLOROBENZENE |
| 74-87-3 | CHLOROMETHANE (METHYL CHLORIDE) |
| 87-86-5 | PENTACHLOROPHENOL |
| | PCDF and PCDD |

As a summary of the different annual measurement campaigns carried out, it should be noted that values of the analysed compounds have not been found above the daily exposure limit values in any of them.

*3-Characteristics and criteria for the use of Personal Protective Equipment for body and respiratory protection*

Throughout the years of preventive work at the sites, improvements in the comfort of personal protective equipment have evolved. Body and respiratory protection equipment is described below, although protection for feet, eyes and hands is also provided.
a) Body protection.
The following types of suits are used in workplaces and areas where contaminants are present:
-Type 3 protective suits are intended for resistance to penetration by a jet of liquid. The materials of these suits shall be tested for resistance to permeation by chemicals specified by the manufacturer, which shall be representative of the intended use of the suits. These suits may be one-piece or two-piece suits worn simultaneously. If the exposure to the chemical in liquid form is not of the magnitude of a pressure jet, but is a spray exposure or even less, such as possible liquid splashes, which may occur accidentally but affect the whole body, a situation arises which can be solved with Type 4 or Type 6 suits.
-Type 4 protective suits are intended for situations with exposure to fine liquid particles.

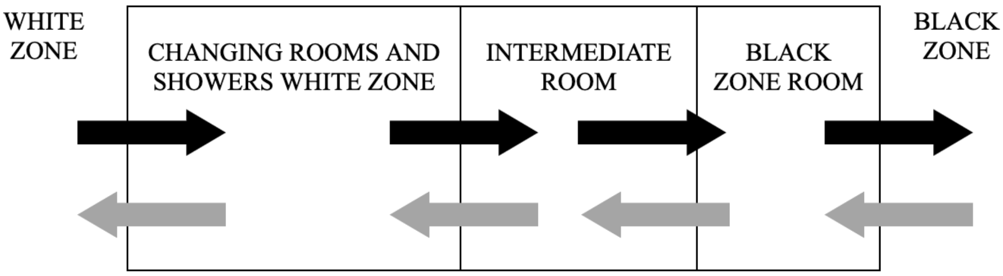
-Type 5 protective suits are suits against suspended solid particles. The tightness of these suits is assessed by means of a test which determines the resistance to the ingress of a fine particulate aerosol through the suit, known in short as the "inward leakage test". The materials of these suits do not have a specific penetration resistance test, but are evaluated as a whole in the above test. They are most often used with additional protective equipment, such as gloves, boots, respiratory protection, etc., which do not form an integral part of the suit but are used in combination, sealed at their junction points or not, as indicated in the equipment information leaflet. In the case of liquids, three situations of worker exposure are differentiated, depending on the type of exposure and assuming that these liquids do not produce significant quantities of vapours, as, if this were the situation, type 1 or 2 suits would be necessary.
-Type 6 protective suits are those which provide the lowest level of chemical protection for the whole body. They are intended for cases where the risk has been assessed as low and a complete barrier against liquid permeation is not necessary, either because the products being worked with are of low hazard, or because exposure is to small sprays or accidental splashes of small volume, and in the event that they are larger, the tasks being performed allow workers to act in a timely and appropriate manner after contamination, for example by replacing clothing with clean clothing.
Summarising the above:
Type 3: Protection against liquids (splashing or low hazard subs.) (EN 14605)
Type 4: Protection against liquid sprays (EN 14605)
Type 5: Protection against dust and solid particulates (EN ISO 13982-1)
Type 6: Protection against small splashes (low level of protection) (EN 13034)

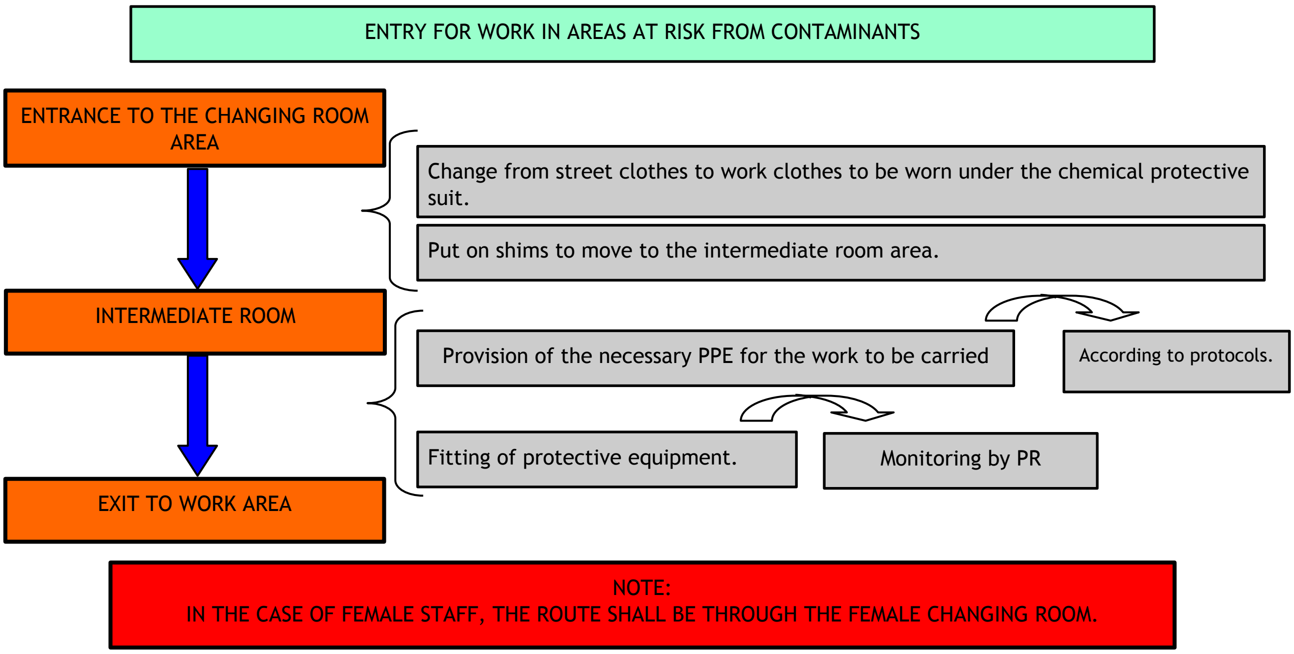


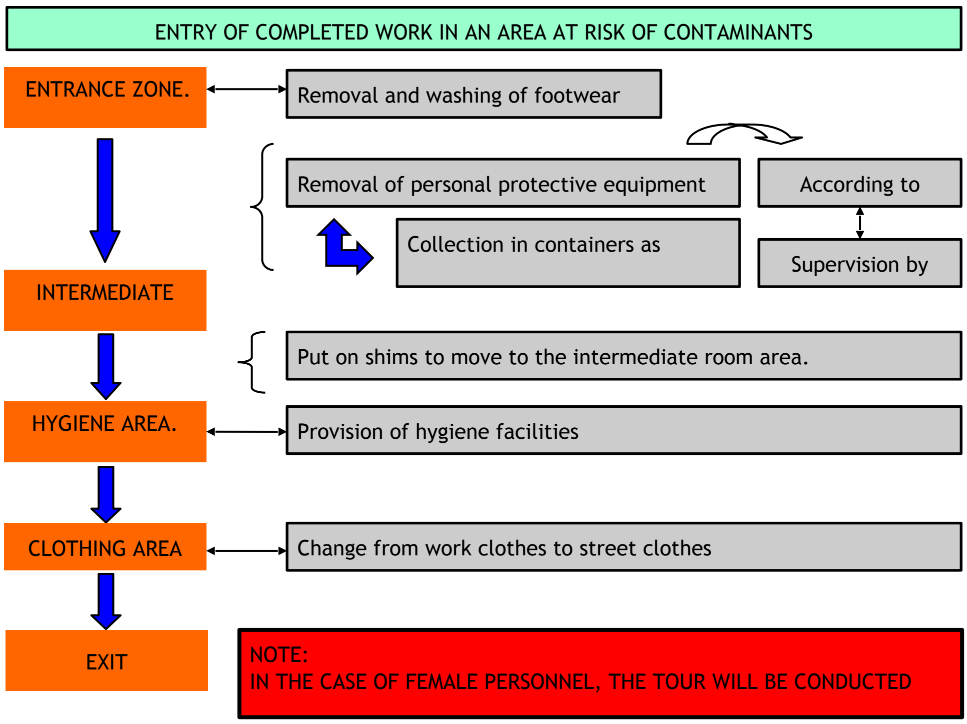

b) Respiratory protection.
The type of respiratory protection used at the sites is type A2P3. These are combined filters for organic vapours with boiling points above 65 degrees Celsius and for particulate filtration. In the case of filters for organic vapours with boiling points above 65 degrees Celsius, class 2 filters are used as they can be used for higher concentrations or for a longer period of time than class 1 filters. In the case of particulate filters, class 3 filters with a filter efficiency of 99.95 percent are used.
The system being used to carry the respiratory protection is a motor-ventilated equipment with head unit. This is the 3M™ Versaflo™ TR-300 motor-ventilated unit and the 3M™ Versaflo™ M-100 series head units. The use of this equipment means greater efficiency in work due to its greater comfort, as well as greater protection as it has a TH3 protection class, better head and eye protection.

*4-Hygiene and welfare installations. Black and white*

There are currently two black and white installations on the sites, a fixed installation and a mobile installation.
The processes for the use of these installations are described below.






*5-Health surveillance of workers*

Health surveillance of workers should be established as a priority for workers involved in tasks where they may be exposed to contaminants at HCH-contaminated sites.

The criteria and protocols described in this guide should be considered as a minimum. Health surveillance criteria and protocols should always be defined by the respective health surveillance services of the companies involved at the sites on the basis of the specific risk assessment.

The content of the tests and analyses to be carried out in the specific medical protocol, which it is considered appropriate to apply to personnel carrying out activities at the sites, is as follows:

- Specific protocol Manual handling of loads
- Specific protocol Forced postures.
- Specific protocol for occupational exposure to pesticides (determination of biological standards).
- Specific protocol for occupational exposure to benzene (determination of biological standards).
- Specific protocol for occupational exposure to Lindane (determination of biological standards).
- Occupational asthma (including spirometry).
- Chest X-ray (AP and L).
- General examination.

- Vision control.
- E.C.G. to people over 40 years old.
- Biological determinations: Gamma-hexachlorocyclohexane in blood, s-phenyl mercapturic acid or t.t. muconic acid, plasma cholinesterase.
- Blood tests including:
  - HEMOGRAM: red blood cells, haemoglobin, haematocrit, MCV, MCH, MCHC, Leukocytes.
  - LEUCOCYTE FORMULA: % and number of leukocytes, monocytes, neutrophils, eosinophils, basophils.
  - Platelet count and coagulation tests.
  - Pregnancy test.
  - Sedimentation rate.
  - Biochemistry: Glucose, Urea, Uric acid, Cholesterol, HDL, VLDL, Triglycerides, Creatinine, GOT, GPT, GGT, Alkaline phosphatase.

The importance of having biological baseline values for the most harmful compounds for the health of workers on HCH-contaminated sites, which as indicated in previous sections of the Guidance are HCH and benzene, as well as the respiratory capacity of workers to be able to make proper and safe use of respiratory protection, makes it necessary to have a "fit" of personnel prior to the start of their activities on HCH-contaminated sites.

It should be noted that pregnant and/or breastfeeding women should be banned from entering HCH contaminated sites.

*Procedure for analysing operational risks and problems in processes and installations*

A risk analysis procedure is currently being implemented for the new lines of action being developed at the sites. These new lines of action are in the field of research and different contamination remediation tests.

The purpose of the procedure is to establish the methodology, determine responsibilities and organisational conditions for carrying out the analysis of risks and operational problems in processes and installations that are executed or developed in HCH contaminated sites within the scope of investigation and/or testing and remediation of contamination.

This analysis will be carried out using the HAZOP study (HAZard and OPeratibility study). This is a structured and systematic risk analysis technique that identifies potential hazards and operational problems in processes, generally documented through process and instrument diagrams (P&ID).

The HAZOP study is a rigorous, systematic and critical verification study of all foreseeable failures, errors or deviations with respect to normal situations and according to a given design concept of a process installation in the project phase or in operation, estimating the hazard potential they generate and their effects. It is a deductive method of qualitative analysis for the detection of failures and their consequences, and the consequent adoption of preventive measures.

**_Acknowledgements_**

This work has been supported by the Government of Aragón, through the public company SARGA.

**_References_**

1. Law 31/1995, of 8 November 1995, on the prevention of occupational hazards.
2. Royal Decree 665/1997 of 12 May 1997 on the protection of workers against risks related to exposure to carcinogens at work.
3. Technical notes on prevention.
4. Practical safety guide for work at HCH-contaminated sites.

# PERSISTENT PESTICIDES IN AIR FROM A FORMER HCH PRODUCTION SITE IN SPAIN


***Navarro, I.[1], De la Torre, A.[1], Arjol, M. A.[2], Fernández, J.[3], Martínez, M. A.[1]***

*[1]Unit of POPs and Emerging Pollutants in the Environment, Department of Environment, CIEMAT, Madrid, Spain*
*[2]Sociedad Aragonesa de Gestión Agroambiental SARGA, Zaragoza, Spain,*
*[3]Department of Agriculture, Livestock and Environment, Government of Aragón, Zaragoza, Spain*



***Summary***

The landfilling and dumping of persistent organic pollutants (POPs) and other persistent hazardous chemicals, such as hexachlorocyclohexane (HCH) isomers can have significant adverse environmental consequences and cause contamination in soil, water, and atmosphere systems. The Government of Aragón implemented remediation and containment measures at derelict production facility (INQUINOSA Factory) and landfill sites located in Sabiñánigo (Aragón, Spain). To protect and assess the local environment, the concentrations of HCH isomers in air were periodically monitored in the Bailín and Sardas landfills and surroundings. Important differences were found between sampling locations (geographic distribution) and sampling campaigns (temporal trend). HCH concentrations obtained during dismantling works at Bailín landfill were statistically higher for all isomers compared to those obtained afterwards. Nevertheless, the levels obtained in Bailín and Sardas landfill and INQUINOSA Factory highlights that even after dismantling works, these facilities are currently HCH air pollution sources.



***Keywords***

POPs, HCH, PeCB, HCB, air monitoring, passive air samplers


### *Introduction*

Hexachlorocyclohexane isomers (α-, β-, γ-, δ-, ε-HCH), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) are pollutants of great concern because of their persistence, toxicity and widespread distribution in the environment. In Spain, the manufacture of lindane has been associated with four production sites that generated nearly 200,000 t of HCH wastes. Approximately 65% of these wastes were generated by the INQUINOSA Factory located in Sabiñánigo (Aragón, Spain) from 1975 to 1992 [1], and were mainly dumped at Bailín and Sardas landfills. Remediation and management of dumpsites is a worldwide problem that must be addressed to protect human health and the environment. Aragon Government's long-term objective is the control of air quality related to landfills used to dump organochlorine waste.

In this study, the concentrations of HCH isomers in air were periodically monitored in the Bailín and Sardas landfills and surroundings since the Bailín dismantling works to the present. Besides, pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) levels were also measured in the Sardas area.

### *Materials and methods*

The present study includes 657 air samples collected in 74 consecutive sampling campaigns (SC) conducted from summer 2014 to autumn 2021. Ten sampling points were selected at the Bailín and Sardas influence area (Figure 1) - Bailín area: P1-P4 (near the landfill) and P5 (in the town of Sabiñánigo); Sardas area: P7 and P8 (possible sources of pollution) and P6, P9 and P10 (residential sites). While HCH isomers were monitored in all locations (from 1st campaign at Baílin area and 17th at Sardas area), chlorobenzenes (CBs) were determined in P7 and P10 from the 24th campaign. At each sampling point, one passive air sampler with a polyurethane foam (PUF) disk was deployed for a month. PUF disks were precleaned by Soxhlet extraction with acetone and diethyl ether for 24 h, then wrapped in aluminum foil and stored in polyethylene bags at -20°C until deployment. Compound-specific sample air volumes were calculated following the Tom Harner Template [2].

Samples spiked with $^{13}$C-labeled surrogate standards ($^{13}C_6$-α-, β-, γ- and δ-HCH, $^{13}C_6$-PeCB and $^{13}C_6$-HCB) were Soxhlet extracted in toluene for 24 h. The extracts were solvent exchanged into hexane and purified by florisil column. The elution was carried out with n-hexane and n-hexane:dichloromethane (50:50, v/v). The final extracts were concentrated under a nitrogen stream, redissolved in nonane and spiked with the $^{13}$C injection standards solutions ($^{13}C_{12}$-PCB 15 and $^{13}C_{12}$-PCB 70) prior to instrumental analysis. Target analytes (α-, β-, γ-, δ- and ε-HCH isomers, PeCB and HCB) were analyzed on a Varian CP-3800 gas chromatograph connected to a 320 MS-TQ mass spectrometer. Quantification was carried out using isotopic dilution method. Isomer concentrations were higher than LODs in all cases. Instrumental blanks (nonane) were run before each sample injection to check instrumental contamination.

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

### *Results and discussion*

The concentrations of HCH in the different areas considered were shown in Figure 2. Important differences were found between sampling locations and sampling campaigns.

*HCH concentration in Bailín area*

HCH concentrations obtained during the first two sampling campaigns -α-HCH (224 $ng/m^3$; median), β-HCH (174 $ng/m^3$), γ-HCH (49 $ng/m^3$), δ-HCH (56 $ng/m^3$) and ε-HCH (28 $ng/m^3$)-, presented statistically higher concentrations (Kruskal-Wallis $p < 0.01$) for all isomers compared to those obtained afterwards -α-HCH (3.9 $ng/m^3$; median), β-HCH (0.6 $ng/m^3$), γ-HCH (1.6 $ng/m^3$), δ-HCH (1.7 $ng/m^3$) and ε-HCH (0.2 $ng/m^3$)-. Levels detected were in accordance to those associated to historical production sites [3]. Considering that the first two sampling campaigns covered the dismantling of the old landfill and the subsequent sealing of the new cell, results indicate that the works performed during the dismantling were a source of HCH contamination. After those, a clear decrease in HCH levels was observed in all sampling points. Nevertheless, some interesting differences between sampling sites were observed: P1 and P2 continued to present having statistically higher values than P3 and P4 and these were higher than those derived from P5. This geographical distribution highlighted that old landfill represents a HCH source even after dismantling work has been completed. Besides, statistically positive correlations were found among HCH isomers in all sampling points, showing a major common source.

Once dismantling works finished, an equilibrium state was reached (from SC5 to SC74) and a similar isomer profile was obtained at P2-P5: α-HCH (45± 5%, mean± SD) followed by γ-HCH (24 ± 5%) and δ-HCH (22 ± 56), and to a lesser extent by β-HCH (7 ± 2%, mean ± SD) and ε-HCH (2 ±1%). A different isomer profile was observed at P1, being γ-HCH the predominant isomer (41± 8%) instead of α-HCH, reflecting the possible influence of DNAPL (Dense Non-Aqueous Phase Liquid) captation cell.

*HCH concentration in Sardas area*

The sum of α-, β-, γ-, δ- and ε-HCH (ΣHCH) concentration in the area evaluated ranged between 0.03 and 64.8 $ng/m^3$. ΣHCH air concentrations obtained at Sardas landfill (P7; 5.11 $ng/m^3$, median) and INQUINOSA Factory (P8; 3.36 $ng/m^3$) showed statistically higher values than the other locations (0.48, 0.51 and 0.23 $ng/m^3$ for P6, P9 and P10, respectively). This result clearly highlights these facilities as currently HCH air pollution sources. Samples obtained from P6, P7, P8 and P10 showed a similar isomer profile with a higher contribution of α-HCH (49 ± 9%, 37 ± 9%, 46 ± 10% and 44 ± 8%; mean ± SD at P6, P7, P8 and P10, respectively) followed by γ-HCH (28 ± 7%, 35 ± 7%, 29 ± 6% and 31 ± 7%), δ-HCH (15 ± 5%, 19 ± 6%, 17 ± 7% and 16 ± 5%), β-HCH (7 ± 4%, 5 ± 3%, 6 ± 3% and 7 ± 4%) and ε-HCH (2 ± 1%, 3 ± 2%, 2 ± 2% and 2 ± 1%). However, in P9 case, the main isomer was γ-HCH (52 ± 11%) followed by α-HCH (29 ± 7%), this suggests the presence of a lindane source hitherto unknown with significant influence at this site.

*PCB and HCB concentration in Sardas area*

CB air concentrations ranged from 0.6 to 318 $pg/m^3$ for PeCB and from 1.0 to 98 $pg/m^3$ for HCB. Positive correlations were found between PeCB and HCB at the two sampling points evaluated (P7: $r > 0.394$, P10: $r > 0.605$; $p < 0.01$), suggesting a major common origin for both chlorobenzenes. PeCB concentrations were statistically higher in P7 (83 $pg/m^3$, median) than P10 (8.4 $pg/m^3$). Levels detected were comparable to values observed in other studies [4].

### *Acknowledgements*

This work has been supported by the Government of Aragón, through the public company SARGA under the contracts no, 5506079-17, 5506079-29, 5507001-18 and 5500011-05.

### *References*

1. Vijgen, J., 2006. The legacy of lindane HCH isomer production.Main report. A global overview of residue management, formulation and disposal. Available at: International HCH & Pesticides Association, IHPA. http://www.ihpa.info/docs/library/reports/lindane%20main%20report%20def20jan06.pdf

2. Harner, T., 2017. 2017_v1_5_Template for calculating effective air sample volumes for PUF and SIP disk samplers. Available at: https://www.researchgate.net/publication/319764519_2017_v1_5_Template_for_calculating_Effective_Air_Sample_Volumes_for_PUF_and_SIP_Disk_Samplers_Sept_15.

3. Fang, Y., Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., Huang, Q., 2017. Chemosphere 178:340–349. https://doi.org/10.1016/j.chemosphere.2017.02.151.

4. De la Torre, A., Sanz, P., Navarro, I., Martínez, M.A., 2016. Environ. Pollut. 217, 26–32. https://doi.org/10.1016/j.envpol.2016.01.040.


FIGURE 1. GEOGRAPHICAL DISTRIBUTION OF SAMPLING SITES

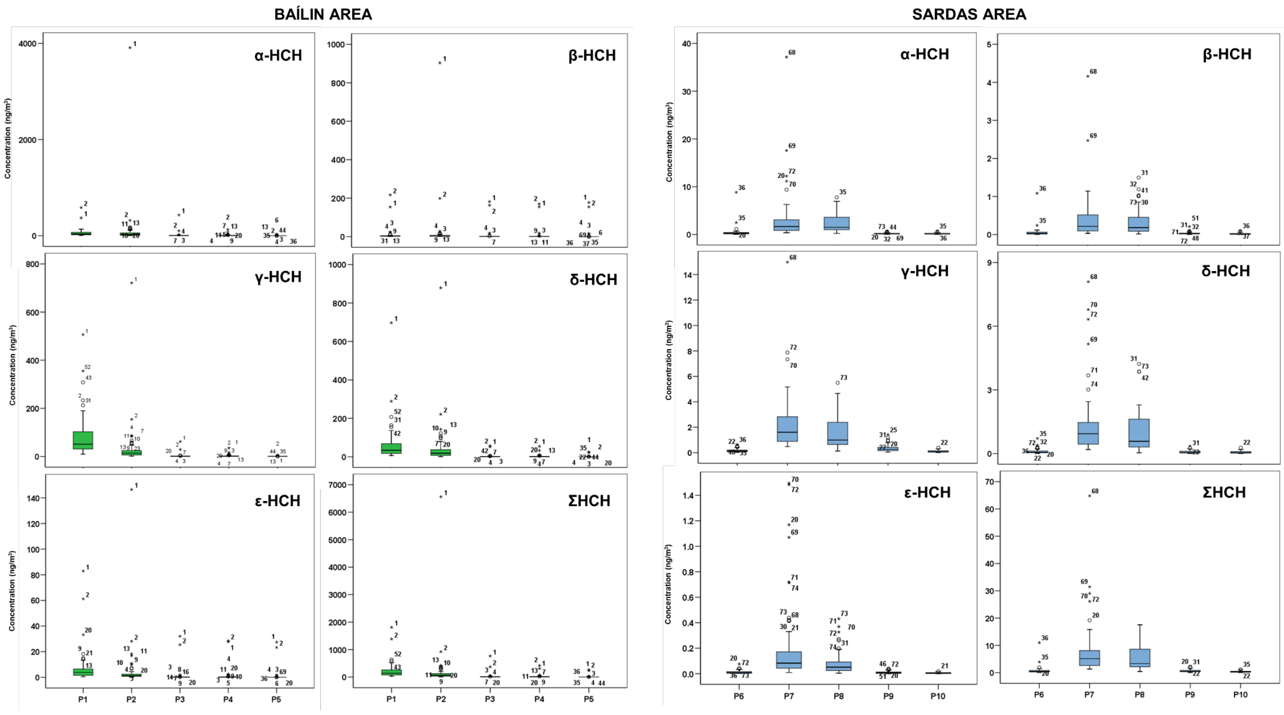



**FIGURE 2. CONCENTRATION (NG/M$^3$) OF HCH IN AIR AT BAILÍN AND SARDAS AREA; OUTLIERS (CIRCLES) AND EXTREME (ASTERISKS) VALUES WERE LABELED WITH SAMPLING CAMPAIGN CODE.**

# ATMOSPHERIC HCH CONCENTRATIONS (2008-2019) FROM THE SPANISH MONITORING PROGAM ON POPS

*Muñoz-Arnanz, J.[1], Colomer-Vidal, P.[1], Ros, M.[1], Vicente, A.[1], Salcedo, C.[1], Bartalini, A.[1], Jiménez, B.[1]*

[1]*Instituto de Química Orgánica General, IQOG-CSIC, Madrid, Spain*

## *Summary*

In Spain, notorious environmental and human health awareness issues related to lindane and other HCH forms have been documented mostly in the north of the country (e.g. Aragón, Basque Country or Galicia regions). Yet, aside from the scientific data available from pointed polluted areas, the presence of HCH in atmospheric air across Spain has been and continues to be systematically investigated since the 2008 inception of the Spanish Monitoring Program on POPs (SMP-POPs). In the SMP-POPs, passive air sampling by means of polyurethane foams (PUFs) is conducted seasonally (winter, spring, summer, fall) at representative urban and background sites scattered through the peninsular and insular Spanish national territory.

In this study we present and evaluate data on HCHs (α, β, ɣ) since 2008 to 2019 from half of the monitoring sites of the SMP-POPs (those investigated by our group at the Spanish National Research Council, IQOG-CSIC), corresponding to seven background and five urban sites made up almost entirely of coastal locations.

Obtained data for over a decade showed greater HCH air concentrations in urban sites than in background locations. In almost all investigated sites, ɣ-HCH was the most abundant species contributing up to ≈70% to ∑HCHs. The seasonality did not seem to influence the total air concentration of HCH. Moreover, no clear temporal trend could be drawn from our data. The fact that HCH air concentrations seem to remain stable over the reported years along with the predominance of the ɣ isomer -the least persistent of them-, highlight the ongoing existence of unidentified HCH sources in the Spanish territory, which warrants further investigation.

## *Keywords*

POPs, HCH, atmosphere, Spain, monitoring

## *Introduction*

Awareness of the risks that POPs pose worldwide led the international community to enact the Stockholm Convention (SC) in 2001 under the United Nations Environment Program (UNEP, 2001). The SC entered into force on 17 May 2004 and, today, there are 152 signatories and 186 parties, being Spain among them. Under the leadership of its Ministry for the Ecological Transition and the Demographic Challenge (MITERD), Spain was a pioneer in fulfilling its obligation of developing and putting into effect a National Implementation Plan (NIP). Specifically, the Spanish NIP was initiated in 2007 encompassing as core part of it a monitoring program of POPs based on passive air sampling (PAS), following the recommendations of the Global Monitoring Plan (GMP) developed by the SC.

As of 2009, the α, β and ɣ forms of hexachlorocyclohexane (HCH) were listed as persistent organic pollutants (POPs) in the Stockholm Convention, becoming, thereby, globally regulated. However, their great-scale production and use since the late 1940s along with their environmental persistence are responsible for the extant global HCH contamination that we face today. In Spain, notorious environmental issues related to lindane and other HCH forms have been documented mostly in the north of the country (e.g. Aragón, Basque Country or Galicia regions). Yet, aside from the scientific data available from pointed polluted areas, the presence of HCH in atmospheric air across Spain has been monitored since the 2008 inception of the Spanish Monitoring Program on POPs (SMP-POPs) based on the use of PAS (Muñoz-Arnanz et al., 2016).

In this study we present and evaluate data on HCHs (α, β, ɣ) since 2008 to 2019 from half of the monitoring sites of the SMP-POPs (those investigated by our group at the Spanish National Research Council, CSIC), corresponding to seven background and five urban sites made up almost entirely of coastal locations (Figure 1).

## *Materials and methods*

### *Sampling*

Since 2008 to 2019, air samples were collected every three months around each season's change (winter, spring, summer and fall). A total of 513 air samples (and 513 associated field blanks) corresponding to 46 field-campaigns were obtained from up to seven background (rural/remote sites located at EMEP stations) and up to five urban sites in Spain by means of passive air samplers (PAS) based on polyurethane foam (PUF) disks. One PUF disk at each site was used for sampling and subsequent analysis of HCHs. Optimized PUF disk pre-treatment, transport conditions and field sampling procedures were followed to avoid any potential PUF contamination as described in Muñoz-Arnanz et al. (2016).

*Sample treatment and instrumental determination*

PUF disks were spiked with a suite of 13C-labeled standards of α-, β-, and ɣ-HCH isomers before undergoing Soxhlet extraction with a mixture of n-hexane:dicloromethane (9:1) for 24h. The obtained extracts were subsequently purified by means of Florisil® before being analyzed by GC-qMS or GC-qqqMS/MS. Further details on the analytical process can be found at Muñoz-Arnanz et al. (2016)

*Data treatment and statistical analysis*

Concentration of α, β, and ɣ isomers, and ∑HCHs are expressed in pg/m$^3$. Data analysis and plots were performed using R software version 4.2.2, and mapping with QGIS software. Data points falling more than 3 times the interquartile range were considered extreme outliers and excluded from the data for plots and statistical analysis. Neither α, β and ɣ-HCH, nor ∑HCHs showed a normal distribution (Shapiro-Wilk test, all $p>0.05$). Concentration comparisons among two groups (cities vs. EMEP stations) were assessed using the Mann-Whitney test, while comparisons among more than two groups (seasons, cities, and EMEP stations) were assessed using the Kruskal-Wallis test including pairwise comparisons of Wilcoxon rank with the significance value adjusted by the Bonferroni correction. Additionally, Spearman's rank correlation coefficient (ρ) analyses were applied to evaluate the relationship between concentrations of α, β, and ɣ-HCH, and ∑HCHs and with years (time trends).

## *Results*

Obtained data for over a decade (n=484) showed a conspicuous variability in the median ΣHCHs concentrations (pg/m$^3$) across the twelve different locations investigated (Figure 1). Statistically significant differences (Kruskal-Wallis, $p<0.05$) were found within both groups, cities and EMEP locations. As for the cities, two stood out with median concentrations of 34.1 pg/m$^3$ (Azpeitia) and 30.6 pg/m$^3$ (Barcelona), although only Huelva was statistically different from the all the rest (Wilcoxon rank, $p<0.05$) owing to the lowest total HCH burden measured there, i.e., 12.6 pg/m$^3$. On the other hand, the two background sampling points with the highest total HCH concentrations, i.e., Cap de Creus (36.5 pg/m$^3$) and Mahón (23.2 pg/m$^3$) were statistically different from the rest of background sampling points (Wilcoxon rank, $p<0.05$).

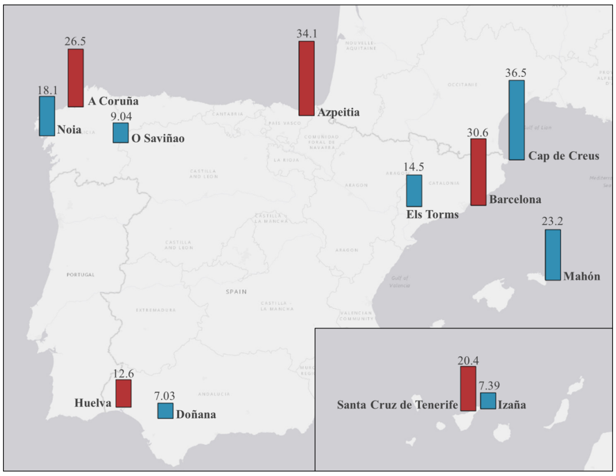



**FIGURE 1. ∑HCHS (MEDIAN, PG/M$^3$) FROM 2008 TO 2019. CITIES ARE RED COLORED AND EMEP STATIONS ARE COLORED IN BLUE**

Interestingly, these values are in consonance with that previously reported by De la Torre et al. (2016) with data corresponding to 2008-2013 from other inner Spanish sampling locations, with median and range values of 18 pg/m$^3$, 0.13-100 pg/m$^3$ (background) and 30 pg/m3, 5.0-154 pg/m$^3$ (cities), respectively. They are, however, up to three orders of magnitude below those reported from a historical lindane production site in Spain (Navarro et al., 2019), with ΣHCHs air concentrations since 2016 to 2018 in the range of 0.07 to 19.2 ng/m$^3$.

Greater HCH air concentrations were found in urban sites than in background locations when splitting all data (n=484) into those two categories. These differences were statistically significant (Mann-Whitney, $p<0.05$) for β and ɣ isomers as well as for ∑HCHs (Fig 2.)

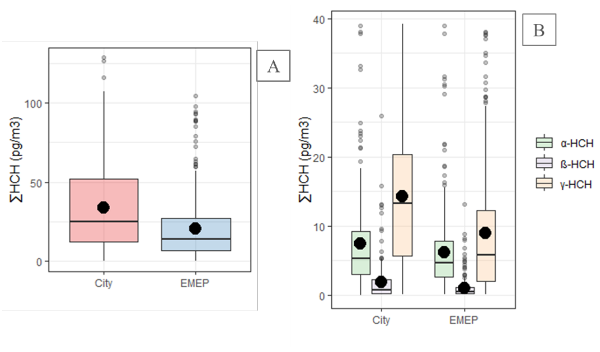



**FIGURE 2. BOX-AND-WHISKERS PLOTS** (BOXES DEPICTED AS FIRST AND THIRD QUARTILES WITH THE MEDIAN INDICATED AS A LINE AND THE MEAN INDICATED AS A CIRCLE; WHISKERS CORRESPONDING TO 5 AND 95% PERCENTILES) OF A) CONCENTRATIONS OF ∑HCHS AND B) CONCENTRATIONS OF Α, Β, AND Ɣ ISOMERS, BOTH IN CITIES AND EMEP LOCATIONS

Higher airborne HCH concentrations were also detected in Spanish locations by De la Torre et al. (2016), which seems to highlight the presence of unidentified HCH sources in urban environments, and for which further investigation is needed since no clear explanation is at hand.

The relative contribution of each isomer to the total content was explored for both, cities (Figure 3) and background locations (Figure 4). Among cities, ɣ-HCH was consistently observed as the most abundant isomer contributing up to ≈70% to ∑HCHs.

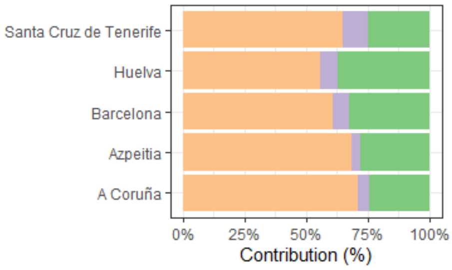



**FIGURE 3. HCH ISOMERS' CONTRIBUTION IN PERCENTAGE (%) FOR CITIES SINCE 2008 TO 2019**

In comparison to urban sampling points, a lesser predominance of ɣ-HCH in background locations was found over the whole study period in agreement with a greater contribution of α-HCH. Thus, the relative abundance of α and ɣ isomers measured about the same in Doñana and Cap de Creus while the α isomer was the most abundant in the Canary location of Izaña.

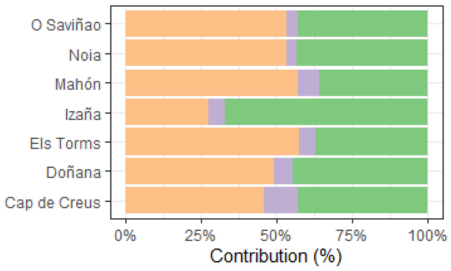



**FIGURE 4. HCH ISOMERS' CONTRIBUTION IN PERCENTAGE (%) FOR EMEP STATIONS SINCE 2008 TO 2019**

Isomeric α-/ɣ- ratios can be informative of the origin of the HCH detected; namely, technical vs. lindane. Usually, ratios about or lower than 1 are deemed related to lindane since the ratio in technical HCH tend to vary between 4 and 7 (Shen et al. 2004). We detected an ample variability in most locations for this ratio; nevertheless, median values of 0.359 for cities and 0.716 for background locations, suggest lindane as an important source for the Spanish ΣHCHs air concentrations detected. Conversely to what was found for other airborne POPs such as PCBs and PCDD/Fs targeted as well in the SMP-POPs (Muñoz-Arnanz et al. 2018), the seasonality did not influence the total HCH air concentrations, but significant differences (Kruskal-Wallis, $p<0.05$) were observed for α and β isomers. Furthermore, it is worth noting the results on ∑HCHs air concentrations showed no clear pattern from a temporal perspective. Only β-HCH, the least abundant isomer, presented a significant negative time trend correlation (Spearman, $p<0.05$, ρ (rho) = -0.353), with a rather small slope of -0.149. Therefore, it seems necessary to widen the number of monitoring years to crystalize the expected decline in Spain of airborne HCHs. The fact that HCH air concentrations seem to remain stable over the years reported along with the predominance of the ɣ isomer -the least persistent of them-, highlight the ongoing existence of HCH sources in the Spanish territory. All in all, SMP-POPs' results build up on numerous international scientific studies that call for attention on these chemicals, for which despite being POPs, further and concrete action is needed.

## *References*

De la Torre, A., Sanz, P., Navarro, I., & Martínez, M. Á. (2016). Time trends of persistent organic pollutants in Spanish air. Environmental Pollution, 217, 26-32.

Muñoz-Arnanz, J., Roscales, J. L., Ros, M., Vicente, A., & Jiménez, B. (2016). Towards the implementation of the Stockholm Convention in Spain: Five-year monitoring (2008–2013) of POPs in air based on passive sampling. Environmental Pollution, 217, 107-113.

Muñoz-Arnanz, J., Roscales, J. L., Vicente, A., Ros, M., Barrios, L., Morales, L., & Jiménez, B. (2018). Assessment of POPs in air from Spain using passive sampling from 2008 to 2015. Part II: Spatial and temporal observations of PCDD/Fs and dl-PCBs. Science of The Total Environment, 634, 1669-1679.

Navarro, I., de la Torre, A., Sanz, P., Arjol, M. A., Fernández, J., & Martínez, M. A. (2019). Organochlorine pesticides air monitoring near a historical lindane production site in Spain. Science of the total environment, 670, 1001-1007.

Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C., & Bidleman, T. F. (2004). Hexachlorocyclohexanes in the North American atmosphere. Environmental Science & Technology, 38(4), 965-975.

# 2D MODEL OF GROUNDWATER FLOW AND DISSOLVED HCH TRANSPORT THROUGH THE GÁLLEGO RIVER ALLUVIAL AQUIFER DOWNSTREAM THE SARDAS HCH LANDFILL (HUESCA, SPAIN)


***Javier Samper[1], Brais Sobral[1], Luis Montenegro[1], Joaquín Guadaño[2], Jorge Gómez[2], Felipe Delgado[3], Javier San Román[3] & Jesús Fernández[4]***

*[1]ET.S. Ingenieros de Caminos, Canales y Puertos. CICA, Centro de Investigaciones Científicas Avanzadas. Universidade de A Coruña. Campus de Elviña 15071 A Coruña*
*[2]Empresa para la Gestión de Residuos Industriales, S.A., S.M.E., M.P., EMGRISA. Madrid*
*[3]Confederación Hidrográfica del Ebro*
*[4]Departamento de Suelos. Gobierno de Aragón*



### *Summary*

The pollutants released from the Sardas landfill have reached the Gállego alluvial aquifer and pose pollution risks to the Sabiñánigo reservoir. Here we present a 2D finite element groundwater flow and total dissolved HCH transport model through the alluvial aquifer of the Gállego river. The oscillations of the level of the reservoir produce a tidal effect in the hydraulic heads in the alluvial aquifer. These oscillations are transmitted in a damped way with some delay to the piezometric oscillations in the aquifer. The offset and the damping of the hydraulic heads attest that the alluvial aquifer is not in direct hydraulic contact with the Sabiñánigo reservoir. The silting sediments of the reservoir and the natural silts of the terrace are interposed between the alluvial aquifer and the reservoir. The direction of the groundwater velocity field changes quickly on a daily basis in response to the oscillations of the reservoir level. The flow direction is E-W/NE-SW under normal conditions when the head in the aquifer is larger than the level in the reservoir. When the reservoir water level increases quickly, the groundwater flow direction reverses to W-E. The E-W/NE-SW flow direction is restored when the hydraulic head in the alluvial rises over the reservoir water level. Model results confirm the validity of the conceptual model and reproduce the measured hydraulic heads in the aquifer. A contaminant transport model in the alluvial aquifer has been performed to simulate the total dissolved HCH. The model is based on the hypothesis that HCH is partitioned between dissolved and sorbed phases by using a constant distribution coefficient, Kd. The computed plume of the concentrations of total dissolved HCH and the mass flux of dissolved HCH are very sensitive to changes in the distribution coefficient. The best fit of the total dissolved HCH concentration data is obtained with Kd ranging from 2 to 5 L/kg. The flux of dissolved HCH leaving the site towards the Sabiñánigo reservoir is estimated equal to 2.1 kg/year for Kd = 10 L/kg.



### *Keywords*

HCH, lindane, landfill, alluvial, numerical model, 2D model, Sardas.


### *Introduction*

HCH was used as a pesticide during the 1950s and 1960s. However, its use was later found to be harmful to human health. Companies started working on the isolation of the ɣ isomer, known as lindane, which in the right concentration would be tasteless and harmless (Vijgen et al., 2019). Lindane was banned in the European Union in 2008 and HCH isomers were included in the Stockholm Convention's list of Persistent Organic Pollutants in 2009 (Schonard, 2016).

The INQUINOSA factory in Sabiñánigo, Huesca (Spain) deposited dust and liquid residues from lindane production in the Sardas and Bailin landfills in the late 1970s (Fernández et al., 2013). In the 1980s, the Sardas landfill was filled with more than 400 $Dm^3$ of urban, construction and industrial solid waste, including those from lindane production in powder and liquid state (Fernandez et al., 2013). In 1997, the N-330 road was built across the Sardas landfill and approximately 50 000 $m^3$ of landfill wastes were moved to the floodplain of the Gállego river. The Sardas landfill is located less than 500 m east of the Sabiñánigo reservoir built in 1963 to supply hydroelectric power to nearby towns and factories (Figure 1). The pollutants released from the Sardas landfill have reached the Gállego alluvial aquifer and pose pollution risks to the Sabiñánigo reservoir. Here we present a 2D finite element groundwater flow and total dissolved HCH transport model through the alluvial aquifer of the Gállego river.

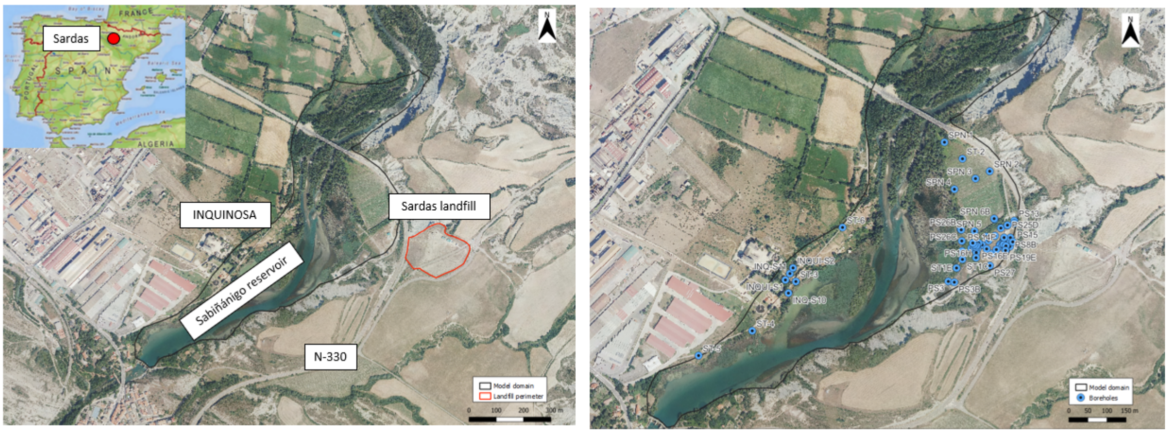



**FIGURE 1. LOCATION OF THE STUDY AREA (LEFT) AND MODEL DOMAIN (RIGHT)**

### *2D groundwater flow numerical model*

A 2D transient horizontal groundwater flow model through the Gállego river alluvial aquifer has been performed with CORE$^{2D}$ V5 code (Samper et al., 2011).

*3.1. Conceptual model*

The model domain extends from the dam of the reservoir on the south to the area upstream the bridge of the N-330 road affected by the fluctuations of the Sabiñánigo reservoir water level on the north (Figure 1). On the right bank of the Gállego river, where INQUINOSA is located, the alluvial floodplain is in contact with the fluvioglacial terrace.

This model aims at quantifying the tidal effect produced by daily fluctuations of the reservoir water level on the aquifer and estimating the hydraulic conductivity of the silting sediments of the reservoir and of the sands and gravels of the aquifer. The conceptual model is based on the following assumptions: 1) The water flows through the sands and gravels; and 2) Groundwater inflows take place through the surroundings fluvioglacial terraces on the right bank and through the Larrés marls on the left bank.

*3.2. Model structure*

The model domain is discretized with triangular finite elements. The mesh has 2348 nodes and 4475 elements (Figure 2). It has been especially refined in areas with presence of DNAPL, areas with large total dissolved HCH concentrations and in the portion of the alluvial located downstream the Sardas landfill. The simulation period is 109 days long and extends from July 15th to October 31st, 2020. This simulation was performed with time increments of 30 minutes.

The spatial variability of hydrogeological parameters was considered by defining two material zones within which all the elements share the same hydrodynamic parameters. Initial estimates of the parameters were derived from the interpretation of pumping tests. The hydraulic conductivity, K, of the alluvial has been calibrated equal to 400 m/d. A larger value of K, 600 m/d, was used in a material zone on the left bank of the alluvial near the Sardas landfill. The estimate of the specific storage coefficient, $S_S$, of the gravels is equal to $6 \cdot 10^{-4}$ $m^{-1}$. The thickness of the silting sediments, natural silts, and sands and gravels have been estimated from boreholes drilled in the reservoir (CHE, 2010), and in the Sardas site downstream the landfill (EMGRISA, 2020).

*3.3. Boundary conditions*

Recharge from rainwater in the areas where the gravels are confined by the silts is equal to 39 mm/year while recharge is higher (51 mm/year) in areas where the gravels outcrop. Boundary conditions along the two banks of the alluvial are simulated with a Neuman condition (fixed flow) by assuming that the flow is uniform by sections. The flow from the Sardas landfill has been assumed equal to 29 $m^3$/d, which is equal to the flow underneath the front slurry-wall (Samper *et al.*, 2023). The rest of the flows have been calibrated by using measured hydraulic head data. The Gállego river has been simulated with a Cauchy condition. External heads have been defined by considering a gentle channel slope of 0.0004 and the fluctuations of the water level in the Gállego river due to the oscillations of the reservoir. The leakage coefficient has been taken equal to 50 $m^2$/d. The water flow exchange between the aquifer and the reservoir has been simulated with a Cauchy condition. The leakage coefficient has been calculated according to: $\alpha = \frac{\left(K_V \cdot A_{node}\right)}{e}$; where $K_V$ is the vertical hydraulic conductivity of the silting sediments or natural silts located below the reservoir, $A_{node}$ is nodal area and $e$ is the estimated thickness of the silting sediments or natural silts underlying the reservoir. The natural silts underneath the reservoir are more compacted than reservoir silting sediments. Therefore, $K_V$ of the reservoir silting sediments is expected to be larger than the $K_V$ of the natural silts. $K_V$ of the silting sediments was calibrated equal to 0.1 m/d and $K_V$

of the silts was taken equal to 0.01 m/d. A Cauchy condition was adopted for the flow underneath the Sabiñánigo dam with a fixed hydraulic head equal to 758 m and a leakage coefficient equal to 80 m²/d.

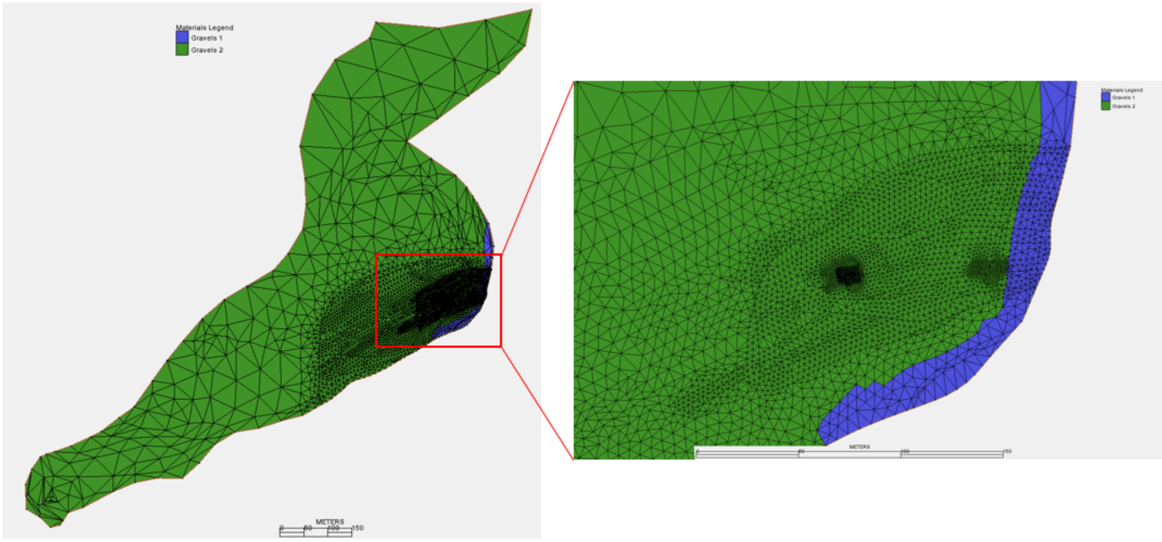


FIGURE 2. 2D MODEL FINITE ELEMENT MESH AND MATERIAL ZONES OF THE ENTIRE AQUIFER (LEFT) AND ENLARGEMENT NEAR THE SARDAS LANDFILL (RIGHT). MODEL CALIBRATION, SENSITIVITY ANALYSES AND RESULTS

Sensitivity runs indicate that increasing the $S_S$ or reducing the $K_V$ of the natural silts and silting sediments reduces the variability of the computed hydraulic head in gravels and increases the time lag between the oscillations of the reservoir water level and the oscillations of the computed hydraulic heads in the aquifer. They also indicate that reducing the leakage coefficient of the Gállego riverbed increases the average computed hydraulic head in the alluvial and reduces its fluctuations. The model was calibrated by using measured hydraulic heads in 8 boreholes monitored with divers from July to October 2020.

The hydraulic gradient is very low in the aquifer due to the large hydraulic conductivity of alluvial and the small inflows into the aquifer. Measured hydraulic heads are closely related to the Sabiñánigo reservoir water level, but they show a slight damping and time lag. The damping and time lag are the result of a combination of the storage effect in the sands and gravels and the flow barrier effect of the natural silts and the silting sediments. The computed hydraulic heads reproduce the oscillations of the measured hydraulic heads (Figure 3).

Reservoir water level fluctuates daily with an amplitude of approximately 1 m. When reservoir water level rises and becomes higher than the hydraulic head in the alluvial, water starts flowing from the Sabiñánigo reservoir into the aquifer and the hydraulic head in the alluvial starts rising. The direction of the groundwater velocity reverses from the usual E-W/NE-SW direction to W-E/SW-NE direction. Once the hydraulic head in the alluvial rises above the reservoir water level, the groundwater velocity recovers its original E-W/NE-SW direction. Figure 4 shows maps of the directions of the groundwater velocity during a reservoir water level rise event which took place from 20:30 September 18 to 05:00 September 19, 2020.

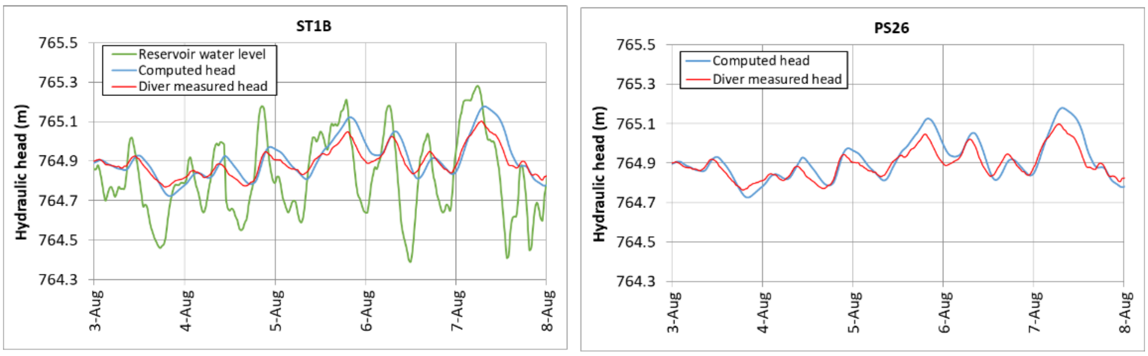



FIGURE 3. MEASURED HYDRAULIC HEADS WITH DIVER (RED LINES), COMPUTED HYDRAULIC HEADS (BLUE LINES) IN ST1B AND PS26 BOREHOLES AND RESERVOIR WATER LEVEL (GREEN LINES) FROM AUGUST 3RD TO AUGUST 8TH 2020

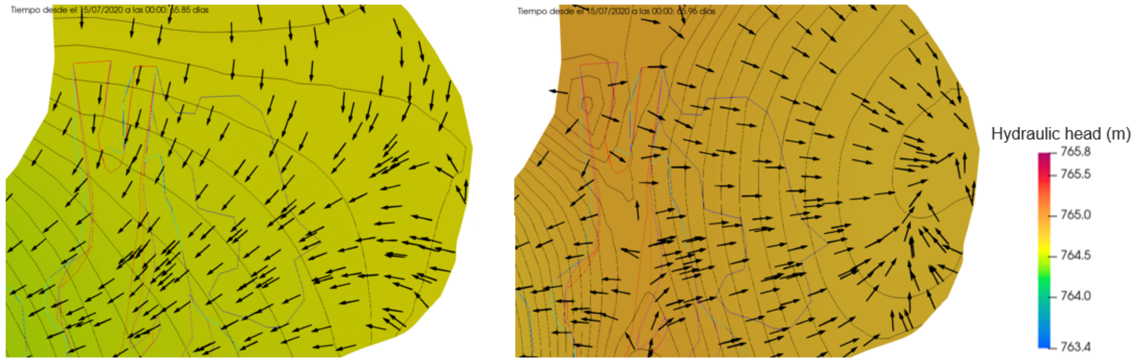



FIGURE 4. CONTOUR LINES OF COMPUTED HYDRAULIC HEADS AND DIRECTIONS OF THE GROUNDWATER VELOCITY FOR LOW RESERVOIR LEVEL (LEFT) AND HIGH RESERVOIR LEVEL (RIGHT)

### *2D contaminant transport model*

#### *3.1. Conceptual model*

A 2D numerical model that simulates the transport of the total dissolved HCH has been performed by assuming steady-state groundwater flow. The simulation period for the transport model extends from 1975 to 2022. Time increments are equal to 3.04 days.

The initial concentration of dissolved HCH is $10^{-9}$ µg/L. The porosity is 0.15. The longitudinal and transversal dispersivities are equal to 10 and 1 m, respectively. The diffusion coefficient in water ($D_0$) is equal to $10^{-10}$ $m^2/s$. The model assumes that the dissolved HCH is in equilibrium with the HCH in the solids and the DNAPL with a constant distribution coefficient, $K_d$, equal to 3 L/kg.

#### *3.2. Boundary conditions and source terms*

The inflow of water from the landfill into the model domain in the period (1976, 1997) was assumed equal to 7.41 $m^3/d$. This inflow was assumed to have a concentration of total dissolved HCH equal to 2348 µg/L. During the construction of the N-300 road, wastes from the landfill were deposited in the Gállego river floodplain, less than 200 m from the Sabiñánigo reservoir. The HCH concentration of the inflow after the construction of the front slurry-wall was reduced to 1174 µg/L. Areas with DNAPL were assumed to be sources of HCH.

#### *3.3. Model calibration and sensitivity analyses*

The extent of the HCH source terms have been calibrated from DNAPL data, measured dissolved COCs concentrations in the boreholes and the plume of measured dissolved HCH. In the first stages of the model calibration, the distribution coefficient was taken from Lorenzo *et al.* (2020). The results of the sensitivity runs indicated that the HCH plume computed with the $K_d$ values reported by Lorenzo *et al.* (2020) was much smaller than the measured HCH plume reported by EMGRISA (2020). The computed plume of the concentrations of total dissolved HCH and the mass flux of dissolved HCH are very sensitive to changes in the distribution coefficient. The best fit of the total dissolved HCH concentration data is obtained with $K_d$ ranging from 2 to 5 L/kg.

#### *3.4. Results*

The total dissolved HCH concentrations measured in boreholes may be affected by the presence of DNAPL at the contact between gravels and the underlying marls (EMGRISA, 2020). The concentrations of total dissolved HCH in two nearby boreholes ST1D and ST1E show large differences. The concentration in borehole ST1D drilled entirely in gravels is equal to 48 µg/L while the concentration in borehole ST1E (which penetrates 60 cm into the underlying marls) is equal to 421 µg/L. Given the large time variability of the measured total dissolved HCH concentration data in the alluvial boreholes and the uncertainties of these measurements, model calibration was not performed on the basis of time series of HCH concentrations. Instead, a HCH concentration interval was computed for each borehole. For a given borehole, the concentration interval is given by $(\mu \pm 2\sigma; \mu + 2\sigma)$ where $\mu$ is the average measured dissolved HCH concentration and $\sigma$ is the standard deviation of the HCH data. The computed total dissolved HCH concentrations at the 35 boreholes having HCH measurements were compared with these intervals. The computed concentrations of HCH are within the uncertainty intervals $[(\mu \pm 2\sigma; \mu + 2\sigma)]$ in 28 out of 35 boreholes.

Figure 5 shows the plume of measured total dissolved HCH concentrations reported by EMGRISA (2020) and computed plume of total dissolved HCH concentrations in December 2020. The plot also shows the concentration intervals for each borehole.

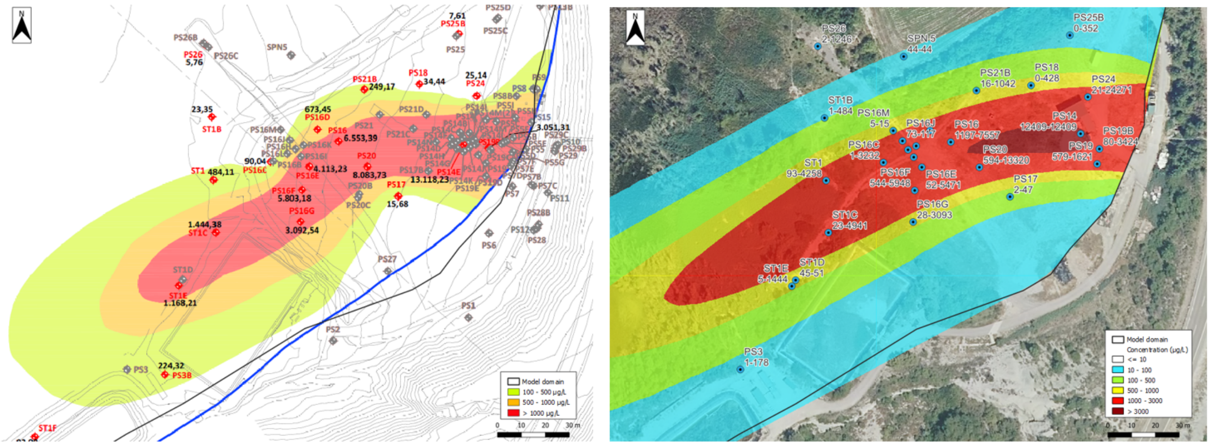


FIGURE 5. PLUME OF MEASURED TOTAL DISSOLVED HCH (EMGRISA, 2020) (LEFT) AND COMPUTED PLUME OF THE DISSOLVED HCH (RIGHT) WITH A DISTRIBUTION COEFFICIENT EQUAL TO 3 L/KG IN DECEMBER 2020. INTERVALS OF TOTAL DISSOLVED HCH CONCENTRATIONS ARE GIVEN FOR EACH BOREHOLE IN THE RIGHT PLOT

## *Conclusions*

2D finite element groundwater flow and total dissolved HCH transport models through the alluvial aquifer of the Gállego river have been presented. The oscillations of the level of the reservoir are transmitted in a damped way and with some delay to the piezometric oscillations in the aquifer. The offset and the damping of the hydraulic heads attest that the alluvial aquifer is not in direct hydraulic contact with the Sabiñánigo reservoir. Water from the alluvial aquifer to the reservoir must go through the silting sediments of the reservoir and the natural silts of the terrace. The direction of the groundwater velocity field changes quickly in a daily basis in response to the oscillations of the reservoir level. The flow direction is E-W/NE-SW under normal conditions when the head in the aquifer is larger than the level in the reservoir. When the reservoir water level increases quickly, the groundwater flow direction reverses to W-E. The E-W/NE-SW flow direction is restored when the hydraulic head in the alluvial rises over the reservoir water level. Model results confirm the validity of the conceptual model and reproduce the measured hydraulic heads in the aquifer.

The computed plume of the total dissolved HCH and the mass flux of dissolved HCH are very sensitive to changes in the distribution coefficient. The best fit to the measured total dissolved HCH data is obtained with $K_d$ values ranging from 2 to 5 L/kg. The flux of dissolved HCH leaving the site towards the Sabiñánigo reservoir is equal to 2.1 kg/year for $K_d$ = 10 L/kg. The lack of recent measured HCH data in the silting sediments prevent a validation of this estimate of the flux. However, this flux estimate is consistent with the HCH fluxes recorded downstream the Sabiñánigo reservoir at the hydropower channel and at the Jabarrella reservoir.

## *Acknowledgments*

This study was performed within the framework of research contracts funded by Ebre Water District and EMGRISA (Company for the Management of Industrial Waste) which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

## *References*

1. CHE, Confederación Hidrográfica del Ebro (2010). Análisis ambiental de los sedimentos y del entorno del embalse de Sabiñánigo (Huesca) y evaluación de riesgos. Informe técnico de la Confederación Hidrográfica del Ebro. Ministerio de Medio Ambiente.

2. Fernández J., Arjol M.A. y Cacho C. (2013) POP-contaminated sites from HCH production in Sabiñánigo, Spain. Environ Sci Pollut Res (2013) 20:1937–1950. DOI 10.1007/s11356-012-1433-8.

3. EMGRISA 2020. Servicio de seguimiento Hidrogeológico de Sardas, Sabiñánigo (Huesca) 2019-2020. Expediente: 1404-4422-2019/19. Memoria anual 2020. Febrero de 2021.

4. Lorenzo, D., R. García-Cervilla, A. Romero, A. Santos (2020). Partitioning of chlorinated organic compounds from dense nonaqueous phase liquids and contaminated soils from lindane production wastes to the aqueous phase. Chemosphere 239, 124798.

5. Samper J, Yang C, Zheng L, Montenegro L, Xu T, Dai Z, Zhang G, Lu C y Moreira S (2011). CORE$^{2D}$ V4: A code for water flow, heat and solute transport, geochemical reactions, and microbial processes, Chapter 7 of the Electronic book Groundwater Reactive Transport Models, F Zhang, G-T Yeh, C Parker & X Shi (Ed), Bentham Science Publishers, pp 161- 186, ISBN 978-1-60805-029-1.

6. Samper, J, B Sobral & B Pisani (2023). 3D groundwater flow and contaminant transport model of the Sardas landfill (Huesca, Spain). 14th

International HCH & Pesticides Forum. Zaragoza, Spain. Government of Aragon, in this issue.
7. Schonard (2016). Directorate General for Internal Policies Policy Department C: Citizens' Rights and Constitutional Affairs. Lindane (persistant organic pollutant) in the EU.
8. Vijgen J, Borst B, Weber R, Stobiecki T, Forter M (2019). HCH and lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue. Enviromental Pollution, 248:696-705.

# TRACER TESTS IN THE HCH-AFFECTED ALLUVIAL AQUIFER DOWNSTREAM THE SARDAS LANDFILL (HUESCA, SPAIN)


*J Gómez[1], J Guadaño[1], Javier Samper[2], Brais Sobral[2], Jesús Suso[3] & Jesús Fernández[4]*

[1]*Empresa para la Gestión de Residuos Industriales, S.A., S.M.E., M.P., EMGRISA. Madrid;*
[2]*ET.S. Ingenieros de Caminos, Canales y Puertos. CICA, Centro de Investigaciones Científicas Avanzadas, Universidade de A Coruña. Campus de Elviña 15071 A Coruña;*
[3]*Profesional libre. Madrid;* [4]*Departamento de Suelos. Gobierno de Aragón*



## Summary

HCH and other COCs have migrated through the Gállego river alluvial aquifer downstream the Sardas landfill, which is located on the left bank of the Gállego river, less than 500 m from the Sabiñánigo reservoir. Tracer tests were performed in 2022 to quantify groundwater velocity under ambient conditions and characterize aquifer parameters and heterogeneities. A dilution test was performed on Feb 8th by adding salt water in borehole PS16H and recording electrical conductivity logs. Darcy velocity was estimated to range from 0.022 m/d to 0.052 m/d. A long-term Br tracer test was performed from June 30 to September 23 by injecting 300 L of a traced NaBr solution in 1 hour into the PS16H borehole. Tracer concentrations were monitored periodically for three months in several downstream boreholes. The test was successful in providing the tracer breakthrough curves in boreholes PS16L and PS16J located around 4 m from the injection borehole. The peak tracer concentration in PS16L occurred after 18 days. The average water velocity was estimated to be about 0.25 m/d. A numerical model of the tracer test was performed to support the design of the tracer test and provide guidance during its execution. The transport parameters and boundary conditions of the numerical model were dynamically updated during the test by incorporating the measured tracer data. The best fit of the numerical model to measured tracer concentration data lead to the following results: 1) Darcy velocity which fluctuated during the test due to the oscillations of the reservoir level ranges from 0.01 m/d to 0.09 m/d); 2) The porosity of the alluvial deposits ranges from 0.15 to 0.25; and 3) The longitudinal dispersivity ranges from 1 to 2 m while the transversal dispersivity varies from 0.25 m to 0.5 m. The results of the tracer test confirm the conceptual model of the groundwater flow through the alluvial aquifer and provide useful information about the heterogeneities of the sands and gravels and the solute transport parameters.



## Keywords

HCH, lindane, landfill, numerical model, 2D model, tracer test, bromide, Sardas.


## Introduction

HCH was used as a pesticide during the 1950s and 1960s. However, its use was later found to be harmful to human health. Companies started working on the isolation of the ɣ isomer, known as lindane, which in the right concentration would be tasteless and harmless (Vijgen et al., 2019). Lindane was banned in the European Union in 2008 and HCH isomers were included in the Stockholm Convention's list of Persistent Organic Pollutants in 2009 (Schonard, 2016). In Spain, the INQUINOSA factory disposed in an uncontrolled manner powder and liquid residues from lindane production at the Sardas landfill (Fernández et al., 2013). Alluvial materials from the Gállego river meander located west of the Sardas landfill are a key element for migration of pollutants into the Sabiñánigo reservoir. A series of hydraulic and tracer tests were performed on the Gállego river alluvial to quantify groundwater flow velocity and characterize the alluvial formation parameters and heterogeneities. Here we present the main results of the tracer tests and the numerical models used to predict and interpret the tracer breakthrough curves.

## Tracer tests

The location of the tracer test area is shown in Figure 1. Two dilution tests were conducted in borehole PS16H to estimate the horizontal groundwater flow velocity on Feb 8th 2022. A high NaCl concentration was used as tracer. Tracer dilution was monitored by performing periodic electrical conductivity logs in the injection well. Darcy velocity was estimated to range from 0.022 m/d to 0.052 m/d. These values are coherent with the Darcy velocities of the 2D groundwater flow model of the alluvial aquifer (see Samper et al., 2023 in this issue).

A long-term Br tracer test was performed from June 30 to September 23 to better quantify groundwater flow velocity and characterize the alluvial formation parameters and heterogeneities. 300 L of a traced NaBr solution were injected in 1 hour into the PS16H borehole (Figure 1). The injected water was recirculated to ensure vertical mixing.

Br concentrations were monitored in 5 observation boreholes (PS16H, PS16L, PS16J, PS16I and PS16K). Only the injection well (PS16H) and boreholes PS16L and PS16J located downstream the PS16H well showed tracer breakthrough curves. PS16L and PS16J concentrations were monitored every 3 hours for the first 6 days, every 4 hours from the 6th day, every 6 hours from the 19th day and every day from the 32nd day onwards. Figure 2 shows the measured Br concentrations in the injection well (PS16H) and the tracer breakthrough curves at the observation boreholes PS16L and PS16J.

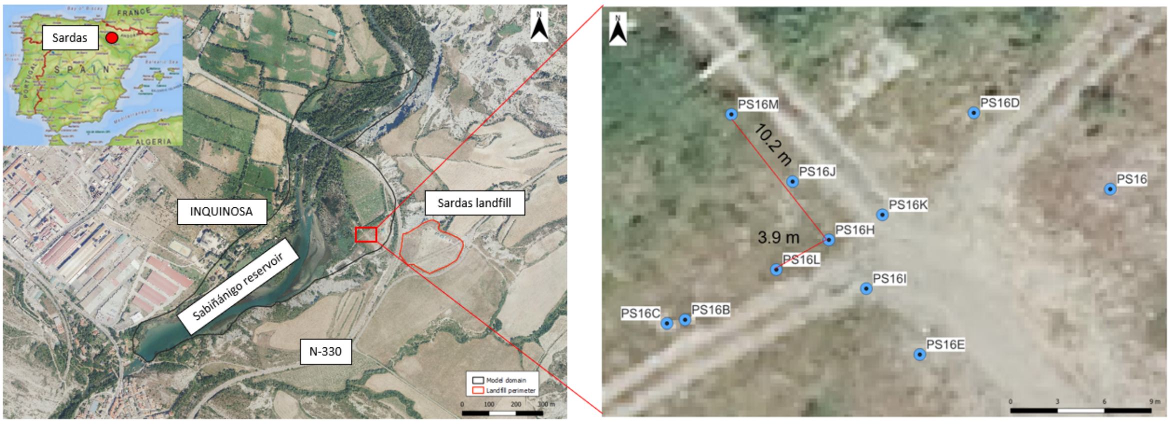



**FIGURE 1. LOCATION OF THE STUDY AREA (LEFT). MODEL DOMAIN, BOREHOLES IN THE TRACER TEST AREA AND DISTANCES OF OBSERVATION BOREHOLES FROM THE INJECTION WELL PS16H (RIGHT).**

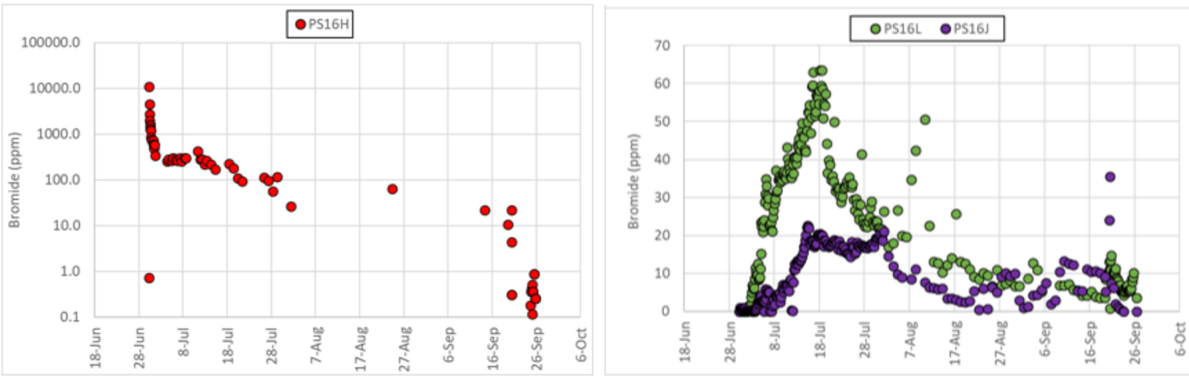



**FIGURE 2. BR CONCENTRATION MEASURED AT THE INJECTION WELL (LEFT FIGURE) AND AT MONITORED BOREHOLES PS16L AND PS16J (RIGHT FIGURE) DURING THE TRACER INJECTION TEST**

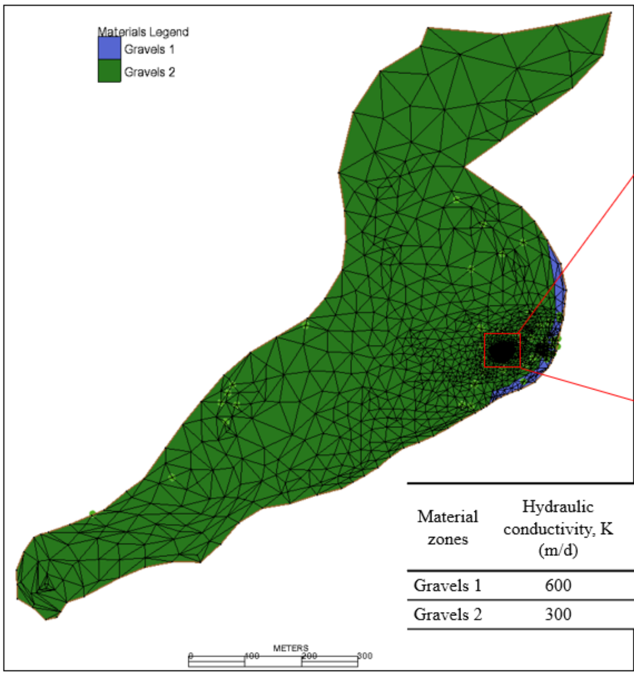
### *Numerical model*

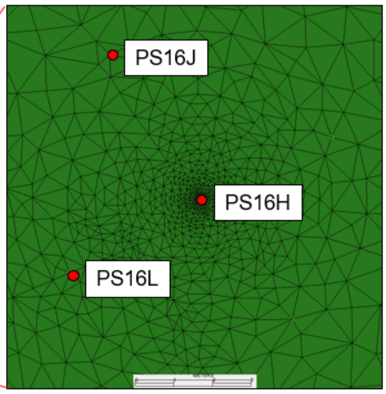
A numerical model of the tracer test was performed to plan and define the tracer test, provide support during its execution, and quantify groundwater flow velocity in the vicinity of the PS16 series boreholes.

The test was modelled with a 2D horizontal groundwater flow model which assumes vertical homogeneous mixing of the tracer and that the water flows through the entire sequence of sands and gravels of the Gállego alluvial system (Samper et al., 2023). The finite element grid of the 2D numerical flow model of the Gállego alluvial aquifer of Samper et al. (2023, in this issue) was reshaped in the vicinity of the test area. The numerical 2D horizontal model domain is discretized with a triangular finite element mesh with 2582 nodes and 5066 elements. The model domain includes the entire influence area of the Sabiñánigo reservoir, from the dam to upstream the N-330 bridge. To ensure the accuracy of the model results around the injection well, the grid was refined near the injection borehole PS16H borehole. Grid size increases from the injection well with a geometric progression. Figure 3 shows the finite element grid, the material zones and the hydraulic and transport parameters.

The simulation period is 109 days long and extends from June 30 to September 18, 2022. Reservoir and borehole hydraulic heads were measured every 2 minutes. Prior models were calculated with 2-minute time increments, however, since the test lasted 88 days in total, the time increments were increased from 2 to 30 minutes. The tracer extraction phase was not considered for model calibration.

The model was solved with CORE$^{2D}$ V5 code (Samper et al., 2011). CORE$^{2D}$ is a finite element code that solves the flow, heat transfer and solute transport equations in media with irregular boundaries and non-uniform physical and geochemical properties.




| Material zones | Hydraulic conductivity, K (m/d) | Specific storage coefficient, $S_S$ ($m^{-1}$) | Porosity, φ | Longitudinal dispersivity (m) | Transversal dispersivity (m) |
|---|---|---|---|---|---|
| Gravels 1 | 600 | $6 \cdot 10^{-4}$ | 0.15 – 0.2 | 0.5 – 2 | 0.25 |
| Gravels 2 | 300 | $6 \cdot 10^{-4}$ | 0.15 – 0.2 | 0.5 – 2 | 0.25 |

**FIGURE 3. 2D MODEL FINITE ELEMENT GRID AND MATERIAL ZONES (LEFT). ENLARGEMENT OF TRACER TEST AREA (RIGHT) AND TABLE OF HYDRODYNAMIC AND TRANSPORT PARAMETERS OF THE TWO MATERIAL ZONES.**

## *Results and discussion*

Predictions of tracer concentrations were calculated with the model by using the a priori estimates of hydraulic and transport parameters. The Br concentration peak in observation borehole PS16L was expected to occur 1 to 2 weeks after injection. Model parameters were re-examined and updated as more tracer data became available. The peak of the Br concentration in borehole PS16L was detected 18 days after tracer injection.

*3.1. Hydraulic heads*

Measured hydraulic heads in the alluvial aquifer are closely related to the water level of the Sabiñánigo reservoir, but they show a slight damping and time delay. The computed hydraulic heads fit the measured data, although the computed heads are slightly higher than measured heads. Inflows through the banks of the Gállego river alluvial were considered constant in the model. The differences between calculated and measured heads could be partly related to the time variability of the inflows from boundaries.

*3.2. Groundwater flow velocities*

The computed Darcy velocity at the injection borehole PS16H increased to 3.4 m/d during the tracer injection. After the tracer injection, ambient conditions were recovered immediately. The computed Darcy velocity is equal to 0.04 m/d. The average flow velocity ranges from 0.29 to 0.22 m/d for porosities ranging from 0.15 and 0.25, respectively.

Figure 4 shows the time evolution of the Sabiñánigo reservoir water level, the measured hydraulic head in borehole PS16C and the angle that the computed groundwater velocity forms with the E-W direction (counterclockwise). As reported by Samper *et al.* (2023, this issue), the oscillations of the reservoir level produce oscillations in the hydraulic heads in the alluvial. The flow direction is E-W/NE-SW under normal conditions when the head in the aquifer is larger than the level in the reservoir. When the reservoir water level increases quickly, the groundwater flow direction reverses to W-E. The E-W/NE-SW flow direction is restored when the hydraulic head in the alluvial rises over the reservoir water level.

*3.3. Tracer breakthrough curves*

Porosity greatly determines the tracer migration velocity because water velocity is equal to Darcy velocity divided by porosity. Prior porosity estimates before the tracer test ranged from 0.05 to 0.08. Figure 5 shows the comparison between measured and calculated Br breakthrough curves in the injection borehole PS16H and the observation boreholes PS16L and PS16J for several combinations of porosity, longitudinal dispersivity and transverse dispersivity.

The best fit of the breakthrough curves is achieved with porosities with the range (0.15, 0.25), a longitudinal dispersivity equal to 1 m and a transverse dispersivity equal to 0.25 m. The model reproduces the shape of the breakthrough curves in observation boreholes PS16L and PS16J. However, it does not reproduce accurately the tail of the breakthrough curves. The breakthrough curve in borehole PS16J shows concentration spikes up to 68 days after injection that cannot be reproduced with the 2D tracer test model which assumes full mixing through the entire thickness of the alluvial aquifer.

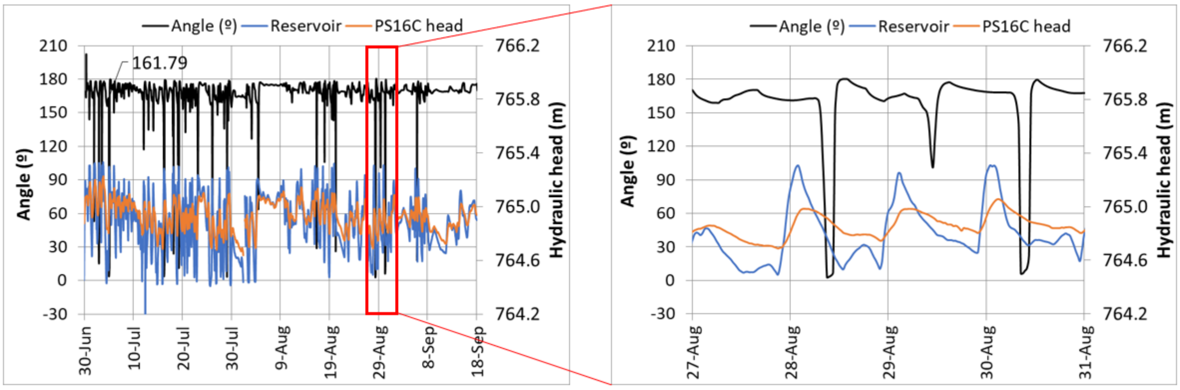



FIGURE 4. TIME EVOLUTION OF THE SABIÑÁNIGO RESERVOIR WATER LEVEL AND MEASURED HYDRAULIC HEADS IN BOREHOLE PS16C AND THE COMPUTED ANGLE THAT THE FLOW DIRECTION FORMS WITH THE E-W DIRECTION (COUNTERCLOCKWISE)

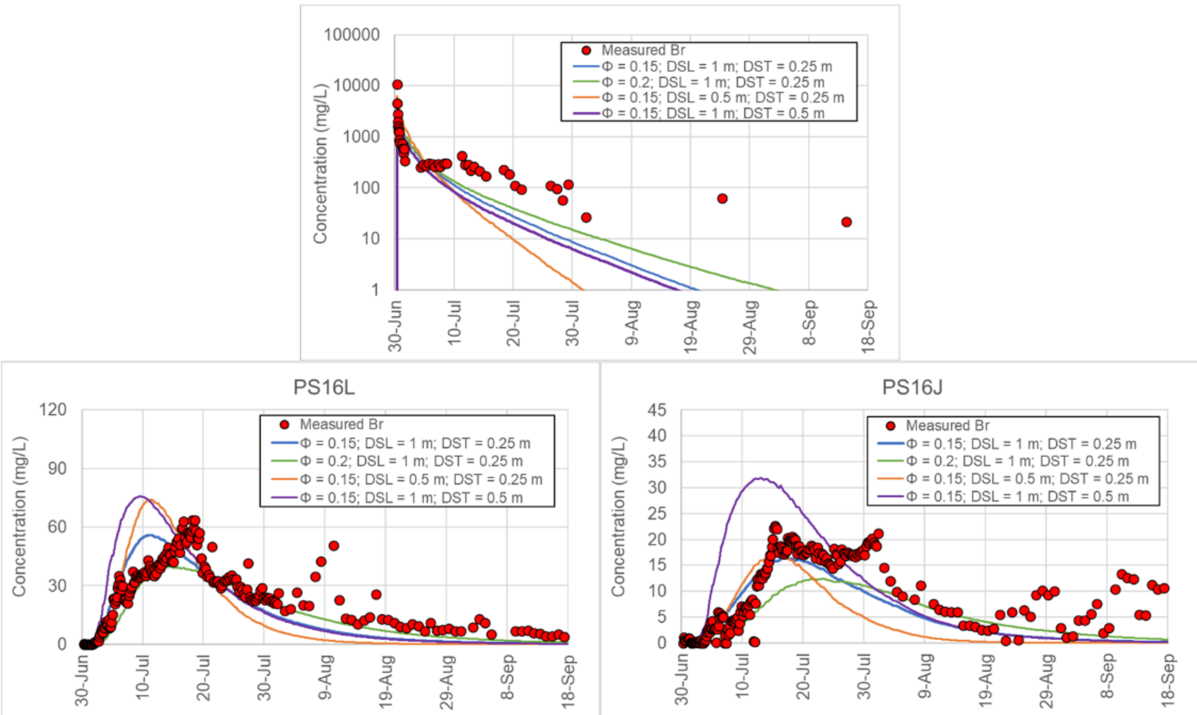



FIGURE 5. MEASURED (SYMBOLS) AND COMPUTED BR BREAKTHROUGH CURVES (SOLID LINES) IN THE INJECTION BOREHOLE PS16H AND THE OBSERVATION BOREHOLES PS16L AND PS16J FOR SEVERAL SENSITIVITY RUNS

## *Conclusions*

We have presented tracer tests which were performed in 2022 in the Sardas site to quantify groundwater velocity under ambient conditions and characterize aquifer parameters and heterogeneities. The dilution test provided an estimate of the Darcy velocity which ranged from 0.022 m/d to 0.052 m/d. The long-term Br tracer test was successful in providing the tracer breakthrough curves in boreholes PS16K and PS16L located around 4 m away from the injection borehole. The peak tracer concentration in PS16L occurred after 18 days. The average water velocity was estimated to be about 0.25 m/d. A numerical model of the tracer test was performed. The transport parameters and boundary conditions of the numerical model were dynamically updated during the test by incorporating the measured tracer data. Darcy velocity fluctuated during the test due to the oscillations of the reservoir level and ranged from 0.01 m/d to 0.09 m/d. The best fit is achieved with a porosity of the alluvial deposits in the range (0.15, 0.25). The longitudinal dispersivity ranges from 1 to 2 m while the transversal dispersivity varies from 0.25 m to 0.5 m. The results of the tracer test confirm the conceptual model of the groundwater flow through the alluvial aquifer and provide useful information about the heterogeneities of the sands and gravels and the solute transport parameters.

## *Acknowledgments*

This study was performed within the framework of research contracts funded by EMGRISA (Company for the Management of Industrial Waste) which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

### *References*

Fernández J., Arjol M.A. y Cacho C. (2013) POP-contaminated sites from HCH production in Sabiñánigo, Spain. Environ Sci Pollut Res (2013) 20:1937–1950. DOI 10.1007/s11356-012-1433-8.

Samper J, Yang C, Zheng L, Montenegro L, Xu T, Dai Z, Zhang G, Lu C y Moreira S (2011). CORE$^{2D}$ V4: A code for water flow, heat and solute transport, geochemical reactions, and microbial processes, Chapter 7 of the Electronic book Groundwater Reactive Transport Models, F Zhang, G-T Yeh, C Parker & X Shi (Ed), Bentham Science Publishers, pp 161-186, ISBN 978-1-60805-029-1.

Samper, J, B Sobral y B Pisani (2023). 2D model of groundwater flow and dissolved HCH transport through the Gállego river alluvial aquifer downstream the Sardas HCH landfill (Huesca, Spain). 14th International HCH & Pesticides Forum. Zaragoza, Spain. Government of Aragon (this issue).

Schonard (2016). Directorate General for Internal Policies Policy Department C: Citizens' Rights and Constitutional Affairs. Lindane (persistant organic pollutant) in the EU.

Vijgen J, Borst B, Weber R, Stobiecki T, Forter M (2019). HCH and lindane contaminated sites: European and global need for a permanent solution for a long-time neglected issue. Enviromental Pollution, 248:696-705.

# 3D GROUNDWATER FLOW AND CONTAMINANT TRANSPORT MODEL OF THE SARDAS LANDFILL (HUESCA, SPAIN)

***Javier Samper[1], Brais Sobral[1], Bruno Pisani[1], Luis Montenegro[1], Joaquín Guadaño[2], Jorge Gómez[2], Jesús Fernández[3]***

*[1]ET.S. Ingenieros de Caminos, Canales y Puertos. CICA, Centro de Investigaciones Científicas Avanzadas. Universidade de A Coruña. Campus de Elviña 15071 A Coruña;*
*[2]Empresa para la Gestión de Residuos Industriales, S.A., S.M.E., M.P., EMGRISA. Madrid;*
*[3]Departamento de Suelos. Gobierno de Aragón*

***Summary***

INQUINOSA's lindane factory in Sabiñánigo (Spain) operated from 1975 to 1992 and produced more than 150 000 t of waste with a high content of HCH (hexachlorocyclohexane) and other chlorinated compounds. This waste was dumped at the Sardas landfill, located on the left bank of the Gállego river. The landfill was poorly sealed in 1997. The average water inflow into the landfill is equal to 36.9 m³/d. Most of the inflow takes place in the lowest areas of the landfill perimeter. Here we present 3-dimensional (3D) transient groundwater flow and contaminant transport models of the Sardas landfill performed with MODFLOW 6. The model domain includes the landfill and the surrounding bedrocks. The simulation period extends from October 1, 2011 to September 29, 2022. Flow model parameters have been calibrated with hydraulic head data collected at 40 boreholes drilled in the landfill and its surroundings. The results of the 3D flow model confirm that water leaves the landfill underneath the frontal bentonite wall through the shallow layer of altered, fractured and decompressed marls. Other outflows include water pumping and water collected in the lowest parts of the landfill perimeter ditches. The transport model accounts for the migration of total dissolved HCH. The total flux of dissolved HCH is estimated to be equal to 12.4 kg/year. The 3D models of the Sardas landfill provide a tool to quantify landfill water inflows and outflows and the contaminant mass flux leaving the landfill. This tool should be most useful to assess and compare landfill management actions regarding pumping rates, water inflow reductions and drainage systems.

***Keywords***

HCH, lindane, landfill, numerical model, 3D model, MODFLOW, Sardas

### *Introduction*

Lindane and other HCH isomers were included in the Stockholm Convention's list of Persistent Organic Pollutants in 2009 (Schonard, 2016). The sites affected by lindane production in Spain include the INQUINOSA factory in Sabiñánigo (Huesca) and the Sardas landfill where more than 400 Dm³ of urban, construction and industrial solid wastes, including those from lindane production (between 30 and 80 Gg) were disposed in the late 1970s in an uncontrolled manner (Fernández et al., 2013). Here we present a 3D transient groundwater flow and contaminant transport model of the Sardas landfill which provides a tool to quantify landfill water inflows and outflows and the contaminant mass flux leaving the landfill.

### *Sardas landfill*

The Sardas landfill is located on a gully system carved on the Larrés marls formation (middle Eocene -Lutetian) by the erosive action of the tributary hydrographic network of the left bank of the Gállego river. It is located near the Sabiñánigo reservoir (Figure 1). The landfill occupies two ravines with an areal extent of 4 ha. The upper surface of the Sardas landfill was sealed with a 2 mm thick HDPE sheet. A slurry-wall 75 m long, 0.5 m thick with variable depth up to the underlying marls was constructed in the downstream part of the landfill to prevent water outflow from the landfill. The rest of the landfill perimeter was sealed with a 0.5 m thick concrete wall reaching the underlying marls to prevent water inflows from the surrounding rock. Perimeter drainage ditches were constructed to collect the surface runoff and the interflow from the landfill. However, the ditches are not collecting all the surface runoff and the interflow, thus allowing for some water inflows into the landfill underneath the concrete wall. Figure 2 shows a conceptual diagram for the water inflows from the perimeter ditches of the landfill at the contact between the cover layer and the bentonite/cement side wall along the perimeter of the landfill.

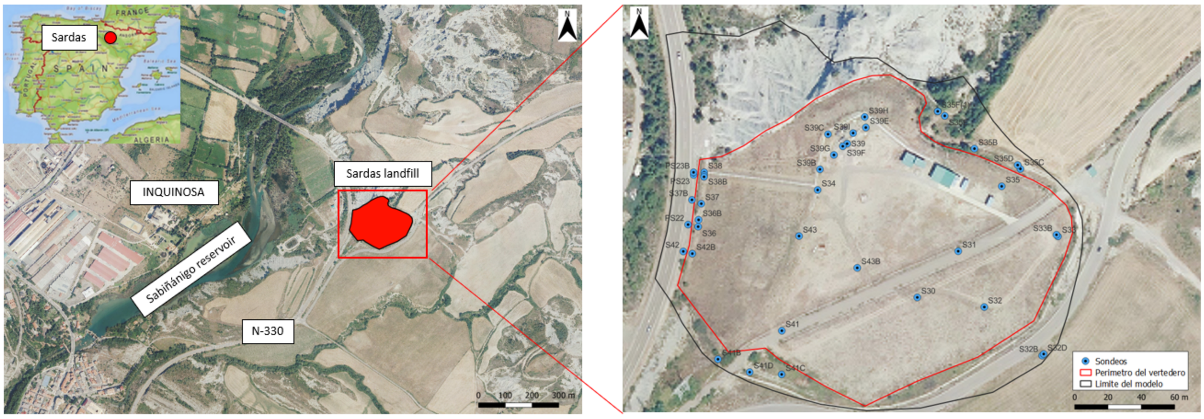



FIGURE 1. LOCATION OF THE STUDY AREA (LEFT) AND MODEL DOMAIN, LANDFILL PERIMETER AND MONITORING BOREHOLES (RIGHT)

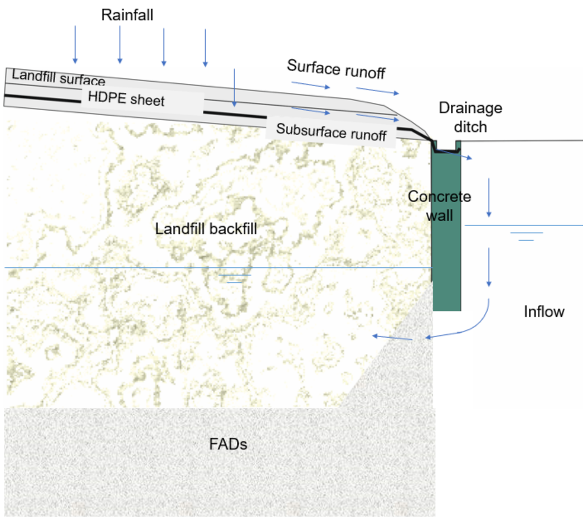



FIGURE 2. DIAGRAM OF THE SURFACE RUNOFF AND INTERFLOW AT THE CONTACT BETWEEN THE LANDFILL COVER LAYER AND THE CONCRETE WALL

### *Transient 3D groundwater flow numerical model*

3D steady-state and transient groundwater flow models of the landfill and the underlying and surrounding geological materials were performed with MODFLOW6 3.0 (Langevin et al., 2020). The model domain in the horizontal plane is shown in Figure 1. The steady-state flow model was calibrated with average hydraulic heads. Then, it was used to specify the upper boundary of the 3D transient flow model.

The thickness of the landfill deposits was estimated from historical digital mapping of the ground surface before the waste disposal. The model includes a 5 m thick layer of fractured, altered and decompressed (FAD) marls underneath the landfill and the surrounding glacis layers. The numerical 3D model domain was discretized with a finite differences grid. ModelMuse 4.3.0 (Winston, 2020) has been used as graphical interface to define the grid and analyze the results. The model has 14 layers and 68 170 cells. Cell size is 4 x 4 m, except near the slurry-wall where the grid was refined with 1 x 1 m cells. The simulation period extends from October 1, 2011, to September 29, 2022. Time increments are all equal to 1 day.

The spatial variability of the hydrogeological parameters was implemented in the model by defining material zones within which all the cells share the same hydrodynamic parameters (hydraulic conductivity, K, specific storage, SS and specific yield, Sy). Eighteen material zones were considered in the numerical model (Fig. 3). Prior estimates for these parameters were derived from the interpretation of pumping and slug tests performed in S30, S32D, S38, S38B and S41D boreholes.

#### *1. Boundary conditions*

Samper *et al.* (2019) identified the following inflows to the Sardas landfill materials upstream the front slurry-wall: 1) Infiltration of surface runoff from ravines upstream the landfill; 2) Flows underneath the perimeter walls coming from the runoff and interflow of the landfill cover; 3) Recharge of a small fraction of rainwater through the cover layer; and 4) Flows underneath the perimeter walls from subsurface flows from the surrounding glacis, silts, and marls. Outflows from the landfill include: 1) Groundwater discharge underneath the front slurry-wall through the shallow marls and through the north end of the slurry-wall; 2) Water pumping in well S37 to control the hydraulic head in the landfill; and 3) Waters collected in drainage systems in near S38C and S35E boreholes.

Water flow into drainage systems was simulated by using a drain boundary condition with a conductance equal to 100 $m^2/d$.

Daily recharge rates were estimated by Samper *et al.* (2020) by using a hydrological water balance model performed with the VISUAL-BALAN code. Daily and monthly pumped water volumes in borehole S37 were provided by EMGRISA. Pumping began in June 2014 and continued intermittently until March 2022.

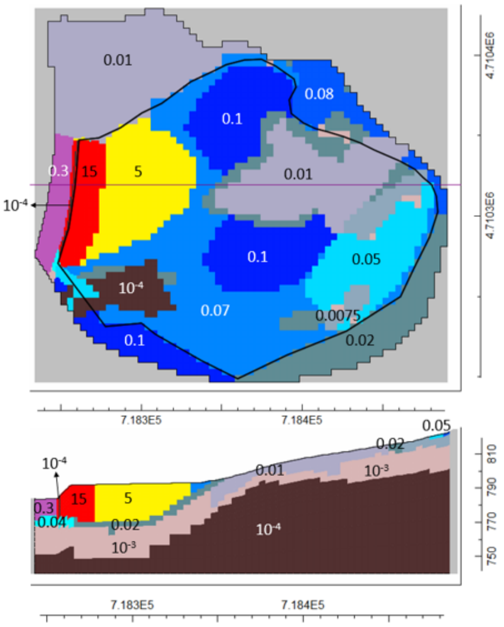
#### *2. Model calibration*

The model was used to simulate and interpret two pumping tests performed in 2011 in several boreholes drilled in the landfill materials. The interpretation of the tests indicated that the northwest corner of the landfill acts as a river-like boundary condition. This is a low point where there is evidence of flooding before the pumping campaigns began in borehole S37 located 25 m south of the northwest corner in a high permeability material zone. Hydrodynamic parameters were calibrated to fit the measured hydraulic head data at 40 observation boreholes.

### 3. *Model Results*

Overall, the hydraulic head fit is good. The RSME (root-mean square error) is equal to 1.52 and the absolute mean residual is equal to 1.05 m. The largest residuals are found in boreholes S35D, S38, S38B, S41B, and S41D. Boreholes S38 and S38B are drilled in deep marls and FADs formations, respectively. Measured hydraulic heads in these boreholes are lower than those measured in S38C, which is drilled in landfill materials. This vertical gradient is not reproduced by the model. The measured heads in the boreholes of the S41 series are similar even though the borehole S41 is screened in the landfill and boreholes S41B, S41C, and S41D are screened in the glacis formation southwest of the landfill. Figure 4 shows the comparison of the measured and calculated hydrographs in boreholes PS23B and S38C, which are located upstream and downstream of the front slurry-wall, respectively.

Figure 5 shows the contour lines of the computed hydraulic heads on the shallow layer in September 2022. The hydraulic gradient is large near the upstream ravine (near borehole S35E) where a drainage ditch was constructed in 2021 and also near S41 boreholes due to a low permeability spot. The hydraulic gradient is smallest upstream the slurry-wall where landfill fillings have a large hydraulic conductivity.




| Material zone | Color |
|---|---|
| Backfill downstream of front slurry-wall | |
| Lower section of the backfills upstream of the front slurry-wall 1 | |
| Lower section of the backfills upstream of the front slurry-wall 2 | |
| Backfills in the S39 area upstream of the front slurry-wall | |
| Backfills in the S33 area upstream of the front slurry-wall | |
| Remaining backfills upstream of the front slurry-wall | |
| Northeast glacis | |
| Southeast glacis | |
| Southwest Glacis | |
| FADs in the central zone of the domain | |
| FADs in the front slurry-wall area | |
| FADs in the S35 area | |
| FADs in the S41 area | |
| Remaining FADs | |
| Marls in the S41 area | |
| Deep marls 1 | |
| Deep marls 2 | |
| Front slurry-wall | |

**FIGURE 3. HYDRAULIC CONDUCTIVITIES (M/D) OF THE MATERIAL ZONES IN THE SHALLOW LAYER (UPPER LEFT) AND ALONG THE E-O VERTICAL PROFILE (LOWER LEFT). THE LEGEND OF THE MATERIAL ZONES IS SHOWN IN THE RIGHT PANEL**

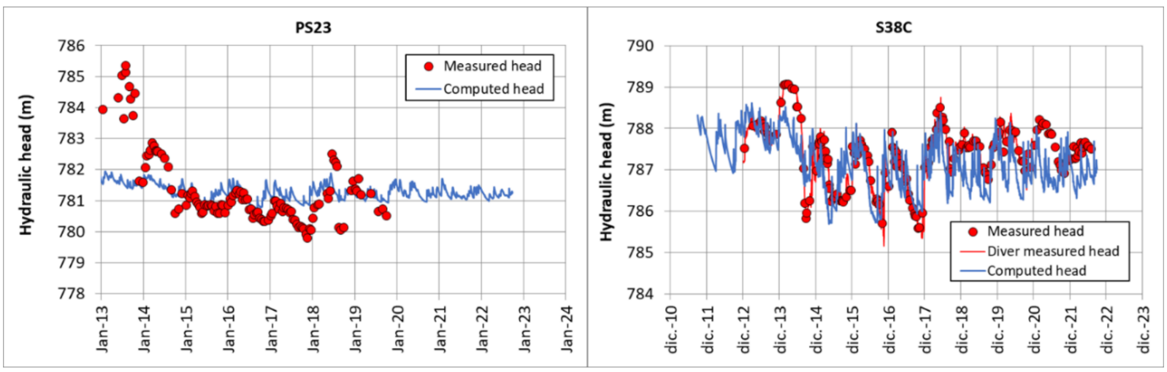



**FIGURE 4. MEASURED (SYMBOLS) AND COMPUTED HYDRAULIC HEADS (BLUE LINE) IN BOREHOLES PS23B AND S38C**

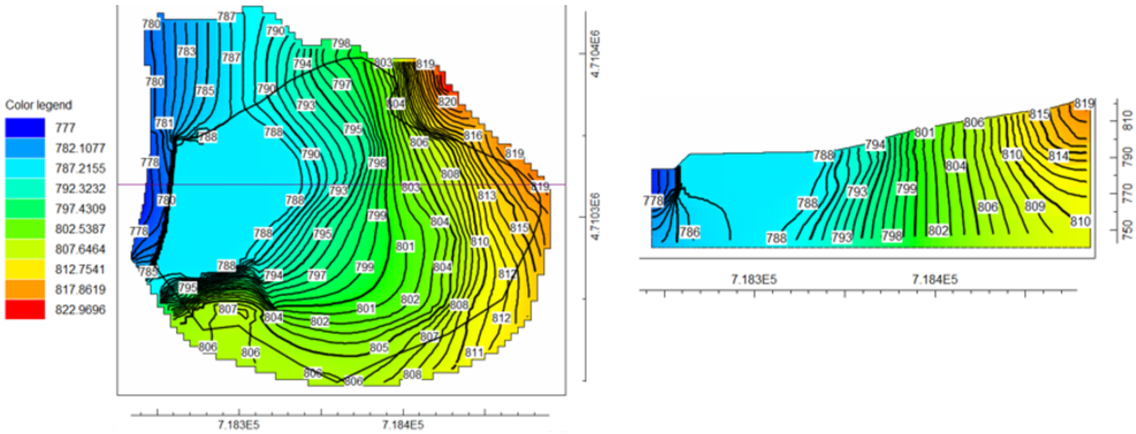



**FIGURE 5. COMPUTED HYDRAULIC HEADS IN THE SHALLOW LANDFILL LAYER (LEFT) AND ALONG A VERTICAL PROFILE THROUGH THE CENTER OF THE LANDFILL (RIGHT) IN SEPTEMBER 2022**

The groundwater balance during the simulation period shows that most of the inflow to the landfill takes place along the NW corner of the landfill with an average inflow of 16.1 $m^3/d$. This amounts to the 44% of the total inflow. The average recharge through the cover is equal to 2.4 $m^3/d$ (7%). The inflows from the rest of the landfill perimeter and from the surrounding bedrock of the model are equal to 18.4 $m^3/d$ (49%). Most of the water discharges underneath the front slurry-wall. This flow is equal to 29.4 $m^3/d$ (77%). The average pumping rate from June 1, 2014 to March 28, 2022, is equal to 5.97 $m^3/d$. The average outflow to the drain located north of the S38 boreholes is equal to 6.40$m^3/d$ from January 2018. The average computed discharge to the drainage ditch located near borehole S35E from April 2021 is equal to 0.53 $m^3/d$.

### *3D contaminant transport model*

A numerical model for the transport of total dissolved HCH has been performed by assuming steady-state groundwater flow conditions. The transport model is based on the 3D flow model presented in the previous section. The simulation period extends from 1975 to 2022. Time increments were taken equal to 10 days.

It is assumed that dissolved HCH is in equilibrium with HCH in the DNAPL phase (in areas where it is present) and HCH sorbed on the solid phase. The equilibrium relationship between the concentrations of total dissolved HCH and sorbed HCH is simulated with a constant distribution coefficient, Kd. Initial estimates of the distribution coefficient, Kd were derived from the values measured by Lorenzo et al. (2020) for 28 COC's from solubility tests in two soil samples taken from the alluvial sediments of the Gállego alluvial aquifer in an area with DNAPL and large HCH concentrations. These values were later adjusted for the conditions of the landfill during the model calibration stage.

The sources of dissolved HCH were estimated from field evidence of DNAPL presence and from measured HCH concentrations in boreholes. Six source areas of dissolved HCH were estimated. The extent of the HCH source zones and the source terms were calibrated to fit the measured total dissolved HCH data in boreholes. These sensitivity runs indicated that: 1) The computed plume of dissolved HCH is very sensitive to the distribution coefficient; and 2) The computed plume of total dissolved HCH migrates very slowly when for the Kd values reported by Lorenzo et al. (2020). The smaller the distribution coefficient, the larger the size of the total dissolved HCH plume. The best fit of total dissolved HCH concentrations is obtained with Kd values ranging from 2 to 5 L/kg. These distribution coefficients are smaller than those reported by Lorenzo et al. (2020) which are deemed to be representative mostly of areas with large HCH concentrations.

The transport model was calibrated with the average measured concentrations of total dissolved HCH because the measured total HCH concentrations data in boreholes show many erratic-like fluctuations. Measuring the total dissolved HCH concentration involves a lot of uncertainties in DNPAL polluted areas.

The fit of the computed total dissolved HCH concentrations to measured data is good, except near the area of the S39 boreholes where DNAPL accumulates and HCH concentrations show a large a large spatial variability. The flux of total dissolved HCH leaving the landfill was estimated as the product of the water flux times the HCH concentration. The estimated HCH mass flux is equal to 12.4 kg/yr and takes place underneath the front slurry-wall.

### *Conclusions*

A 3D transient groundwater flow and contaminant transport model of the Sardas landfill has been presented. Flow parameters were calibrated with hydraulic head data collected at 40 boreholes. The results of the 3D flow model confirm the previous hypotheses about the water inflows and outflows. Most of the inflow to the landfill takes place along the NW corner of the landfill with an average value of 16.1 $m^3/d$. Inflows from the rest of the landfill perimeter and from the surrounding bedrock of the model are equal to 18.4 $m^3/d$. Most of the water discharges underneath the front slurry-wall 29.4 $m^3/d$. The average pumping rate from June 1, 2014 to March 28, 2022, is equal to 5.97 $m^3/d$. The average outflow to the drain located north of the S38 boreholes is equal to 6.40 $m^3/d$ from January 2018. The transport model accounts for the migration of total dissolved HCH. The computed flux of total dissolved HCH leaving the landfill is estimated to be equal to 12.4 kg/year and takes place underneath the front slurry-wall.

***Acknowledgments***

This study was performed within the framework of research contracts funded by EMGRISA which was awarded a Contract for the Hydrogeology of the Sardas landfill by the Aragon Regional Government. We acknowledge the support received from the Aragon Government (Elena Cano) and EMGRISA (Raúl López).

***References***

Fernández J., Arjol M.A. & Cacho C. (2013) POP-contaminated sites from HCH production in Sabiñánigo, Spain. Environ Sci Pollut Res (2013) 20:1937–1950.

Langevin, C.D., Hughes, J.D., Banta, E.R., Provost, A.M., Niswonger, R.G., and Panday, Sorab, 2020, MODFLOW 6 Modular Hydrologic Model version 6.2.0: U.S. Geological Survey Software Release, 22 October 2020, https://doi.org/10.5066/F76Q1VQV.

Lorenzo, D., R. García-Cervilla, A. Romero, A. Santos (2020). Partitioning of chlorinated organic compounds from dense nonaqueous phase liquids and contaminated soils from lindane production wastes to the aqueous phase. Chemosphere 239, 124798

Samper J., Sobral B., Mon A., Pisani B., Naves A., Guadaño J., Motenegro L., y Fernández J. (2019). Modelo de flujo y transporte de solutos del emplazamiento de sardas en Sabiñánigo (Huesca). En: Estudios de la Zona no Saturada Vol XIV, Madrid, 28-30 octubre. 978- 84-948550-8-5.

Samper, J, B Sobral y B Pisani (2020). Hidrogeología y modelos de balance hidrológico, y modelos de flujo subterráneo y transporte de contaminantes en los emplazamientos afectados por INQUINOSA. Actividad 1: La actualización del modelo hidrológico de balance del vertedero, la realización de un modelo preliminar tridimensional (3D) de flujo y transporte de masa del relleno del vertedero y el acoplamiento del modelo de balance con el modelo 3D. Informe Final (Fase 2) de la Actividad 1, ETS Ingenieros de Caminos, Coruña, UDC, agosto 2020.

Schonard (2016). Directorate General for Internal Policies Policy Department C: Citizens' Rights and Constitutional Affairs. Lindane (persistant organic pollutant) in the EU.

Winston, R.B., 2020, ModelMuse version 4.3: U.S. Geological Survey Software Release, 16 August 2020, https://doi.org/10.5066/P9XMX92F.

# DIAGNOSIS OF LINDANE CONTAMINATION OF THE SARDAS LANDFILL (SABIÑÁNIGO) IN THE GÁLLEGO RIVER AND PROPOSAL FOR ACTION

***Rodríguez-Arévalo, J.[1], Castaño, S.[1], Martín-Ruiz, M.[1], Rodríguez-Abad, R.[1], Asanza, E.[1], Delgado, F.[2], San Román, J.[2]***

*[1]Centre for Studies and Experimentation in Public Works (CEDEX); [2]Ebro River Basin Authority (CHE)*

### *Summary*

A study of the effect of lindane on the Gállego river was commissioned to the CEDEX by the CHE during 2021. The study focused on the knowledge of the system formed by the Sabiñánigo reservoir, the Sardas landfill facilities, located on its left bank, and the geological substratum. The work consisted of the compilation and analysis of the information generated over decades by centres of the Central Administration, through the CHE, by the Government of Aragón, and by experts in multiple disciplines. The results obtained include: 1) a better definition of the hydrogeological functioning of the low permeability substrate of the Sardas landfill; 2) the evaluation of the landfill sealing system and its stability; 3) the mass balances of water and HCH in the reservoir and the distribution of pollutants in the seasonal episodes analysed; and 4) the selection and preliminary evaluation of the most plausible hypotheses to explain these pollution episodes. A series of future actions are proposed to evaluate these hypotheses, and to prioritise HCH pollution containment techniques over clean-up activities and treatment of contaminated soil and water. These are: 1) a modification of the water monitoring network, based on a better knowledge of the water renewal time in the reservoir and of the mass balances of circulating HCH; 2) the additional characterisation of the silts at the top of the lower terrace of the Gállego river and the sediments filling the reservoir on its right bank with non-destructive techniques; 3) the reinforcement of the screen and passive leachate drainage in front of the Sardas landfill; and 4) the application of retention techniques that enhance the natural biodegradation of lindane in the aquifer and the materials that confine it.

### *Key words*

Landfill, lindane, contamination, surface water, groundwater, conceptual modelling

### *Introduction and background*

The Ebro River Basin Authority (CHE) commissioned the Centre for Applied Techniques Studies (CETA) and the Geotechnical Laboratory (LG) of CEDEX to collaborate in the study of lindane contamination of the Gállego river in the Sabiñánigo reservoir. This assignment, which was carried out during 2021, responds to the CHE's interest in resolving the problem of toxic and hazardous waste dumps and historical contamination, which give rise to the affection and poor qualitative state of the water bodies of the Gállego river located downstream of the Sabiñánigo reservoir, due to the indicator lindane, the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane (HCH). The affection is shown in episodes in which the concentration of HCH isomers in the water of the Gállego river in the Jabarrella reservoir, belonging to the alert network managed by the CHE downstream of the Sardas and Bailín landfills, exceeds the concentration reference values of Royal Decree 817/2015, of 11 September, which establishes the criteria for monitoring and evaluation of the state of surface waters and environmental quality standards. The CEDEX study has focused the study on the seasonal episodes of pollution that originate upstream of the Sabiñánigo dam and cannot be attributed to the old Bailín landfill site, neither by surface runoff from the Paco stream, nor by groundwater draining from the layer of sandstone known as "layer M" that cuts through the Gállego river (Figure 1).

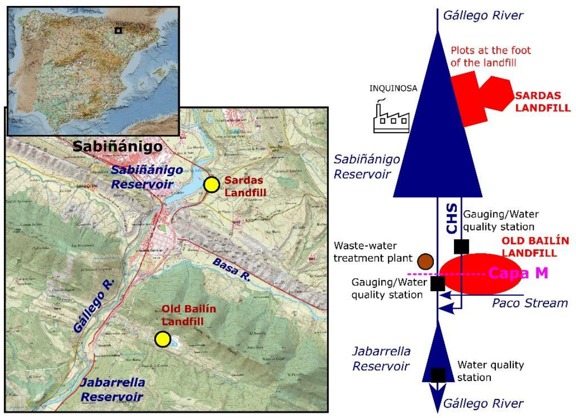



**FIGURE 1. LOCATION AND SCHEMATIC OF THE HYDROLOGICAL SYSTEM OF INTEREST**

The Sardas landfill wastes were disposed in the vicinity of the Sabiñánigo reservoir on two gullies on the left bank of the Gállego river, excavated in marls of low permeability. Since the 1960s it has been in operation for some 30 years for the deposit of a total of some 400,000 m$^3$ of urban and industrial waste. Some of these wastes were considered hazardous, such as lindane, produced by the former factory belonging to Industrias Químicas del Noroeste S.A. (INQUINOSA). The landfill was sealed in 1994 by a waterproof sheet sealing the upper part, with perimeter screens and a front screen at the lower edge, next to the N-330/ E-7 road. From the point of view of the subject of this contract, it should be noted that between 35,000 and 50,000 m3 of waste mobilised during the construction of the road was deposited on the plots located at the foot of the landfill, east of the N-330/E-7 to the left bank of the Sabiñánigo reservoir. No insulating material was installed on top or underneath these materials. It is also relevant that the front screen of the landfill only partially contains the infiltration waters, so that through its base and through the substratum the pollutants migrate towards the detrital sediments of the fluvio-glacial group of the Gállego river, which form an aquifer through which pollution can reach the waters of the river.

### *Objective and scope*

The results of the water quality monitoring programmes for the river Gállego show that there are open pathways for pollutants to enter the river in the Sabiñánigo reservoir. The aim of this work of CEDEX has focused on studying deeply the results of the previous studies to formulate hypotheses that explain the seasonal episodes of pollution detected at the water quality sampling point operating in the Sabiñánigo Hydroelectric Channel (CHS), and which have their unquestionable origin upstream of the Sabiñánigo dam. The study addresses the definition of the hydrological system of interest (composition, geometry, boundary conditions and mass balance), postulates conceptual models of hydrogeologic functioning and scenarios of possible effects of HCH isomers on the waters of the Sabiñánigo reservoir, and on the spatial and temporal distribution of the pollution episodes observed, and proposes actions and future work to help evaluate these hypotheses and limit the impact of pollution.

### *Definition of the hydrological system of interest*

In accordance with the purpose of the assignment, the hydrological system of interest on which the study of the effect of lindane on the Gállego river is focussed is defined by the Sabiñánigo reservoir itself and the fluvioglacial terraces and the underlying marly substratum. This system is therefore only affected by sources of pollutants located upstream of the Sabiñánigo dam. On the right bank of the Sabiñánigo reservoir is the former INQUINOSA factory and on its left bank the Sardas landfill site, which constitute its main potential sources of pollution by waste resulting from the manufacture of lindane (Figure 1).

### *Background information and study methodology*

The work has included the evaluation of the previous studies carried out up to 2021, among which the 4 monitoring reports on pollution in the Gállego river carried out during 1989 and 1990 by CEDEX at the request of the General Directorate for Public and Hydraulic Works, and Environment (DGOPHMA), the remediation project resulting from the "Acuerdo de encomienda de gestión" of the Ministry of the Environment, Rural and Marine Affairs (MARM) to the Empresa para la Gestión de Residuos Industriales S. A. (EMGRISA) in 2009, the work coordinated by the CHE in the vicinity of the Sabiñánigo reservoir in 2010 and the various lines of work coordinated by the GA commissioned to different companies since an initial diagnostic study in 1991, subsequently developed under the "European Regional Development Fund Operational Programme for Aragon 2014-2020, Building Europe from Aragon". Among the results of this latest Programme, the annual "hydrogeological monitoring of Sardas" reports since 2010 and the "ecological status of the riverbeds in the basin of the Gállego river " since 2006 stand out.

The study of this information has been organised according to its usefulness for the objective of the work in the following blocks:

- Physical environment: The geological information about the substratum of the reservoir and its possible pollutant sources has been studied. This substratum is composed of the following formations, from bottom to top: Larrés marls, from the upper Eocene; topographically lower Quaternary fluvioglacial terraces, which include a stretch of sands and gravels that constitute an aquifer at their base, and a stretch of semi-confining clayey silts at the top that buffer the vertical upward flow of water and the transport of pollutants from the aquifer to the river; and recent sediments (silts and sands) from the flood plain of the current course of the Gállego river, which are filling the reservoir and contributing to the semi-confinement of the aquifer.
- Sabiñánigo reservoir and dam: The information provided by the gauging and sampling networks for water and recent sediments has been used to draw up mass balances of water and pollutants in the reservoir, to estimate the residence time of the water in the reservoir, and to evaluate the effect of daily variations in the water level in the reservoir on the mobilisation of pollutants.
- Potential sources of contamination: The results of the characterisation programmes of the Sardas landfill, the plots located at its foot and the INQUINOSA factory.

In addition, field surveys have been carried out, the results of which have shown, for example, that the marly substratum admits a flow of groundwater that feeds the landfill, and which will be difficult to limit because it affects its entire surface area at the bottom.

### *Characterisation of the HCH isomers contamination episodes in the water of the Sabiñánigo reservoir*

The study has focused on the observations and measurements carried out at the CHS, in the years 2017 to 2019. The water and HCH mass balances carried out show that, although the gauging and quality network immediately downstream of the Sabiñánigo dam must be completed in the future, the CHS conveys most of the outflow from the Sabiñánigo reservoir and the information provided by its monitoring is sufficiently representative of the reservoir outflows for the purpose of this work.

The identification and quantification of episodes has been approached based on the mass flux, calculated as the product of the concentration of HCH isomers by the circulating flow. Figure 2 shows that the total cumulative mass of HCH circulating in the CHS is 8 kg in 2017, 11 kg in 2019, and 12 kg in 2018, a function not only of the concentration, which was higher in 2017 and 2019, but also of the circulating flow, which was higher in 2018. This HCH mass flux has been correlated with precipitation and temperature, and with the water level in the reservoir. As shown in Figure 2, temperature appears to be a key factor in triggering the process of HCH mobilisation into the reservoir waters or increasing its effect. The content of each of the HCH isomers has also been analysed, expressed as a percentage of the total concentration measured in the CHS waters. Figure 3 distinguishes the autumn-winter months, in which only the α-HCH isomer is detected, and the spring-summer months, in which all isomers are detected in an order (α-HCH, γ-HCH, δ-HCH, β-HCH and ε-HCH), according to their different leaching rate or intensity. This information can help to know the origin of the contamination in the reservoir waters with the help of a more intensive characterisation of the environment, as proposed in this study.


FIGURE 2. DAILY MEAN AIR TEMPERATURE AT THE SABIÑÁNIGO STATION AND ANNUAL ACCUMULATED HCH MASS FLUX

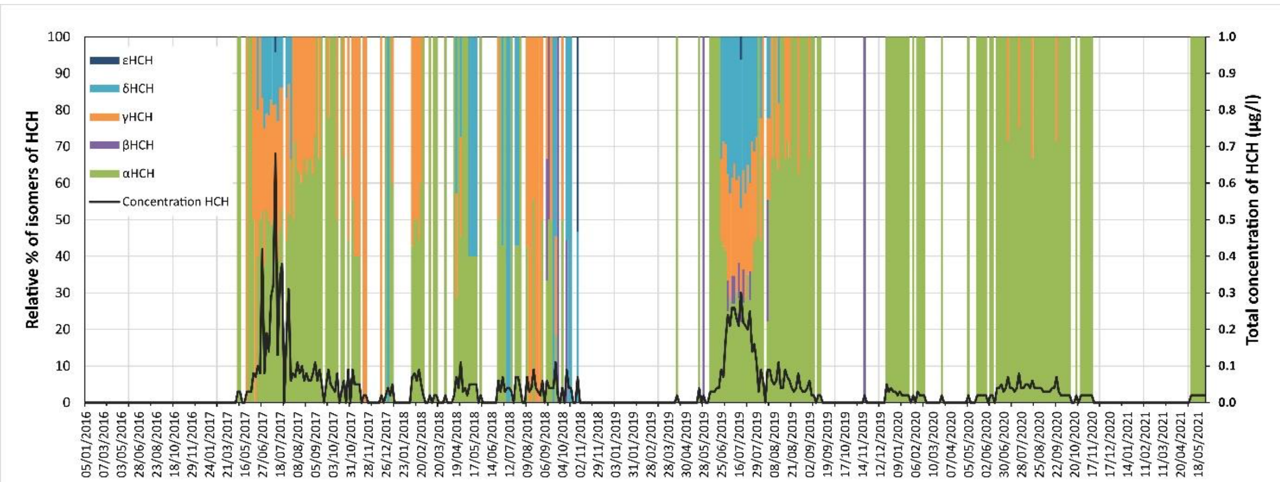



FIGURE 3. HCH ISOMERS´ PERCENTAGE RELATIVE TO HCH TOTAL CONCENTRATION IN THE CHS

### *Water pollution scenarios in the Sabiñánigo reservoir*

The compartments of potential origin of the HCH contamination of the waters of the Gállego river in the CHS and the hypotheses that have been postulated and evaluated in a preliminary way to explain the episodes of contamination observed are set out below:

- Aquifer. Vertical percolation upwards towards the reservoir from the fluvioglacial gravels and sands affected by leachate from the Sardas landfill, through the silts at the top of the lower terrace of the Gállego river.
- Fluvioglacial silts. Leaching by the waters of the reservoir of the sandy silts on the top of the lower terrace of the Gállego river, in the most superficial strip that constitutes its flood plain. In this strip it is easier to postulate an intense effect of the temperature increase, and it is subject to daily cycles of flooding and drying. These silts are affected by the wastes from the Sardas landfill site, which were disposed on these formations, and by the leachate from the slope of the landfill.
- Recent sediments filling the reservoir. Leachate from sediments potentially contaminated by discharges from the INQUINOSA factory on the right bank or by leachate from the Sardas landfill on the left bank of the Sabiñánigo reservoir.
- Other hypotheses on the origin of contamination:
  - Leakage from the settling ponds at the foot of the Sardas landfill.
  - Diffuse contribution by seasonal deposition of evaporated or volatilised HCH isomers from the landfill and soils in the area.
  - Impact of restoration, extraction, control, or monitoring actions in the surroundings of the Sardas landfill.

The first two hypotheses have been assessed as the most plausible. However, the persistence of the pollution process and the difficulty of remediation will be much greater in the first case than in the second. Clarifying this point is key to defining the short, medium, and long-term management strategy that applies to each case. The additional characterisation of the fluvioglacial silts proposed in the Conclusions is key to assessing both hypotheses.

### *Conclusions*

The Sabiñánigo reservoir is currently a recipient of lindane contamination in the waters of the Gállego river. Weekly integrated water sampling (Ebro River Basin Authority) and bi-weekly integrated water sampling (Government of Aragón) have been key to identify the pollution pulses that occur in this reservoir and to postulate several hypotheses to explain these periodic pollution episodes. The increase in temperature in spring and summer seems to be a determining factor in the contamination of the reservoir waters by HCH.

The most plausible hypotheses are: 1) leaching of the silts of the top the lower terrace of the Gállego river that are contaminated from the Sardas landfill by the reservoir waters; and 2) underground flow from the aquifer through these silts in favour of its sandier lenses.

The answer to the doubts and the evaluation of the hypotheses raised in this work require:

1.Extension of the monitoring networks during pollution episodes that considers the dynamics of the reservoir and the time of water renewal in the reservoir, the possibility that HCH isomers are mobilised in different modes (solution, suspension), and the complex interplay of other pollutants.

2.Characterisation of the flow, HCH contamination, and the parameters that regulate its transport in the shallowest stretch of the silts at the top of the lower terrace of the Gállego river. The application of less destructive techniques than drilling boreholes to the aquifer is recommended, including the use of passive flow meters in mini-piezometers, gas sampling, and the analysis of interstitial water and riparian and aquatic vegetation.

3.Design and application of retention and confinement techniques in all the contaminated components of the system as a priority over decontamination techniques, especially in the aquifer and the materials that confine it, and in the Sardas landfill itself through the reinforcement of the frontal screen and the passive drainage of leachates upstream.

Among the objectives and possible beneficial outcomes of this future work are a better integration of field and laboratory monitoring and experimental efforts with ongoing conceptual and numerical modelling efforts; reduced management costs in the short, medium, and long term; and increased confidence of scientists, managers, and society at large in the environmental assessment and management undertaken, and in the achievement of the environmental objectives of hydrological planning. The final report of this work is available at www.chebro.es.

### *Acknowledgements*

CEDEX acknowledges the attention received by the Government of Aragon (GA), EMGRISA, SARGA and AECOM during the field visits to the Sardas landfill site on 26 November 2019, 15 April 2021 and 11 November 2021, and that received by the representatives of the Demarcation of State Roads in Aragon of the Ministry of Transport, Mobility and Urban Agenda, UTE and Technical Assistance during the field visit and study of the slopes of the A-23 motorway route on the Sabiñánigo East - Sabiñánigo West section in Huesca. The invitation of the CHE and the GA to the meetings to present the results of the Hydrogeological Monitoring is also acknowledged.

# MASS DISCHARGE TEMPORAL EVALUATION IN A TRANSECT LOCATED IN THE DISCHARGE ZONE TO THE GALLEGO RIVER IN BAILIN LANDFILL, SABIÑANIGO (HUESCA)

***Alonso T.[1], Alcalde D.[1], Escobar-Arnanz J.[1], Encinas R.[1], Fernández J.[2]***

*[1]AECOM, Environment and Sustainability Department, Remediation. Madrid, Spain;*
*[2]Department of Agriculture, Livestock and Environment. Aragon's Government, Spain*

***Summary***

Since 2015, Mass Flux (J) and Mass Discharge (Md) studies have been conducted in a control area of the former lindane landfill in Sabiñanigo, Huesca (Spain) close to the Gallego River, by using the methodology of Passive Flux Meters (PFM).

Lindane and other Persistent Organic Pollutants (POP) dumped in the landfill created a dissolved plume in a complex fractured bedrock media that contains, in order of amount in the groundwater, monochlorobenzene, benzene and HCH (lindane and non-commercial isomers). This plume reaches the Gallego River in a zone called Discharge Zone, and the knowledge of the scope of its discharge to the river is the main objective pursued with the calculations of the Mass Discharge, in order to implement control and corrective actions during the increasingly frequent remediation activities that are being carried out on the site in recent years.

PFM devices consist of a permeable sorbent infused with soluble tracers packed in nylon mesh tubes. They are placed in the boreholes or monitoring wells for a known exposure period where they intercept the groundwater flow, causing dissolved contaminants to be sorbed and the soluble tracers to leach out. Measurements of the contaminant concentration and remaining resident tracers can then be used to estimate groundwater and contaminant fluxes. The integration of these fluxes throughout a control area (transect) is used to calculate the total Md of each contaminant.

The results obtained for Mass Discharge estimations have shown an increase in Mass Flux and, consequently, in the Mass Discharge of the Discharge Zone transect, and suggest that some remediation tests, especially those involving intensive injection events, have been able to produce a 'washout' effect process in the fractures that favors the contaminant mass to move downgradient with a higher velocity within the groundwater flow. In addition, the evaluation of the Mass Discharge in those situations in which the aquifer is not in equilibrium highlights that it could increase when carrying out on site remediation activities that have a direct impact on the hydraulic head of the aquifer, e.g., injection events from the source zone that push the most contaminated groundwater downstream.

***Keywords***

Mass Discharge; Mass Flux; PFM; benzene, monochlorobenzene, HCH; mass balance

***Introduction***

In the last eight years, Mass Discharge studies have been carried out at different locations within Bailin landfill site by using the PFM methodology [1]. Based on these studies, it has been possible to evaluate the Mass flux that flows through the main fracture network that constitutes the aquifer.

The dissolved plume, generated from lindane and other POP dumped in the former unlined landfill, migrates through a fissured aquifer formed by a sequence of vertical fractured sandstone and mudstone layers. These layers are parallel to Bailin Stream, that delimit the south boundary of the site and drains to the Gallego River. The so-called M layer is the only sandstone layer that has enough longitudinal continuity to connect the landfill and the river. In depth, the lithological alternation with different fracture distributions controls the preferential groundwater pathways. The understanding of the relationship among fractures, hydraulic conductivities, hydrochemistry and depth was crucial to develop the conceptual site model. Although the principal contaminated area is close to the source zone, preferential pathways in the sandstone layers constitute the main pathways that contribute to spread the plume [2].

For five years, Mass Discharge values have been obtained in the transect of the so-called Discharge Zone, an area located immediately upgradient of the aquifer discharge into the Gallego River. The study of the temporal evolution of Md values has able to identify patterns of behavior of the main pollutants (benzene, monochlorobenzene and HCH), related to an increase in groundwater flow velocities and concentration of some contaminants, especially in 2021, when the last Md estimation was calculated. These increases could be related not only to the nature of the components of the dissolved plume but also due to some actions carried out on the site

### *Materials and methods*

The Mass Flux (J) is the mass of a chemical compound passing through a perpendicular plane to the groundwater flow (transect) per unit time (e.g., $g/d/m^2$). The Mass Flux determines the amount of a contaminant mass moving in the groundwater based on the groundwater flow velocity, and it´s delimited in a defined area. Mass Discharge (Md) represents the total contaminant mass transported by groundwater (e.g., g/d). Mathematically, Mass Flux (J) is the product of the contaminant concentration in the groundwater and the groundwater flux: $J = q_0 \cdot C = -K \cdot i \cdot C$, where $q_0$ = groundwater flux, $L^3/L^2/t$ (e.g., volume/area/d), K = saturated hydraulic conductivity, L/t, (e.g., m/d), i = hydraulic gradient, dimensionless (e.g., m/m), and C = contaminant concentration, $M/L^3$ (e.g., mgvolume); and Mass Discharge is the integration of the contaminant mass fluxes across the selected transect: $Md = \int_A J \cdot dA$, where A = area of the control plane, $L^2$ (e.g., $m^2$), and J = spatially variable contaminant flux, as previously defined [3].

Mass Flux varies temporal and spatially along the transect of the Discharge Zone (Figure 1) due to changes in the concentration of contaminants and in the groundwater flow: i) when groundwater levels are high, Mass Flux increases mainly because the groundwater flow velocitity increases. Therefore, the mass flow is greater the higher the hydraulic head of the aquifer; ii) the natural infiltration that occurs in the source area allows a greater mobility of the contaminants, which migrate downgradient through the complex fracture network. However, groundwater does not progressively flow at the same velocity through all the fractures, so the effect in the Discharge Zone will take days or weeks to manifest depending on the conditions; iii) the different transport mechanisms of the contaminants in the groundwater (advection, diffusion, dispersion, sorption) and the degree of the hydraulic connectivity condition both the concentration of the contaminants observed in the boreholes and their mobility; iv) when the groundwater levels decrease in the absence of prolonged rainfall, the hydraulic gradients decrease as well and, therefore, the groundwater flow velocity. If the concentrations do not vary significantly, the Mass Flux decreases.

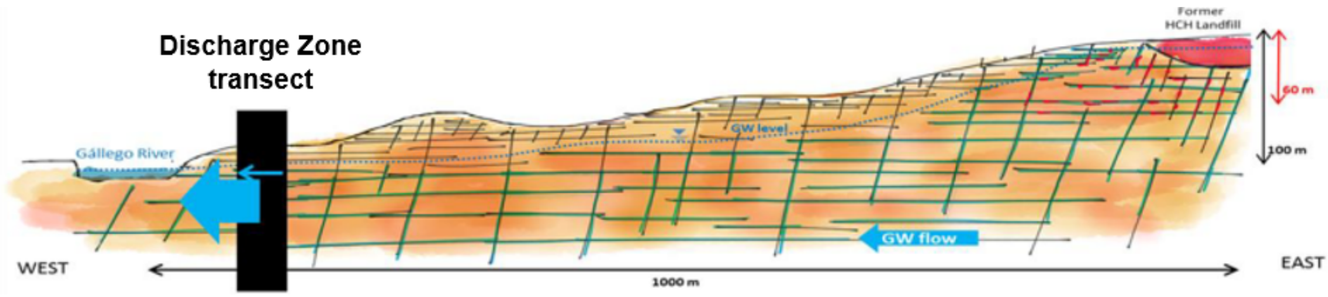



FIGURE 1. TRANSECT IN THE DISCHARGE ZONE CLOSE TO THE GALLEGO RIVER. GROUNDWATER FLOWS FROM THE SOURCE LOCATED 1.000 M UPGRADIENT THROUGH THE FRACTURE NETWORK OF THE MAIN SANDSTONE LAYER (M-LAYER)

Mass Flux was evaluated with 6 PFM (Figure 2). These devices are designed to determine the concentration of contaminants present in the groundwater and the groundwater flow velocity at the same time. Samplers are composed of a mixture of activated carbon, which retains the contaminants, and several alcohols that act as tracers, in order to estimate the groundwater flow velocities based on the solubility coefficients of the alcohols. Each PFM had a length of 1.5 m and was divided into 4 sections.

There are 3 monitoring wells in the Discharge Zone, screened at different depths that intercept the main fracture sections where the dissolved plume migrates. Monitoring well P141 intercepts the section of the fissured aquifer from 17 to 21 m deep; P140 from 27 to 31 m deep; and P142 from 40 to 47 m deep. In these sections, PFM have been installed to assess the Mass Flux at depth and calculate the total Mass Discharge in the Discharge Zone transect.

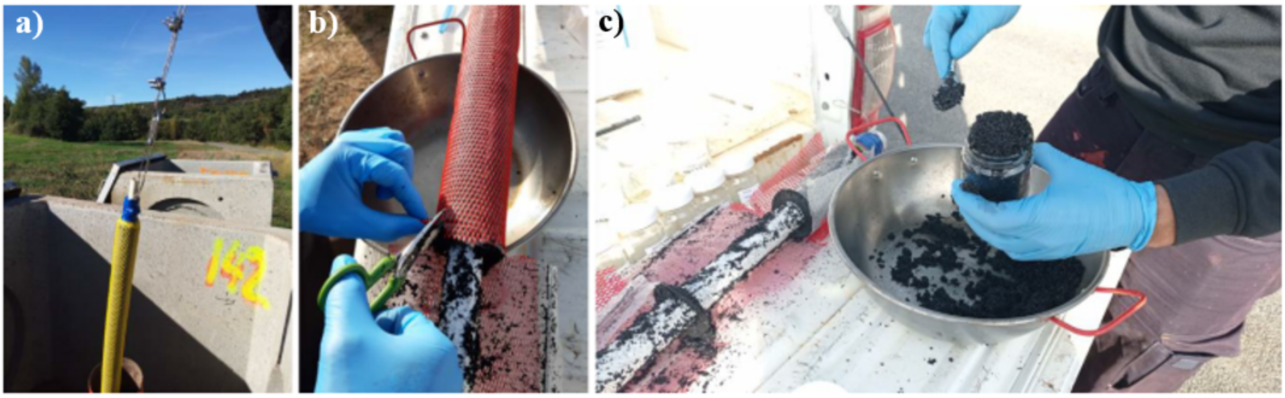



FIGURE 2. PASSIVE FLUX METERS. PICTURE A) SHOWS THE DEPLETION OF THE PFM IN THE WELL; WHILE PICTURES B) AND C) SHOW THE SAMPLING PROCESS OF THE ACTIVED CARBON THAT CONFORM THE BODY OF THE PFM

### *Results and discussion*

Data related to the number of existing fractures and their area (depending on the thickness or opening of each fracture) and the thickness of the M-layer in the Discharge Zone were collected to estimate the discharge area. Several conservative aspects were assumed to define the system parameters to carry out the calculations: i) an average value of 3 m was used for the M-layer thickness, although this thickness is estimated to be lower in the Discharge Zone; ii) a 63% of the fractures identified in the saturated section of the boreholes located in the Discharge Zone has a maximum thickness of 1 mm, a 23% has a maximum thickness of 2 mm, a 8% has a maximum thickness less than 1 mm, a 4% has a maximum thickness of 3 mm, and only the 2% of the fractures has a maximum thickness of 10 mm. However, in order to obtain a conservative range of values, a minimum value of 4 mm and a maximum value of 10 mm were attributed to all fractures. Thus, the range of values for Mass Discharge were calculated based on the minimum and maximum area estimations (from 0.012 $m^2$ to 0.03 $m^2$); iii) in some sections of the wells where samplers could not be placed, and Mass Flux could not be estimated directly, the average value of the Mass Flux of the existing fractures above and below these sections measured with the PFM was applied, assuming that all fractures present in these sections had a good hydraulic connection.

The results obtained in the Mass Discharge studies over the years were integrated to represent the evolution of the minimum and maximum values for benzene, monochlorobenzene and HCH (Figure 3). The results shown an increase in the contaminant mass that passes through the Discharge Zone. The monochlorobenzene was the compound that presented the highest Md values while HCH presented the lowest. It should be noted that the aquifer was in equilibrium conditions during studies from 2015 to 2019; that is, no intensive remediation activities were carried out either before or during the deployment of the PFM that could alter the natural groundwater flow. On the other hand, PFM deployment in 2021 was conducted after the execution of some injection tests in which significant volumes of water were injected upgradient in the source area.

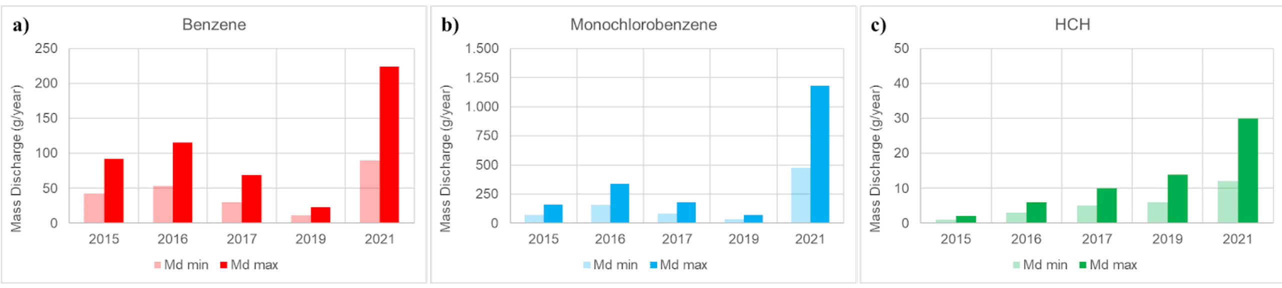



FIGURE 3. TEMPORAL EVOLUTION OF THE MD (G/YEAR) IN THE DISCHARGE ZONE. DARKEST COLORS IN THE GRAPHICS REPRESENT THE MAXIMUM VALUE OF THE MD WHILE LIGHTER COLORS REPRESENT THE MINIMUM VALUE OF THE MD. GRAPH A) SHOWS THE EVOLUTION OF BENZENE MD; GRAPH B) SHOWS THE EVOLUTION OF MONOCHLOROBENZENE MD; AND GRAPH C) SHOWS THE EVOLUTION OF HCH MD

Groundwater flow velocities analyzed in 2021 in the three monitoring wells of the Discharge Zone shown an increase that could be related to a possible combined effect of a fracture washout in the source area where the injection tests were carried out together with a greater hydraulic head associated with the injection water volumes. Particularly, a notable increase was detected in the deepest sections of the Discharge Zone (well P142), whose main fracture area is located between 40 and 50 m deep, and groundwater flow velocity presented values between 25 to 44 cm/day. At these depths, most of the contaminant mass circulates compared to the shallower areas of the fracture network. Thereby, Mass Discharge values are significantly higher in well P142 than P140 and P141.

In the case of monochlorobenzene, the concentration also shows a slight upward trend in recent years. Instead, the concentration of benzene seems to decrease and HCH remains more or less stable (Figure 4).

In order to evaluate a potential impact on the quality of surface waters in Gallego River, in regard to the discharge of groundwater from the fractures of the M-layer in the Discharge Zone, a mass balance was carried out considering the Mass Discharge values from the 2021 study. Mass balance was calculated to estimate the maximum concentration expected in the river ($C_{river}$) if the maximum Md values for each contaminant occurred in the most unfavorable case. The mass balance was calculated by using the formula

$$C_{river} = Md_{max}/Q_{river},$$

where $Md_{max}$ = maximum Mass Discharge value obtained in the PFM studies, M/t (e.g., mg/d), and $Q_{river}$ = river flow, $L^3/t$, (e.g., volume/d). The river flow value used was 0.67 $m^3/s$, that is the minimum flow rate recorded in the river the month in which the PFM were deployed.

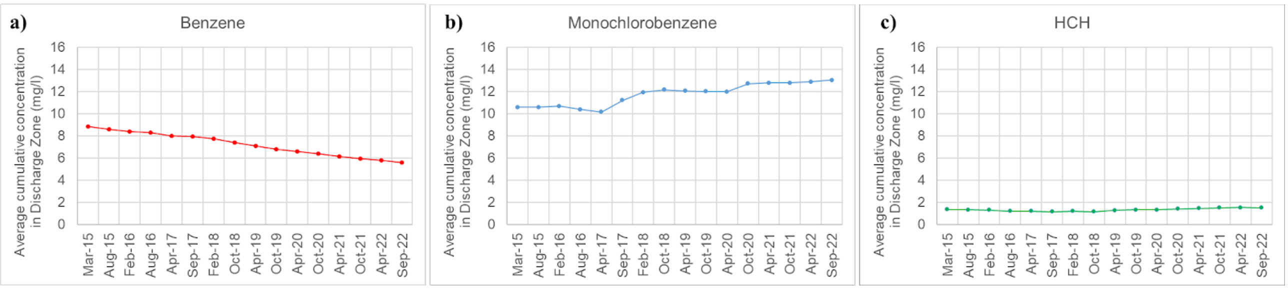



**FIGURE 4. EVOLUTION OF THE AVERAGE CUMULATIVE CONCENTRATION (MG/L) ANALYZED IN THE WELLS OF THE DISCHARGE ZONE IN SAMPLING CONTROL EVENTS CARRIED OUT SINCE 2015. GRAPH A)** SHOWS THE TEMPORAL EVOLUTION OF BENZENE AVERAGE CONCENTRATION, GRAPH B) SHOWS THE TEMPORAL EVOLUTION OF MONOCHLOROBENZENE AVERAGE CONCENTRATION, AND GRAPH C) SHOWS THE TEMPORAL EVOLUTION OF HCH AVERAGE CONCENTRATION

The results obtained in the mass balance were compared with the regulatory standard values published on the Royal Decree (R.D.) 817/2015, of September 11 [4] (Table 1). None of the concentration of the contaminants calculated from the mass balance would break the standards for surface waters, and the maximum potential concentration that would be detected in the surface waters of the Gallego River because of the discharge of contaminant mass by the M-layer would be lower than the regulatory values set by the R.D., even under the most unfavorable conditions (minimum river flow and maximum Mass Discharge).

**TABLE 1. MASS BALANCE CALCULATIONS COMPARED TO REGULATORY STANDARDS FOR SURFACE WATERS**

| Concept | Benzene concentration (µg/l) | Monochlorobenzene concentration (µg/l) | HCH concentration (µg/l) |
|---|---|---|---|
| Average annual standard published in the R.D. 817/2015 | 8 | 20 | 0.02 |
| Maximum allowable standard published in the R.D. 817/2015 | 50 | Not available | 0.04 |
| Estimated surface water concentration because of the discharge of the M-layer calculated in the mass balance | 0.011 | 0.06 | 0.0014 |

### *Conclusions*

The Mass Discharge values associated with the Discharge Zone transect on the M-layer depend on several factors such as the concentration of the contaminants and groundwater flow velocity. These parameters depend to a great extent on the fluctuations that occur in the dissolved plume as a function of the hydraulic head, which varies mainly according to the seasonal regime and specific actions carried out in different areas of the site.

Specifically, intensive remediation activities, such as injections into plume source areas, mostly promote a fracture washout effect that could increase flow rates through the fracture network. When this kind of activity is carried out in source areas, in addition to fracture washout, it is possible that the increase in the hydraulic head of the upstream aquifer generates a greater push effect from areas where contamination is notably higher. According to the evolution of recent years, remediation activities, not only in frequency but also in scope and intensity, tend to increase in source and central areas of the plume, and may generate an increase in Mass Discharge, as the observed increase in the study of 2021 seems to be related with one of these actions. Even so, the mass balance of the system M-layer discharge-Gallego River shows lower values than the regulatory standards.

However, there are several uncertainties that could underestimate the results, e.g., if Mass Discharge occurs not only by the fractures of the M-layer, or its width is greater than 3 m; and/or Mass Discharge varies very quickly depending on the stress submitted to the aquifer and it is not possible to capture the moment of the Mass Discharge peak. Any action carried out along the M-layer can cause fluctuations in the aquifer system that generate rises and falls in the contaminant mass that flows within the dissolved plume towards Gallego River, so it is indispensable to perform a good previous design of the action, considering the application of control and corrective measures downgradient and upgradient the test area that minimize the potential increase in the migration of the polluting mass.

### *References*


1. Hatfield K., Annable M.D., Cho J., Rao P.S.C., Klammer H. (2004). A direct passive method for measuring water and contaminant fluxes in porous media. Journal of Contaminant Hydrology, 75 (3-4), 155-181.
2. Alcalde D., Rodriguez R., Needham S. Groundwater modelling of a HCH DNAPL plume migration in a fissured aquifer (Bailin, Huesca, Spain). Paper, 12th International UFZ. Deltares Conference (AquaConSoil, 2013, Barcelona).
3. ITRC (Interstate Technology & Regulatory Council). (2010). Use and Measurement of Mass Flux and Mass Discharge. MASS FLUX-1. Washington, D.C.: Interstate Technology & Regulatory Council, Integrated DNAPL Site Strategy Team, 65-72.
4. Royal Decree 817/2015, of September 11, on which the criteria for monitoring and evaluating the state of surface waters and environmental quality standards are based. Published on BOE 219, on September 12, 2015. Ministry of Agriculture, Nutrition and Environment. BOE-A-2015-9806.