

DIOXIN CONTAMINATION FROM FORMER LINDANE (γ -HCH) PRODUCTION IN SARDAS LANDFILL AND SURROUNDINGS (SABIÑÁNIGO, SPAIN)

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Introduction

For over two decades the Sardas landfill (Sabiñánigo, Spain) was used for industrial wastes as well as municipal and construction waste¹. In total approx. 350,000 m³ waste were deposited directly onto the ground, consisting of Eocene marls without a bottom liner¹. The industrial waste contained residues from the chlorine production and in particular approximately 70,000 tonnes of waste isomers from the hexachlorocyclohexane (HCH) production for the manufacture of lindane (γ -HCH).¹ Lindane production was carried out by chlorination of benzene in a photochemical processes using ultraviolet radiation. For the production of 1 tonne of lindane approximately 10 tonnes of HCH waste isomers were generated which were largely deposited in the past around the former lindane productions^{2,3}. These wastes are present in the Sardas landfill in solid form and in liquid form (as Dense Non Aqueous Phase Liquid, DNAPL).¹

The landfill site was assessed through a governmental project supported by joint funding from the National and Regional environmental authorities. A part of the work consisted in the drilling and construction of more than seventy monitoring and pumping wells and the environmental characterisation of soil and groundwater. Currently, the environmental monitoring of the site, the extraction of the DNAPL phase by pumping and the control and treatment of leachate is ongoing.

From former lindane production it has been documented that polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in 100 kg TEQ scale have been formed and disposed from one factory in Germany^{4,5}. Also, the residues from chlorine production can be highly contaminated by PCDD/Fs⁶⁻⁸. Therefore, it was concluded by the remediation team that PCDD/Fs need to be considered and assessed for the remediation measures at the site.

The aim of this study was to assess the presence and distribution of PCDD/Fs in the landfill site of Sardas, and to determine which sources whether the origin of these compounds is related to thermal or other processes within the landfill itself, or the production lindane. The assessment of the PCDD/Fs contamination is a starting point for further risk assessment for the environment and ecosystems and for human health in respect to these pollutants including the occupational exposure of hydrogeological monitoring of the landfill.

Materials and methods

We analyzed the concentrations of PCDD and PCDF in different types of waste from landfill, surface soils in the immediate environment, as well as leachate and groundwater. In total, used 21 liquid samples and 13 solid samples.

Solid samples are from surveys of surface soil and sludge and, leachate ponds were taken with single-use material in glass jars of 250 ml sealed, without exposure to light and at room temperature.

Liquid samples are from piezometers and surface upwelling. Sampling piezometers was performed after the purge of the same and in each case were carried out with sample material for single use only and were introduced in airtight bottles. Samples were protected from light and kept at room temperature until arrival at the laboratory.

All samples were analysed by a commercial laboratory (Alcontrol AB in Sweden). The analytical method of analysis was based on SS - EN- 1948 using high resolution GC/MS. The laboratory is accredited by Swedak Accrediting according to 1006 ISO / IEC 17025.

Results and discussion

In all samples analysed PCDD/Fs were detected. Some of the samples showed quite unique PCDD/F patterns. and some of the samples had high PCDD/F levels above the provisional low POPs limit of the Basel Convention.

Deposited residues from lindane production

Residues from lindane production (largely HCH waste isomers) contained relatively high PCDD/PCDF levels (Figure 1). The TEQ in the analysed production residues were frequently above the provisional low POPs limit of the Basel Convention (15 µg TEQ/kg) with peak values of 79 µg TEQ/kg. Considering the PCDD/F content this categorize these residues as POPs waste. Since the waste largely consists of HCH waste isomers^{1,2}, which have been listed in 2009 in the Stockholm Convention, the waste is anyway POPs waste. For some of the residues the 1,2,3,4,7,8-HxCDD was the main 2,3,7,8-substituted congener (Figure 1). However, other waste from HCH production showed a different pattern (Figure 1), indicating that different PCDD/F generating processes were present in the former HCH production.

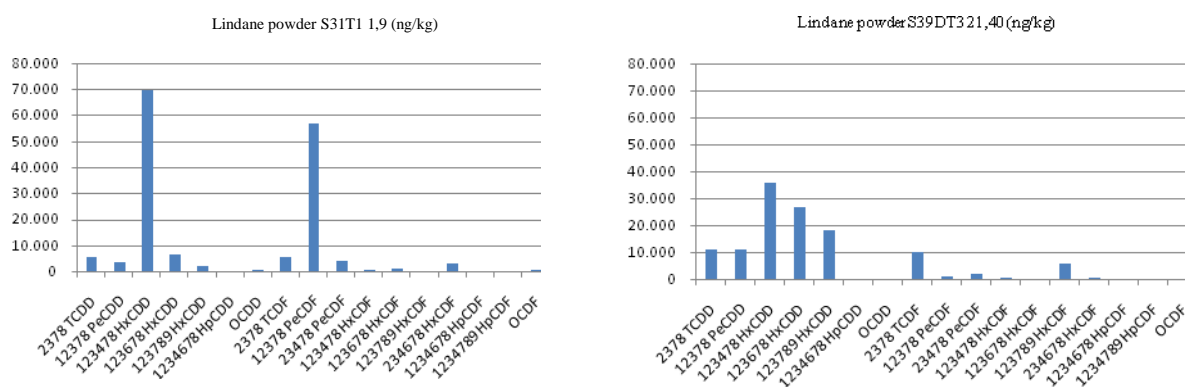


Figure 1: PCDD/Fs congener profiles from lindane production residues powder (the samples were taken from the solid residue of lindane inside the landfill).

PCDD/Fs in deposited combustion residues

In some areas, the landfill residues from unknown combustion processes have been disposed. Samples of combustion residues from the landfills were taken at different depths. The congener profiles of two samples are shown in figure 2. Some of the samples showed a dominance of PCDD, indicating that waste containing chlorinated phenols (PCP) were probably present in the process. Other samples contained PCDD and PCDF at similar levels still with highly chlorinated congeners. The TEQ concentrations of the samples were moderate with levels below 1 µg TEQ/kg.

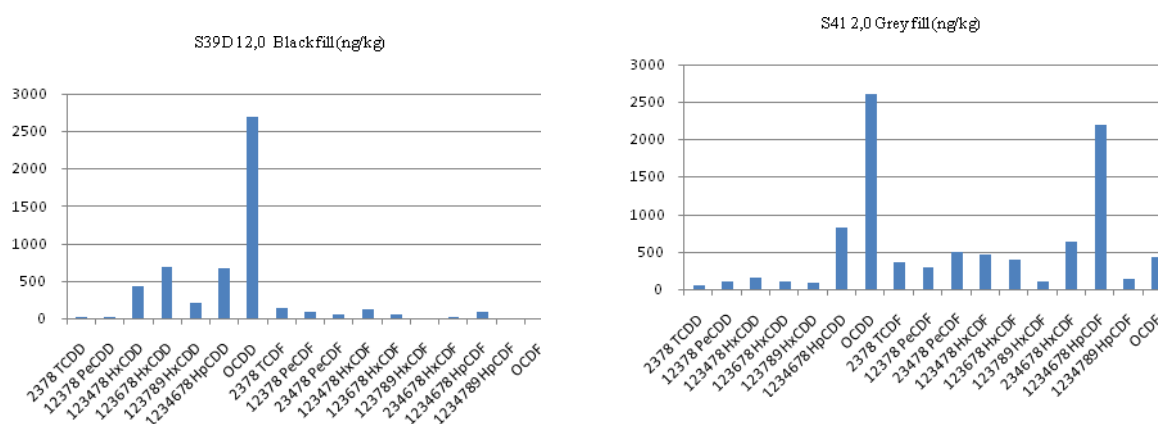


Figure 2: PCDD/Fs congener profiles in disposed combustion residues.

PCDD/Fs in mixed wastes from the landfill

Samples were also taken from the landfill, at areas with heterogeneous materials. Levels in these areas were also moderate (below 1 µg TEQ/kg) (Figure 3) and showed some impact of the marker congener of the above described HCH waste residues (Figure 1). This indicates that these wastes impact also other areas in the landfill.

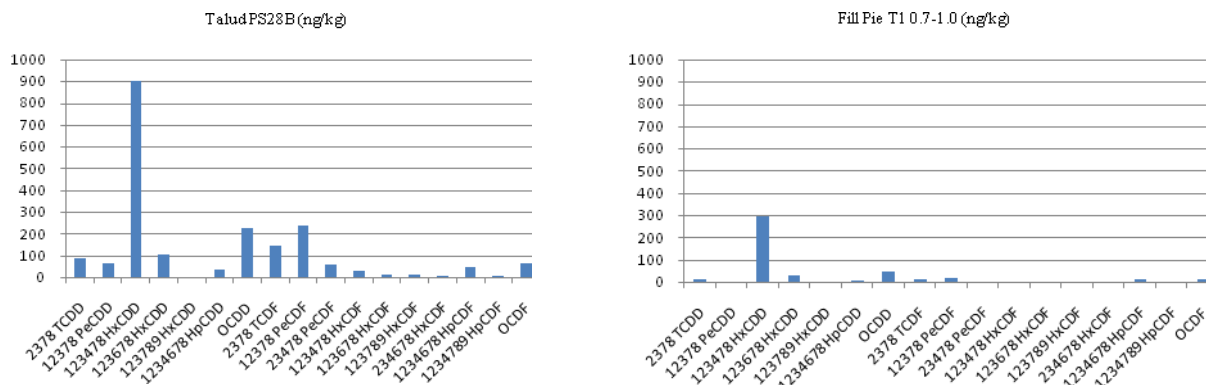


Figure 3: PCDD/Fs congener profiles in two mixed waste samples from the landfill.

PCDD/Fs in leachate samples and in sludges

As mentioned, the landfill had several 2000 tonnes of highly chlorinated DNAPL phase consisting of chlorobenzenes, chlorphenols, HCH isomers and other compounds¹, samples have been taken in leachates in aqueous phase, which have been in contact with dense phases. In this initial assessment, the leachates contained mainly lower chlorinated PCDD in some cases in relatively high levels of 500 ng TEQ/l (Figure 4a). The enrichment might be triggered to some extent by solubility. However, the pure PCDD pattern with the absence of lower chlorinated PCDFs indicates that the pattern rather reflects a contamination from a specific source.

High PCDD/F levels were detected in a sludge pond where leachates from the landfill end-up. The pattern in the pond was dominated by the above mentioned 1,2,3,4,7,8-HxCDD with minor presence of 2,3,7,8-TeCDD and the virtual absence of PCDF. This specific pattern is for the PCDDs similar to the HCH production waste (Figure 1). The virtual absence of the PCDF could mean that the PCDD/F pattern in the measured HCH production waste is a mixed pattern of different processes and the pattern in the sludge from a particular process. Further measurements of HCH production residues and more detailed assessment of the congener fingerprint are necessary to draw more detailed conclusions (in this first assessment only 2,3,7,8-substitute congeners data were generated while for a detailed assessment, the entire set of congeners is required).

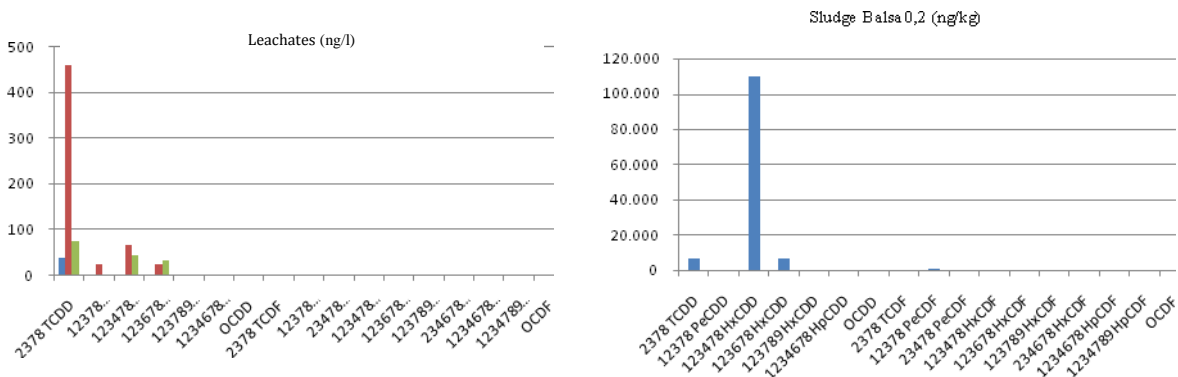


Figure 4a: PCDD/F in leachate samples (DNAPL)

4b: PCDD/F in sludge samples

In this initial PCDD/F screening also a groundwater sample taken in the alluvial Gallego river close to the landfill has been measured. The PCDD/F were below the detection limits. Also here, a more detailed assessment including POP-accumulating biota are needed for a conclusion on a potential impact on the river. For more water soluble HCH, a yearly release of HCH in the order of 100 kg has been measured.¹

PCDD/Fs levels in surface samples at and around the landfill

Surface samples were taken in the close environment of the landfill (soil samples) and top filling (Figure 5). The samples had TEQ levels below 20 ng TEQ/kg and were therefore not specifically contaminated but had levels

below e.g. the German limit for playgrounds. The congener pattern of some samples had partly an influence from the HCH residues (Figure 4) showed lower of landfill fillers and surface exhibit a mixed pattern, being enriched in with elevated 1,2,3,4,7,8-HxCDD and OCDD and still predominant enrichment in 1,2,3,4,7,8-HxCDD in samples of landfill filling 1,2,3,7,8-PentaCDF (Fig. 5 (left) versus Fig. 1) or a pattern dominated by higher chlorinated compounds (Fig. 4 (right)) with potential impact from ashes (Fig. 2).

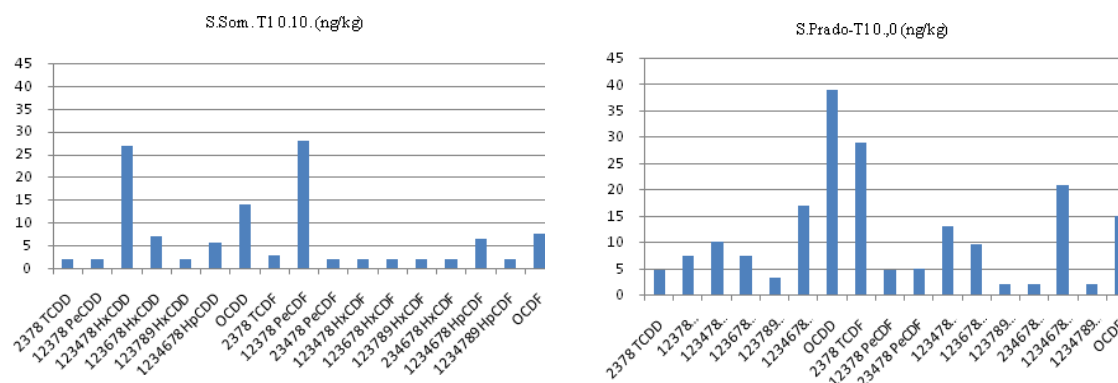


Figure 5: PCDD/Fs congener profiles in two samples from the surface soil at and around the landfill.

Conclusions and further considerations

This first assessment revealed that PCDD/Fs were generated during the former lindane production and were disposed to the landfill. The levels in the production residues were higher compared to the provisional low POPs limits of the Basel Convention (15 µg TEQ/kg). These PCDD/Fs levels were however far lower compared to the waste disposed from a German former lindane production, where residues from the recycling of HCH waste isomers (to chlorobenzenes) had PCDD/F concentrations in the percent range^{3,4}. While the Spanish factory has also considered to recycle HCH waste isomers, this seems not to have taken place in large scale, considering that from this Spanish factory approximately 140,000 tonnes of waste isomers have been disposed¹. Further assessments are needed to conclude if PCDD/Fs are relevant for further remediation process.

The current monitoring also revealed that PCDD/Fs are released in leachates from the landfill. The release of PCDD/Fs has also been reported from the major landfill of the former lindane production in Hamburg^{4,5}.

The initial assessment of soil samples close to the landfill indicated that no major PCDD/F contamination of the surrounding soil has taken place similar to the detailed investigated landfill in Germany⁴. However, more measurements are needed for a sound assessment of this important question.

Since groundwater samples taken in the alluvial river Gallego did not show detectable concentrations, no larger migration of PCDD/Fs through groundwater seem to take place while HCH is released¹. The assessment of bio-accumulation biota, such as fishes, is needed to conclude in respect of PCDD/Fs in the river system.

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