# PRESENCE OF HCB and PCBs IN SPANISH SEWAGE SLUDGE

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**Abstract**

Hexachlorobenzene (HCB) has been historically used extensively in agriculture and industry. As its production was banned in the 1980s, a sharp reduction of its presence in the environment was observed. Presently, HCB emissions are mainly due to by-products of several industrial processes, as well as combustion processes. Taking into account that the main intake way of organochlorinated pollutants to humans is the diet, to control the exposure through this way, it is important to restrain the intake from agriculture products and, therefore, from those products working as manure: sewage sludge case. Sewage sludge could contain traces of many organic pollutants, such as HCB and PCBs that should be monitored. Thus, in the present work, levels of HCB and PCB congeners 28, 52, 101, 118, 153, 138, and 180 have been determined in Spanish sewage sludges. Up to our knowledge, these are the first Spanish data corresponding to HCB levels in this matrix.

**Introduction**

Historically, Hexachlorobenzene (HCB) has been used extensively in agriculture and industry[1]. In 1933 it was introduced in agriculture as a fungicide on seeds, onions, sorghum and crops, whereas in the industry it has been used for the carbon anode treatment, as a fluxing and degassing agent in the Aluminium industry, in organic synthesis as an intermediate, and other industrial applications. HCB has also been utilised in military pyrotechnic smokes and in wood preservation.

The period of highest HCB production was from 1960s to early 1980s, showing a peak of HCB production in the late 1970s[2]. From the decade of 1980s the production of HCB declined as a result of restriction in its use. Nowadays, HCB is formed as by-product during the synthesis of pesticides and other organochlorinated compounds. Additionally, its generation has also being observed in combustion processes.

The HCB toxicity has been well documented since the incident of Turkey in the 1950s[3], when the population ingested HCB-treated seed grain. The main HCB toxic effects observed are porphyria, induction of liver-cell tumors, renal adenomas, haemangioendotheliomas, tyroid adenomas, neurological disease,and also acts as a promoter of cancer as observed in several studies[4,5,6,7,1].

Taking into account the main intake way of this pollutant to humans is the diet[8], to control the exposure through this way, it is important to restrain the intake from agriculture products and, therefore, from those products working as manure.

Since year 2000, due to the application of the European Directive 91/271/CEE, the quantity of sewage sludge production in Europe have risen and concretely, in Spain, this one is mainly used to amend agricultural land. Land application of raw or treated sewage sludge can reduce significantly disposal cost component of sewage treatment as well as providing a large part of organic matter supply demanded by many crops. However, this matrix could contain traces of many persistent organic pollutants, such as HCB and polychlorobiphenyls (PCBs) that should be monitored

PCBs are ubiquitous pollutants, extensively studied in the last century. As well as HCB, the PCB production has been banned in the late 1970s, early 1980s, due to their toxicity. They have been analysed in several matrices especially in food, but little works have been reported about indicator PCBs (PCBs 28, 52, 101, 118, 153, 138 and 180) in sewage sludge.

The content of dioxin-like compounds in sewage sludge has already been reported widely, but, the HCB content corresponding to this matrix rarely has been evaluated. Thus, in the present work, levels of HCB and PCB congeners 28, 52, 101, 118, 153, 138 and 180 have been determined in Spanish sewage sludges. Up to our knowledge, these are the first Spanish data corresponding to HCB levels in this matrix.

## Material and Methods

**Sample collection**:

Four sewage sludges were sampled from Wastewater Treatment Plants (WWTPs) at different locations throughout Spain:

- Samples S1 and S2 (Figure 1) were taken from WWTPs flowing into the Duero River. In these sampling locations the main pollution sources are agricultural activities.
- Sample S3 was taken from a WWTP located in the basin of Guadiana River near the border with Portugal. Its pollution is also mainly due to agricultural activities.
- Sample S4 was taken from a tributary of the Tajo River. In this case, the WWTP is located downstream a high industrialized area.

All these sampling locations are pointed out in Figure 1.

Samples were taken by plant staff, air-dried (or at 40°C) until constant weight and poured into sealed amber-glass flasks. Upon receiving in the laboratory, they were ground to a fine powder, reducing as much as possible time between collection and analysis.


*Figure 1. Sewage sludge sampling locations.*

**Sample Extraction and Clean-up**:

Approximately 0.5 g of dried sewage sludge was extracted in an ASE 100 system (Accelerated Solvent Extraction), as published elsewhere[9]. A mixture of hexane:dichloromethane (1:1) as extraction solvent was used. Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to remove organic matter. Clean-up stage was performed in an automated purification Power PrepTM System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. Purified extracts were spiked with $^{13}C$ PCBs (70, 111 and 138) and analyzed by HRGC-HRMS at 10,000 resolving power using a 40 m chromatographic column (DB-5MS from J&W).

**Results and Discussion**

Levels of PCBs and HCB are represented separately:

PCB concentration obtained is represented in Figure 2 The most significant result is the variation between levels for S4 and those for the other samples. Thus, its total content ranged from 3 folds when compared with S3 up to 6 folds when compared with S2. S1 could not be compared owing to several were not detected (LOD is 0.0012 ng/g for PCBs 52 and 101).

Congener profile is very similar, independently on concentration level associated with each sample. In this way, it can be observed that PCB congeners 153, 180 and 138 are showing the highest concentration. However, a noticeable difference is shown in profile corresponding to congener 28. Whereas, PCB 28 contribution to total concentration is very low in S1, S2 and S3, this congener is the fourth most weighty in S4 sewage sludge.

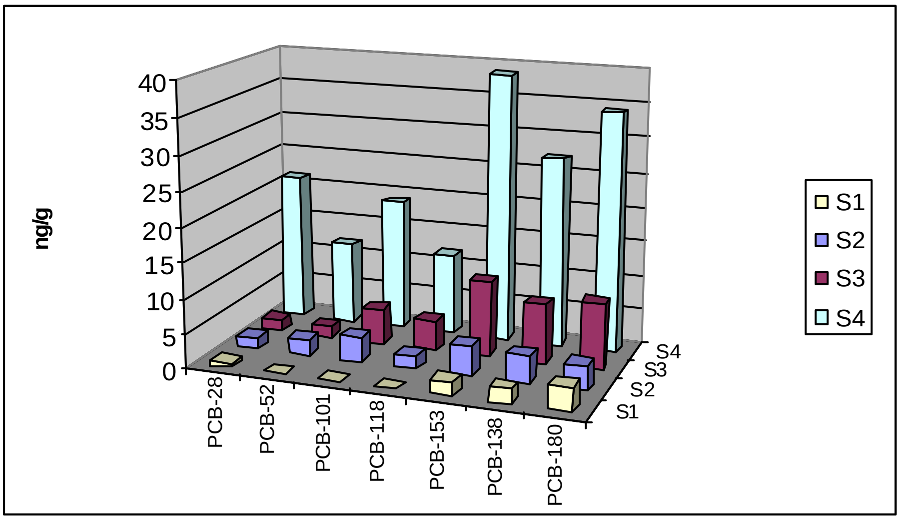


*Figure 2. PCB levels of Spanish sewage sludge samples.*

Data related to the HCB of the Spanish sewages sludges evaluated are plotted in Figure 3. Similarly to the PCB study, the highest concentration correspond to S4. But, in this case, the difference with S3 is not so significant. The HCB increase in S4 ranges from 1.4 folds in comparison with S3 up to 6 folds by contrasting with S2. HCB in S1 was not detected, presenting a limit of detection of 0.002 ng/g.

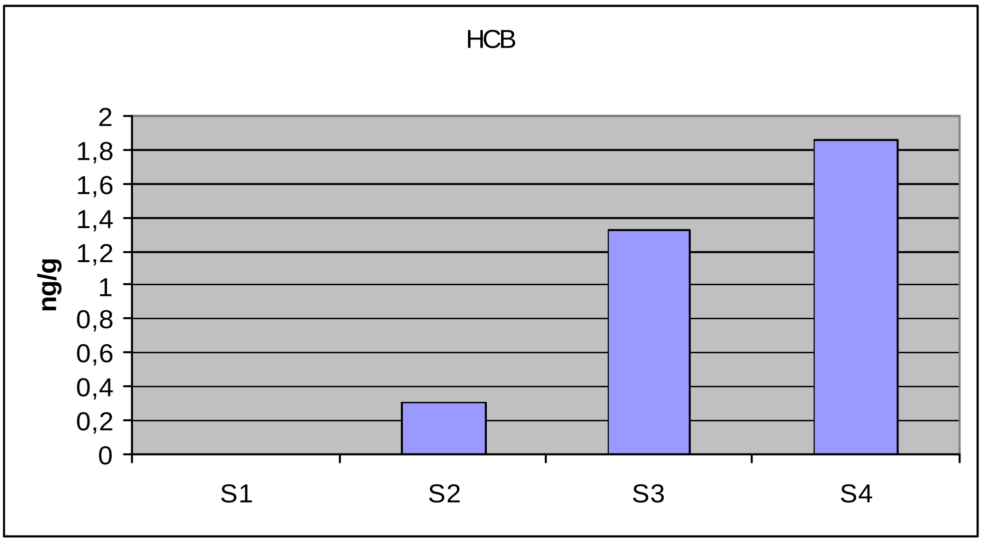


*Figure 3. HCB levels in Spanish sewage sludge samples.*

By comparing Figures 2 and 3, it can be concluded that levels of PCBs and HCB correlate with the location of the wastewater treatment plants assayed. Thereby, S1 is the sample with the lowest concentration of both groups of organic pollutants. As mentioned previously, S1 has been taken from a WWTP located in the middle course of a Duero River tributary. This sampling point is mainly influenced by agricultural activities, showing residuals levels of PCBs and HCB. S2 and S3 are also samples proceeding from agricultural activities but with a higher contribution of urban influents and, therefore, PCB and HCB concentrations are intermediate. Finally, S4 is resulting from an industrial and highly populated area and, consequently, the PCB and HCB pollution is the most important.

Considering these results, it could be concluded that a better knowledge of these compounds in sewage sludge for land application would be desired. Type of effluent, agricultural, urban or industrial, as well as likely influence and environmental fate of these substances in the soil should be assessed. In accordance with other European countries, further studies on this filed are recommended. Current data only constitute a first approach and, consequently, these observations need to be confirmed by enlarging number of samples and facilities evaluated, in order to provide more information, which may be useful for making-decision support systems at both national and international regulatory scale.

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