# PCDDs AND PCDFs IN SOILS NEAR A CLINICAL WASTE INCINERATOR IN MADRID, SPAIN. CHEMOMETRIC COMPARISON WITH OTHER POLLUTION SOURCES

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Polychlorinated dibenzo-p-dioxins (PCDD) and Polychlorinated dibenzo-p-furans (PCDF) are widely distributed in soil and air particulate from industrialise and heavily populated environment[1-3]. Due to the widespread concern over the presence of these compounds in the environment, it would be very important to determine their sources and transport mechanism, as well as their ultimate effects and fate in the environment.

According to the literature the major sources of PCDD/Fs soils contamination include combustion processes in the presence of chlorine such as municipal, sewage sludge, hospital and industrial waste incinerators, metallurgic and industrial processes and a widely used of organochlorine compounds[4-5]. There is pronounced differences in both isomeric patterns and congener profiles of PCDDs and PCDFs between a) industrial related and b) combustion emissions The number of congeners present in industrial sources are limited and characteristic, whereas in the case of combustion emissions most congeners are present. It is possible to take advantage of those differences in the knowledge of the pollution sources using multivariate data analysis techniques.

The aims of this work is:

1. To determine if there is a PCDD/F contamination in soils surrounding the CWI located near Madrid, Spain.
2. To determine whether the PCDD/F profile and pattern in these soil are similar or different from those associate with known or suspected environmental sources, using multivariate analysis techniques.
3. To determine whether more than one potential source could explain the presence of these compounds in the studied soils

## MATERIAL AND METHODS

### *Study area*

The clinical waste incinerator was located in Valdemingomez at 15 km east Madrid, Spain, near the metropolitan dump site. Nearby, there are several uncontrolled scrap car reclamation sites. In close proximity there is a busy high way, and a secondary road leading to

Valdemingomez area with Diesel trucks heavy traffic . All these activities are suspected sources of PCDD/F emissions. The incinerator burns plastic medical waste enclosed in plastic containers. These plastic containers, themselves, could possibly contain significant amounts of PCDD/Fs.

Sampling sites were selected considering the prevailing wind direction (north west) at distances of 0.4, 1, 2 and 4.5 km from the suspected emission source.Additionally, to obtain background levels, two remote sites, where emission of PCDD/Fs could be excluded, were selected in the same region.

*Quantitative analysis*

The extraction, clean up and HRGC/HRMS analysis have been reported elsewhere[6]. Basically the method consists in a extraction with toluene in a Soxhlet apparatus during 36 hours followed by a series of columns of silica gel, acid modified silica gel ( 44 % concentrated sulphuric acid), basic modified silica gel (33 % 1M NaOH). Extracts were concentrated to 1 ml and fractionated on liquid chromatography using Florisil activated a 130° C at least 18 h. using methylchloride and hexane. The quantitative analysis was carried out by HRGC/HRMS in mode SIM using the dilution isotopic technique.

*Multivariate analysis*

A data base which contents more than 120 pieces of data from soils and effluents polluted by typical emission of PCDD/Fs was gathered from the available literature and put together. From this data base two matrices were formed. One containing analytical data of 2,3,7,8-substituted PCDD/F congeners (pattern), and the other one containing total tetra to octa PCDD/Fs (profiles). Both matrices included the data from the studied soils

The chemometric comparison was done using Principal Components Analysis (PCA), which is a technique for dimension reduction that decomposes the pre-treated data (x) into a sample score matrix (T) times loading matrix (p) plus a residual matrix (E) as shown in equation (1):

$$X = TP' + E$$

The objective of PCA is to derive a few new components as linear combinations of the original variables which will provide a description of the structure of the data with a little loss of information as possible.

The data were scaled to minimise any statistical bias associated with the orders of magnitude differences in chemical concentrations. Data were normalised by expressing the concentration of individual variables as a percentage of the combined sum of the total variables

## RESULTS AND DISCUSSION

The PCDD/Fs levels found in the 14 soils analised near the CWI were between 0.82 and 11.42 ng/kg of I-TEQ. The lower values were similar to those found in the two control points located at 4.5 km far from the CWI. The higher values correspond to the soils located between 0.4 and 1 km under the wind direction

The 2,3,7,8 substituted PCDF congeners have been found in almost all the samples analysed. Levels are decreasing with the chlorination degree from tetra to octafurans. Only one of the samples exhibits very high levels for all the PCDF congeners, and their concentrations are increasing with the chlorination degree from tetra to octa furans. We have not found any explanation for so high levels found in this soil, located in the south direction 2.5 km from the CWI.

Dioxin levels were lower than Furans, and all the 2,3,7,8 substituted congeners were found in soils down wind of the CWI.

The percentage of the 2,3,7,8 substituted PCDD/F congeners with respect to each homologue congener group was very small ( around 10 %), for the lower chlorinated congeners such as tetra, and penta dioxins and furans, and between 50 and 70 % for hexa and hepta congeners.

**Multivariate analysis**

*Comparison of the homologue profile*

The calculation of the principal components of the homologue profile ( total tetra to octa PCDD/Fs) of the different soils polluted by different emission sources, indicate that 67.12 % of the total variability is accounted for in the first three principal components..

The first principal component axis was mainly formed by tetra and penta furans, and octadioxins, the second one was formed by tetra, penta and octadioxins, and heptafurans, and the third one by penta and hexa dioxins, and tetrafurans

The chemometric comparison of the PCDD/F homologue profile for soils near a CWI and other polluted sources let us to know that these soils have a typical combustion profile, mainly characterised by tetra, penta and hexa furans. This profile is similar to other clinical waste incinerator and very close to soils polluted by combustion of PCBs or materials with high PCB content , probably due to the characteristics of the waste incinerated in the clinical incinerator that probably contains plastics with PCBs.

*Comparison of the 2,3,7,8, substituted PCDD/F congeners pattern*

The calculation of the principal components of the 2,3,7,8 PCDD/F pattern ( the 17 2,3,7,8 substituted congeners) of the different soils polluted by different emission sources, indicate that 69.31 % of the total variability is accounted for in the first three principal components.

The first principal component axis was mainly formed by 1,2,3,7,8-P5CDF, 1,2,3,4,7,8-HxCDF, OCDD and OCDF. The second P.C. axis was formed by 1,2,3,7,8,P5CDF, 2,3,4,7,8-P5CDF and 1,2,3,4,7,8-HxCDF, 1,2,3,7,8,-P5CDD and 1,2,3,4,7,8-HxCDD. The third PC axis was mainly formed by the 2,3,7,8- HxCDDs, 2,3,4,7,8,9, HxCDF and 1,2,3,4,7,8,9,-HpCDF.

The results of the Principal component calculations for the pattern of 17 congeners 2,3,7,8 substituted of PCDD/Fs in soils polluted by different sources showed various fingerprint patterns in the dimensional space formed by the three first principal components, corresponding to combustion and no combustion sources. The studied soils, as occurred in the profile study, were included with soils polluted by combustion sources, being very close to other CWI, soils with typical combustion sources, soils polluted by the combustion of PCBs, and soils polluted by traffic emissions.

## CONCLUSIONS

The soils surrounding the clinical waste incinerator, near Madrid, Spain, have a typical combustion profile , mainly characterised for high levels of low chlorinated congeners as tetra, penta and hexa dioxins and furans, and low levels of higher chlorinated congeners.

The chemometrics comparison of the PCDD/Fs congener distribution of the studied soils with PCDD/Fs polluted sources, indicate that they have a similar profile and pattern to combustion sources. They are very close to emissions from Clinical Waste Incinerators, and soils polluted by heavy traffic and combustion of material containing PCBs.

Principal Component Analysis is a powerful tool for detecting compositional similarities and differences in chemical residues among environmental samples.

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