

PATTERNS OF DIOXINS AND FURANS IN URBAN, NON URBAN AND MARINE SEDIMENTS IN SOME ENVIRONMENTAL SYSTEMS OF CONCEPCION, REGION DEL BIO BIO, CHILE

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Introduction

The sources that produce polychlorinated dibenzo-p-Dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) have been well documented, being the anthropogenic sources the most important, such as; medical waste incineration, internal combustion, backyard burn, wood combustion and some specific industrial processes like the bleaching of wood pulp during the cellulose pulp production^{1,2,3}. Environmental and health authorities have defined, that, of the total Dioxins and Furans identified by the scientific community, just 17 congeners, ten furans and seven dioxins, have deleterious effects on the human health⁴. Several authors have concluded that the relative proportions of each PCDD/F in the same sample are differs for different sources⁵. That difference in the relative proportion is a powerful tool for associate a fingerprint to a specific source⁶.

After being released to the environment, the Dioxins and Furans are exposed to different weathering processes, such as photodegradation by ultraviolet radiation, biodegradation and bioaccumulation⁶. That weathering process produces a modification in the relative proportions of each Dioxin and Furan, and consequently a modification in the fingerprint. Those environmental processes difficult the final source identification⁶. Different methods have been described for standardization of the sample before the application of fingerprint technics, such as; 2, 3, 7, 8-Sum, Relative homologue, Relative TEQ (Toxic equivalents) and total homologue⁶. Relative homologue and Relative TEQ show an advantage over the other methods despite neutralizing the effect of some weathering processes⁶.

Different statistical tools may be used for the analysis of the normalized concentrations of Dioxins and Furans, which can vary from histograms, that only represent the profile for each homologue of TCDD/F in different samples, to more complex statistical tools, like principal components analysis (PCA), that allow to compare a large number of data and classify it by similar fingerprints⁶.

Concepcion is a city located in the central zone of Chile, about 500 km south from Santiago City, the capital of Chile, and 12 km from the coast. The city is placed in the middle of a complex hydrological system composed by several lagoons and the river Bio-Bio, which are affected by the urban activities which develop in the surroundings. The main urban activities that take place in the city are; residential wood burning, automotive transport and petrochemical activities. Moreover the city is surrounded by large extensions of pine and eucalyptus forests that in the summer season are dramatically affected by fire forests.

The main objective of this work is to identify common sources of Dioxins and Furans in sediments of five lagoons: Lo Galindo (LG), Las Tres Pascualas (LLTP), Lo Mendez (LM), Redonda (LR), located in the urban area of Concepcion City and Quinenco (LQ) located 30 km south from the city in rural area. And two corers of marine sediments (COR1 and COR2) from Coliumo bay, which is located at around 32 Km north from Concepcion city.

Materials and methods

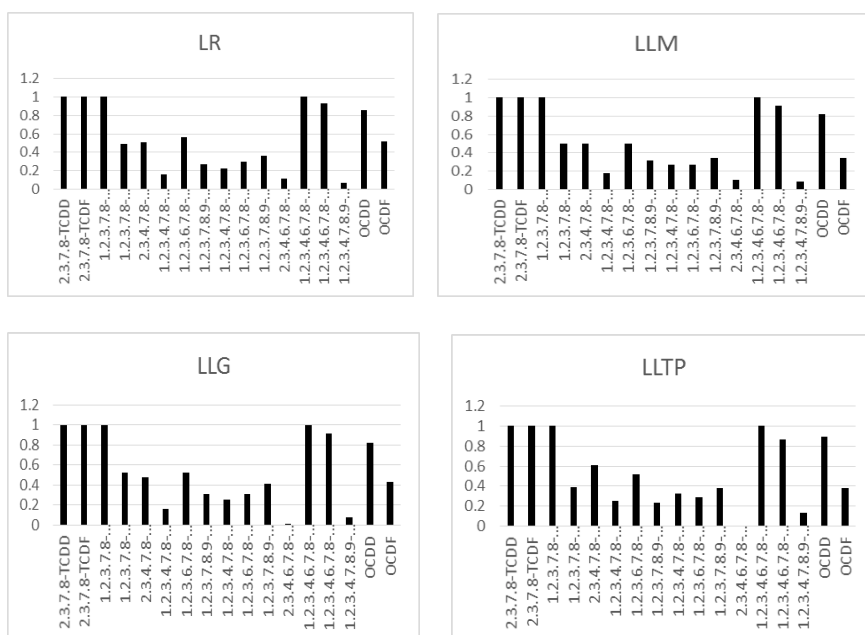
Freeze dried samples were extracted using an automated pressurized liquid extraction system (FMS.Inc. USA) with a mixture of n-Hexane: Dichloromethane 1:1, at 120°C and 1700 psi. The extracts were then purified using the automated Power Prep system provided by FMS. The final extract containing the Dioxins and Furans were dried and suspended with nonane to a final volume of 20 μL . Quantification was carried out using the standards; EDF-9999, EDF 8999, EDF-5999 and EDF-6999 provided by Cambridge Isotope Laboratory, USA. Extracts were analyzed using a High resolution Gas Chromatograph, Trace 1310, Thermo, coupled to a High Resolution Mass Spectrometer, DFS, Thermo. Separation was made with a specific TG-Dioxin column, 60m x 0,25mm x 0,25 μm . Chromatographic conditions were; inlet temperature 260°C, oven temperature ramp 120 to 315°C, transfer line 280°C. The Mass spectrometer configuration; source temperature 250°C, electron energy 48eV, resolution, no less than 10000 and, MID mode. Extraction, analysis and quantification methods were based on EPA 1613 Rev. B protocol⁷.

The statistical analysis was made using the software SIMPCA-P version 10.0

Results and discussion:

PCDD and PCDF were present in all the analyzed sediments. For both lagoon and marine sediments, OCDD was the congener with the dominant concentration, followed by 1,2,3,4,6,7,8-HpCDD. Congener 2,3,7,8-TCDD was under the detection limit for all samples (LoD for 2,3,7,8-TCDD in sediment was 0.0001ng g⁻¹, and 0.0002 ng g⁻¹ for penta through Octa). The Toxic Equivalent Factor assigned for 2,3,7,8 TCDD is 1. The absence of this congener in the studied sediments reduces the toxic charge in them. This can be seen in the calculated total TEQ values for the studied samples (97.06-2250.54 TEQ ng kg⁻¹). For the normalization of the 2,3,7,8 TCDD, half of the limit of detection value was used. To gather more information related to the fingerprint for Dioxins and Furans founds in the sediment samples, two additional samples were extracted and analyzed. The first one was an air particle filter from our laboratory, around 1 km from the downtown of the city. This filter is used for cleaning the air that is injected to the laboratory used to generate positive pressure. The second one, was an automotive air engine filter, from a car that is only used within the limits of Concepcion city.

The normalization of concentrations for Dioxins and Furans in each sample was made using the Relative Homologue method (RH), in which each concentration is divided by the total concentrations of the same homologue⁶. Figure 1, shows the histograms with the profiles generated using the RH normalization method, for LR, LLM, LLG, LLTP, LQ, Engine filter, Air filter and superficial marine sediments (COR1, 0-1cm and COR2, 0-1cm).



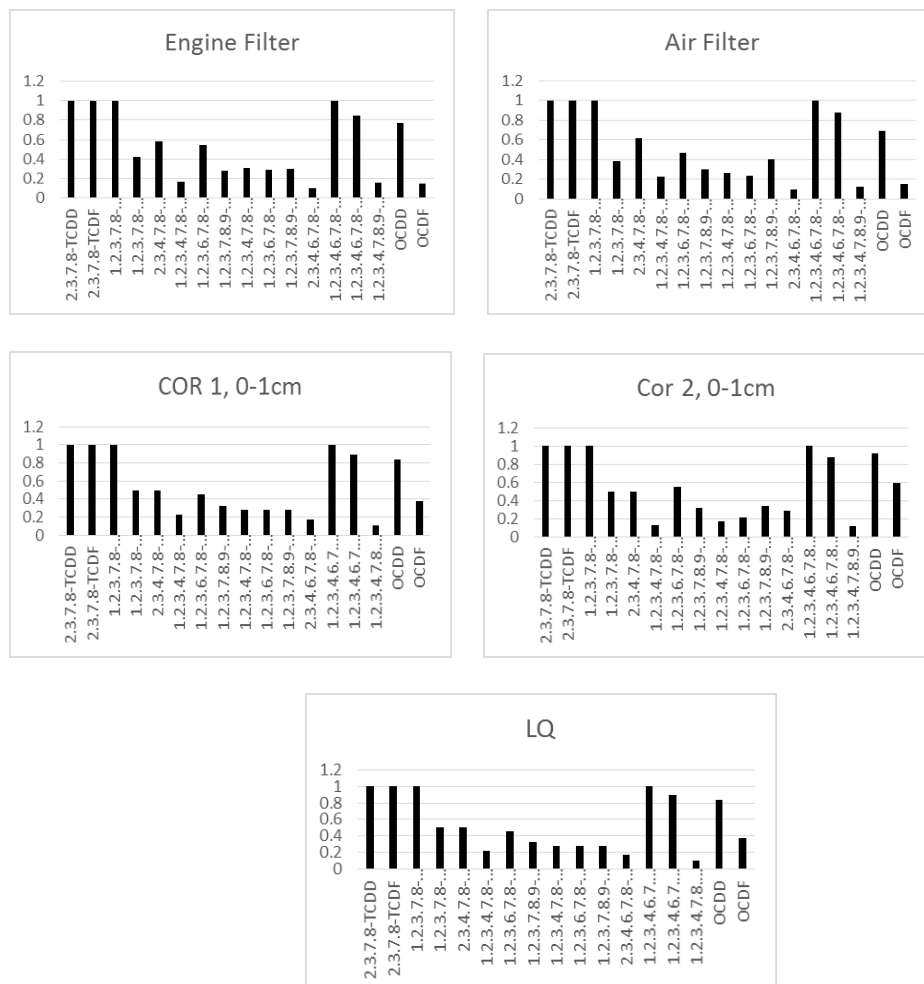


Figure N°1. Profiles found for Dioxins and Furans using the relative homologue normalization method, for samples of sediments analyzed.

The histograms allows the clustering of the samples with similar profiles. Three clusters were identified, conformed by: Engine filter, Air Filter and LLTP; LR, LLM and LG; LQ, Cor1, 0-1 cm. and Cor2, 0-1cm. Cor1 and Cor2, have a total length of 42 cm and 38cm respectively. Both were sectioned and analyzed one by one centimeter, for the first 10 cm., and the remaining length, by each two centimeters. The profiles for segments between 2cm. to 42cm and 2cm to 38cm respectively, were different than the superficial profiles. That variation may be produced by weathering effects.

Figure 2, shows PCA analysis for sediment samples, using relative homologue normalization method. This statistical analysis clusters the samples according to their fingerprint profile. PCA analysis suggest that Dioxins and Furans for LLTP come from the same source than Engine Filter and Air Filter. Same source is suggested for LLG, LR, LLM and segment 2-3 for COR1. LQ have the same profile that COR1,0-1cm. The remaining samples form different clusters. The deeper segments of the corers have a long period of deposition and long periods of weathering processes. Those processes change the original signatures of Dioxins and Furans.

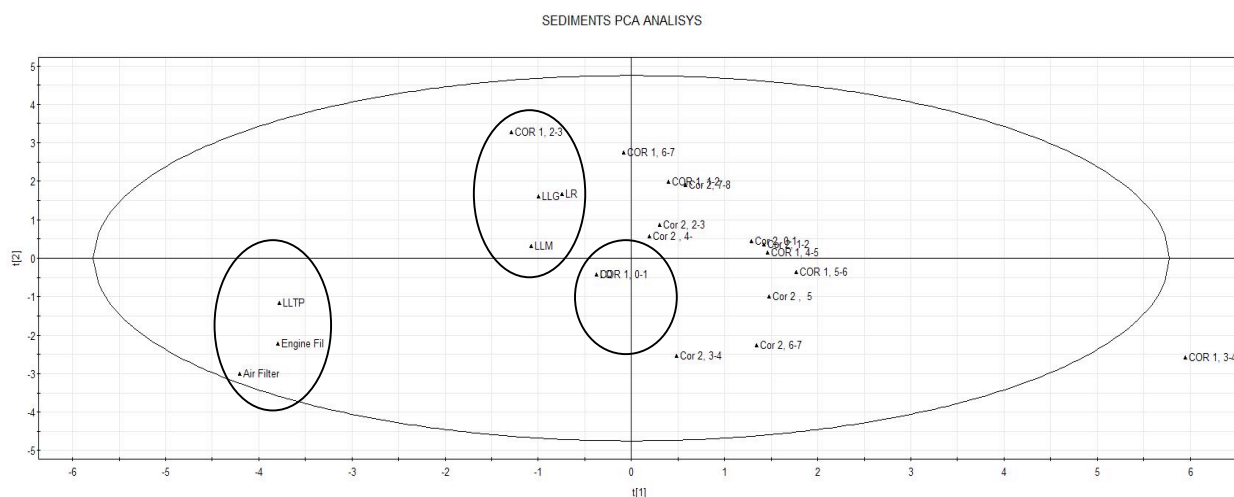


Figure N°2: Principal components analysis for sediments samples analyzed.

The results of this study suggests that the input of Dioxins and Furans in the superficial sediment of the lagoons located in the urban area of Concepcion city have the same composition than particulated material trapped by the filters. Superficial sediments of the non urban lake and superficial marine sediments of corers have input of Dioxins and Furans with a different signature than the urban area. This suggests that the sources of Dioxins and Furans are different for each cluster.

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