# DIOXINS, FURANS AND DIOXIN LIKE PCB LEVELS IN AGRICULTURAL AND FOREST SOIL FROM SÃO PAULO STATE, BRAZIL

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## Introduction

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) are present in the environment primarily as a result of human activities. These compounds are persistent, bioaccumulative and at elevated levels are known to be toxic to humans and other organisms. They are subject to long-range transport and have been measured in remote soils from human activities[4]. They are included in the list of Stockholm Convention Persistent Organic Pollutants (POPs) and Brazil as a Part of this Convention has been working to develop strategies and action plans to reduce the emission of these pollutants.

According to the Brazilian Inventory of sources and estimation of emissions of dioxins and furans[1], the southeast region with a high degree of industrialization and agricultural activity, contributes with 58.8% of emissions of dioxins and furans and São Paulo State is the biggest national contributor for the emissions (28.9%). The national action plan proposed to reduce PCDD/PCDF emissions and highlights the need (1) to evaluate the effectiveness of the strategies implemented by monitoring these pollutants in the environment and (2) to review the national regulations and guidelines lists to include dioxins and furans in the regulation/guideline to evaluate the monitoring results.

In Brazil, for the evaluation of soil quality monitoring activities there is a national orientative guideline list that includes inorganic and organic substances, but till now do not include dioxin like compounds. The use of guideline values lists have been common practices in countries with tradition in protecting the soil and groundwater quality and for control of contaminated areas. The guiding values are concentrations of chemicals that provide guidance on the condition of soil and groundwater quality and amendments imposed by anthropic action. São Paulo State has established guideline values for chemical substances in soil and ground water, were are defined soil quality reference (QRV), preventive values (PV) and intervention values (IV). The QRV is the background concentration of chemicals in soil or ground water and it was considered only the group of naturally occurring inorganic substances on the basis of geochemical processes. Anthropic organic compounds were considered naturally absent and therefore QRV was not applicable, but it is known that some organic compounds like PCDDs and PCDFs can be formed at natural conditions like incomplete combustion of organic material by forest fires, volcanic activity and the action of micro organism on chlorinated phenolic compounds can produce PCDD/PCDF[2].

CETESB has just started the study for dioxin like compounds to increase the understanding the level of these compounds in soil and in the future subsidize the establishment of guiding values in São Paulo State and for national guide.

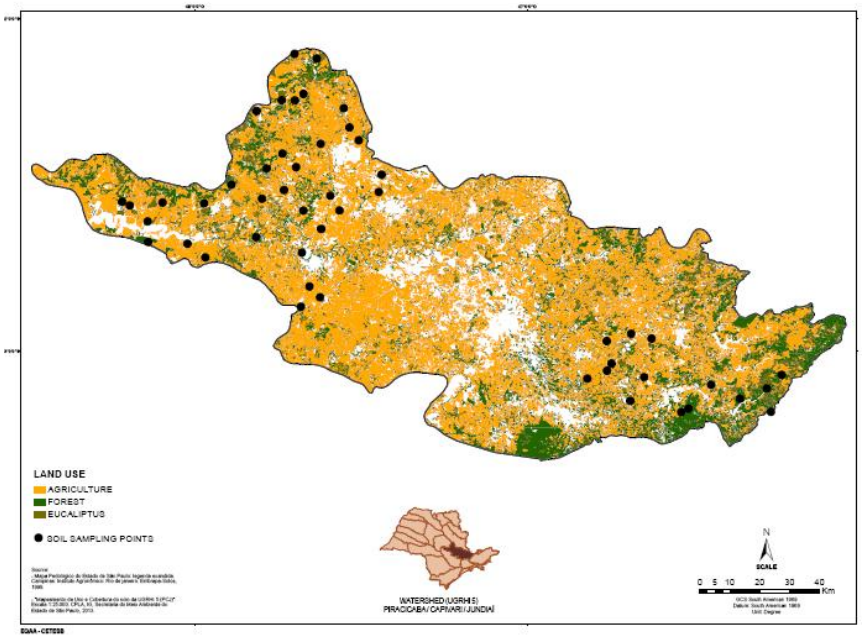
## Materials and methods

The area chosen for the study is one of the 22 Watershed Management Units of São Paulo State (UGRHI 5) and consists of basins of Piracicaba (11,320km$^2$), Capivari (1,570km$^2$) and Jundiaí (1,150km$^2$) rivers. The basin of these rivers covers 57 municipalities and, according to the IBGE (Brazilian Institute of Geography and Statistic) projection for 2012, comprises over 12% of the state population, of which 96% lives in urban areas.

Traditionally agricultural (mainly sugarcane and coffee plantations), the region has become in recent decades a major industrial centers in the country.

Composite soil samples were collected at a depth of 0 to 20 cm, with stainless steel auger, homogenized and packed in glass jars. The total of 49 samples (21 samples from forest fragments and 28 samples from agricultural area) were collected during 2011 and 2012. Two types of land use were considered for this study: agricultural and forest fragments. The Figure 1 shows the location of sampling points.

**Figure 1 – Sampling site**




Soil samples were extracted and analysed according to the method US EPA 8290A[3]. The samples were spiked with 13C12-PCDD/F internal standards (Wellington Laboratories) and extracted for 24 hours in a Soxhlet extractor with toluene: acetone (9:1). The extracts were purified in an acid silica column (40% $H_2SO_4$ and 10% $AgNO_3$) and then in an Alumina column. The final extracts were concentrated to dryness and ressuspended with 10µL of internal standards (13C12-1234-TCDD and 13C12-123789-HxCDD). The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatographic coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS), operating with electron impact ionization of 35eV at a mass resolution of 10.000. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 µm film thickness). The limit of detection/quantitation (LOD/LOQ) was calculated for each sample considering the signal/noise of 3 for LOD and 10 for LOQ using the MassLynx software (Waters).

**Results and discussion**

The results of total PCDD/PCDF and dl-PCBs expressed as $WHO_{05}$ TEQ are summarized in Table 1. The total TEQ was calculated using lower and upper bound concept. For TEQ calculation using lower bound, all results below limit of quantitation/detection (LOQ/LOD) was considered as zero and for upper bound all results below LOQ/LOD are considered equal to LOD/LOQ value.
As can be seen at Table 1, there are significant differences when are used zero, LOD or LOQ for results below detection/quantitation limit (LOD/LOQ). Therefore, for the establishment of guideline value is necessary to define criteria to calculate PCDD/PCDF/dl-PCB results expressed as TEQ. For concentrations below LOD/LOQ, there are several different treatments to estimate the TEQ that can be based upon including unquantified concentration as zero contributors, others took ½ of LOD values[4] or LOQ values .

**Table1 – Concentration of PCDD/PCDF+dl-PCBs in soil samples (ng TEQ $WHO_{05}$/kg d.w.)**

| Land use/culture | $TEQ_{\sum PCDD/F+dl-PCB}$ (<LOD = 0) | $TEQ_{\sum PCDD/F+dl-PCB}$ (<LOD = LOD) | $TEQ_{\sum PCDD/F+dl-PCB}$ (<LOQ = LOQ) |
|---|---|---|---|
| Forest fragments (n=21) [min – max] | 0.11 [0.001 – 0.37] | 0.89 [0.47 – 1.45] | 2.50 [1.40 – 4.08] |
| Sugarcane (n=18) [min - max] | 0.09 [0.0008 – 0.42] | 0.81 [0.07 – 1.52] | 2.28 [1.36 – 3.72] |
| Sugarcane (n=2)* [min - max] | 4.79 [3.58 – 6.00] | 6.07 [4.64 – 7.49] | 6.55 [4.85 – 8.24] |
| Bean (n=1) | 0.27 | 1.28 | 3.29 |
| Citrus (n=1) | 0.005 | 0.50 | 1.67 |
| Eucalyptus (n= 2) [min - max] | 0.08 [0.01- 0.14] | 1.22 [0.82 – 1.62] | 3.45 [2.52 – 4.39] |
| Pumpkin (n=1) | 0.03 | 1.16 | 3.35 |
| Roses (n=1) | 1.43 | 3.09 | 5.76 |
| Sorghum (n=1) | 0.001 | 0.80 | 2.62 |
| Strawberry (n=1) | 1.67 | 2.65 | 4.79 |

*Sugarcane culture: two samples results were well above the average and were calculated separated

Considering the results below LOD/LOQ as zero, and comparing the values with the Dutch guide for ecological risk evaluation of PCDD/F and dioxin like PCBs in soil (2ng TEQ/kg)[5], only 2 samples from sugarcane culture are higher than this guide. Considering the LOD/LOQ values for results below these limits, this number increases to 4 samples and 31 (63%) samples respectively. For regulatory purposes the laboratories in São Paulo usually express the results using the LOQ value, therefore for low concentration of PCDD/F and dl-PCBs evaluation it is necessary to have care and consider the analytical limits. It was calculated TEQ values considering the Dutch reference (Nato88 for PCDD/F) but as the concentrations are very low, there were not observed significative differences.

**Table2 – Concentration profile of PCDD, PCDF and dl-PCBs in agricultural and forest fragments soil samples (ng TEQ $WHO_{05}$/kg d.w.), considering results <LOD=zero for TEQ calculation**

| | Forest fragments (n=21) | Sugarcane (n=18) | Sugarcane* (n=2) | Eucalyptus (n=2) |
|---|---|---|---|---|
| $TEQ_{\sum PCDD\ (mean)}$ [min - max] | 0.07 [0.0008 – 0.29] | 0.06 [0.0006 – 0.37] | 2.90 [1.63 – 4.17] | 0.02 [0.010 -0.022] |
| $TEQ_{\sum PCDF\ (mean)}$ [min - max] | 0.01 [0.00 – 0.17] | 0.017 [0.00 – 0.13] | 1.82 [1.82 – 1.82] | 0.00 |
| $TEQ_{\sum PCDD/F\ (mean)}$ [min - max] | 0.08 [0.0008 – 0.30] | 0.08 [0.0006 – 0.37] | 4.72 [3.46 – 6.00] | 0.02 [0.010 - 0.022] |
| $TEQ_{\sum dl-PCB\ (mean)}$ [min - max] | 0.03 [0.0002 – 0.13] | 0.01 [0.0001 – 0.10] | 0.06 [0.005 – 0.12] | 0.06 [0.0008 – 0.12] |
| $TEQ_{\sum PCDD/F+dl-PCB\ (mean)}$ [min - max] | 0.11 [ 0.001 - 0.37] | 0.09 [0.001 – 0.42] | 4.79 [3.58 – 6.00] | 0.08 [0.01 - 0.14] |

*Sugarcane culture: two samples results were well above the average and were calculated separated

The dl-PCB contribution for the total TEQ are lower than PCDD/F and are very similar profile for all kind of cultures and forest fragments. Evaluating the individual profile of PCDDs and PCDFs, the most abundant PCDD was the octa chlorinated dioxin (OCDD) that was quantified in all 49 samples analysed followed by heptachlorinated dioxin (1234678-HpCDD) quantified in 41 samples (84%) and heptachlorinated furan

(1234678Hp-CDF) quantified in 26 samples (53%) whereas the octa chlorinated furan (OCDF) was quantified in 22 samples (45%). The other congeners was quantified in a very low percentage. The most toxic tetrachlorinated dioxin (2378-TCDD) was detected in 16 samples but all of them were lower than LOQ.

**Table3 – Concentration profile of PCDD, PCDF and dl-PCBs in agricultural soil samples (ng TEQ $WHO_{05}$/kg d.w.), considering results <LOD=zero for TEQ calculation**

| | Bean | Citrus | Pumpkin | Roses | Sorghum | Strawberry |
|---|---|---|---|---|---|---|
| $TEQ_{\sum PCDD}$ | 0.03 | 0.001 | 0.02 | 0.89 | 0.001 | 1.50 |
| $TEQ_{\sum PCDF}$ | 0.18 | 0.004 | 0.01 | 0.22 | 0.000 | 0.09 |
| $TEQ_{\sum PCDD/F}$ | 0.21 | 0.005 | 0.03 | 1.12 | 0.001 | 1.59 |
| $TEQ_{\sum dl-PCB}$ | 0.07 | 0.0001 | 0.0004 | 0.31 | 0.0002 | 0.08 |
| $TEQ_{\sum PCDD/F+dl-PCB}$ | 0.27 | 0.005 | 0.03 | 1.43 | 0.001 | 1.67 |

n=1 for all cultures

Comparing the results with Amazon Basin soils in Brazil (0.02 – 0.4ng TEQ/Kg)[6], the results are similar or slightly above the Amazon region. Comparing the results with other forest soils from Austria (0.01-64ngTEQ/kg), Germany (10-30ng TEQ/kg), Ireland (4.8 ng TEQ/kg), Luxemburg (6.0 ng TEQ/kg d.w.) and any tipe of soils from Belgium (2.7 – 8.9 ng/TEQ/kg), Italy (0.057 – 0.12 ng TEQ/kg), UK (0.78 – 87 ng TEQ/kg)[7], the results are very similar or even below.

According to the Brazilian Inventory of sources and estimation of emissions of dioxins and furans[1], sources of emissions to soil identified are fires and burning in open air, accidental or not (54%) and biomass burning in open air (46%). The deposition from the air can be one of source of dioxin like compounds found in the samples. The samples from sugarcane culture with higher concentration levels (n=2) indicate that it can be due to the application of residue from sugarcane industry but it was not possible to confirm.

Thorough this study results, can the concluded that the study area are not impacted with high level of dioxin like compounds but as these compounds can accumulate in soil with a long memory it can concentrate in a long period. The results of this study will contribute for the debate of environmental quality and pollutants monitoring. The knowledge of sources and emissions reduction are priority actions to fulfill the objectives of the Stockholm Convention.

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