

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. According to the Brazilian Inventory of sources and estimation of emissions of dioxins and furans¹, 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%). 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. 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.

Table1 – Concentration of PCDD/F+dI-PCBs in soil samples (ng TEQ WHO₀₅/kg d.w.)

| Land use/culture | TEQ _{ΣPCDD/F+dl-PCB} (<lod 0)<="" =="" th=""><th>TEQ_{ΣPCDD/F+dI-PCB} (<lod =="" lod)<="" th=""><th>TEQ_{ΣPCDD/F+dl-PCB} (<loq =="" loq)<="" th=""></loq></th></lod></th></lod> | TEQ _{ΣPCDD/F+dI-PCB} (<lod =="" lod)<="" th=""><th>TEQ_{ΣPCDD/F+dl-PCB} (<loq =="" loq)<="" th=""></loq></th></lod> | TEQ _{ΣPCDD/F+dl-PCB} (<loq =="" loq)<="" th=""></loq> |
|-------------------|--|--|--|
| Forest fragments | 0.11 | 0.89 | 2.50 |
| (n=21) | [0.001 - 0.37] | [0.47 - 1.45] | [1.40 - 4.08] |
| [min – max] | | | |
| Sugarcane (n=18) | 0.09 | 0.81 | 2.28 |
| [min - max] | [0.0008 - 0.42] | [0.07 – 1.52] | [1.36 – 3.72] |
| Sugarcane (n=2)* | 4.79 | 6.07 | 6.55 |
| [min - max] | [3.58 – 6.00] | [4.64 – 7.49] | [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) | 0.08 | 1.22 | 3.45 |
| [min - max] | [0.01- 0.14] | [0.82 – 1.62] | [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 |

Materials and Methods

Sampling Site

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 (11,320km²), Capivari (1,570km²) and Jundiaí (1,150km²) rivers. The basin of these rivers covers 57 municipalities and comprises over 12% of the state population. Traditionally agricultural (mainly sugarcane and coffee plantations), the region has become in recent decades a major industrial centers in the country.

The total of 49 composite samples were collected during 2011 and 2012. Two types of land use were considered for this study: agricultural and forest fragments.

Figure 1 – Sampling sites: São Paulo State Watershed Management Unit 5 (UGRHI 5)

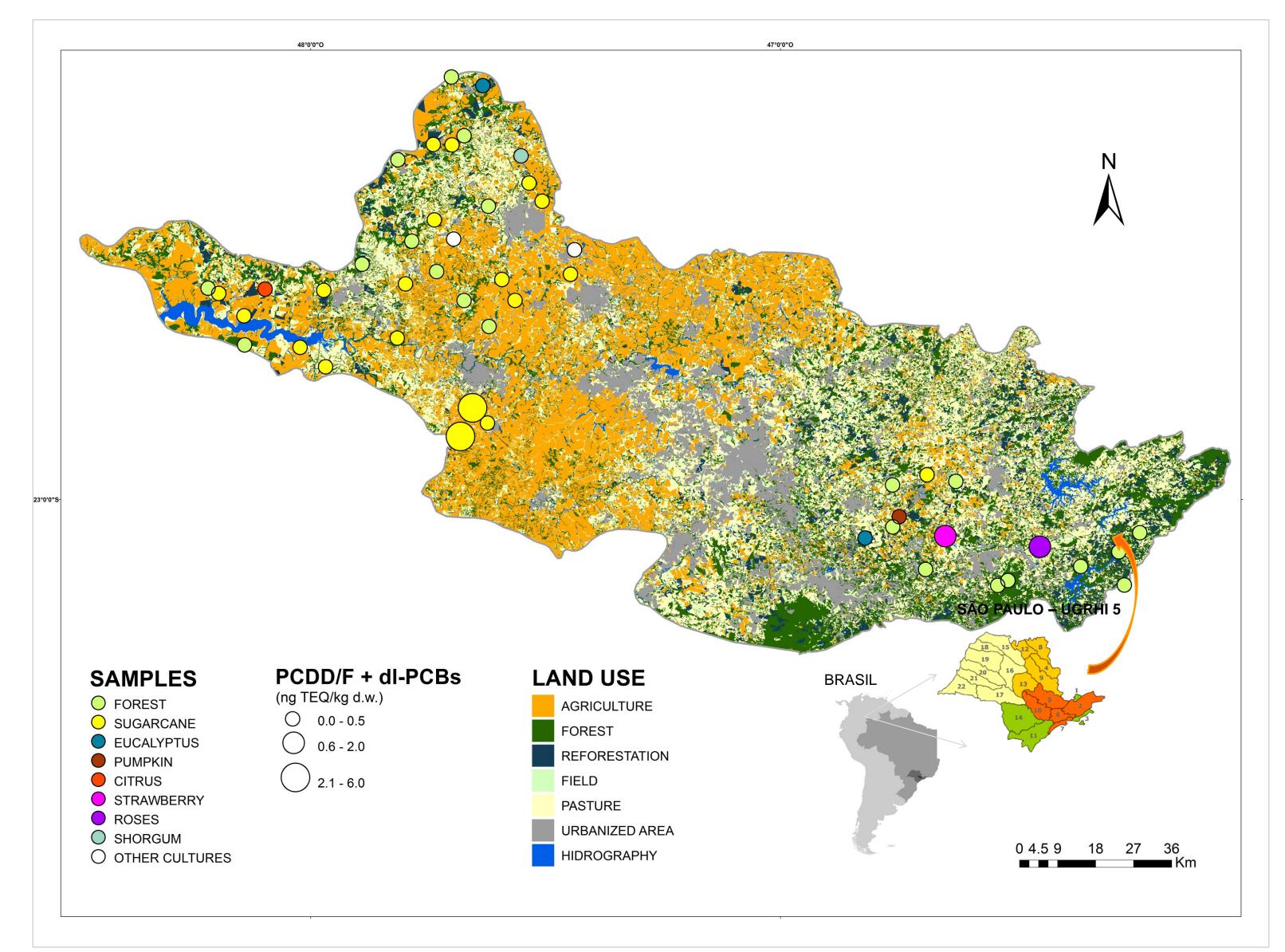


Table2 – Concentration profile of PCDD/F and dI-PCBs in agricultural /forest fragments soils (ng TEQ WHO₀₅/kg d.w.), considering results <LOD=zero for TEQ calculation

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

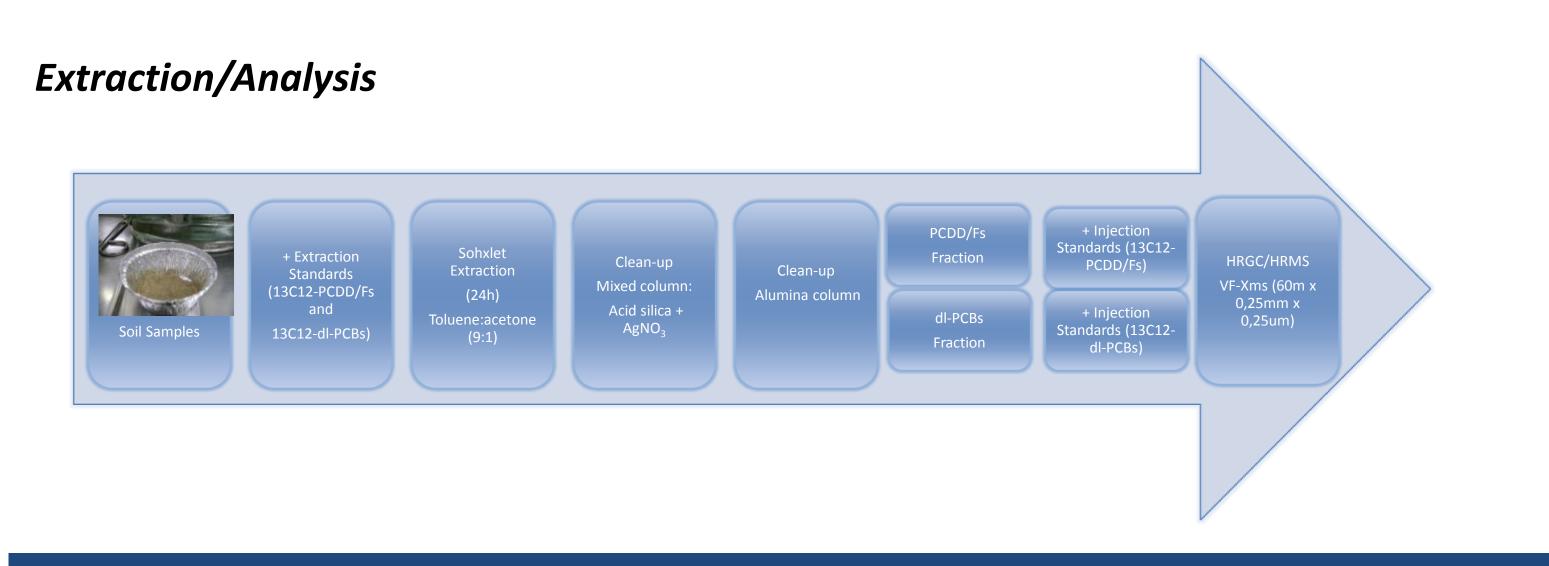


Table 3 – Concentration profile of PCDD, PCDF and dI-PCBs in agricultural soil samples (ng TEQ WHO₀₅/kg d.w.), considering results <LOD=zero for TEQ calculation

| Concentration (ng TEQ/kg) | Bean | Citrus | Pumpkin | Roses | Sorghum | Strawberry |
|------------------------------|------|--------|---------|-------|---------|------------|
| ∑PCDD | 0.03 | 0.001 | 0.02 | 0.89 | 0.001 | 1.50 |
| ∑PCDF | 0.18 | 0.004 | 0.01 | 0.22 | 0.000 | 0.09 |
| ∑PCDD/F | 0.21 | 0.005 | 0.03 | 1.12 | 0.001 | 1.59 |
| ∑dI-PCB | 0.07 | 0.0001 | 0.0004 | 0.31 | 0.0002 | 0.08 |
| ∑PCDD/F+dI-PCB | 0.27 | 0.005 | 0.03 | 1.43 | 0.001 | 1.67 |

Results and Discussion

The PCDD/F results (Table 1, 2 and 3) are similar or slightly above the Amazon basin⁶ soils and very similar or even below other countries (Austria, Germany, Ireland, Luxemburg)⁷ forest soils. According to the Brazilian Inventory of sources and estimation of emissions of dioxins and furans¹, sources of emissions to soil identified are fires and burning in open air (54%) and biomass burning in open air (46%). The deposition from the air can be one of sources 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.

Acknowledgements

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References

 BRASIL, MMA. Inventário Nacional de fontes de estimativa de emissões de dioxinas e furanos. Brasília, MMA, 2013. http://www.pnuma.org.br/admin/publicacoes/texto/Inventario_Dioxinas_Furanos_web_-_ISBN978-85-7738-180-7.pdf
Moche W, Szabo Z. Horizontal Standardization for soil, sediment, sludge and bio-waste. 2004.
[US EPA] Method 8290A, 2007
[CCME] Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health - Polychorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDD/Fs), 2002.
Health Council of the Netherlands: Committee on Risk Evaluation of Substances/Dioxins. Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls. Rijswijk: Health Council of the Netherlands, 1996; publication nº1996/10E. ISBN: 90-5549-115-2.

6. [UNEP] Regionally Based Assessment of Persistent Toxic Substances - Eastern and Western South America Regional Report, 2002.

7. Fiedler H. The Handbook of Environmental Chemistry, v.30, 2003. P. 123-201.

8. [US EPA] Method 1668C, 2010.