ASSESSMENT OF PCDD-PCDF EMISSIONS FROM THE COPESUL/SOUTH PETROCHEMICAL COMPLEX LOCATED IN SOUTHERN BRAZIL

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Introduction

COPESUL is the Raw Material and Utilities Central of the South Petrochemical Complex, this, being the most modern industrial facility of its type in Brazil, and the second largest naphtha cracker in the country. Responsible for more than 40% of Brazilian olefins production, it is also among the largest crackers (on the same site) in the world. The majority of COPESUL products are transformed by downstream industries of the Complex into thermoplastics resins, synthetic rubber, styrene and solvents that are widely used in the manufacturing of packing material (food, hygiene, cleaning), electronic appliances, medical and surgical supplies, toys and in the car industries, to be consumed in Brazil and foreign countries.

At the request of the local state Environmental Protection Agency, an Environmental Assessment of Priority Pollutants (EAPP) was performed at the end of the year 2000 and at the beginning of the year 2001. This large-scale EAPP was requested after it was determined that the previous EAPP (1997) was non-conclusive for a defensible and reliable environmental assessment. Among the different (organic and inorganic) parameters tested, PCDD-PCDF was a main concern to the local State Agency with regards to the Complex activities and of it's potential impact on the human health and the environment, despite the fact that the Complex does not uses or produces any organo-chlorinated product. More specifically, potential sources of PCDD-PCDF such as waste water effluents, sludge from the drinking water treatment unit of COPESUL (where chlorine is used in water treatment) and combustion gases and ashes mainly from COPESUL's stacks (low chlorine content coal powered boiler) were to be investigated. As well, potentially impacted environmental matrices (from the possible releases of Priority Pollutants), such as surface and groundwater, soil, aquatic sediments, fishes and ambient air were to be tested in order to establish an assessment of the environmental conditions prevailing at the Petrochemical Complex.

Methods

The list of sampling points, matrices and analytical parameters used for the year 2000 EAPP included 105 sampling points for PCDD-PCDF analyses.

This list included reference sites for each of the potentially impacted environmental matrices in order to establish and compare background conditions outside the areas of influence of the Petrochemical Complex. Sampling and laboratory analytical methods were all adapted from the most recent methodologies referable to numerous sources including Environment Canada[1,3,4], USEPA, Ministries of

Environment of Ontario and Quebec. More specifically, PCDD-PCDF were tested using an improved and adapted version of the EPA 8290-A (HRGC/HRMS), except for combustion gases and ambient air tested with Environment Canada method EPS 1/Rm/3. The adapted version of the method EPA 8290-A allowed the achievement of lower detection limits (DL) than this method normally allows.

All laboratory analyses were performed at Maxxam Analytics (High Resolution facility) in Waterloo, Ontario, Canada while external quality control analyses were conducted by the Dioxin and Toxic Organics Section of the Laboratory Services Branch of the Ontario Ministry of Environment in Toronto, Ontario, Canada. All samples were sent to Canada by cargo plane using refrigerated containers (with T° control) suitable for aircraft shipping.

Results and Discussion

As Brazil has not yet adopted nor established criteria, guidelines, or standards for the type of environmental quality guidelines required for this project, the selection of appropriate guidelines to perform the environmental assessment of the Complex utilized North American environmental standards. More specifically, the emphasis was put on the Canadian (Federal or Provincial Governments)[5] guidelines and regulations.

Potential Emission Sources of Priority Pollutants of the Petrochemical Complex

- None of the four (4) potential emission sources of Priority Pollutants from the Petrochemical Complex investigated in this study can be regarded as significant sources of PCDD-PCDF (boilers stack emissions, boilers stack ash, process waste water effluents and the drinking water treatment facility of COPESUL). All total TEQ presented here are calculated with non-detects = 1 time DL.
  - *Boilers Stack emissions*
    Release of PCDD-PCDF was measured at between 0.96 to 1.16 pg/m^3 (I-TEQ at 11% 0_2) which represent only 0.3% of the Canadian guideline for stack emissions (500 pg/m^3).
  - *Boilers Stack Fly Ashes*
    None of the 17 PCDD-PCDF congeners used to calculate total TEQ were detected above detection limits.
  - *Process Waste Water Effluents*
    This included individual industries process waste waters before complete treatment, the global waste water effluent that is directed to the Integrated System for the Liquid Effluents Treatment, the final treated effluent and the stabilization pond, which is the last stage of treatment before land disposal.
    Process Waste Water Effluents were measured between 4.74 and 26.04 pg/L for PCDD-PCDF (I-TEQ) which represents respectively 8 and 43% of the Canadian guideline (Province of Ontario) for effluent discharge to the environment (60 pg/L).
  - *Drinking Water Treatment Facility*
    No PCDD-PCDF was detected in the drinking water sample of the facility. Regarding the sludge generated by the facility, a low trace level of 1.04 ng/kg (I-TEQ) which represents only 1.04% of the Canadian guideline (Province of Ontario) for sludge application to agricultural lands (100 ng/kg).

Potentially Impacted Environmental Matrices

- *Groundwater*

  The I-TEQ values are between 7.65 and 9.65 pg/L (except for QA/QC duplicate samples showing slightly higher I-TEQ values because of higher reported DL), well below the Canadian guideline of 15 pg/L for drinking water. Thus, based on this, and in comparison with the values of the reference sites, no significant environmental impact from PCDD-PCDF is occurring on the groundwater and drinking water monitoring points.

- *Surface Water*

  The I-TEQ values are between 9.38 pg/L and 9.67 pg/L (except for one QA/QC duplicate sample showing slightly higher TEQ value because of higher reported DL). Despite the absence of guidelines for PCDD-PCDF in surface water, the comparison with the 15 pg/L Canadian drinking water guideline is a valuable indication of the water quality. Thus, based on this, and in comparison with the value of the reference site no significant environmental impact for PCDD-PCDF is occurring on the surface waters monitored for this study.

- *Soils*

  For the area where final treated effluent wastewater is sprayed over the soil as a means of final discharge to the environment, the I-TEQ values vary between 0.475 ng/kg to 0.515 ng/kg (except for one QA/QC duplicate sample showing higher TEQ of 1.26 ng/kg because of higher reported DL). These are well below the Canadian Industrial and Agricultural land use guidelines (respectively 750 and 2 ng/kg from the Province of Quebec). Thus, based on this, and in comparison with the reference sites values, no environmental impact from PCDD-PCDF is occurring on the monitored soils of this area.

  For the atmospheric deposition area (downwind of COPESUL's boiler stacks) I-TEQ values are 0.487 ng/kg and 0.771 ng/kg, also well below the Canadian guidelines for Industrial and Agricultural land use. Thus, based on this, and in comparison with the reference sites values, no significant environmental impact from PCDD-PDDF appears to be occurring.

- *Aquatic Sediments*

  The I-TEQ values are between 0.469 ng/kg and 0.541 ng/kg (except for QA/QC duplicate samples showing higher I-TEQ values of 2.36 and 2.87 ng/kg, because of higher reported DL). These values are below the Canadian Sediments Quality guideline (No Probable Effect) of 0.85 ng/kg (soon to-be-released by the CCME). Thus, based on this, and in comparison with the reference site values, no environmental impact from PCDD-PCDF is likely occurring on the sediments, in terms of adverse biological effects.

- *Fishes*

  Among the 7 sampling points monitored for fishes, the geometrical mean concentrations of PCDD-PCDF found are between:

	I-TEQ (Human consumption)	WHO-TEQ Birds	WHO-TEQ Mammals
0.0 DL	0.00 and 0.40	0.00 and 1.64	0.00 and 0.49
0.5 DL	0.24 and 0.60	0.37 and 1.99	0.29 and 0.71
1.0 DL	0.47 and 0.89	0.74 and 2.32	0.57 and 0.99

  - For human consumption, results obtained are lower than 10% of the Canadian guideline (10 ng/kg from the Province of Ontario).

- For bird consumption, results obtained are lower than 50% of the guideline (4.75 ng/kg). This guideline is soon-to-be-released by the CCME.
- For mammal consumption, Fisheries and Ocean Canada recommends use of the 0.5 DL approach for the congeners not detected above DL. Using this approach, results obtained are equal or lower than the mammal guideline (0.71 ng/kg; soon-to-be-released by the CCME). On the other hand, Environment Canada recommends to use the 0.0 DL approach, which leads to results lower than the mammal guideline. If we use the 1.0 DL approach also used in this study, results found for some samples could exceed the mammal guideline. Based on the above mentioned information and the fact that there are no mammals likely to feed on Lambari in this area of Brazil, we consider that the application of the mammal guideline does not represent a problem.

- *Ambient Air*
  - The I-TEQ values are between 0.02 and 0.08 pg/m^3, well below the Canadian guideline of 5 pg/m^3. Thus, based on this, and in comparison with the reference site value, no significant impact for PCDD-PCDF is occurring on ambient air.
    The PCDD-PCDF ambient air pollutant concentrations monitored in this study were similar to rural background levels found in three other countries[2].

Conclusions

None of the 4 potential emission sources of PCDD-PCDF from the Petrochemical Complex investigated in this study can be regarded as significant sources. Along the same trend, none of the 6 potentially impacted environmental matrices monitored for this project are showing significant impact from PCDD-PCDF. However, since this is based on a sole sampling and analyses campaign, it is recommended to pursue PCDD-PCDF testing in the future (with a revised program), to gain additional data for a more definite assessment and to monitor potential environmental impacts from any variations in the industrial process of the Complex.

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