2003 Assessment of PCDDs-PCDFs 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 state of Rio Grande do Sul Environmental Protection Agency (Fundação Estadual de Protecão Ambiental or FEPAM), an Environmental Assessment of Priority Pollutants (EAPP) was performed by Copesul at the end of the year 2003. EAPPs have been voluntarily performed at the Petrochemical Complex since 1986 on a basis of once every three year. It is now performed as a requirement which is part of the petrochemical plant operational license. Among the different (organic and inorganic) parameters tested, PCDDs-PCDFs remained 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 use nor produce any organo-chlorinated product.

Despite the numerous data accumulated over the years, some inconsistencies related to sampling and analytical methodologies did not allow appropriate environmental assessments until the year 2000 campaign. On this year 2000, Copesul, SNC◆Lavalin and FEPAM all agreed on the procedures to be used for the Environmental Assessment of Priority Pollutants of the South Petrochemical Complex, which also included the assessment of volatile (VOCs) and semi-volatiles (SVOCs) compounds (base neutrals, polycyclic aromatics and phenols). VOCs and SVOCs compounds are the main focus of the assessment, since these are the compounds that are produced on the site.

The previous EAPP of 2000[1] concluded that none of the 3 potential emission sources of PCDDs-PCDFs of the Petrochemical Complex investigated could be regarded as significant sources. Along the same

trend, none of the 7 potentially impacted environmental matrices monitored showed significant impact from PCDDs-PCDFs. However, since this was based on a sole sampling and analyses campaign, it was recommended to pursue PCDDs-PCDFs 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.

Thus, the main objective of the year 2003 EAPP was to validate and confirm the previous 2000 EAPPs results and diagnosis, according again to a scientifically sound and defensible environmental assessment of the Petrochemical Complex and of it's surroundings, based on reliable analytical data. As a result, an important adjustment in the year 2003 program was the reduction in the number of sampling points (from 105 to 30) and matrices sampled and tested (from 10 to 6) for PCDDs/Fs, in order to focus monitoring only on sampling points and matrices that are considered as potential concerns for these compounds (environmental sinks or sources of contamination). More specifically, potential sources of PCDDs-PCDFs such as waste water effluents (also tested in previous EAPPs) and sewage sludge from the waste water treatment facility of the Complex (hereafter SITEL, and tested for the first time) were investigated. Drinking water was also tested in order to verify it's quality level for human consumption. Finally, potentially impacted environmental matrices (from the possible releases of Priority Pollutants), such as soils and fresh water aquatic sediments were also 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 2003 EAPP included 30 sampling points for PCDDs-PCDFs 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, USEPA, Ministries of Environment of Ontario and Quebec and Standard Methods for the Examination of Water and Wastewater. More specifically, PCDDs-PCDFs were tested this year using (for the first time) the test method EPA 1613. In previous EAPPs, test method EPA 8290 (adapted version in 2000) had been used. This change, requested by Copesul, is considered by SLEI and by the analytical laboratory (Maxxam Analytical) as a significant improvement with regards to detection limits and recovery rates as explained hereafter:

- EPA method 1613 allows for greater variation in the methodology, which may lower method detection limits (MDLs) for specific samples. EPA 1613 allows for variations in the extraction procedure, amount of recovery standards added to the matrix, column type, equipment configuration, and sample size, which allow MDLs to be lowered. Procedures used are documented in the analyst notes (generally in the case narrative).

- EPA method 1613 allows for greater latitude for the extraction procedures, thus generally permitting better recovery rates for surrogates and for native compounds (spiked blanks) than with EPA method 8290.

The detection limits generally achieved for 2003 were the following :

- For Liquid samples : 0.3 to 6.1 pg/L (from 2 to 30 pg/L in 2000)

- For Solid samples : 0.1 to 0.4 ng/kg (from 0.1 to 1.5 ng/kg in 2000)

All laboratory analyses were performed at Maxxam Analytics (High Resolution facility) in Waterloo, Ontario, Canada All samples were sent to Canada by cargo plane using refrigerated containers (controlled at 4° C) 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 default 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)[2,3] guidelines and regulations. However, it should be emphasized that the Canadian guidelines don't necessarily reflect of the conditions prevailing in this part of Brazil, and therefore the applicability (and limitations) of foreign guidelines should only be regarded in the context of an alternative, in absence of site (region)-specific guidelines.

Potential Emission Sources of Priority Pollutants of the Petrochemical Complex

- None of the two (2) potential emission sources of Priority Pollutants from the Petrochemical Complex investigated in this year's study can be regarded as significant sources of PCDDs-PCDFs (process waste water effluents and sewage sludge from waste water treatment (SITEL)). The previous EAPP of 2000 had concluded that none of the 3 potential emission sources of PCDDs-PCDFs tested at that time (boilers stack emissions, stack fly ashes and process waste water effluents) were to be regarded as significant sources (all well below selected guidelines), thus no testing of these sources (with the exception of a few process waste water effluents) was conducted in 2003. All total TEQ presented here are calculated with non-detects = 1 time DL.

  – *Process Waste Water Effluents*

    This included one downstream industry (for styrene production) individual process waste waters (before complete treatment), as well as the global waste water effluent (of all of the industries of the Complex) that is directed to SITEL's Effluents Treatment (one organic effluent and one inorganic).

    Process Waste Water Effluents were measured between 2.13 pg/L to 2.17 pg/L I-TEQ. These values are all below the Canadian guideline of 60 pg/L I-TEQ (Effluent Monitoring and Effluent Limits – Organic Chemical Manufacturing Sector (Ministry of Environment of Ontario). Each of the 3 sampling sites tested are showing the presence of Octa and /or Hepta CDD. In 2000, some of them (the downstream industry and the waste water treatment facility for inorganic effluent) also showed low level traces of PCDDs/Fs.

  - *Sewage Sludge from the Industrial Waste Water Treatment Facility (SITEL)*

    PCDDs/PCDFs were detected at concentrations of 3.41 ng/kg (or 4.48 ng/kg for the laboratory duplicate sample) which is well below the Canadian guideline applicable of 100 ng/kg (for land-application of sludge).

  – *(Drinking Water Treatment Facility)*

No PCDDs-PCDFs congeners were detected in the drinking water sample of the facility.

Potentially Impacted Environmental Matrices

- *Groundwater and Surface water*

  Groundwater and surface water were not tested for PCDDs/PCDFs in 2003 considering that, no significant environmental impact from PCDDs-PCDFs on theses matrices was identified in 2000, and also because PCDDs/PCDFs are considered to be hydrophobics.

- *Soils*

  1) In the State of Rio Grande do Sul, there is a regulation specifically introduced for the South Petrochemical Complex that forbids the discharge to the surface water of any kind of effluent (including treated effluents). For this reason, final treated effluent waste water is sprayed over the soil as a mean of final discharge to the environment. The WHO-TEQ values for these soils vary between 0.41 ng/kg to 0.42 ng/kg. These are well below the Canadian Industrial land use guideline (4 ng/kg WHO-TEQ) and they are equivalent to the TEQ values measured in the reference sites. Strictly as in informal comparison, mean background concentration for rural soils in North America[4] is at 2.5 ng/kg WHO-TEQ (with non detects set to 0 for TEF calculations). Thus, as in 2000, in comparison with the reference sites values, no environmental impact from PCDDs-PCDFs is occurring on the soil of this area. Total TEQ results of this year are very comparable to the year 2000 results, though slightly lower, because of lower detection limits achieved this year.

  Congeners (and homologues) profiles between this year's and 2000's are generally showing good similarity, even though this year's results tend to show more detailed profiles. Octa CDD is present in each sample (total of 5). Hepta CDD is also present (3 out of 5 samples) and so is Hexa CDF (2 out of 5 samples) and Hexa CDD (one sample). In 2000, we noted a predominance of Octa CDD and Hepta CDD/CDF.

  Considering the non detection in 2000 (not tested this year) of any PCDDs-PCDFs in the final treated effluent of SITEL, the trace presence of PCDDs/PCDFs congeners in the soils (this year and the previous years) could possibly be linked to atmospheric deposition from airborne PCDDs-PCDFs (from the Copesul's stack or/and from other background sources). The above PCDDs-PCDFs patterns are consistent with the combustion gases pattern of COPESUL's stack (industrial boilers) identified in 2000 (with emissions measured at trace levels). However, as explained in 2000, this "congeners pattern" is quite common and can be associated with other sources or normal background. It is also interesting to note that the average congeners profile for all soils samples of this project is very similar to the typical congeners profile for North American soil[4] which shows a predominance of Octa CDD, followed by Hepta CDD. This year's profile may be somehow closer to the urban soil profile, while the year 2000 profile was closer to the rural soil profile.

  2) For the Sitel's sludge farm areas (2 fields tested out of 13) where sewage sludge is injected into the surface soil as a mean of disposal, the WHO-TEQ values vary between 0.42 ng/kg and 0.45 ng/kg. These are also well below the Canadian Industrial land use guideline and they are equivalent to the TEQ values measured in the reference sites. Thus, as in 2000, in comparison with the reference site value, no environmental impact from PCDDs-PCDFs is occurring on the soil of this area.

Congeners profiles for both field of the sludge farm areas are comparable. Hepta and Octa CDD are present in both sampling sites, while Hexa CDD (Field no 2) and Hexa and Hepta CDF (field no 2, duplicate sample) and Penta CDF (MOE's results) are also present in one of the two samples. Actually, the only congeners not detected in the soil samples are the Penta CDD and the Tetra CDD/CDF. In comparison, the congeners profile of the Sitel's sludge is also indicating the presence of nearly all PCDDs/PCDFs congeners (with the exception of Tetra CDD), as outlined in the previous section on sludge analytical results.

In 2000, analytical results (only field no 2 was tested) only indicated the presence of total Hepta CDD (homologue). No congeners were detected.

- *Fresh Water Aquatic Sediments*

The WHO-TEQ values measured are between 0.41 ng/kg and 0.58 ng/kg, with the exception of Sitel's Lagoon no 1 (tertiary treatment) at 12.29 ng/kg, with 17 of the 18 congeners (detected at 0.50 ng/kg in 2000) and from Safety Basin no 7. These values (except 12.29 ng/kg) are below the Canadian Sediments Quality Guideline of 0.85 ng/kg WHO-TEQ (as in 2000). On the other hand, the result from Lagoon no 1 is exceeding the SQG guideline (Threshold Effect Level) but remains below the PEL guideline of 21.5 ng/kg (Probable Effect Level). Thus, according to the definition of the guidelines, and in comparison with the reference site values, environmental impact from PCDDs-PCDFs is *possibly* occurring on the sediments from Lagoon no 1, in terms of adverse biological effects. The significant difference in concentration between the results of Lagoon no 1 of 2000 and 2003 is likely related to the modification in the sampling procedure of this year (composite sampling over the whole lagoon vs grab sampling at the exit point of the lagoon in 2000).

However, we should remember that the purpose of Lagoon no 1 is to finalize wastewater treatment at the petrochemical complex and therefore it is not intended to serve as an aquatic ecosystem. Nevertheless, it appears indeed, that ecosystem has settled in Lagoon no 1, and has underwent, throughout the years, a certain evolution (presence of fish, birds, mammals (i.e. capivara, etc.) and amphibians (i.e caymans, turtles, etc.)). Thus, considering the connections and interactions between the aquatic ecosystem (and the various interconnected trophic chains) of this water-body and of the aquatic ecosystems located outside the Complex (for instance, the adjacent Cai river), adverse biological effects along higher levels of the trophic chains (predatory fish, birds and mammals) are also *possibly* occuring.

The remaining sediment sampling sites, in comparison with reference sites values are not indicating the occurrence of environmental impact. All of the 13 sampling points have shown hits of PCDDs-PCDFs congeners. Beside the almost ubiquitous presence of Hepta and Octa CDD, the other congeners detected most frequently are the Hepta and Octa CDF. This is a similar profile to the one identified at the reference points, as well as for monitoring sampling points of 2000. Occasional hits of Hexa and Penta CDF were also reported in 2000.

Conclusions

None of the 2 potential emission sources of PCDDs-PCDFs from the Petrochemical Complex investigated in this year's study can be regarded as significant sources. Along the same trend, none of the 2 potentially impacted environmental matrices monitored for PCDDs/PCDFs for this project (soils and aquatic sediments) are showing significant impact (inside or outside the Complex), with the exception of one sediment sampling point located in Lagoon no 1 (tertiary treatment) of the Complex

waste water treatment facility. The concentration measured (12.29 ng/kg WHO-TEQ) is above the Canadian guideline (0.85 ng/kg = Threshold Effect Level or possible effect level) but below the PEL guideline (21.5 ng/kg = Probable Effect Level), which according to the definitions of the guidelines means that adverse biological effects is ***possibly*** occurring. However, since this is based on a sole composite sampling campaign and that only limited information is known on the interconnections with adjacent aquatic ecosystem (Cai river), it was recommended to re-sampled this site in the future again (using composite sampling) to validate these data, and also to start identifying the different biological components and interactions of this aquatic ecosystem. As for the remaining sampling sites of this study that are not indicating PCDDs-PCDFs potential impact or presence, testing in the future should be pursued 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.

Acknowledgments

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References

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