LEVELS OF PCDD/Fs IN DUST PRECIPITATION SAMPLES WITHIN THE METROPOLITAN REGION OF RIO DE JANEIRO.

Reichel, K[1*], Takaki, T[1], Lemos, L[1], Almeida Fortes, RM[1], Castro, RR[1], Torres, JPM[2], Rocha, DAM[3].

[1]Integrated Petroleum Expertise Company, IPEXCo, Rio de Janeiro, Brazil; [2]Institute of Biophysics, Rio de Janeiro Federal University, Rio de Janeiro, Brazil; [3]Chemistry Institute, Fluminense Federal University, Niterói, Brazil.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF) are extremely toxic pollutants that have serious health effects on the nervous, endocrine, reproductive and nervous system and also acts as highly carcinogenic. Since of the beginning of the Dioxin problem, air, dust and dust precipitation in the ambient air had an important contribution to the understanding the complex Dioxin toxicity and the whereabouts of them.

Components, particularly Dioxins and Furans in dust precipitation can lead to toxic pollution of soil. About cultivation of plants or animal use, they can get into the human food chain and harm the health of humans and animals sustainably. In large cities, it can be expected significant dust deposits and their components due to high traffic and intensive industrial activities.

With the background of results of extensive European studies and urban programs of monitoring [1 – 4] the dust precipitation, research on the levels of the pollutants could have a great importance and necessity in the metropolitan region of Rio de Janeiro. Rio de Janeiro has several disordered industrial sources of potential environmental pollutants. A special local peculiarity are the frequent encountered uncontrolled fire at the street edges of the traffic arteries, lit by residents and homeless, that could possibly make a very important contribution to the levels.

Materials and methods

-Sampling

This study presents the PCDD/F levels in thirteen specially selected sampling points of the metropolitan region of Rio de Janeiro shown in Table 1.

Table 1. Sampling points

District	Address	Sample-ID	Description
Ramos	Estrada do Engenho da Pedra	PMRJ1401	Close to a busy highway called "Avenida Brasil". This district includes several metal industries.
Marechal Hermes	Avenida Engenheiro Assis Ribeiro	PMRJ1402	Surrounded by several metal industries one crematory and "Avenida Brasil".
Caju	Rua União, 28	PMRJ1403	The harbor district of Guanabara Bay. Close to metal industries and "Avenida Brasil".
Tijuca	Rua São Francisco Xavier	PMRJ1404	Tijuca includes metal industries and incinerators.
Santa Cruz	Avenida João XXIII	PMRJ1405	Close to a steel plant and close to "Avenida Brasil".
Campo Grande	Rua Maurício de Andrade	PMRJ1406	Close to several metal industries and "Avenida Brasil".
Seropédica	BR 465 - km 8	PMRJ1407	Close to metal industries, "Avenida Brasil" and another highway "Rodovia Presidente Dutra".
Queimados	Rua Professora Joana D'Arc	PMRJ1408	In the center of the city, surrounded by several metal industries and "Rodovia Presidente Dutra".
Nova Iguaçu	Rua Arararia	PMRJ1409	Close to Industries and "Rodovia Presidente Dutra".
Belford Roxo	Rua Gonçalves Gato	PMRJ1410	Surrounded by metal industries, incinerator and close to " Rodovia Presidente Dutra".
Duque de Caxias	Rua Silva Jardim	PMRJ1411	Close to Industries and "Rodovia Presidente Dutra".
Nova Friburgo	Rua Marechal Floriano	PMRJ1412	140 km from the city center of Rio de Janeiro, where no significant effect of PCDD/F sources are expected.
Teresópolis	Parque National da Serra dos Orgãos - PARNASO	PMRJ1413	100 km from the city center of Rio de Janeiro, directly in the national park, “Parque Nacional da Serra dos Orgãos”. No effects of PCDD/F sources are expected.

Sampling point Nova Friburgo and Teresópolis were included to the study in order to assess the levels of the other points in a comparative manner. Sampling was performed according to VDI 211 sheet 2 [5], the analysis was carried out in accordance with USEPA 1613 [6] and USEPA 8290A [7].

The sampling sites were chosen most closely to possible sources (incinerator, crematory, metal industry, cement industry, traffic arteries, oil refinery).

For each measuring point ten glasses (Bergerhoff collectors) were installed in parallel with a respective volume between 2L and 2,4 L and a diameter of 11cm. Glasses were combined into one monthly composite sample. They were placed as high as possible and on a free-standing place (roof) to prevent disturbing influences (leaves, birds, windless caused by walls) and to take into account non-specific wind directions, according to the German twenty second-Regulation implementing the Federal Pollution law [8].

In the Lua report states that the wind direction is the direction from which the wind blows, and must be specified at the level of Anemometer, in an exact degree as an angle against the north clockwise direction. When circulating winds occur, a uniformly distributed random wind direction from the range of 1 ° to 360 ° should be chosen [9]. In our study, no specific wind direction could be observed

At the time of the glasses changing, each of them got a unique identification number and was sealed with a lid. At the laboratory the glasses were registered by the laboratory management system and stored cool and dark in a storeroom.

The time period between collecting the glasses from each sample place and registering in the laboratory was two days. The time period between storing and analyzing the samples was between 14 and 21 days.

-*Analytical process*
In this study, totally 39 samples, three sample collection of each of thirteen sampling locations, were taken to evaluate those individual compounds of PCDD and PCDF for by NATO / CCMS (North Atlantic Treaty Organization / Committee on the Challenges of Modern Society), or according to WHO (World Health Organization) toxic equivalency factors have been adopted. There were also determined the total of the tetra- to hepta chlorinated compounds and octa-chlorinated OCDD and octa-chlorinated OCDF of polychlorinated dibenzo-dioxins PCDD and polychlorinated dibenzofurans PCDFs. The analysis was performed by capillary gas chromatography and detection by high resolution mass spectrometry (GC / HRMS) according to US methods 1613B and 8290A.

-*Preparation*
Filters for each sample were equilibrated one day before weight. If one or more glasses contained water, this water was filtered. The glasswall of each glass was 6 times carefully cleaned with a spatula and rinsed with distilled/ionized water. The water was also passed through the filter. After following the process for each glass, the filters were dried at maximum 40C° until constant weight. The liquid phase of all ten glasses was 3 times extracted by liquid/liquid process, each time with 50mL Toluene.

-*Extraction*
The Toluene phase was completed with Toluene and Acetone until 400mL (Toluene 9 : Acetone 1) and used for the hot Soxhlet extraction. The filters were placed into the glass apparatus, a defined internal 13C-labeled PCDD / F standard (Quantification Standard) was added, and extraction was carried out over a period of 16 hours. 75% from the extract were used for further analysis. The remaining 25% of the extract served as a reserve sample.

75% of the extract was concentrated until 0,5mL and for further purification different column liquid chromatography techniques were using. To determine the recoveries of the internal standard (Quantification Standard) more 13C-labeled PCDD / F (recovery standard) were added immediately before the measurement to the purified extract.

-PCDD/F analyses
Separation, identification and quantification of the various PCDD / F compounds were determined by measuring by capillary gas chromatography and detection by high resolution mass spectrometry (GC / HRMS).

In use, there was a fused silica capillary column, which was coated with a non-polar stabilized stationary phase. The gas chromatographic conditions separated the isomers from each other (compounds with the same empirical formula, with the same molecular weight but different structure). The detector identified the components to be analyzed based on their molecular weights.

The identification of PCDD/F- components was carried out by relative retention times and on two characteristic masses and their Isotope ratios. Quantification was performed by the method of the internal standard.

The HRGC/HRMS analyses were performed according to the US EPA Method 1613B and US EPA 8290A on Trace GC Ultra DFS High Resolution Magnetic Sector MS using a 60m DF5-MS column. (Agilent 0,25mm ID, 0,25µm film). The following conditions were applied: SIM mode, constant flow, helium as the carrier gas (1,5mL/min), splitless injection (260C°), energy electrons 40eV, temperature interface 260C°, detector condition 2 X 10^{-6} Amps. Temperature regime was applied as follows: 120C° for 4 min, from 120C° to 200C° with 15C°/min, from 200C° to 240C° with 1,5C°/min, 240C°for 2min, from 240C° to 310C° with 3C°/min, 310C° for 10min.

Results and discussion
Table 2 shows the results of the first sample collection (07/04/14 – 05/05/14) of the thirteen sampling locations.

Table 2. Concentrations of PCDDF (pg/m^2/d)

Local	Ramos	Marechal Hermes	Caju	Tijuca	Santa Cruz	Campo Grande	Seropédica	Queimados	Nova Iguaçu	Belford Roxo	Duque de Caxias	Novo Friburgo	Teresópolis
Sample-ID	PMRJ1401	PMRJ1402	PMRJ1403	PMRJ1404	PMRJ1405	PMRJ1406	PMRJ1407	PMRJ1408	PMRJ1409	PMRJ1410	PMRJ1411	PMRJ1412	PMRJ1413
Congeners	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d	i-TEQ de Nato pg/m²/d
PCDDs													
2,3,7,8-TCDD	N.C.	0,7206	0,1600	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	0,2607	N.C.	N.C.
1,2,3,7,8-PeCDD	0,5470	2,417	0,8147	N.C.	0,4173	N.C.	0,2290	0,5288	0,7569	1,099	1,043	N.C.	N.C.
1,2,3,4,7,8-HxCDD	0,1504	0,5684	0,1192	N.C.	0,06391	0,04142	0,08480	0,07115	0,1178	0,1829	0,1313	N.C.	0,02153
1,2,3,6,7,8-HxCDD	0,3075	1,022	0,3486	0,1507	0,1910	0,1014	0,1540	0,1974	0,2967	0,3991	0,3644	0,05502	0,03768
1,2,3,7,8,9-HxCDD	0,2835	0,8879	0,2147	N.C.	0,1346	0,07310	0,1038	0,1569	0,2456	0,3474	0,3474	N.C.	0,04785
1,2,3,4,6,7,8-HpCDD	0,3017	0,7085	0,3204	0,2124	0,1435	0,06759	0,1242	0,1508	0,2384	0,2934	0,2636	0,06764	0,05419
OCDD	0,08872	0,1001	0,1038	0,06969	0,02984	0,01979	0,02135	0,03882	0,07550	0,06008	0,05376	0,02154	0,01402
TCDD (non-targeted)	9,586	38,72	13,90	4,673	3,624	7,515	6,009	6,287	10,51	18,10	13,66	1,429	0,9749
PeCDD(non-targeted)	8,84	50,5	11,94	2,309	2,936	5,070	6,850	5,270	10,07	15,86	14,43	0,4964	N.C.
HxCDD(non-targeted)	4,119	21,99	4,223	1,796	1,947	0,1594	2,670	2,604	3,208	6,100	5,808	0,3983	0,1603
HpCDD(non-targeted)	0,3670	0,8115	0,3614	0,2110	0,1561	0,1055	0,1388	0,1771	0,2436	0,3453	0,3217	0,07404	0,0544
PCDFs													
2,3,7,8-TCDF	0,1195	0,2939	0,2480	0,07576	0,06278	0,07846	0,05556	0,1101	0,1694	0,3456	0,2100	0,06818	0,03648
1,2,3,7,8-PeCDF	0,1368	0,2678	0,2135	0,08054	0,03440	0,06506	0,03655	0,11470	0,1890	0,3393	0,2095	0,03888	0,02392
2,3,4,7,8-PeCDF	1,496	3,787	2,928	0,9968	0,5038	0,8187	0,5726	1,435	2,581	4,055	3,023	0,3559	0,2480
1,2,3,4,7,8-HxCDF	0,3962	0,7004	0,5676	0,2488	0,1350	0,1520	0,1238	0,3168	0,4892	0,7680	0,5815	0,07057	0,06699
1,2,3,6,7,8-HxCDF	0,3981	0,6972	0,5356	0,1882	0,1372	0,1345	0,1218	0,2943	0,4321	0,8250	0,5799	0,04605	0,05921
2,3,4,6,7,8-HxCDF	0,4680	0,7109	0,5859	0,2544	0,1199	0,1647	0,1399	0,3860	0,5178	0,7412	0,6742	N.C.	0,0789
1,2,3,7,8,9-HxCDF	0,05000	0,04575	0,05432	N.C.	N.C.	N.C.	0,01803	0,02729	0,06115	0,07149	0,06667	N.C.	N.C.
1,2,3,4,6,7,8-HpCDF	0,1260	0,1736	0,1490	0,05534	0,03662	0,03821	0,03519	0,08923	0,1254	0,1795	0,1570	0,01824	0,02644
1,2,3,4,7,8,9-HpCDF	0,01207	0,0153	0,01608	N.C.	N.C.	N.C.	N.C.	0,01033	0,008972	0,01807	0,01143	N.C.	N.C.
OCDF	0,006383	0,006474	0,007693	0,003684	0,001316	0,001652	0,002130	0,005249	0,006361	0,005776	0,007248	0,001220	0,002344
TCDF (non-targeted)	3,754	9,481	8,628	1,633	1,755	2,235	1,516	3,209	5,216	9,726	6,036	1,189	0,4659
PeCDF(non-targeted)	21,72	35,55	35,46	10,04	5,06	6,39	4,450	10,11	24,35	38,65	28,90	0,8640	0,5590
HxCDF(non-targeted)	0,5985	0,7749	0,7874	0,2185	0,1628	0,2802	0,1369	0,4269	0,6802	0,9452	0,7895	0,07356	0,06878
HpCDF(non-targeted)	0,04335	0,06717	0,06320	0,02368	0,01526	N.C.	N.C.	0,04084	0,04972	0,05750	0,007313	N.C.	N.C.
TOTAL PCDD/Fs (targeted)	4,888	13,12	7,391	2,336	2,011	1,757	1,823	3,935	6,312	9,730	7,984	0,7432	0,7178

N.C. not calculated because none of the congeners are detected above LOQ.

For the polychlorinated dioxins and furans (PCDD / F), in dust precipitation, no pollution limits are set. Alternatively, the target value for the long-term air pollution, defined as a deposition value of 4 pg per m² and day can be mentioned [10]. The deposition value is to be understood as the total value of the dioxin and furan congeners and the coplanar PCBs. Several measurements in the literature indicate that in the steel production the deposition value is generated to 30% by TE coPCBs, while shredders causing 30% to 90% of the TE coPCBs [11].

In this study, the PCDD/F concentrations were determined exclusively. Despite the lack of coPCBs concentrations the first PCDD/F results of five sampling locations – Marechal Hermes, Caju, Nova Iguaçu, Belford Roxe e Duque de Caxias - listed in Table 2, are significantly higher than the target value for the long-term air pollution [10].

The profiles of all measured locations are the same, which was expected due to the same matrix. The results of the eastern districts, Santa Cruz, Campo Grande, Seropédica and also still Queimados are in the same range. Also, the results of the northern districts, Nova Iguaçu, Belford Roxo and Duque de Caxias are in the same range, but much higher than the results in the eastern districts. The highest concentrations we found in the district of Marechal Hermes, relatively near to the district Caju which also shows relatively high results. The concentrations of the two sampling points far from Rio de Janeiro, Nova Friburgo and Teresópolis, are significantly lower than the target value for the long-term air pollution [10].

This previous results obtained in the study will be continuously hedged with the next sampling and analysis and can provide more detailed and far-reaching interpretation and thus initiate possible follow-up studies.

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