DIOXINS AND FURANS LEVELS IN TSP AND PM 2.5 COLLECTED IN NITERÓI / RIO DE JANEIRO STATE

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), trivially known as dioxins and furans, are two groups of trace pollutants that are listed Annex C of the Stockholm Convention due to their physico-chemical and toxicological properties. PCDD/Fs are unintentionally generated by-products from industrial und combustion processes, such as paper bleaching and incineration of residues. The main distribution route of these contaminants is atmospheric transport principally when originated from thermal emission source. The emitted PCDD/Fs are partitioned between gas-phase and suspended particles, and their removal to the other environmental compartments occurs by wet or dry deposition.

In Brazil, the release of PCDD/Fs to air was estimated (Toolkit) to be 1,169 g TEQ/a for the year 2008 that is 52.2% of the total estimated release[1]. In 2005, Assunção et al.[2] reported total air concentrations of PCDD/Fs in São Paulo City and Schuster et al.[3] showed recently PCDD/F air concentrations obtained with passive air samplers in several countries of the GRULAC region, inclusive in three locations in Brazil. Besides this, very few is known about PCDD/Fs in the Brazilian atmosphere and even less in total suspended particulate (TSP) and particulate matter smaller than 2.5 µm (PM 2.5).

The objective of this study was to have data on PCDD/Fs in TSP and PM 2.5 collected in Brazil. The sampled area is situated in Niterói, which is the fifth most populated city of Rio de Janeiro State (~ 500,000 inhabitants), with a high Human Development Index. This area was chosen because there are already data available for polycyclic aromatic hydrocarbons (PAH) in TSP and PM 10 that indicate an increase of PAH concentrations during the last six years probably caused by increased traffic volume[4]. PCDD/F emissions through vehicles in Brazil were already shown by high PCDD/Fs level in soot collected in automobile tunnels of Rio de Janeiro City[5].

Materials and methods

Samplers for TSP and PM 2.5 were placed at the entrance of Campus Valonguinho, Federal University Fluminense (UFF) that is located in the center of Niterói (figure 1). The altitude of the sampling location was approximately 5 meters above sea level. The sampling site is situated nearby the two main public transport stations, Araribóia Ferry Station (900 m) and João Goulart Bus Terminal (~ 1.5 km), and one of the main traffic streets of Niterói.

Two high volume samplers, AGV-PTS and AGV PM 2.5 (Energética, Rio de Janeiro/Brazil), were employed for sampling of TSP and PM 2.5, respectively. Sampling occurred in short periods during 09/10/2014 and 13/10/2014 (5 days), and during 29/10/2014 and 06/11/2014 (8 days). The flow rates were approximately 1.5 m^3/min for TSP and 0.9 m^3/min for PM 2.5. TSP and PM 2.5 capture happened on glass fiber filters provided by Energética with 1 µm pore size and an area of 20.3 x 25.4 cm. Filters were replaced every 24 hours and stored in freezer at – 20° C until analysis. TSP and PM 2.5 samples were taken simultaneously.

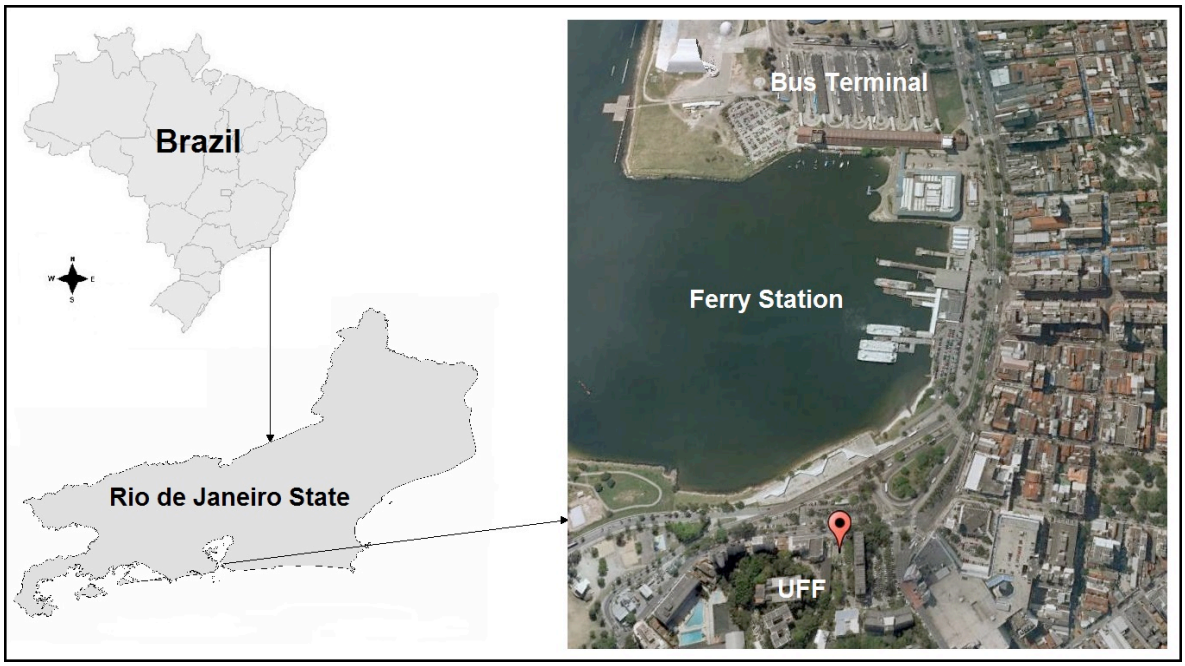

Figure 1: Sampling location at UFF; GPS data: 22º 53' 46.89" S, 43º 7' 32.01" W (Image source: Google Earth)

Each filter were analyzed individually. Three quarters of each filter were used for dioxin analysis and the remaining quarter for analysis of PAH. Extraction were conducted in a Soxhlet extractor with toluene pesticide grade (TEDIA, Fairfield/USA) during 24 hours (~ 200 cycles). After extraction, the solution was fortified with all seventeen ^{13}C-labelled 2,3,7,8-congeners, evaporated with a rotary evaporator and dissolved in n-hexane pesticide grade (TEDIA, Fairfield/USA). First cleanup step was performed on multi-layer column (silica; silica/sulfuric acid; silica) for destruction of the main interfering components followed by Florisil column for separation of dioxins and polychlorinated biphenyls. The clean solution was concentrated and transferred to injection vial equipped with a 200 µL insert. After transfer, the remaining volume was reduced to dryness under nitrogen flux and then dissolved in 12 µL (final volume) of isooctane pesticide grade (MERCK, Darmstadt/Germany).

Instrumental analysis were conducted on a gas chromatograph (Agilent 6890N Series) coupled to low resolution mass spectrometer (Agilent 5973). Separation occurred on DB-5ms (60 m length, 0.25 mm diameter, 0.25 µm film thickness; Agilent) with a carrier gas (helium) flow of 1.5 mL/min. Injector and transfer line were hold on 300° C and the injection volume was 2 µL. The mass spectrometer was operated in selected ion monitoring mode, tracing two ions for native and two ions for labelled compounds in each homologue group. Compounds were identified when retention time and isotope ration were in the established range.

Results and discussion

TSP and PM 2.5 concentrations are shown in figure 2. Both concentrations are following more or less the same trend during the sampling periods and TSP concentration were always higher than the respective PM 2.5 concentration. There is also trend to lower concentrations on Sunday, except for TSP in the second period. However, more data points are necessary for determination of general trends.

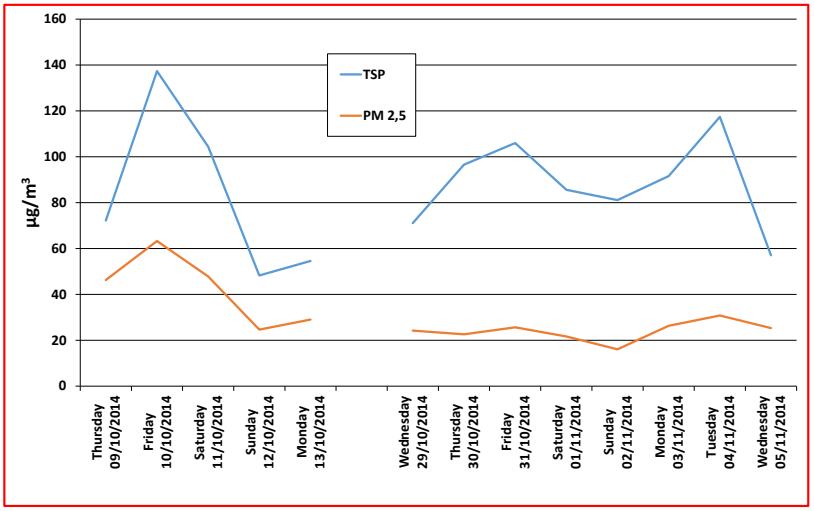

Figure 2: TSP and PM 2.5 concentrations during the two sampling periods.

The results for PCDD/F concentrations (ng/g) in TSP and PM 2.5 are listed in table 1. All tetra and penta 2,3,7,8-congeneres were always below quantification limit, as well as 1,2,3,7,8,9-HxCDF. Upperbound I-TEQ levels for PM 2.5 varied between 1.21 to 1.96 ng/g in the first sampling period, and between 1.74 and 2.49 ng/g in the second period. The variation of upperbound I-TEQ for TSP was between 0.41 and 0.53 ng/g in the first period, and between 0.21 and 0.44 ng/g in the second period. The overall average (upperbound) for PM 2.5 and TSP was 1.76 and 0.44 ng I-TEQ/g, respectively.

For comparison reasons, the obtained concentrations were transformed also in pg per volume. The overall average for PM 2.5 and TSP was 0.054 and 0.039 pg I-TEQ/m^3, respectively. These amounts are in the same range as reported by Assunção et al.[2] for total air in November in São Paulo City. In this month levels varied between 0.047 and 0.063 pg I-TEQ/ m^3, but higher amounts were found in February, May and August. Lower amounts were informed by Schuster et al.[3] in the polyurethane foam of passive samplers (0.025 pg TEQ/m^3 in São Paulo and 0.030 pg TEQ/m^3 in São Luís). This indicates that particulate matter, especially PM 2.5, contributes with a high amount to the PCDD/F burden in air.

However, the partially high difference between upper- and lowerbound levels (table 1) showed that the determination of PCDD/Fs in PM 2.5 and TSP with low resolution mass spectrometry reached its limits. On the other hand, weekly pooled or pooled samples of a ten-day period should resolve this problem, which could be a suitable method for continuous monitoring programs, especially for PM 2.5.

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Table 1: PCDD/F levels in PM 2.5 and TSP (ng/g) collected in Niterói/Rio de Janeiro State, 2014

PM 2.5	***09/10/14***	***10/10/14***	***11/10/14***	***12/10/14***	***13/10/14***	***29/10/14***	***30/10/14***	***31/10/14***	***01/11/14***	***02/11/14***	***03/11/14***	***04/11/14***	***05/11/14***
	Thurs	**Fri**	**Sat**	**Sun**	**Mon**	**Wed**	**Thurs**	**Fri**	**Sat**	**Sun**	**Mon**	**Tues**	**Wed**
2,3,7,8-TCDD	< 0.18	< 0.13	< 0.17	< 0.18	< 0.27	< 0.32	< 0.35	< 0.31	< 0.36	< 0.49	< 0.30	< 0.26	< 0.31
1,2,3,7,8-PeCDD	< 0.30	< 0.25	< 0.27	< 0.35	< 0.52	< 0.60	< 0.69	< 0.59	< 0.65	< 0.86	< 0.52	< 0.46	< 0.52
1,2,3,4,7,8-HxCDD	1.37	< 0.30	< 0.22	< 0.25	< 0.41	< 0.50	< 0.49	0.53	< 0.51	< 0.66	< 0.41	0.67	1.61
1,2,3,6,7,8-HxCDD	2.37	0.91	0.75	0.66	< 0.43	1.23	< 0.46	1.03	0.93	< 0.68	0.82	0.79	2.45
1,2,3,7,8,9-HxCDD	1.49	0.54	< 0.24	< 0.26	< 0.40	< 0.48	< 0.49	< 0.41	< 0.46	< 0.66	0.57	0.57	1.57
1,2,3,4,6,7,8-HpCDD	21.48	10.00	6.78	5.76	7.87	10.85	12.65	5.90	14.97	1.87	9.93	12.23	23.21
OCDD	36.37	14.99	13.11	9.91	12.29	24.39	19.41	10.79	22.72	12.21	18.78	15.91	43.60
2,3,7,8-TCDF	< 0.20	< 0.18	< 0.22	< 0.23	< 0.31	< 0.38	< 0.45	< 0.37	< 0.44	< 0.59	< 0.42	< 0.32	< 0.39
1,2,3,7,8-PeCDF	< 0.35	< 0.23	< 0.31	< 0.33	< 0.51	< 0.63	< 0.60	< 0.62	< 0.68	< 0.91	< 0.59	< 0.49	< 0.57
2,3,4,7,8-PeCDF	< 0.34	< 0.25	< 0.33	< 0.31	< 0.49	< 0.61	< 0.57	< 0.59	< 0.67	< 0.94	< 0.53	< 0.51	< 0.52
1,2,3,4,7,8-HxCDF	1.78	1.57	1.04	1.13	0.94	0.91	1.26	0.72	2.02	< 0.60	1.22	1.57	1.56
1,2,3,6,7,8-HxCDF	1.42	1.69	1.05	1.05	1.05	0.78	1.06	0.51	2.00	< 0.66	1.12	1.46	1.21
2,3,4,6,7,8-HxCDF	2.01	2.04	1.73	1.62	1.60	1.16	1.87	0.83	4.34	< 0.64	1.86	2.17	2.48
1,2,3,7,8,9-HxCDF	<0.25	< 0.21	< 0.29	< 0.27	< 0.36	< 0.46	< 0.42	0.49	< 0.52	< 0.64	< 0.40	< 0.37	< 0.30
1,2,3,4,6,7,8-HpCDF	9.47	7.92	7.66	6.01	6.46	5.35	5.66	3.92	11.61	2.33	8.08	7.84	10.78
1,2,3,4,7,8,9-HpCDF	0.85	0.99	1.17	0.85	0.82	0.88	< 0.52	< 0.57	1.12	< 0.76	1.22	1.04	0.77
OCDF	5.41	4.99	4.95	3.11	3.81	3.62	5.43	3.67	7.39	3.78	5.90	4.48	5.65
Sum I-TEQ upperbound	***1.96***	***1.35***	***1.21***	***1.21***	***1.52***	***1.74***	***1.87***	***1.54***	***2.49***	***2.01***	***1.76***	***1.79***	***2.41***
Sum I-TEQ lowerbound	***1.40***	***0.88***	***0.63***	***0.58***	***0.53***	***0.61***	***0.63***	***0.48***	***1.24***	***0.06***	***0.78***	***0.95***	***1.48***

TSP	***09/10/14***	***10/10/14***	***11/10/14***	***12/10/14***	***13/10/14***	***29/10/14***	***30/10/14***	***31/10/14***	***01/11/14***	***02/11/14***	***03/11/14***	***04/11/14***	***05/11/14***
	Thurs	**Fri**	**Sat**	**Sun**	**Mon**	**Wed**	**Thurs**	**Fri**	**Sat**	**Sun**	**Mon**	**Tues**	**Wed**
2,3,7,8-TCDD	< 0.07	< 0.03	< 0.04	< 0.05	< 0.08	< 0.06	< 0.05	< 0.04	< 0.05	< 0.05	< 0.05	< 0.04	< 0.07
1,2,3,7,8-PeCDD	< 0.10	< 0.06	< 0.08	< 0.08	< 0.15	< 0.11	< 0.08	< 0.07	< 0.90	< 0.09	< 0.08	< 0.05	< 0.12
1,2,3,4,7,8-HxCDD	0.39	0.23	< 0.06	< 0.06	< 0.09	< 0.07	< 0.05	< 0.04	0.21	< 0.06	0.15	0.22	0.18
1,2,3,6,7,8-HxCDD	0.56	0.41	0.28	0.29	< 0.10	0.35	0.45	0.15	0.35	< 0.06	0.35	0.40	0.22
1,2,3,7,8,9-HxCDD	0.19	0.24	0.18	0.15	< 0.09	< 0.08	< 0.05	< 0.04	0.18	< 0.06	0.15	0.26	0.16
1,2,3,4,6,7,8-HpCDD	3.32	4.42	2.87	2.39	5.43	4.08	4.58	1.98	6.04	0.67	2.54	3.28	2.16
OCDD	5.65	7.15	5.39	5.04	9.87	8.69	7.26	2.75	8.92	4.13	5.26	5.50	5.12
2,3,7,8-TCDF	< 0.09	< 0.04	< 0.05	< 0.05	< 0.10	< 0.08	< 0.06	< 0.06	< 0.07	< 0.06	< 0.05	< 0.04	< 0.09
1,2,3,7,8-PeCDF	< 0.11	< 0.06	< 0.09	< 0.09	< 0.16	< 0.11	< 0.09	< 0.07	< 0.10	< 0.09	< 0.09	< 0.07	< 0.15
2,3,4,7,8-PeCDF	< 0.12	< 0.06	< 0.08	< 0.09	< 0.17	< 0.11	< 0.09	< 0.08	< 0.10	< 0.09	< 0.08	< 0.06	< 0.14
1,2,3,4,7,8-HxCDF	0.41	0.59	0.41	0.46	0.36	0.38	0.21	0.17	0.48	< 0.07	0.28	0.36	0.31
1,2,3,6,7,8-HxCDF	0.39	0.61	0.42	0.44	0.45	0.39	0.26	0.15	0.58	< 0.07	0.31	0.33	0.32
2,3,4,6,7,8-HxCDF	0.47	0.86	0.68	0.65	0.67	0.55	0.42	0.19	0.80	< 0.06	0.42	0.50	0.37
1,2,3,7,8,9-HxCDF	< 0.09	< 0.05	< 0.06	< 0.06	< 0.11	< 0.09	< 0.07	< 0.06	< 0.07	< 0.07	< 0.06	< 0.05	< 0.10
1,2,3,4,6,7,8-HpCDF	1.91	2.94	2.76	2.34	2.13	1.71	1.10	0.78	2.31	0.28	1.84	1.73	1.37
1,2,3,4,7,8,9-HpCDF	< 0.09	0.38	0.36	0.18	< 0.10	< 0.08	< 0.06	0.14	0.41	< 0.06	0.23	0.27	0.23
OCDF	0.72	1.72	1.63	1.20	1.09	1.25	1.00	0.67	1.69	0.43	1.81	0.91	0.76
Sum I-TEQ upperbound	***0.50***	***0.49***	***0.41***	***0.41***	***0.53***	***0.44***	***0.36***	***0.24***	***0.93***	***0.21***	***0.36***	***0.37***	***0.43***
Sum I-TEQ lowerbound	***0.30***	***0.38***	***0.26***	***0.25***	***0.23***	***0.23***	***0.20***	***0.10***	***0.36***	***0.01***	***0.22***	***0.27***	***0.20***