

MINISTÉRIO DO
MEIO AMBIENTE E
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Final Brazil Report of

the UNEP-GEF Project

Continuing regional support for the POPs Global Monitoring Plan under the
Stockholm Convention in the Latin American and Caribbean Region

GEF ID4881

Elaboration

CETESB

Brazil

November 2023

1 Introduction

This report addresses activities and the results developed in Brazil in support of the Global Monitoring Plan (GMP) as established by the Stockholm Convention on Persistent Organic Pollutants (POPs) and according to the project “Support in the implementation of the global monitoring plan for POPs in the countries of Latin America and the Caribbean” coordinated by Centro Coordinador del Convenio de Basilea y Centro Regional del Convenio de Estocolmo para América Latina y el Caribe (BCCC-SCRC) – Laboratório Tecnológico del Uruguay (LATU).

The objective of the project is to strengthen the monitoring capacity at the national level and contribute to the generation of data for the global monitoring plan and support the establishment of regional analytical capacities for the global POPs monitoring plan (GMP), thus enabling countries of Latin America and the Caribbean - GRULAC contribute to the global report to be presented at the Conference of the Parties to the Stockholm Convention.

2 Organizational Arrangements

Brazil is one of participant countries from GRULAC (Group of Latin America and Caribbean Region) and the Brazilian Ministry of the Environment and Climate Change, focal point of the Stockholm Convention, indicated CETESB (Companhia Ambiental do Estado de São Paulo) to coordinate the activities related to the air and water monitoring.

For the development of the activities it was signed a Memorandum of Understanding between BCCC-SCRC / LATU and CETESB and were established the activities listed below.

Activities	GEF Funds USD	Co-Financing (UD\$)
Overall project coordination for the entire project duration including nomination of project staff and development of a national workplan and timetable, coordination of air and water sampling, and national samples; miscellaneous costs	--	25,000
Undertake air sampling (includes servicing of the site, consultation with stakeholders, documentation, shipment of samples to the international labs, etc.)	7,000	5,000
Undertake sampling of matrices of major national interest (includes identification, shipment and analysis in national laboratory)	--	5,000

Analyse PUFs and matrices of major national interest in national laboratory	22,000	746,700
Plan for sustainable monitoring plan for GRULAC developed	--	2,800
National workshops and travel for sampling	2,100	10,000
National reports presenting implementation and results of GMP 2	-	5,500
Total (1st part)	50,000	800,000
Undertake 8 water sampling (includes servicing of the site, consultation of the stakeholders, documentation, shipment of the samples to the international labs, etc.)	10,800	--
Release from the customs, installation and maintenance of the active air sampler, shipment of the exposed PUFs (polyurethane foam) to international laboratories	5,500	--
Analyse PFAS in 8 PUFs	3,000	--
Analyse PFAS in 8 water samples	3,000	--
Total (2nd part)	22,300	--
Grand Total (Including Amendment)	72,500	800,000

The project offered sampling material and technical assistance to the participants to undertake chemical analysis in their laboratories. During the project, the national laboratory has been trained by one of the expert laboratories – CSIC Barcelona or MTM Örebro University according to item 4.1.

3 National Activities

3.1 Air Sampling (Passive - PAS and High Volume Sampling - HVS)

Coordination: CETESB – Companhia Ambiental do Estado de São Paulo

3.1.1 Methodology

3.1.1.1 Passive Air Sampling (PAS) methodology

The passive air sampling was carried out according to the procedure provided from the project coordination (UNEP, 2016) and the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants (UNEP/GMP, 2015).

The persistent organic pollutants that are considered to be sampled with Passive Air Sampler (PAS) are: Basic POPs (aldrin, dieldrin, endrin, cis-chlordane, trans-chlordane, cis-nonachlor, transnonachlor, oxychlordane, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, mirex, hexachlorobenzene, toxaphene), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs).

The same procedure also applies to the sampling of the nine POPs listed by the Conference of the Parties at its fourth session: Lindane (γ -HCH), α -HCH, β -HCH, polybrominated diphenyl ethers (PBDEs), hexabromobiphenyl (PBB), chlordecone, pentachlorobenzene, perfluorooctane sulfonic acid, its salt and perfluorooctane sulfonyl fluoride; at its fifth session: endosulfan; at its sixth session: hexabromo cyclododecane (HBCD).

3.1.1.2 High Volume sampling (HVS) methodology

The active air sampling was carried out according to the procedure provided from CSIC (2018) and the training provided from them (2018).

The persistent organic pollutants that are considered to be sampled with HVS are:

Basic POPs (aldrin, dieldrin, endrin, cis-chlordane, trans-chlordane, cis-nonachlor, transnonachlor, oxychlordane, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, *p,p'*- DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, mirex, hexachlorobenzene, toxaphene, lindane (γ -HCH), α -HCH, β -HCH, chlordecone, pentachlorobenzene, endosulfan, endosulfan sulfate).

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB).

Polybrominated diphenyl ethers (PBDE), hexabromobiphenyl (PBB), hexabromo cyclododecane (HBCD).

Perfluorooctane sulfonic acid, its salt and perfluorooctane sulfonyl fluoride.

3.1.2 Sampling

3.1.2.1 Passive Air Sampling Site Information

Urban site- São Paulo City at CETESB's Air Monitoring Station “Cerqueira César”

Land use: traffic

Address: Avenida Dr. Arnaldo, nº 725 (Faculdade de Saúde Pública), São Paulo

Geographical coordinates

Latitude: 23° 33' 12.8" S

Longitude: 46° 40' 21.9" W

Altitude: 820 m above sea level

Institution responsible for Air sampling: CETESB- Air Sampling and Analysis Laboratory and Organic Chemistry Laboratory.





3.1.2.2 Passive Sampling – Exposure Periods

The deployment time was three-month periods during one year (02/01/2017 – 28/12/2018), with total of 6 PUF disk samples for each group of compounds for the Expert laboratories (PUF number: 1, 3, 5, 7, 9, 11) and 6 PUFs disk samples for each group of compounds for the National laboratory (PUF number 2, 4, 6, 8, 10, 12). The detailed information are presented at Table 1 and Table 2.

Table 1 - Passive Air Sampling Schedule – 2017-2018 (Expert Laboratory samples)

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure	Date the PUF was sent to expert lab
BRA-1 (2017-I)	1	CSIC	OCPs	2-jan-2017	31-mar-2017	88	17-abr-2017
BRA-3 (2017-I)	3	CSIC	PCB(6)	2-jan-2017	31-mar-2017	88	17-abr-2017
BRA-5 (2017-I)	5	CSIC	dl-POPs	2-jan-2017	31-mar-2017	88	17-abr-2017
BRA-7 (2017-I)	7	CSIC	dl-POPs	2-jan-2017	31-mar-2017	88	17-abr-2017
BRA-9 (2017-I)	9	CSIC	PBDE, HBCD, HxBB	2-jan-2017	31-mar-2017	88	17-abr-2017

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure	Date the PUF was sent to expert lab
BRA-11 (2017-I)	11	MTM	PFOS	2-jan-2017	31-mar-2017	88	17-abr-2017
BRA-1 (2017-II)	1	CSIC	OCPs	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-3 (2017-II)	3	CSIC	PCB(6)	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-5 (2017-II)	5	CSIC	dl-POPs	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-7 (2017-II)	7	CSIC	dl-POPs	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-9 (2017-II)	9	CSIC	PBDE, HBCD, HxBB	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-11 (2017-II)	11	MTM	PFOS	31-mar-2017	30-jun-2017	91	10-jul-2017
BRA-1 (2017-III)	1	CSIC	OCPs	30-jun-2017	29-set-2017	91	9-out-2017
BRA-3 (2017-III)	3	CSIC	PCB(6)	30-jun-2017	29-set-2017	91	9-out-2017
BRA-5 (2017-III)	5	CSIC	dl-POPs	30-jun-2017	29-set-2017	91	9-out-2017
BRA-7 (2017-III)	7	CSIC	dl-POPs	30-jun-2017	29-set-2017	91	9-out-2017
BRA-9 (2017-III)	9	CSIC	PBDE, HBCD, HxBB	30-jun-2017	29-set-2017	91	9-out-2017
BRA-11 (2017-III)	11	MTM	PFOS	30-jun-2017	29-set-2017	91	9-out-2017

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure	Date the PUF was sent to expert lab
BRA-1 (2017-IV)	1	CSIC	OCPs	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-3 (2017-IV)	3	CSIC	PCB(6)	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-5 (2017-IV)	5	CSIC	dl-POPs	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-7 (2017-IV)	7	CSIC	dl-POPs	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-9 (2017-IV)	9	CSIC	PBDE, HBCD, HxBB	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-11 (2017-IV)	11	MTM	PFOS	29-set-2017	29-dez-2017	91	22-jan-2018
BRA-1 (2018-I)	1	CSIC	OCPs	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-3 (2018-I)	3	CSIC	PCB(6)	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-5 (2018-I)	5	CSIC	dl-POPs	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-7 (2018-I)	7	CSIC	dl-POPs	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-9 (2018-I)	9	CSIC	PBDE, HBCD, HxBB	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-11 (2018-I)	11	MTM	PFOS	29-dez-2017	29-mar-2018	90	9-abr-2018
BRA-1 (2018-II)	1	CSIC	OCPs	29-mar-2018	29-jun-2018	92	17-jul-2018
BRA-3 (2018-II)	3	CSIC	PCB(6)	29-mar-2018	29-jun-2018	92	17-jul-2018

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure	Date the PUF was sent to expert lab
BRA-5 (2018-II)	5	CSIC	dl-POPs	29-mar-2018	29-jun-2018	92	17-jul-2018
BRA-7 (2018-II)	7	CSIC	dl-POPs	29-mar-2018	29-jun-2018	92	17-jul-2018
BRA-9 (2018-II)	9	CSIC	PBDE, HBCD, HxBB	29-mar-2018	29-jun-2018	92	17-jul-2018
BRA-11 (2018-II)	11	MTM	PFOS	29-mar-2018	29-jun-2018	92	17-jul-2018
BRA-1 (2018-III)	1	CSIC	OCPs	29-jun-2018	28-set-2018	91	10-out-2018
BRA-3 (2018-III)	3	CSIC	PCB(6)	29-jun-2018	28-set-2018	91	10-out-2018
BRA-5 (2018-III)	5	CSIC	dl-POPs	29-jun-2018	28-set-2018	91	10-out-2018
BRA-7 (2018-III)	7	CSIC	dl-POPs	29-jun-2018	28-set-2018	91	10-out-2018
BRA-9 (2018-III)	9	CSIC	PBDE, HBCD, HxBB	29-jun-2018	28-set-2018	91	10-out-2018
BRA-11 (2018-III)	11	MTM	PFOS	29-jun-2018	28-set-2018	91	10-out-2018
BRA-1 (2018-IV)	1	CSIC	OCPs	28-set-2018	28-dez-2018	91	8-jan-2019
BRA-3 (2018-IV)	3	CSIC	PCB(6)	28-set-2018	28-dez-2018	91	8-jan-2019
BRA-5 (2018-IV)	5	CSIC	dl-POPs	28-set-2018	28-dez-2018	91	8-jan-2019

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure	Date the PUF was sent to expert lab
BRA-7 (2018-IV)	7	CSIC	dl-POPs	28-set-2018	28-dez-2018	91	8-jan-2019
BRA-9 (2018-IV)	9	CSIC	PBDE, HBCD, HxBB	28-set-2018	28-dez-2018	91	8-jan-2019
BRA-11 (2018-IV)	11	MTM	PFOS	28-set-2018	28-dez-2018	91	8-jan-2019

CSIC: Consejo Superior de Investigaciones Cientificas, Barcelona, Spain
MTM research Centre, Örebro University, Sweden

Table 2 - Passive Air Sampling Schedule – 2017-2018 (National Laboratory samples)

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure
BRA-2 (2017-I)	2	CETESB	OCPs	2-jan-2017	31-mar-2017	88
BRA-4 (2017-I)	4	CETESB	PCB(6)	2-jan-2017	31-mar-2017	88
BRA-6 (2017-I)	6	CETESB	dl-POPs	2-jan-2017	31-mar-2017	88
BRA-8 (2017-I)	8	CETESB	dl-POPs	2-jan-2017	31-mar-2017	88
BRA-10 (2017-I)	10	CETESB	PBDE, HBCD, HxBB	2-jan-2017	31-mar-2017	88
BRA-12 (2017-I)	12	CETESB	PFOS	2-jan-2017	31-mar-2017	88
BRA-2 (2017-II)	2	CETESB	OCPs	31-mar-2017	30-jun-2017	91
BRA-4 (2017-II)	4	CETESB	PCB(6)	31-mar-2017	30-jun-2017	91

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure
BRA-6 (2017-II)	6	CETESB	dl-POPs	31-mar-2017	30-jun-2017	91
BRA-8 (2017-II)	8	CETESB	dl-POPs	31-mar-2017	30-jun-2017	91
BRA-10 (2017-II)	10	CETESB	PBDE, HBCD, HxBB	31-mar-2017	30-jun-2017	91
BRA-12 (2017-II)	12	CETESB	PFOS	31-mar-2017	30-jun-2017	91
BRA-2 (2017-III)	2	CETESB	OCPs	30-jun-2017	29-set-2017	91
BRA-4 (2017-III)	4	CETESB	PCB(6)	30-jun-2017	29-set-2017	91
BRA-6 (2017-III)	6	CETESB	dl-POPs	30-jun-2017	29-set-2017	91
BRA-8 (2017-III)	8	CETESB	dl-POPs	30-jun-2017	29-set-2017	91
BRA-10 (2017-III)	10	CETESB	PBDE, HBCD, HxBB	30-jun-2017	29-set-2017	91
BRA-12 (2017-III)	12	CETESB	PFOS	30-jun-2017	29-set-2017	91
BRA-2 (2017-IV)	2	CETESB	OCPs	29-set-2017	29-dez-2017	91
BRA-4 (2017-IV)	4	CETESB	PCB(6)	29-set-2017	29-dez-2017	91
BRA-6 (2017-IV)	6	CETESB	dl-POPs	29-set-2017	29-dez-2017	91

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure
BRA-8 (2017-IV)	8	CETESB	dl-POPs	29-set-2017	29-dez-2017	91
BRA-10 (2017-IV)	10	CETESB	PBDE, HBCD, HxBB	29-set-2017	29-dez-2017	91
BRA-12 (2017-IV)	12	CETESB	PFOS	29-set-2017	29-dez-2017	91
BRA-2 (2018-I)	2	CETESB	OCPs	29-dez-2017	29-mar-2018	90
BRA-4 (2018-I)	4	CETESB	PCB(6)	29-dez-2017	29-mar-2018	90
BRA-6 (2018-I)	6	CETESB	dl-POPs	29-dez-2017	29-mar-2018	90
BRA-8 (2018-I)	8	CETESB	dl-POPs	29-dez-2017	29-mar-2018	90
BRA-10 (2018-I)	10	CETESB	PBDE, HBCD, HxBB	29-dez-2017	29-mar-2018	90
BRA-12 (2018-I)	12	CETESB	PFOS	29-dez-2017	29-mar-2018	90
BRA-2 (2018-II)	2	CETESB	OCPs	29-mar-2018	29-jun-2018	92
BRA-4 (2018-II)	4	CETESB	PCB(6)	29-mar-2018	29-jun-2018	92
BRA-6 (2018-II)	6	CETESB	dl-POPs	29-mar-2018	29-jun-2018	92
BRA-8 (2018-II)	8	CETESB	dl-POPs	29-mar-2018	29-jun-2018	92
BRA-10 (2018-II)	10	CETESB	PBDE, HBCD, HxBB	29-mar-2018	29-jun-2018	92

PUF Code	Sampler No.	Destination lab for analysis	Analytes	Actual exposure start date (d-mmm-yyyy)	Actual exposure end date (d-mmm-yyyy)	Effective days of exposure
BRA-12 (2018-II)	12	CETESB	PFOS	29-mar-2018	29-jun-2018	92
BRA-2 (2018-III)	2	CETESB	OCPs	29-jun-2018	28-set-2018	91
BRA-4 (2018-III)	4	CETESB	PCB(6)	29-jun-2018	28-set-2018	91
BRA-6 (2018-III)	6	CETESB	dl-POPs	29-jun-2018	28-set-2018	91
BRA-8 (2018-III)	8	CETESB	dl-POPs	29-jun-2018	28-set-2018	91
BRA-10 (2018-III)	10	CETESB	PBDE, HBCD, HxBB	29-jun-2018	28-set-2018	91
BRA-12 (2018-III)	12	CETESB	PFOS	29-jun-2018	28-set-2018	91
BRA-2 (2018-IV)	2	CETESB	OCPs	28-set-2018	28-dez-2018	91
BRA-4 (2018-IV)	4	CETESB	PCB(6)	28-set-2018	28-dez-2018	91
BRA-6 (2018-IV)	6	CETESB	dl-POPs	28-set-2018	28-dez-2018	91
BRA-8 (2018-IV)	8	CETESB	dl-POPs	28-set-2018	28-dez-2018	91
BRA-10 (2018-IV)	10	CETESB	PBDE, HBCD, HxBB	28-set-2018	28-dez-2018	91
BRA-12 (2018-IV)	12	CETESB	PFOS	28-set-2018	28-dez-2018	91

3.1.2.3 High Volume Air Sampling (HVS) Site Information

The passive samplers for the GMP-2 project were installed at CETESB's Air Monitoring Station "Cerqueira César" in an urban site of São Paulo City. During the training (February, 2018) the Expert Lab suggested to install the High Volume Sampler at CETESB's Pinheiros air monitoring station that is located inside the company because it is a safer place to keep the active sampler than the GMP-2 Passive Sampling site.

Sampling site information

Urban site- São Paulo City at CETESB's Air Monitoring Station "Pinheiros"

Land use: traffic

Address: Avenida Prof. Frederico Hermann Jr., nº 345 (CETESB), São Paulo

Geographical coordinates

Latitude: 23° 33' 41.32" S

Longitude: 46° 42' 7.51" W

Altitude: 728 m above sea level

Institution responsible for Air sampling: CETESB - Air sampling and Analysis Lab and Organic Chemistry Lab



3.1.2.4 High Volume Air Sampling (HVS) Periods

For the active sampling, it was provided materials (PUF, XAD) for Expert Lab analysis, but not for National Lab analysis.

It was collected 3 samples for basic POPs analysis (2018-2019), 3 samples for dl-POPs analysis (2018/2019), 2 samples for PBDE analysis (2019) and 2 samples for PFAS analysis according to the Table 3.

Table 3 - Active Air Sampling Schedule – 2018-2019 (Expert Laboratory samples)

CAV Code	Destination lab for analysis	Analytes	Actual sampling start date	Actual exposure end date	Volume of Air collected (m3)	Date the PUF was sent to expert lab
BRA-CAV1 (2018-I)	CSIC	Basic POPs	01-Oct-2018	04-Oct-2018	2158,3	10-Oct-2018
BRA-CAV-2 (2018-I)	CSIC	dl-POPs	24-Sep-2018	27-Sep-2018	2139,3	10-Oct-2018
BRA-CAV1 (2019-I)	CSIC	Basic POPs	07Jan 2019	10Jan2019	2158,5	10 Ap2019
BRA-CAV2 (2019-I)	CSIC	dl-POPs	14 Jan2019	17 Jan2019	2158,5	10 Ap2019
BRA-CAV3 (2019-I)	CSIC	PBDE	21 Jan2019	24 Jan2019	2158,2	10 Ap2019
BRA-CAV4 (2019-I)	MTM	PFAS	28 Jan2019	31 Jan2019	2107,9	10 Ap2019
BRA-CAV1 (2019-II)	CSIC	Basic POPs	5 Fev2019	8 Fev2019	2158,7	10 Ap2019
BRA-CAV2 (2019-II)	CSIC	dl-POPs	11 Fev2019	14 Fev2019	2158,8	10 Ap2019
BRA-CAV3 (2019-II)	CSIC	PBDE	18 Fev2019	21 Fev2019	2158,3	10 Ap2019
BRA-CAV4 (2019-II)	MTM	PFAS	25 Fev2019	28 Fev2019	2158,7	10 Ap2019

CSIC: Consejo Superior de Investigaciones Cientificas, Barcelona, Spain

MTM research Centre, Örebro University, Sweden

3.2 Water Sampling

Coordination: CETESB – Companhia Ambiental do Estado de São Paulo

3.2.1 Water Sampling – 2017

3.2.1.1 Water Sampling Site – 2017

Amazon River in Itacoatiara county, Manaus metropolitan region - Amazon

Geographical coordinates

Latitude (deg): 03° 09' 00.3" S

Longitude (deg): 58° 29' 13.6" W

Latitude (decimal): -3,15008333

Longitude (decimal): -58,487111

Narrative: Middle of the river

Distance from shore: 1600m

Sampling procedure: by boat

Institution responsible for Water sampling: CETESB- Divisão de Amostragem



3.2.1.2 Water Sampling Schedule - 2017

It was collected 4 water samples at Amazon river for Expert Lab and 4 water samples for National Lab Analysis according to Table 4

Table 4 - Water Sampling Schedule – 2017 (Expert and National Laboratory)

Sampling code	Weather observation	Water temperature (°C)	Sampling date	Time	Storage conditions	Shipment date to laboratory
BRA-A (2017-1)	Stable during the sampling but it was rainy during the night before sampling	28.5	30-mar-2017	9:15 – 9:20	2-6°C	17/04/2017 (MTM)
BRA-B (2017-1)						Not Applicable (CETESB)
BRA-A (2017-2)	Stable	29.1	29-jun-2017	13:26 – 13:42	2-6°C	10/07/2017 (MTM)
BRA-B (2017-2)						Not applicable (CETESB)
BRA-A (2017-3)	Stable	30.7	28-set-2017	11:45 – 12:10	2-6°C	09/10/2017(MTM)
BRA-B (2017-3)						Not Applicable (CETESB)
BRA-A (2017-4)	Stable	29.7	21-dez-2017	10:48 – 10:53	2-6°C	22/01/2018 (MTM)
BRA-B (2017-4)						Not Applicable (CETESB)

MTM research Centre, Örebro University, Sweden

3.2.2 Water Sampling - 2018

3.2.2.1 Water Sampling Site 2018

São Vicente Channel – São Paulo

Geographical coordinates

Latitude (deg): 23° 56' 08.4" S

Longitude (deg): 46° 23' 28.2" W

Latitude (decimal): -23,93566667

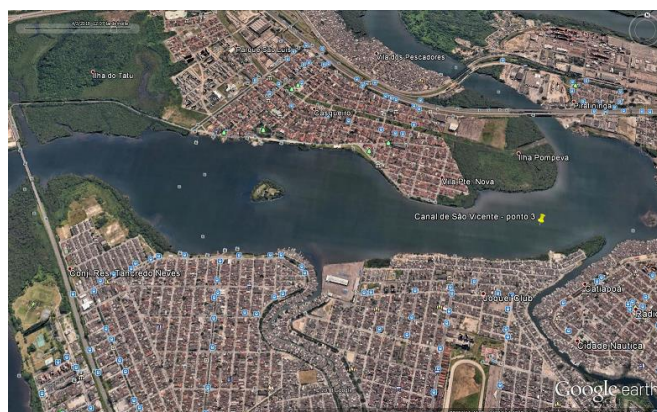
Longitude (decimal): -46,39116667

Narrative: Middle of the river

Distance from shore: 200m

Sampling procedure: by boat

Institution responsible for Water sampling: CETESB- Sampling Division



3.2.2.2 Water Sampling Schedule 2018

Four water samples were collected in São Paulo for Expert Lab and 4 water samples for National Lab Analysis according to Table 5.

Table 5 - Water Sampling Schedule – 2018 (Expert and National Laboratory)

Sampling code	Weather observation	Water temperature (°C)	Sampling date	Time	Storage conditions	Shipment date to laboratory
BRA-A (2018-1)	Rainy (24h)	29.4	5-mar-2018	15:16 – 15:26	2-6º	09/03/2018 (MTM)
BRA-B (2018-1)						Not Applicable (CETESB)
BRA-A (2018-2)	Stable	21,4	24-jul-2018	14:37 – 14:42	2-6º	30/07/18 (MTM)
There is no Bottle B						Not Applicable (CETESB)
BRA-A (2018-3)	Raining	22.7	28-set-2018	12:20 – 12:25	2-6º	10/10/2018 (MTM)
There is no Bottle B						Not Applicable (CETESB)
BRA-A (2018-4)	Stable	28.4	20-dez-2018	12:16 -12:21	2-6°C	08/01/2019 (MTM)
There is no Bottle B						Not Applicable (CETESB)

MTM research Centre, Örebro University, Sweden

3.3 National Samples

In 2017 national abiotic samples were sent to the Expert Labs: 3 sediment samples, 2 total suspended particulate (TSP) samples, 2 transformer oil for PCB analysis and one solid waste sample for chlordecone analysis (Table 6).

In October of 2018 it was recommended to send fish samples (mandatory) to the Expert La (MTM) and it was decided to collect fish and sediment sample at the same site of water sampling for PFAS (2018) in São Paulo.

The sediment sample was collected according to the CETESB's internal procedures SQPR/LB-139 "Sampling in Aquatic Environment", SQPR/LB-129 "Strategy for sediment and sewage sludge sampling" and SQPR/LB-132 "Strategies for sample preservation". The laboratory responsible for sampling has ISO17025:2017 accreditation for sediment sampling for PCB, OCP, Dioxins and furans analysis. The fish samples were prepared from a pool of several fish samples.

The Fundação Oswaldo Cruz (FIOCRUZ), prepared and send 2 freeze dried fish samples, 1 freeze dried chicken eggs sample, 1 powdered cow milk and 1 butter sample (Table 7). The fish sample were obtained at a fish stand on the free market that Copacabana/Rio de Janeiro. The chicken eggs, powdered cow milk and butter were bought at a normal supermarket.

Table 6 – National Abiotic Samples - 2017

Sample ID	Sample information	Compounds to analyse
Sediment 1	Rio Grande Reservoir - São Bernardo do Campo- São Paulo/Brazil (RGDE02030; RGDE02900)	PBDE, PBB, PCB-6 and If possible to include: dl- POPs
Sediment 2	Pond near Terminal Tequimar - Santos - São Paulo/Brazil	PBDE, PBB, HBCD, PFOS
Sediment 3	Sorocaba River, Cerquilha- São Paulo/ Brazil (SORO02700)	PFOS
TSP1	Cerqueira César Air Monitoring Station – São Paulo Apr.-jun2017	dl-POPs, PCB(6), PBDE, PBB
TSP-1b	Cerqueira César Air Monitoring Station – São Paulo Apr.-jun2017	PFAS
TSP2	Cubatão – Vila Parisi Air Monitoring Station – São Paulo Apr – Jun 2017	PBDE, PBB, PCB-6, dl- POPs
TSP-2b	Cubatão – Vila Parisi Air Monitoring Station – Jan – Mar 2017	PFAS
TSP-2c	Cubatão – Vila Parisi Air Monitoring Station – São Paulo Jul – Sep 2016	HBCD
Transformer Oil 1	Transformer oil EC-89	PCB
Transformer Oil 2	Transformer oil EC247	PCB
Solid Waste	Solid waste from São Paulo	Chlordecone

TSP = total suspended particulate (air sample)

Table 7 – National Biotic and Abiotic Samples – 2018/2019

Sample ID	Sample information	Compounds to analyse
Sediment 4	<p>São Vicente Channel – São Paulo – Brazil GPS coordinates: 23°56'08.4''S / 46°23'28.2''W Sampling date: 20/Dec/2018 Sample preparation: 21-28 Dec/2018 Sample dried at ambient temperature: total 100g Moisture (ambient temperature): 66.52% Moisture (at 105°C): 70.92% Shipment to the Expert Lab (MTM): 08/Jan/2019</p>	PFAS
Fish – BRA-F1 (2018)	<p>São Vicente Channel – São Paulo – Brazil GPS coordinates: 23°56'08.4''S / 46°23'28.2''W Fish specie: White Mullet Sampling date: 10 Dec-2018 Freeze dried and packaging: Dec2018 - 02/Jan/2019 Institution responsible for Fish sample preparation: CETESB, Toxicological Analysis Lab Shipment to the Expert Lab (MTM): 08/Jan/2019 – 2 bottles 50g total 100g (d.w.)</p>	PFAS
Fish – BRA-F2 (2018)	<p>São Vicente Channel – São Paulo – Brazil Fish specie: Largehead Hairtail “Swordfish” Sampling date: 10 Dec-2018 Freeze dried and packaging: Dec2018 - 02/Jan/2019 Institution responsible for fish sample preparation: CETESB, Toxicological Analysis Lab Shipment to the Expert Lab (MTM): 08/Jan/2019 – 2 bottles 50g total 100g (d.w.)</p>	PFAS
Fish – BR-INCQS-01	<p>Fisch Specie: Tilapia (<i>Cichlidae pseudcrenilabrinae</i>) – Freshwater fish raised in captivity Sample from fish stand on the free Market – Copacabana/Rio de Janeiro – Brazil Sample Amount: 100g freeze dried (900 g total) Water content: 75,0% Institution responsible for fish sample preparation: FIOCRUZ – INCQS</p>	dl-POPs, indicator PCB, OCP
Fish – BR-INCQS-02	<p>Fisch Specie: Linguado (<i>Paralichthys patagonicus</i>) – marine fish commonly consumed in Brazil Sample from fish stand on the free Market – Copacabana/Rio de Janeiro – Brazil Sample Amount: 100g freeze dried (900 g total) Water content: 76,9% Institution responsible for fish sample preparation: FIOCRUZ – INCQS</p>	dl-POPs, indicator PCB, OCP

Powdered cow milk – BR-INCQS-03	Powdered cow milk from supermarket – Rio de Janeiro – Brazil (with no additional treatment, weighted and directly into the container) Sample Amount: 150g Institution responsible for the sample acquisition : FIOCRUZ – INCQS	dl-POPs, indicator PCB, OCP
Butter – BR-INCQS-04	Butter sample from supermarket – Rio de Janeiro – Brazil (with no additional treatment, weighted and directly into the container) Sample Amount: 100g Institution responsible for the sample acquisition : FIOCRUZ – INCQS	dl-POPs, indicator PCB, OCP
Chicken eggs – BR-INCQS-05	Chicken eggs sample from supermarket – Rio de Janeiro – Brazil Sample Amount: 56g (freeze dried) Water content: 75,7% Institution responsible for the sample preparation : FIOCRUZ – INCQS	dl-POPs, indicator PCB, OCP

3.4 International Inter-Calibration Study

The interlaboratory assessment is part of the United Nations Environment Programme's (UNEP) capacity building program for laboratories analyzing Persistent Organic Pollutants (POPs). The interlaboratory exercises are often used to assess the effectiveness of quality assurance/quality control (QA/QC) practices among several participating labs and to provide a measure of interlaboratory comparability.

During the GMP-2 project, two interlaboratory assessments were offered and some Brazilian laboratories participated in 2016 and 2018 rounds including OCPs, PCB/dl-PCB, Dioxin and furans, PBDE and PFAS analysis in several matrices. In 2016, it was registered 4 national laboratories for the interlaboratory assessment and in 2018 it was registered 10 national laboratories. The data are confidential and it was not possible to verify how many national laboratories really sent the results, but was informed from the coordination, that not all laboratories sent the results. One national laboratory has achieved 325 z-scores, of these 74% were satisfactory. Considering the new POPs (PBDE/PBB and PFAS) and dl-POPs, more than 80% of the results were satisfactory and for indicator PCBs and Toxaphene results, 100% of the results were satisfactory.

Considering the interlaboratory assessment results, it is possible to conclude that the analytical capacity for the new POPs PBDEs/PBB and PFAS analysis were built in Brazil but need more participating laboratories in the future assessments.

National PAS and Water Samples analysis laboratory characteristics

Equipments: GC-dual- μ ECD, GCMS, GCMSMS, GC-HRMS, LCMSMS, LC-Q-TOF, APGC-MSMS. The maintenance are performed by the technician from equipment representative in Brazil.

Analysis: the laboratory perform analysis of OCPs, PCB indicator, dl-PCBs, dioxins and furans in water, soil, sediment, passive air samples, residues and biological tissue samples and other organic compounds analysis. With the support of this UN project, the laboratory started to analyse PBDEs/PBB and PFAS analysis in abiotic samples

QA/QC: the laboratory has the ISO 17025:2017 accreditation for OCPs, PCB indicator, dl-PCBs and dioxins and furans analysis. The laboratory complies with ISO 17025 requirements such as participation in intercalibration studies, use of standard reference materials, analyte spike, surrogate spike, blank control, etc.

3.5 Analytical Methodology – National Laboratory

Basic POPs (PUF sampler 2 + 4): the PUF sample was extracted by Soxhlet with Hexane:Acetone (1:1), during 24h. The extract was cleaned up by gel permeation (GPC) and then by silica gel column (U.S.EPA method 3640A and 3630C). The final extracts were analyzed in a Agilent 7890 model gas chromatography/electron capture detector GC- μ ECD-ECD. The GC was fitted with a DB 1701 (60m x 0.25mm id. x 0.25 μ m film thickness) and a SLB-5MS (60m x 0.25mm id. x 0.25 μ m film thickness) fused silica column.

dl-POPs/PCB-I/PBDE/PBB (PUF sampler 6 and 8): PCDD/Fs, PCBs, PBDE and PBB were analyzed according to the method U.S. EPA 8290A, U.S. EPA 1668B and EPA1614A, respectively. PUF samples were spiked with $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ PCBs and $^{13}\text{C}_{12}$ -PBDE extraction standards. The extraction was performed in a Soxhlet for 24 hours with toluene:acetone (8:2 v/v). The extracts were purified in an acid silica column (40% H_2SO_4 and 10% AgNO_3) using n-hexane as eluent, following by Alumin column using a solution toluene:hexane (2:1 v/v) to elute PCBs and PBDEs (fraction 1) then, dichloromethane to elute PCDD/Fs and other PBDEs (fraction 2). Fraction 2 was cleaned up with a carbon column using dichloromethane/n-hexane (1:1) as eluent to collect PBDE congeners into fraction 1. PCDD/Fs was eluted with toluene. The two fractions obtained were concentrated until 25 μ L

and added the $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ PCBs and $^{13}\text{C}_{12}$ -PBDE injection standards before analysis. The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatographic coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS). The equipment was operating with electron impact ionization of 35eV at a mass resolution of 10000 for PCDD/F and PCB and a resolution of 5000 for PBDE analysis. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 μm film thickness) for PCDD/F and PCBs analysis and DB5-ms UI capillary column (15m x 0.25mm id x 0.25 μm) for PBDE/PBB analysis and for BDE-209 congener analysis was used a RTX-1614 capillary (15m x 0.25mm x 0.10 μm) additional column.

The PBB/PBDEs were analysed together with dl-POPs (sampler 6+8) and the sampler 10 (PBB/PBDE) was used to blank analysis for dl-POPs, PBB/PBDE and OCP. Depending on the period was chosen one of compounds to prepare a blank analysis because it was not possible to analyse blank for all compounds in all periods.

PFAS (PUF sampler 12): The PUF sample was extracted by soxhlet with methanol and SPE/Wax clean-up and isotopic dilution method according to the UNEP/GEF/Orebro University procedure – Revision 1 – February 2018.

Basic POPs (sediment): the sediment samples were air dried at room temperature, grinded and sieved (1mm) and then extracted in a microwave oven (U.S. EPA method 3546) with hexane:acetone (1:1). The extract was cleaned up by gel permeation, silica gel and sulfur cleanup with copper (U.S.EPA methods 3640A, 3630C and 3660B). The final extracts were analyzed in a Agilent 7890 model gas chromatography/electron capture detector GC- μECD -ECD. The GC was fitted with a DB1701 (60m x 0.25mm id. x 0.25 μm film thickness) and a SLB-5MS (60m x 0.25mm id. x 0.25 μm film thickness) fused silica column.

dl-POPs + PBB/PBDEs (sediment): PCDD/Fs, PCB-I, dl-PCBs, PBDE and PBB were analyzed according to the method U.S. EPA 8290A, U.S. EPA 1668B and EPA 1614A, respectively. Sediment sample (air dried, grinded and sieved) was extracted in a microwave extractor with toluene:acetone (8:2 v/v). The sample was spiked with $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ -PCBs, $^{13}\text{C}_{12}$ -PBDEs extraction standards before extraction. The extract was purified in an acid silica column (40% H_2SO_4 and 10% AgNO_3) using n-hexane as eluent, following by Alumin

column using a solution toluene:hexane (2:1 v/v) to elute PCBs and PBDEs (fraction 1) then, dichloromethane to elute PCDD/Fs and other PBDEs (fraction 2). Fraction 2 was cleaned up with a carbon column using dichloromethane/n-hexane (1:1) as eluent to collect PBDE congeners into fraction 1. PCDD/Fs was eluted with toluene. The two fractions obtained were concentrated until 25 μ L and added the $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ PCBs and $^{13}\text{C}_{12}$ -PBDE injection standards before analysis. The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatographic coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS). The equipment was operating with electron impact ionization of 35eV at a mass resolution of 10000 for PCDD/F and PCB and a resolution of 5000 for PBDE analysis. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 μ m film thickness) for PCDD/F and PCBs analysis and DB5-ms UI capillary column (15m x 0.25mm id x 0.25 μ m) for PBDE/PBB analysis and for BDE-209 congener analysis was used a RTX-1614 capillary (15m x 0.25mm x 0.10 μ m) additional column.

dl-POPs + PBDEs/PBB (fish): PCDD/Fs, dl-PCBs, PBB/PBDEs were analyzed according to the method U.S. EPA 8290A, U.S. EPA 1668B and EPA1614A, respectively. Fish sample (lyophilized) was extracted in a Soxhlet extractor with toluene. The sample was spiked with $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ -PCBs and $^{13}\text{C}_{12}$ -PBDE extraction standards before extraction, and extracted for 24 hours, then the extract was concentrated till dryness to determine the fat content. The same dried extract was resuspended in n-hexane and purified in an acid silica column (40% H₂SO₄ and 10% AgNO₃) using n-hexane as eluent, following by Alumin column using a solution toluene:hexane (2:1 v/v) to elute PCBs and PBDEs (fraction 1) then, dichloromethane to elute PCDD/Fs and other PBDEs (fraction 2). Fraction 2 was cleaned up with a carbon column using dichloromethane/n-hexane (1:1) as eluent to collect PBDE congeners into fraction 1. PCDD/Fs was eluted with toluene. The two fractions obtained were concentrated until 25 μ L and added the $^{13}\text{C}_{12}$ -PCDD/F, $^{13}\text{C}_{12}$ PCBs and $^{13}\text{C}_{12}$ -PBDE injection standards before analysis. The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatographic coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS). The equipment was operating with electron impact ionization of 35eV at a mass resolution of 10000 for PCDD/F and PCB and a resolution of 5000 for PBDE analysis. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 μ m film thickness) for PCDD/F and PCBs analysis and DB5-ms UI capillary column (15m x 0.25mm id x 0.25 μ m) for PBDE/PBB analysis and for BDE-209 congener analysis was used a RTX-1614 capillary (15m x 0.25mm x 0.10 μ m) additional column.

PFAS (water): The water sample was extracted by SPE/Wax and analysed by isotopic dilution method according to the UNEP/GEF/Orebro University procedure – Revision 1 – February 2018.

Passive sampler air volume calculation

The passive air sampler volumes were calculated according to the Harner (2021) Template. This Excel template allows users of PUF disk (GAPS, MONET and CSIC types) and SIP disk samplers (GAPS type) to estimate the effective sample air volumes for their passive samplers. This effective air volume allows conversion of amount collected on the sampler to a concentration value in air. The calculation takes into account deployment time and average temperature. For the compounds not listed in the Template, was considered an air volume of 4 m³/day.

3.6 POPs Analysis Results – Passive Air Samples

3.6.1 PCDD and PCDF results - Passive Air Samples

The National and Expert Labs results of PCDD and PCDF analysis in passive air samples are presented at Table A1 (Annex1) and Figure 1A and 2B (CETESB results) and at Table 3 (Annex2) and Figures 1B and 2B (CSIC results). The PCDD/Fs profile are dominated by Cl₈-DD, 1234678Cl₇-DD and 1234678Cl₇-DF and the profile of CSIC and CETESB results are very similar (Figures 1A/B and 2A/B). These PCDD/Fs pattern are very similar to previous study in São Paulo using active sampler (Assunção et al., 2005) and GMP-1 results (Table 8).

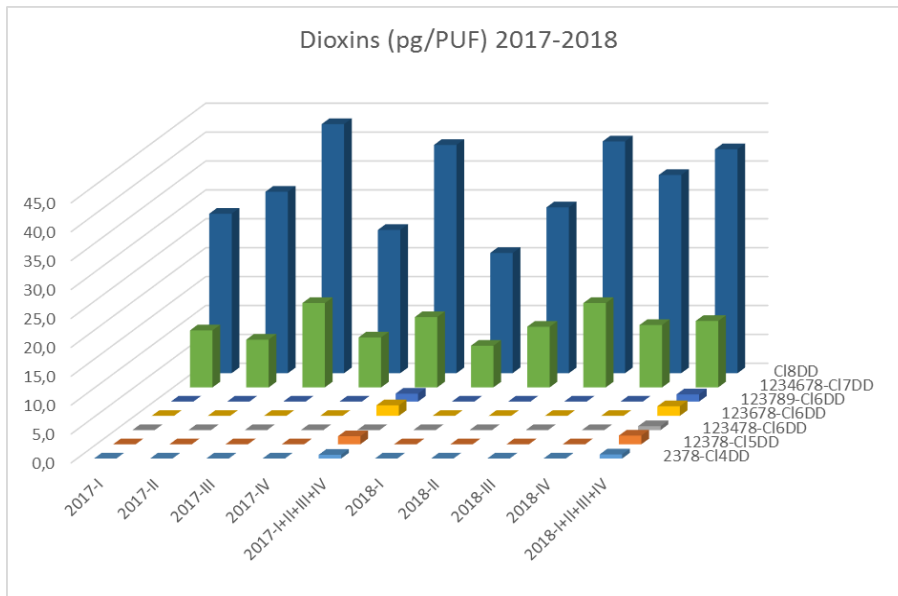


Figure 1A. Dioxin concentration in São Paulo city (Cerqueira Cesar Air Monitoring Station) 2017 – 2018 – CETESB's results

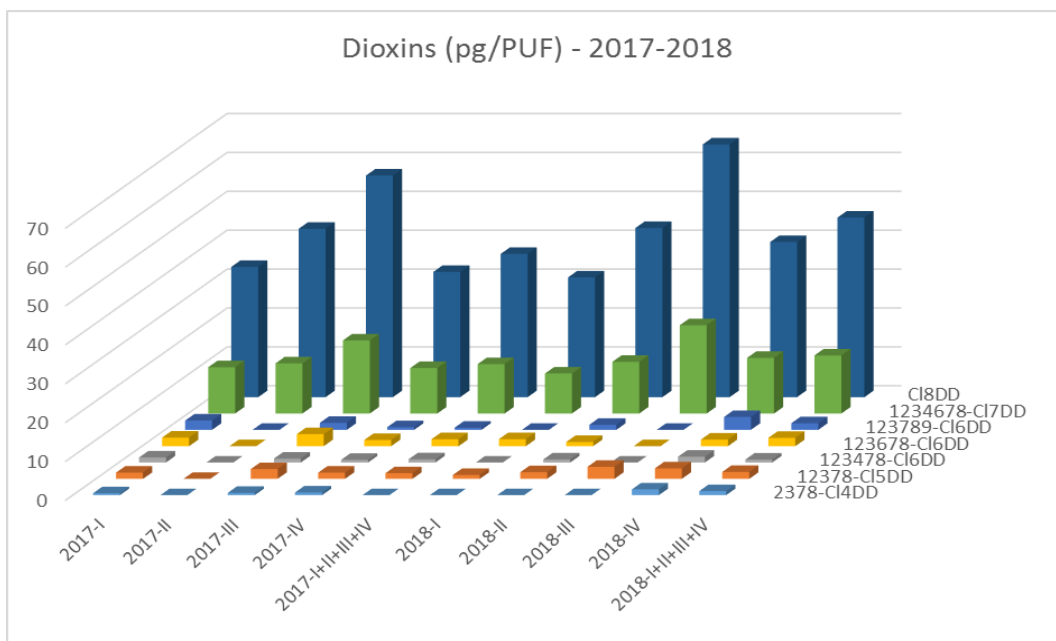


Figure 1B. Dioxin concentration in São Paulo city (Cerqueira Cesar Air Monitoring Station) 2017 – 2018 – CSIC's results

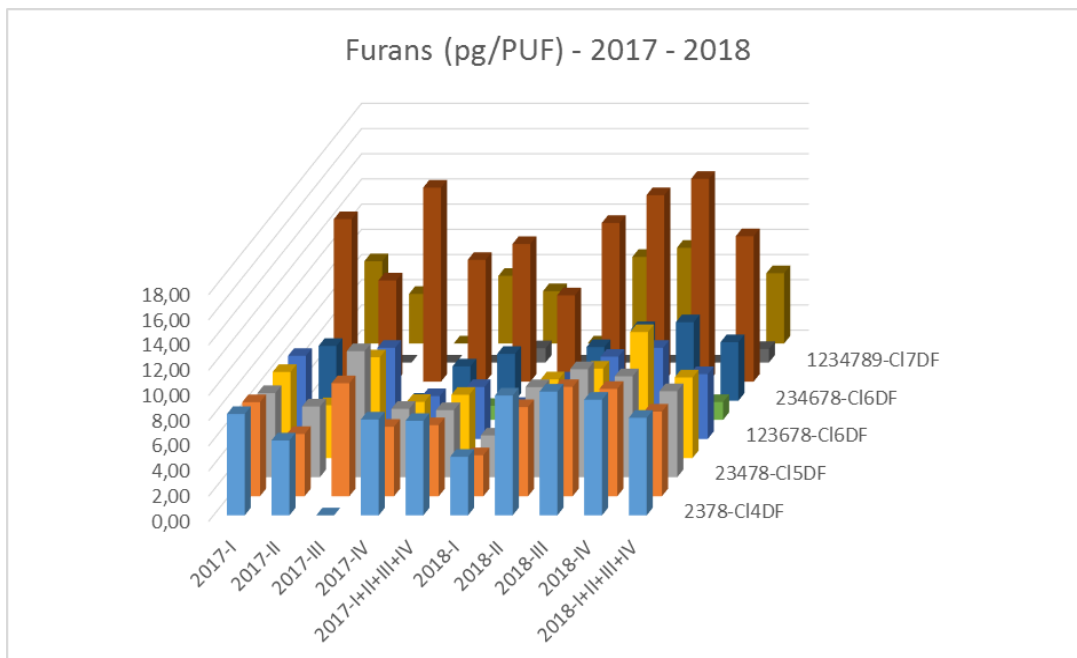


Figure 2A. Furans concentration in São Paulo (Cerqueira Cesar Air Monitoring Station) 2017 – 2018 – CETESB’s results

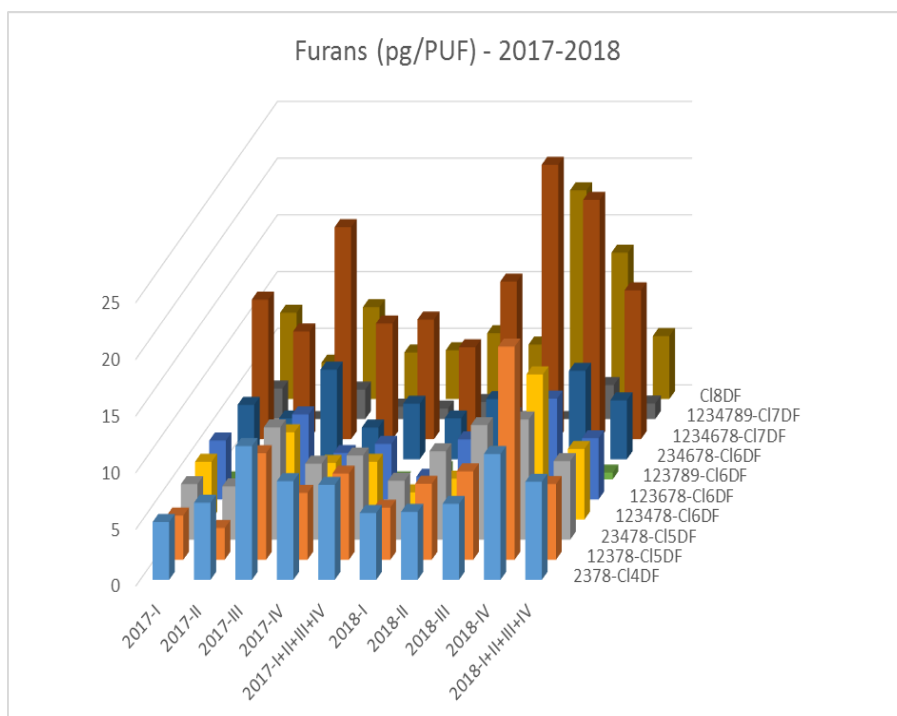


Figure 2B. Furans concentration in São Paulo (Cerqueira Cesar Air Monitoring Station) 2017 – 2018 – CSIC’s results

Considering 3 months samples, most of the PCDD/Fs are below limit of quantitation but considering the annual sample (2017-I+II+III+IV/2018-I+II+III+IV), almost all PCDD/PCDF congeners were quantified and the annual samples are better than 3 months samples for PCDD/F quantitation in air samples in São Paulo city.

The Table 8 shows the concentration of dioxins and furans results for the GMP-2 period from the National and Expert Lab. The GMP-1 site and GMP-2 site are both urban sites and 3 Km distance each other. The sampling sites (GMP-1 and GMP-2) were located in an intense vehicular traffic where many cars fueled with gasohol or ethanol and buses with diesel circulate. So, the main source of dioxins and furans are probably vehicular emission.

The GMP-1 site (2010-2015) results samples presented higher concentration of hepta and octachlorinated dioxins and furans, but the GMP-2 (2017-2018) samples presented higher concentration of total TEQ (Toxic equivalent to the most toxic dioxin 2378TCDD) for dioxins, furans and dl-PCB (Table 8). Considering the TEQ values, PCDF were present in higher concentration than PCDD and dl-PCB concentration were below PCDD/F concentrations.

Table 8 – Dioxin and Furans and dl-PCBs concentrations in Passive Air Samples (PUF) - GMP-1 site and GMP-2 samplings results (National Lab) and GMP-2 results from Expert Lab

Dioxins/Furans	National Lab results		Expert Lab results	
	GMP-1 site Results* 2010-2015 Min.-Max (fg/m ³)	GMP-2 – 2017/2018 ∑annual 4PUFs (fg/m ³)	GMP-2 -2017/ 2018 ∑annual 4 PUFs (fg/m ³)	GMP-2 2017/ 2018 Min–Max (fg/ m ³)
2378-C14DD	<LOQ (100%)	5.07 / 5.60	< LOQ/ 8.26	< LOQ – 11.5
12378-C15DD	<LOQ (92.3%) – 4.63	10.8/ 11.7	11.3/ 13.7	< LOQ – 23.5
123478-C16DD	<LOQ (100%)	<LQ/ 5.17	6.35/ 5.72	< LOQ – 11.4
123678-C16DD	<LOQ(76.9%) – 9.38	14.0/ 12.7	13.8/ 16.4	< LOQ -23.5
123789-C16DD	<LOQ(92.8%) – 6.24	10.6/ 9.57	4.23/ 13.0	< LOQ – 25.0
1234678-C17DD	20.8 – 121	93.2/ 87.3	97.2/ 113	78.8 – 172
OCDD	10.0 – 569	302/ 293	281/ 350	236 – 492

2378-CI4DF	<LOQ (7.69%) - 36.9	59.8/ 61.4	66.8/ 68.5	40.4 – 90.1
12378-CI5DF	<LOQ (15.4%) – 39.8	15.7/ 18.6	21.1/ 18.5	7.69 – 51.6
23478-CI5DF	<LOQ(23.1%) – 33.7	41.4/ 52.7	57.8/ 53.5	35.7 – 80.6
123478-CI6DF	<LOQ(7.69%) – 44.9	38.8 / 49.0	39.3/ 47.6	18.4 – 97.1
123678-CI6DF	<LOQ(15.4%) – 46.0	31.8/ 39.4	37.8/ 41.3	15.3 – 67.5
234678-CI6DF	<LOQ(30.8%) – 25.2	28.7/ 35.5	37.7/ 39.7	< LOQ – 59.9
123789-CI6DF	<LOQ (100%)	8.56/ 10.8	< LOQ/ 4.58	< LOQ – 6.90
1234678-CI7DF	7.73 – 96.9	83.8/ 87.9	80.9/ 99.9	62.0 – 183
1234789-CI7-DF	<LOQ (84.6%) – 9.41	8.69/ 8.16	7.08/ 10.4	< LOQ – 22.7
OCDF	5.86 – 119	31.7/ 42.2	32.8/ 42.1	24.2 – 139
\sum PCDD TEQ.m ⁻³)* (fg	1.19 – 8.84-	19.4/ 21.0	14.8/ 26.7	1.07 – 38.1
\sum PCDF TEQ.m ⁻³)* (fg	5.20 – 23.6	30.6/ 37.0	37.0/ 37.9	21.2 – 58.5
\sum PCDD/F TEQ.m ⁻³)* (fg	6.42 -31.1	50.0/57.9	51.8/64.6	22.3 – 96.5
\sum PCB (fg TEQ.m ⁻³)*	0.71 -11.9	17.1/ 18.2	17.3/24.6	6.13 – 29.8
\sum PCDD/F/PCB (fg TEQ.m ⁻³)*	7.48 – 42.9	67.1/ 76.2	69.1/89.2	37.8 – 121

* GMP-1 site results: Tominaga et al, 2016

3.6.2 Polychlorinated Biphenyls (PCBs) results - Passive Air Samples

The National and Expert Labs results of dl-PCB analysis in passive air samples are presented at Table A2 (Annex1) and Figure 3A (CETESB results) and at Table 3 (Annex2) and Figures 3B (CSIC results). The dl-PCB profile are dominated by PCB118 congener, followed by PCB105 and PCB77 congeners and the profile of CSIC and CETESB results are very similar (Figures 3A/B). The dl-PCB contribution for total TEQ (PCDD/PCDF/PCB) were 23.9 – 25.5% (2017 and 2018 results – Table 8).

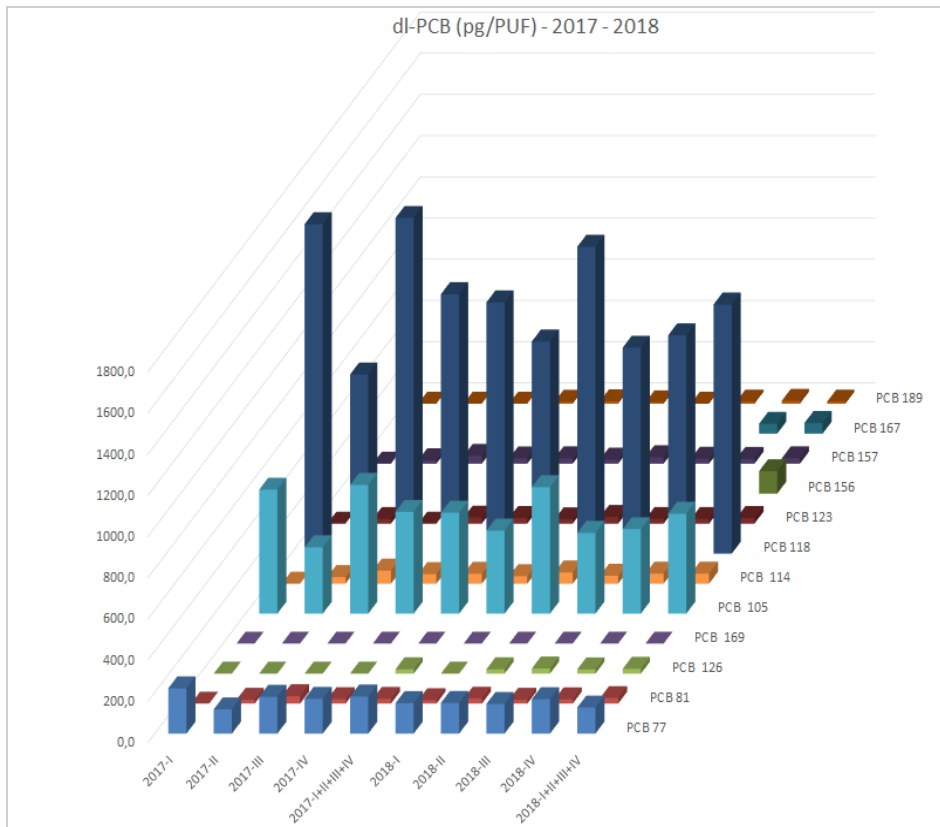


Figure 3A. dl-PCB concentration in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station) – CETESB’s results

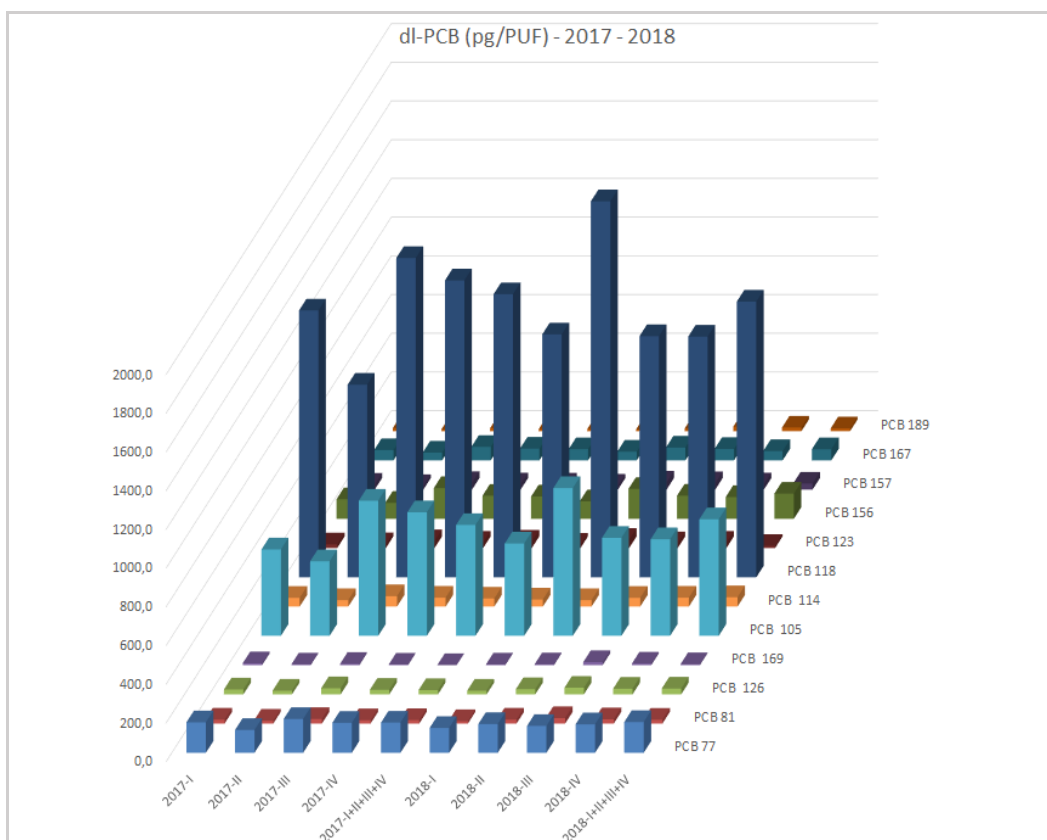


Figure 3B. dl-PCB concentration in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station) – CSIC’s results

PCB indicators results are presented in the Figure 4, Tables A3 and A4: The lower chlorinated PCB 28 and PCB 52 were the most abundant congener and the higher chlorinated PCB 180 was the less abundant. The PCB indicator results from the GMP-1, GMP-2 and Expert Lab results are presented at Table 9. The lower chlorinated PCB 28 was the most abundant congener during GMP-1 period but for the GMP-2 period the PCB 28 and PCB 52 are the most abundant congeners. Considering the 3 months period sampling, some results are below quantitation and the sum of annual 4 PUFs (2017-I+II+III+IV/2018-I+II+III+IV) provide better information with results higher than LOQ values for São Paulo city samples.

Table 9 – PCB Indicator concentrations in Passive Air Samples – Results of National Lab (GMP-1 and GMP-2) and Expert Lab (GMP-2)

PCBs	National Lab Results (pg/m ³)			Expert Lab Results (pg/m ³)
	GMP-1 2010-2015 Min.-Max	GMP-2 2017/2018 Min.-Max	GMP-2 2017/2018 – – ∑annual 4 PUFs	GMP-2 Min.-Max
PCB 28	5.71 – 75.7	5.72 – 35.5	36.2 - 45.4	18.6 – 36.1
PCB52	2.68 – 27.4	2.00 – 37.8	39.0 – 54.6	23.8 – 34.7
PCB 101	1.79 – 21.0	<LOQ – 24.3	17.6 - 21.7	14.8 – 26.5
PCB 138	0.97 – 11.2	<LOQ – 10.2	8.37 -9.21	6.17 – 14.5
PCB 153	1.05 – 10.9	<LOQ – 12.9	10.9 – 11.1	8.40 – 14.5
PCB 180	0.25 – 6.07	<LOQ – 3.17	2.84 – 3.34	2.58 – 4.32
Sum 6 PCBs	12.0 – 124	<(LQ) - 123	116 – 145	83.2 – 117
PCB118	0.91 – 8.94	6.66 – 12.7	9.87 – 9.72	7.62 – 14.7
Sum 7 PCB	13.4 – 129	< (LQ) – 136	126 – 154	90.8 – 130

* GMP-1 site results: Tominaga et al, 2016

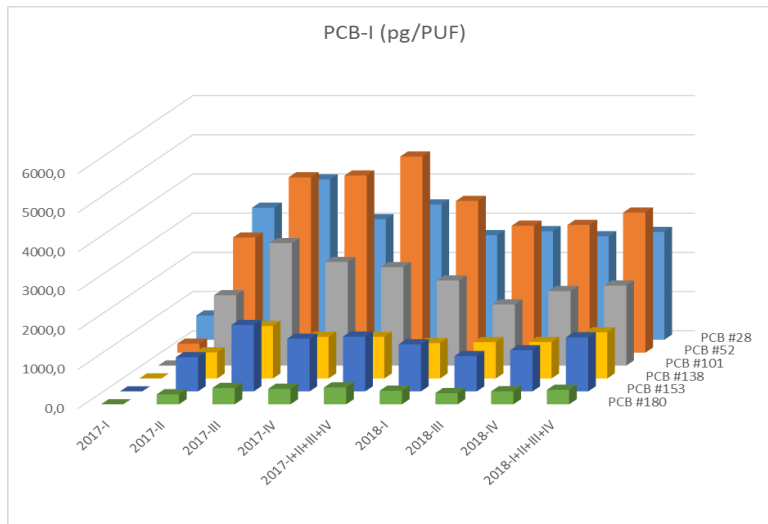


Figure 4. PCB-I concentration in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station) – CETESB’s results

Considering the past use of PCB in Brazil, the PCB presence in air samples may be related to the storages of used equipment, old equipments still in use, wastes and contaminated areas.

3.6.3 Organochlorine Pesticides (OCPs) results – Passive Air Samples

The OCPs detected in passive air samples in São Paulo city are dieldrin, DDE, DDT, HCB and g-HCH (Tables A5/A6, Figure 5). The Table 10 present the OCP results of GMP-2 samples analysed from National Lab and Expert Lab and results of GMP-1 samples.

The endosulfan (I, II and sulfate) concentrations were very low (Expert Lab results) or below quantitation limit (Expert Lab and National Lab), but at the GMP-1 period, the endosulfan concentration was very high (Table 10).

The Expert Lab analysed OCP by GC-HRMS equipment and the national Lab by GC-ECD and then the Expert Lab reached lower quantitation limits and they detected some other OCPs (Annex 2, Table 1) not detect by national Lab (Pentachlorobenzene, a-HCH, d-HCH-, heptachlor, cis-heptachlor epoxide, trans-chlordane, cis-chlordane, trans nonachlor, aldrin, endrin and mirex) probably because of low concentration.

Table 10 – Organochlorinated Pesticides concentrations in Passive Air Samples- GMP-1 and GMP-2 samplings results (National Lab) and GMP-2 results from Expert Lab

OCPs detected	GMP-1 Results 2010-2015 Min.-Max (pg/m ³)	GMP-2 - 2017 Min.-Max. (pg/m ³)	GMP-2 – 2018 Min. – Max (pg/m ³)	GMP-2 Expert Lab results Min.-Max. (pg/m ³)
Dieldrin	<LQ (11.8%) – 29,0	12.3 - 18.3	13.7 – 20.3	26.5 – 48.3
p,p'-DDD	<LQ(82.3%) – 2.87	<LQ (100%)	<LQ (100%)	1.67 – 4.19
p,p'-DDE	10.9 - 43.0	26.4 – 50.4	36.3 – 52.4	56.9 – 109
p,p'-DDT	<LQ (5.88%) – 95.6	<LQ (50%) – 32.2	<LQ(50%) – 26.2	21.2 – 45.8
HCB	15.3 – 51.8	19.88 – 57.3	23.2 – 40.1	39.7 – 97.7
Gamma- HCH	30.9 – 72.8	34.3 – 52.5	41.2 – 61.4	47,5 – 102
Endosulfan 1	<LQ (11.8%) – 1348	<LQ (100%)	<LQ (100%)	8.00 – 80.0
Endosulfan 2	<LQ(52.9%) – 72.2	<LQ (100%)	<LQ (100%)	<LQ (25%) – 10.0 NQ(50%)
Endosulfan sulfate	<LQ(52.9%) - 36.2	<LQ (100%)	<LQ (100%)	<LQ (37.5%) – 2.07 NQ (50%)

* GMP-1 site results: Tominaga et al, 2016

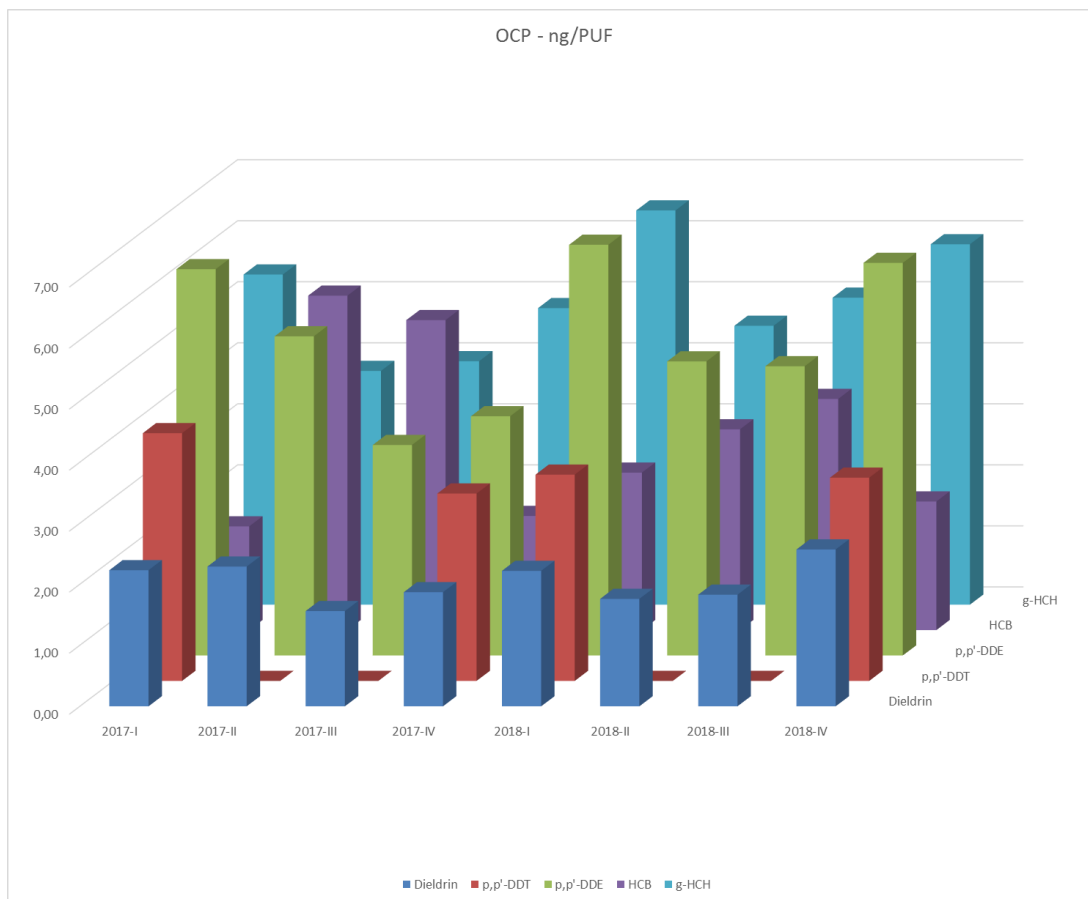


Figure 5. OCP detected in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station)

3.6.3.1 DDT, DDE and DDD

It was detected the presence of pp'-DDE and pp'-DDT in the PUF samples (Tables A5 and A6, Figure 5). The Expert Lab detected the presence of DDD probably because of high resolution equipment used to analyse OCPs. The DDD concentration was lower than DDT and DDE. The DDT concentration decreased from GMP-1 to GMP-2 period and the degradation compound (DDE) concentration increased during the same period.

DDT has been banned in Brazil since 1985 for agricultural use (Brasil, 1985) and in 2009 for all uses (Brasil, 2009). From 1959 to 1982, Brazil produced 75,500 tonnes of DDT and also imported 31,300 tonnes between 1959 and 1975. From 1989 to 1991, 3,200 tonnes of DDT were imported and between 1996 and July of 2003, 7,059kg were purchased (Almeida et al., 2007).

The presence of DDT, DDE and DDD may be related to the past use and production of DDT in the country. DDT and DDE has been detected, although in low frequency and or low concentration, in drinking water monitoring programs in Brazil (Bergamasco et al., 2011), sediment samples in São Paulo State (Tominaga et al., 2011 and 2015a), soil samples in São

Paulo State (CETESB, 2008; Lemos et al., 2009; Tominaga et al., 2015b), fish samples in Brazil, including São Paulo State (Torres et al., 2010), human milk samples (Krauss, 2004) and blood samples (Nascimento *et al.* 2017).

In ambient air samples, Meire et al. (2010) has detected DDT (op'-DDT + pp'-DDE) in two National Parks at concentration range of ND to 57pg/m³. In the GMP-1 monitoring in São Paulo city (2010-2015), the pp'-DDE concentration range was 10.9 – 43.0 pg/m³ (Table 10).

3.6.3.2 Aldrin, dieldrin and endrin

Aldrin and endrin were banned in 1985 in Brazil for agricultural use (except for use against ants and termites) and in 1998 for public health use. Aldrin and endrin were formulated by Shell Company in Brazil (São Paulo State), during 1977 and 1990 resulting in an industrial area contaminated with aldrin, endrin and dieldrin. Between 1961 and 1982, 17,000 tonnes of aldrin and 10,600 tonnes of endrin were imported. Between 1989 and 1995, 300 tonnes of aldrin were imported and between 1997 and 1998, the import rate decreased to 20 tonnes (Almeida et al., 2007; UNEP 2002).

The presence of dieldrin in PUF sample (12.3 – 20.3 pg/m³) confirm the data found in the literature and may be related to the past use and production of these compounds in São Paulo. In ambient air samples, Meire et al. (2010) has detected dieldrin in two National Parks in Brazil at concentration range of ND to 19 pg/m³ and Guida et al. (2018a) detected drins in National Parks in Southeas Brazil at concentration range of ND to 79 pg/m³ (sum of dieldrin and endrin). Guida el al. (2018b) has detected dieldrin at concentration range of 9 to 365 pg/m³ in São Paulo. In the GMP-1 monitoring in São Paulo city (2010-2015), dieldrin concentration range was <LOQ - 29 pg/m³ (Table 10). Aldrin and dieldrin have been detected in drinking water monitoring programs in Brazil (Bergamasco et al., 2011), soil samples from São Paulo State (CETESB, 2008; Lemos et al., 2009). According to Torres et al (2010), among cyclodiene compounds, dieldrin is more marked in São Paulo State fish samples than other states in Brazil. Dieldrin has been detected in milk sample in São Paulo State (Krauss et al., 2004). In the GRULAC region, the detection frequency of dieldrin in PUF samples from GAPS (Global Atmospheric Passive Sampling) program during 2005 was 33% (UNEP, 2009).

3.6.3.3 Hexachlorobenzene (HCB)

The main environmental input of HCB occurs as a by-product in the industrial manufacturing of chlorinated solvents as well as some pesticides such as pentachlorophenol. In Cubatão-São Paulo, there are highly contaminated sites and stockpiles of HCB which are a potential source of pollution in the region (CETESB, 2001; UNEP 2002).

The detection of HCB in PUF sample confirms some data found in the literature. HCB has been detected in drinking water monitoring in Brazil (Bergamasco, 2011), in superficial water samples (Del Grande et al., 2003), in soil and sediment samples from São Paulo State (CETESB, 2008; Lemos et al., 2009; Tominaga et al. 2011, Almeida et al., 2007; Bicego, 2006); in fish samples (Almeida et al., 2007) and human milk samples (Krauss et al., 2004).

In the GMP-1 monitoring in São Paulo city (2010-2015), HCB concentration range was 15.3 – 51.8 pg/m³ (Table 10) and the concentration range in 2017/2018 is still similar (19.9 – 57.3 pg/m³ (Table 10) to 2010-2015).

3.6.3.4 Endosulfan

Endosulfan was not detected or was below quantitation limit for all 2017 and 2018 samples analysed by national laboratory (A1-Table 5 and A1- Table 6), but was detected and quantified in all GMP-1 PUF samples (2010 and 2011 (GMP-1 samples) and the concentrations found were higher than other OCPs (Tominaga et. al., 2016). The Expert Lab detected and quantified endosulfan in 2017 and 2018 (Tabel 10 and Annex 2-Table 1) samples but the concentration was very low compared to 2010-2015 samples (Table 10).

Brazil started to import endosulfan in the 60s (Londres, 2011) and in 2010 was established a progressive ban of endosulfan and it was concluded in July 2014 (MMA, 2015). It can be the reason of the decrease of endosulfan level in the last years.

3.6.4 PBDE/PBB results – Passive Air Samples

The PBDE results are presented at Tables A7, A8 and Figure 10. The BDE-209 is the most abundant (Table 11) BDE, followed from BDE 47, 99, 183, 28 and 100. This profile is very similar to other studies such as GMP-1 ambient air results in São Paulo City (Martrat et al., 2012), sediment samples from São Paulo city (Tominaga et al., 2019), indoor dust in Araraquara City in São Paulo State (Cristale et al., 2017) and in Atlantic spotted dolphin (BDE47>99>100>153>154), captured in southern and southeastern Brazil (Leonel et al., 2012).

The GMP-2 results for PBDEs concentration in Air samples are very similar to the Expert Laboratory results and GRULAC Urban area concentrations (Table 11).

According to the inventory from the Brazilian National Implementation Plan for the Stockholm Convention (MMA, 2015), these substances were not produced in Brazil and it was not possible to verify if these POPs were imported as a substance. However, data from the inventory indicated that these substances are present in electrical and electronic equipment and in imported vehicles, and that recycling parts of these products contain PBDEs.

Table 11 – PBDE concentrations in passive air samples- GMP-2 sampling results (National Lab) and GMP-2 results from Expert Lab and concentration in the GRULAC region

BDE	GRULAC Urban area* 2013-2016 Average.-Max (pg/m ³)	GMP-2– National Lab results 2017/2018 Min. – Max (pg/m ³)	GMP-2 Expert Lab results Min. – Max (pg/m ³)
BDE-17	--	0.14 – 0.71	<LQ(37.5%) – 0.48
BDE-28	0.156 – 0.83	0.47 – 1.15	0.48 – 1.08
BDE-47	1.267 – 11.155	0.65 – 9.82	4.16 – 5.69
BDE-66	--	<LQ (37.5%) – 1.16	0.31 – 0.61
BDE-77	--	<LQ(50%) – 0.24	NA
BDE-100	0.106 – 1.021	0.54 – 1.10	0.45 – 0.68
BDE-99	0.414 – 4.982	1.88 – 4.39	1.88 – 3.48
BDE-85	--	<LQ (75%) – 0.11	<LQ (100%)
BDE-126	--	<LQ (100%)	NA
BDE-154	0.036 – 0.417	<LQ(12.5%) – 0.48	<LQ (100%)
BDE-153	0.081 – 1.708	0.28 – 0.51	<LQ (100%)
BDE-156	--	<LQ (100%)	NA

BDE-183	--	<LQ (12.5%) – 1.29	<LQ (87.5%) – 18.9
BDE-49	--	0.21 – 0.45	NA
DBE-209	1.398 – 7.875	18.9 – 137	NA

* UNEP-GMP report, 2021

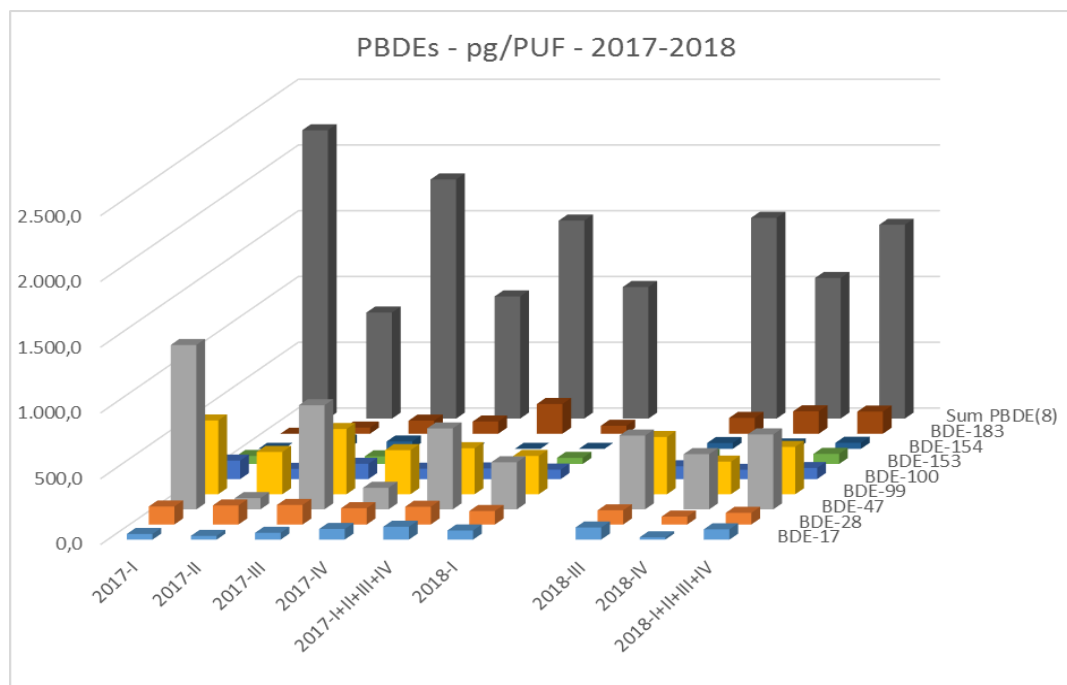


Figure 6. PBDE concentration in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station)

3.6.5 PFAS – Passive Air Sampling Analysis Results

The national Lab results for PFAS in passive air samples were not considered because of the low recovery of the labeled standards and interferences. The UN procedure for PFAS analysis is very good for standard analysis but for real air extract analysis, the results were not good. It has been tested some procedure to clean up the extract but the results were still not good and for future samples extract clean up will be tested new material (Supelclean ENVI-Carb tube), according to Gonzáles et al., 2021).

The PFAS results from the Expert Lab in passive air samples are presented at Annex 3 and Figure 7. The most abundant PFAS in passive air samples were PFOS followed by PFOA.

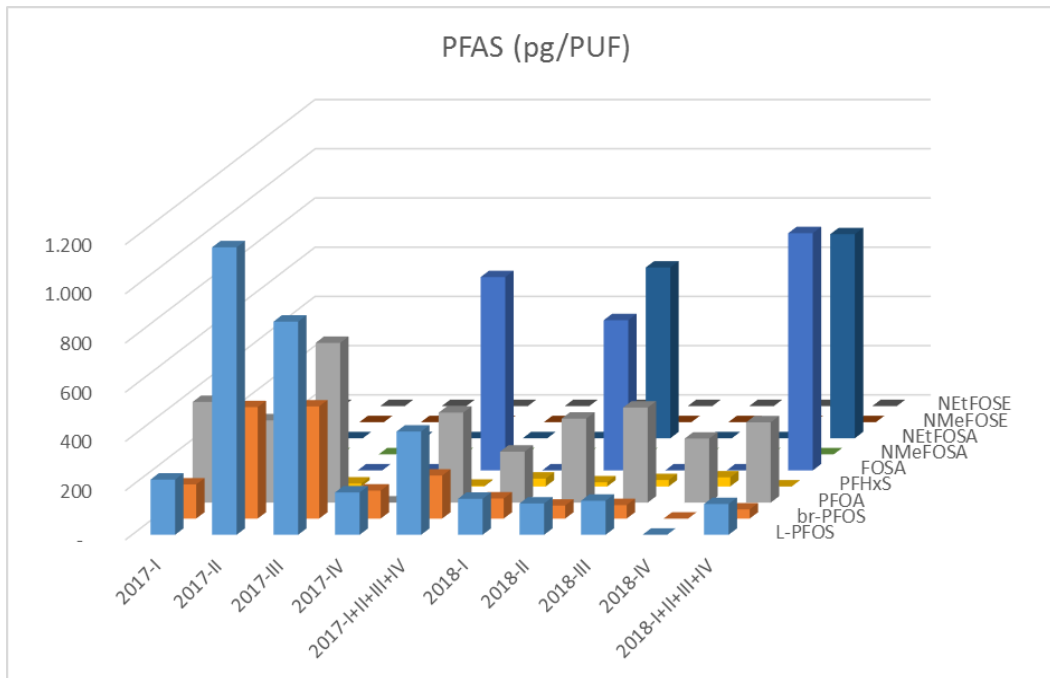


Figure 7. PFAS concentration in São Paulo City - 2017-2018 (Cerqueira Cesar Air Monitoring Station) – MTM Research Center results

3.7 POPs Analysis Results – Active Air Samples

For the Active Air sampling, it was not provided materials (PUF, XAD-2) for the POPs analysis at national laboratories, but only at expert laboratories. The active air samples collected using PUFs, XAD-2 and total suspended particulate (TSP) filters (Table 3) were analysed all together (PUF+XAD-2+ TSP) at expert labs and the results are presented at Table 12 (dl-POPs), Table 13 (Indicator PCBs), Table 14 (PBDEs), Table 15 (HBCD) and Table 16 (PFAS). According to the Expert Labs, only very few data could be generated due to deterioration of the PUFs or loss of sample extracts during clean-up. A comparison with the PAS/PUF results can be made only on the pattern for dl-POPs and PFAS. The Figure 8 shows the concentration of PCDD/F (fg/m^3 and $\text{fg TEQ}/\text{m}^3$) and dl-PCBs ($\text{fg TEQ}/\text{m}^3$) concentrations results from active and passive air samplers. The Figure 9 shows the concentration of PFAS in active (2019) and passive air samples (2017/2018).

The HBCD was analysed only in active air samples (Table 15) and there is no previous data to compare the results. HBCD is used in the building, electronics, automotive and textile industries in Brazil (MMA, 2015) as flame retardant in expanded polystyrene (EPS); extruded polystyrene (XPS) and high-impact polystyrene (HIPS).

Table 12 - Active Air sample: dl-POPs results (Expert Lab)

Original Sample-ID	BRA-CAV-2 2019-I (11-14/01/19)	BRA-CAV-2 2019-II (14-17/02/19)	BRA-CAV-2 2019-I (11-14/01/19)	BRA-CAV-2 2019-II (14-17/02/19)
	Total pg	Total pg	fg/m ³	fg/m ³
PCDD/PCDF			Air vol.: 2158,2 m ³	Air vol.: 2158,3 m ³
2378-Cl ₄ DD	3,5	2,7	1,6	1,2
12378-Cl ₅ DD	15,7	10,1	7,3	4,7
123478-Cl ₆ DD	14,8	10,2	6,9	4,7
123678-Cl ₆ DD	54,8	28,4	25,4	13,2
123789-Cl ₆ DD	39,2	20,9	18,1	9,7
1234678-Cl ₇ DD	309,9	229,3	143,6	106,3
Cl ₈ DD	485,4	393,9	224,9	182,5
2378-Cl ₄ DF	50,6	33,7	23,5	15,6
12378-Cl ₅ DF	74,0	33,4	34,3	15,5
23478-Cl ₅ DF	89,1	66,7	41,3	30,9
123478-Cl ₆ DF	171,7	131,3	79,6	60,8
123678-Cl ₆ DF	111,9	91,6	51,9	42,5
123789-Cl ₆ DF	14,0	11,8	6,5	5,5
234678-Cl ₆ DF	126,3	125,9	58,5	58,3
1234678-Cl ₇ DF	514,3	469,2	238,3	217,4
1234789-Cl ₇ DF	113,0	86,3	52,4	40,0
Cl ₈ DF	601,4	477,2	278,7	221,1
WHO₂₀₀₅-TEQ_{PCDD}	33,4	21,1	15,5	9,8
WHO₂₀₀₅-TEQ_{PCDF}	82,9	66,1	38,4	30,6
WHO₂₀₀₅-TEQ_{PCDD/PCDF}	116,3	87,3	53,9	40,4
dl-PCB				
PCB 77	875,6	622,4	405,7	288,4
PCB 81	73,5	58,2	34,0	27,0
PCB 126	97,0	68,3	44,9	31,7
PCB 169	18,1	14,9	8,4	6,9
PCB 105	2780,0	1872,6	1288,1	867,6
PCB 114	219,6	155,2	101,8	71,9
PCB 118	7407,8	5035,5	3432,4	2333,1
PCB 123	105,7	86,7	49,0	40,2
PCB 156	447,5	303,8	207,4	140,8
PCB 157	86,4	64,1	40,0	29,7
PCB 167	234,1	157,6	108,5	73,0
PCB 189	55,0	42,1	25,5	19,5
WHO₂₀₀₅-TEQ_{no-PCB}	10,3	7,4	4,8	3,4
WHO₂₀₀₅-TEQ_{mo-PCB}	0,34	0,23	0,2	0,1
WHO₂₀₀₅-TEQ_{PCB}	10,69	7,59	4,95	3,52
WHO₂₀₀₅-TEQ_{total} (PCDD/F+dl-PCB)	127,0	94,9	58,8	44,0

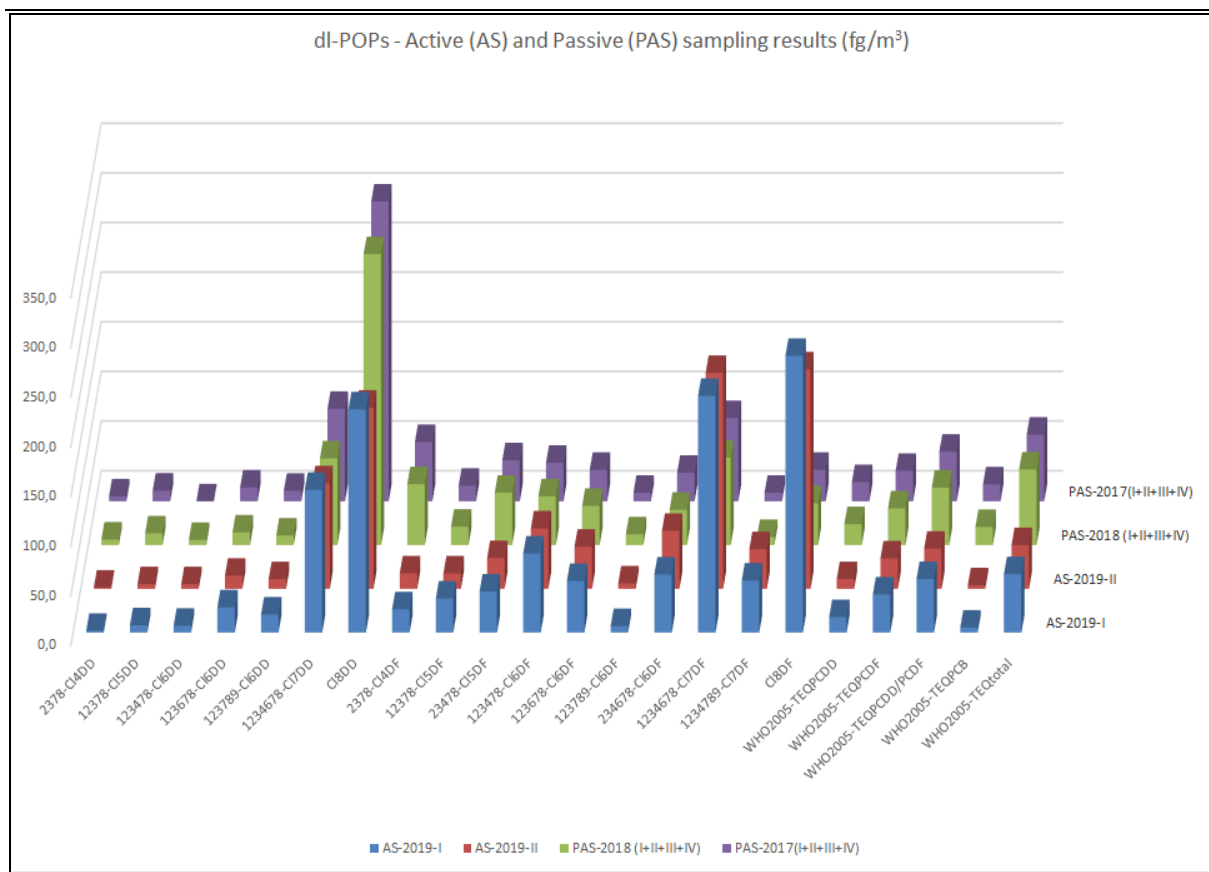


Figure 8. dl-POPs concentrations in Active Air samples (Expert Lab) and PAS samples (National Lab)

Table 13 - Active Air sample: PCB-I results (Expert Lab)

Sample complete to report	BRA-CAV-1 2019-I (07-10/01/19)	BRA-CAV-1 2019-II (05-08/02/19)	BRA-CAV-1 2019-I (07-10/01/19)	BRA-CAV-1 2019-II (05-08/02/19)
Unit	Total pg	Total pg	pg/m ³	pg/m ³
Indicator PCB			Air Vol.: 2158,2 m ³	Air vol.: 2158,3 m ³
PCB 28	n.a.	n.a.		
PCB 52	n.a.	24965		11,567
PCB 101	11220	8222	5,199	3,810
PCB 153	6314	4059	2,926	1,880
PCB 138	6622	3874	3,068	1,795
PCB 180	2668	1744	1,236	0,808
Sum Indicator PCB	26825	42864	12,4	19,9

Table 14 - Active Air sample: PBDE results (Expert Lab)

Sample complete to report	BRA-CAV-3 2019-I (21-24/01/19)	BRA-CAV-3 2019-II (18-21/02/19)	BRA-CAV-3 2019-I (21-24/01/19)	BRA-CAV-3 2019-II (18-21/02/19)
Unit	Total pg	Total pg	pg/m ³	pg/m ³
PBDEs			volume: 2158,2	volume: 2158,3
BDE-28	359	240	0,166	0,111
BDE-47	2597	2196	1,203	1,018
BDE-100	394	324	0,182	0,150
BDE-99	1461	1261	0,677	0,584
BDE-154	907	539	0,420	0,250
BDE-153	1620	n.a.	0,751	
BDE-183	7800	n.a.	3,614	
Sum PBDEs	15138	4559	7,01	2,11

Table 15 - Active Air sample: HBCD results (Expert Lab)

Sample complete to report	BRA-CAV-3 2019 (2019-I + 2019-II)	BRA-CAV-3 2019 (2019-I + 2019-II)
Unit	Total ng	pg/m ³
HBCD		Air vol.:4316,5 m ³
a_HBCD	0,670	0,155
b_HBCD	< 0.03	< 0.007
g-HBCD	0,940	0,218
Sum HBCD	1,61	0,37

Table 16 - Active Air sample: PFAS results (Expert Lab)

Lab ID	CAV-4	CAV-4	2 CAV-4	2 CAV-4
Sampling year	2019	2019	2019	2019
Month	1	2	1+2	1+2
Volume recorded (m ³)	2107,9	2158,7	4266,6	4266,6
Temperature (°C)	28,7	23,7	26,2	26,2
From	2019-01-28	2019-02-25		
To	2019-01-31	2019-02-28		
Year-season	2019-I	2019-I	2019	2019
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2019-1)	BRA (2019-2)	BRA 2019	BRA 2019
Unit	Pg	Pg	pg	fg/m ³
L-PFOS			3.480	815,6
br-PFOS			308	72,2
Sum PFOS			3.788	887,8
PFOA			2.680	628,1
PFHxS			<200	-
FOSA			4.238	993,3

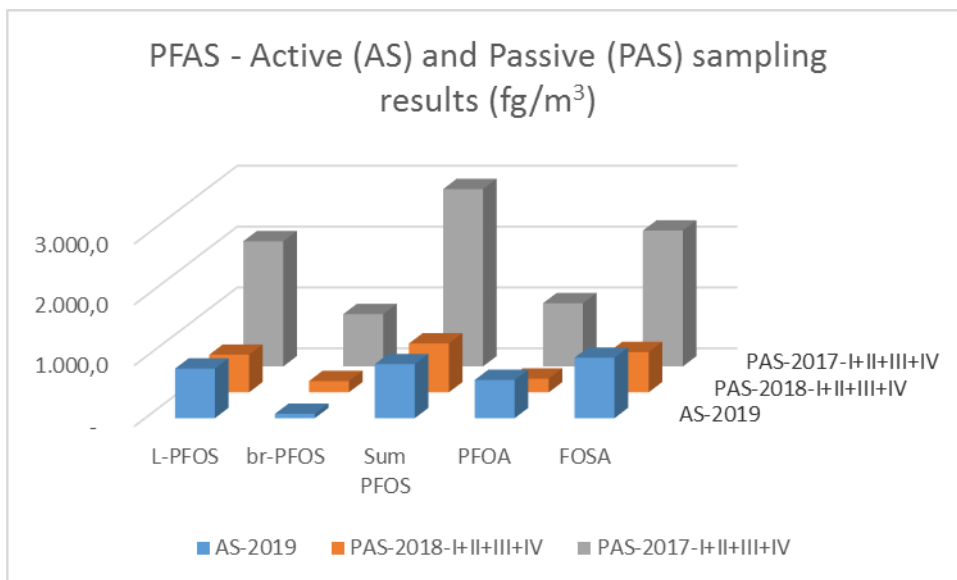


Figure 9. PFAS concentrations in Active Air samples (Expert Lab) and PAS samples (Expert Lab)

3.8 PFAS – Water Sample Analysis Results

The PFAS results from National Lab in water samples are presented at Tables A11, A12 and Table 17. The Expert Lab results are presented at Annex 4, Table 17 and Figure 10. The difference between Expert Lab and National Lab results probably is because of low concentration and/or close to detection levels and lab interference for the National Lab results, mainly for PFOA analysis at the beginning of the method development in 2017.

Table 17 – PFAS concentrations in water samples - GMP-2 samplings results (National Lab) and GMP-2 results from Expert Lab and concentration in the GRULAC region

PFAS	GRULAC 2017/2018 Average.- Max (pg/L)	GMP-2– National Lab results 2017 Min. – Max (pg/L)	GMP-2 Expert Lab results 2017 Min. – Max (pg/L)	GMP-2– National Lab results 2018		GMP-2 Expert Lab results 2018	
				Min.	Max (pg/L)	Min.	Max (pg/L)
L-PFOS	--	20.0 – 40.0	40.0 – 330	1,050	1,650	1,510	2,640
br-PFOS	--	10.0	<25.0 – 30.0	<LOQ	360	790	1,440
ΣPFOS	1,174-3,315	30.0 – 50.0	40.0 – 350	1050	1990	2,300	4,080
PFOA	552 – 1,045	NR/280 – 550	50.0 – 150	<LOQ	910	650	860

PFHxS	239 – 705	20.0 – 30.0	<25.0 – 50.0	650 – 1,790	560 – 810
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NR: not reported because of interferences

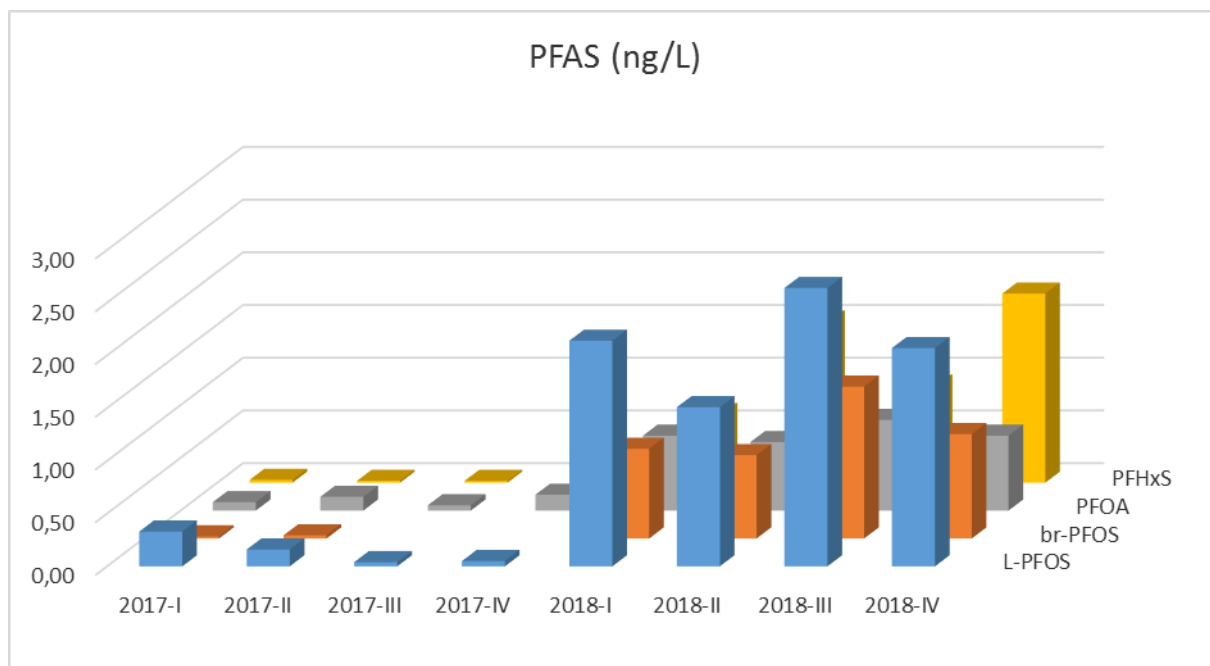


Figure 10. PFAS concentration in Water samples – 2017: Amazon River/ 2018: São Vicente Channel - SP – MTM results

3.9 National Sample Analysis results

3.9.1 PFAS results in National Samples

The PFAS results in National samples analysed by reference Lab are presented at Tables 18, 19 and 20. The sediment sample (Table 18) from Santos, São Paulo, presented very high levels of PFAS compared to other two sediment samples. The sediment sample from Santos was collected in an area where film-forming foams to extinguish a fire in a petrochemical terminal of Port of Santos. Pozo et al (2021) estimated that at least 635.96 g of PFAS were introduced in the Santos estuary to extinguish this fire. The water samples from this region was analysed (Table 21) by the National Lab and the concentration of PFAS are very high compared to São Vicente Channel and Amazon river water samples (Table 17).

The PFAS present in aqueous film forming foam (AFFF) used to extinguishing fires in Brazil probably are related to the high concentrations of PFAS in sediment and water samples collected after AFFF use to extinguish the fire at Port of Santos.

Table 18 – PFAS concentrations in National Sediment Samples (pg/g d.w.)

Sample Information	L-PFOS	br-PFOS	ΣPFOS	PFOA	PFHxS
Sediment 2: Porto de Santos, São Paulo, Brazil	961,969	260,554	1,222,523	5226	24019
Sediment 3: Cerquilho – São Paulo, Brazil	257	34.22	292	25.15	12.26
Sediment 4- São Vicente Channel – São Paulo, Brazil	347	35.88	383	17.13	14.86

PFAS analysis performed by Expert Lab

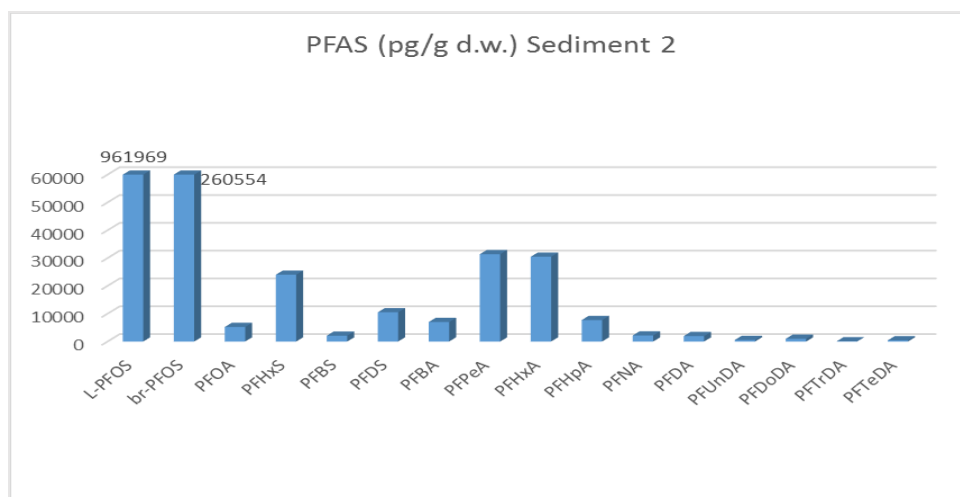


Figure 11. PFAS concentration in sediment sample contaminated with film-forming foam

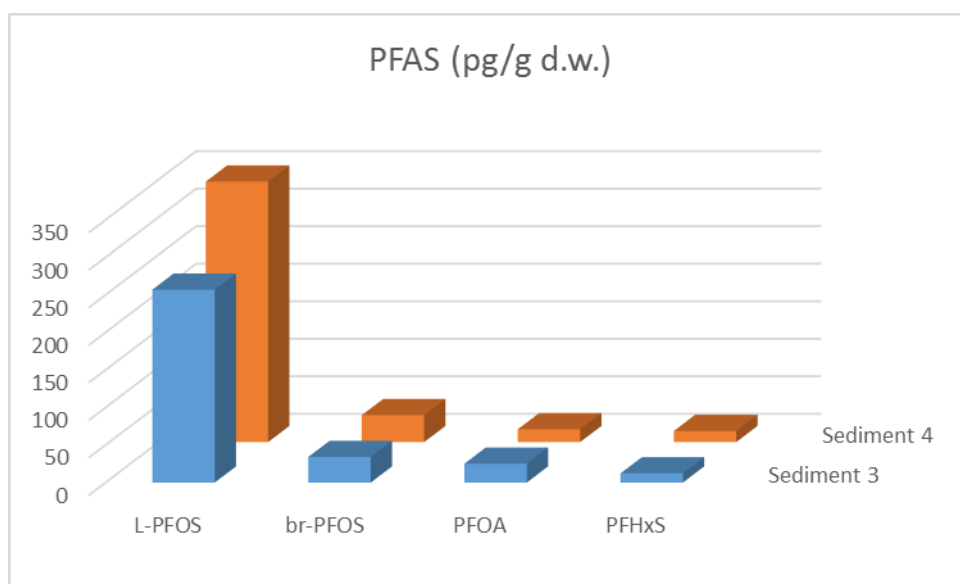


Figure 12. PFAS concentration in national sediment samples

The PFAS analysis in national fish samples are presented at Table 19. The White Mullet and Largehead Hairtail fish were both collected in São Paulo, Canal de São Vicente region in the same place where water (Table 17- GMP-2/2018) and sediment (Table 18 –sediment 4) samples were collected.

The fish samples obtained at a fish stand on the free market in Copacabana/Rio de Janeiro and prepared from FIOCRUZ presented lower levels of PFAS compared to São Paulo fish samples. The fish from São Paulo were obtained in local area where was collected water and sediment sample and not for commercial purpose.

Table 19 – PFAS concentrations in National Fish Samples (pg/g fresh weight*)

Sample Information	L-PFOS	br-PFOS	∑PFOS	PFOA	PFHxS
Dried White Mullet muscle– São Vicente Channel – São Paulo- Brazil	907	191	1,098	45.72	17.32
Dried Largehead Hairtail (Swordfish) muscle– São Vicente Channel region – São Paulo- Brazil	1,496	154	1,650	8.11	22.85
INCQS-01 – Dried Tilapia (<i>Cichlidae Pseudocrenilabrinae</i>) muscle– Fish Market – Rio de Janeiro – Brazil	301.27	57.47	358.74	1.96	3.16
INCQS-02- Dried Linguado (<i>Paralichthys patagonicus</i>) muscle– Fish Market – Rio de Janeiro – Brazil	17.40	2.41	19.81	4.25	<5.6

PFAS analysis performed by Expert Lab *the fish sample were freeze dried and the Expert Lab report the results adjusted to fresh weight using the assumptions for loss of mass of 80% for fish samples

The national biotic samples (butter, cow milk and chicken egg) analysis results are presented at Table 20. These samples were bought at a normal supermarket. The butter and cow milk samples received no additional treatment and were weighted directly into the container. The whole chicken egg samples (10 eggs), without shell were homonized with a Turrax disperser and the resulting liquid freeze-dried. The dry matter was then homogenized with an industrial mixer.

Table 20 – PFAS concentrations in National Biotic Samples (pg/g fresh weight*)

Sample Information	L-PFOS	br-PFOS	∑PFOS	PFOA	PFHxS
INCQS-04-Butter – Rio de Janeiro – Brazil	73.97	28.83	102.80	<6.2	<5.6
INCQS-03-Powdered Cow Milk – Rio de Janeiro – Brazil	1.93	0.79	2.72	<6.2	<5.6
INCQS-05-Dried Chicken Egg – Rio de Janeiro – Brazil	35.77	13.84	49.61	4.33	<5.6

PFAS analysis performed by Expert Lab *the eggs samples were freeze dried and the Expert Lab report the results adjusted to fresh weight using the assumptions for loss of mass of 70% and for powdered milk samples it was assumed 90% of loss of mass.

The PFAS concentrations in butter, powdered cow milk and chicken egg samples are lower than average PFAS concentration in fish samples. The PFAS concentration in fish samples for consumption are lower than fish samples from polluted area and these data are confirmed with other PFAS data in fish samples in Brazil (Torres et al., 2022)

Table 21 – PFAS concentrations in National Water Sample (ng/L) contaminated with fire extinguishing foam

Sample Information	L-PFOS	br-PFOS	∑PFOS	PFOA	PFHxS
Porto de Santos, São Paulo, Brazil	12526	NR	NR	244	2796

PFAS analysis performed by National Lab ; NR: not reported because of interferences

3.9.2 PBDEs results in National Sediment Samples

The PBDEs analysis in National Samples performed by National lab are presented at Table 22. The results from Expert Lab was not received yet, but the National Lab has been analysing PBDE in sediment samples since 2017 and the results has been checked with sediment reference material. There are no regulations or quality standards values for PBDE in Brazil to evaluate environmental quality monitoring and the results were compared to Canadian Environmental Quality Guidelines (EC, 2013). The national sediment samples 1, 2 and 3

results for PBDEs are below the Canadian Environmental Quality Guidelines. The sediment monitoring during 2017/2018 (n=47) in São Paulo State indicate a total of 40.9% of the BDE-209 results were above the Canadian Guideline and all the samples exceeding the Canadian Guidelines values are from Industrial land use areas (Tominaga et. al., 2019). According to the inventory from the Brazilian National Implementation Plan for the Stockholm Convention (MMA, 2015), these substances were not produced in Brazil and it was not possible to verify if these POPs were imported as a substance. However, data from the inventory indicated that these products are present in electrical and electronic equipment and in imported vehicles, and that recycling parts of these products contain PBDEs.

Table 22 – PBDEs concentrations in National Sediment Sample (National Lab results)

BDE	Sediment 1 (pg/g d.w.)	Sediment 2 (pg/g d.w.)	Sediment 3 (pg/g d.w.)
BDE-17	19.6	<5.00	<5.00
BDE-28	372	<10.0	<10.0
BDE-47	NR	NR	NR
BDE-100	39.1	<20.0	<20.0
BDE-99	173	<100	<100
BDE-154	21.5	<10.0	13.3
BDE-153	34.1	<10.0	10.2
BDE-183	35,99	30,99	21,27
BDE-49	126	<10.0	18.3
BDE-209	6982	NR	3674

NR: not reported, presence of interferences

3.9.3 dl-POPs results in National Sediment Samples

The dl-POPs analysis in National Samples performed by National Lab and Expert Lab are presented at Table 23. The sediment 1 are from a contaminated site with dioxins and furans and PCBs and the results are in agreement with previous monitoring data (CETESB, 2021). The sediment 2 was collected in the Port of Santos where a fire occurred and it can explain

higher level of dioxin and furans when compared with “non contaminated” place sediment (sediment 3). The sediment 3 was analysed by National Lab and was not expected to find high concentration of dl-POPs. Some National and Expert Lab results are not in agreement, mainly OCDD/F and the national analysis were checked with the use of sediment reference material, but the results were still the same and not possible to find the source of the analytical problem or interferences.

Table 23 – Dioxin and Furans and dl-PCBs concentrations in sediment samples - National Lab and Expert Lab results (pg/g d.w.)

Dioxins/Furans	Sediment 1 (pg/g d.w.)		Sediment 2 (pg/g d.w.)		Sediment 3 (pg/g d.w.)		Sediment 1 (pg/g d.w.)		Sediment 2 (pg/g d.w.)	
	National Results	Lab	National Results	Lab	National Results	Lab	Expert Results	Lab	Expert Results	Lab
2378-C14DD	<0,92		<0,86		<0,57		0,58		0,09	
12378-C15DD	1,7		3,52		<0,72		2,3		1,3	
123478-C16DD	3,15		8,87		<0,91		3,8		3,1	
123678-C16DD	16,4		114		<0,91		19,9		18,6	
123789-C16DD	5,53		22		<0,91		7,0		6,2	
1234678-C17DD	681		3510		15,2		561,8		425,0	
OCDD	4750		30100		138		4186,4		3618,4	
2378-C14DF	35,2		1,56		<0,70		40,9		1,1	
12378-C15DF	64,5		3,31		<0,53		68,2		2,0	
23478-C15DF	27,3		2,43		<0,53		33,40		2,26	
123478-C16DF	354		27,8		<0,68		360,92		21,36	
123678-C16DF	153		12,1		<0,65		173,09		6,12	
123789-C16DF	53,3		7,53		<0,85		19,64		0,21	
234678-C16DF	24,8		8,32		1,1		138,81		5,61	

1234678-CI7DF	2,69E+03	585	3,57	3155,1	118,7
1234789-CI7-DF	513	61,9	2,28	505,5	7,3
OCDF	7,27E+04	2,13E+03	18,5	2,9	385,9
∑PCDD (pg TEQ/g d.w.)	12,44	62,1	0,19	12,82	9,52
∑PCDF (pg TEQ/g d.w.)	126	13,67	0,17	122	5,55
∑PCDD/F (pg TEQ/g)	138,4	75,8	0,37	134,8	15,07
dl-PCBs					
PCB 77	396	24,6	13,5	437,9	89,8
PCB 81	<18,5	<1,36	<0,98	18,0	4,2
PCB 126	49,3	2,12	<1,41	57,3	7,8
PCB 169	<8,64	<0,89	<0,45	54,0	3,3
PCB 105	2,71E+03	176	48,7	2933,5	569,6
PCB 114	707	3,09	<2,14	768,0	18,9
PCB 118	2,19E+04	873	208	Saturated	1186,1
PCB 123	285	6,25	<2,06	193,6	23,8
PCB 156	3,00E+03	93,3	17,4	3238,3	255,5
PCB 157	340	14,9	4,36	378,7	67,8
PCB 167	1,41E+03	46,8	9,10	1494,4	126,2
PCB 189	790	13,2	1,34	911,4	34,7
∑PCB (pg TEQ/g d.w.)	5,90	0,25	0,01	7,70	0,958
∑PCDD/F/PCB (pg TEQ/g d.w.)	144	76	0,38	143	16

4 Capacity building activities

4.1 Training provided from Expert Laboratories

During the project development it was provided practical trainings as presented below.

Training Period: 19 – 23 February, 2018 (total: 40h)

Training Place: CETESB – Physical Chemical Analysis Division, Organic Chemistry Lab and Toxicological Analysis Lab - São Paulo

Expert Laboratories:

- MTM Research Center - Örebro University, School of Science and Technology, Sweden

Dr Heidelore Fiedler

Dr Leo W. Yeung

- CSIC – Consejo Superior de Investigaciones Científicas – Laboratorio de Dioxinas –

Instituto de Diagnóstico Ambiental y Estudios del Agua (IDAEA)

Dr Esteban Abad

Training topics

- Active sampler operational procedures

- Sample preparation techniques discussions and POPs analysis by GCMS-NCI and GCMSMS

- PBDE analysis by GCMS-NCI and GCMSMS

- Extraction, cleanup, identification and quantitation of PFAS in milk and serum samples by LC-Q-TOF

- Extraction, cleanup, identification and quantitation of PFAS in water and ambient air samples by LC-Q-TOF

Training participants

A total of 12 national participants were trained, including 01 participant from FIOCRUZ, 02 participant from CETESB's Air Sampling and Analysis Lab, 06 participant from CETESB's Organic Chemistry Lab, 02 participants from CETESB's Toxicological Analysis Lab and one participant from CETESB's Physical Chemical Analysis Division.

Training Outputs

- Active sampler in operation, samples collected and sent to Expert Labs

- PBDE/PBB analysis methodology implemented, samples analysed

- PFAS analysis methodology implemented for water samples, water samples analysed. For air samples, the methodology need improvements and will be included additional clean up step.

5 Collaboration and synergies with other national/regional initiatives on POPs monitoring and capacity building

5.1 Latin American Passive Atmospheric Sampling Network (LAPAN)

Third Regional Monitoring Report – Latin America and the Caribbean Region, 2021

5.2 Global Atmospheric Passive Sampling (GAPS) Network

Saini, A.; Harner, T.; Chinnadhurai, S.; Schuster, J.; Yates, A.; Sweetman, A.; Zuluaga, B.A.; Jiménez, B.; Manzano, C.A.; Gaga, E.; Stevenson, G.; Falandysz, J.; Ma, J.; Miglioranza, K.; Kannan, K.; Tominaga, M.Y.; Jariyasopit, N.; Roa, N.Y.R.; Amador, O.; Sinha, R.; Alani, R.; Suresh, R.; Nishino, T.; Shoeib, T. GAPS-Megacities: A new global platform for investigating persistent organic pollutants and chemicals of emerging concern in urban air. *Environ. Pollut.*, 267 (115416), 2020. <https://doi.org/10.1016/j.envpol.2020.115416>.

5.3 University of São Paulo – School of Public Health

Francisco, A.P.; Nardocci, A.C.; Tominaga, M.Y.; Silva, C.R.; Assunção, J.V. Spatial and seasonal trends of polychlorinated dioxins, furans and dioxin-like polychlorinated biphenyls in air using passive and active samplers and inhalation risk assessment. *Atmos. Pollut. Res.*, 8(5), p.979-987, 2017

5.4 University of São Paulo – Institute of Chemistry

Silva, C.R.; Masini, J.C. Ethylene vinyl acetate copolymer is an efficient and alternative passive sampler of hydrophobic organic contaminants. A comparison with silicone rubber. *Environ. Pollut.*, 323 (121258), 2023. <https://doi.org/10.1016/j.envpol.2023.121258>

5.5 NILU - Norwegian Institute for Air Research, Kjeller, Norway

Melymuk, L.; Nizzetto, P.B.; Harner, T.; White, K.B.; Wang, X.; Tominaga, M.Y.; He, J.; Li, J.; Ma, J.; Ma, W.; Aristizábal, B.H.; Dryer, A.; Jiménez, B.; Muñoz-Arnanz, J.; Odabasi, M.; Dumanoglu, Y.; Yaman, B.; Graf, C.; Sweetman, A.; Klánová, J. Global inter-comparison of polyurethane foam passive air samplers evaluating sources of variability in SVOC measurements. *Environ. Sci. Policy*, 125, 1-9, 2021.

5.6 EMBRAPA – Empresa Brasileira de Pesquisa Agropecuária

Stockholm Convention National Implementation Plan: Formation of PFOS from the use of formicides baits containing sulfluramid

6 Sustainability Plan

The main challenge for the POPs monitoring in the country has been the need of infrastructure with high cost/quality equipments, highly qualified technical staff, financial support for the activities development and ongoing equipment maintenance.

Most of POPs monitoring studies and programs developed in Brazil are funded by the Federal and State Government through its research and teaching funding agencies and are carried out mainly by public universities within their postgraduate programs. Some other monitoring programs have also been carried out by specific public institutions, such as CETESB, EMBRAPA and FIOCRUZ. Currently, the Ministry of Health is trying to develop and implement a national biomonitoring program that also covers many POPs. Some measures to improve national analytical capacity on POPs have been successfully implemented in Brazil. We highlight the development of analytical capacity within the NIP update project in which analytical methods were developed and implemented by the Federal University of Rio de Janeiro, at the Carlos Chagas Filho Institute of Biophysics, Eduardo Penna Franca Radioisotope Laboratory. The Laboratory has all the necessary instrumental steps for the

identification and quantification of SCCPs, PCNs, POP brominated flame retardants (HBCD, PBDES, including decaBDE) and some organochlorine pesticides and their by-products (dicofol, HCB and PCP).

The UNEP/GEF GMP projects built analytical capacities at CETESB and FIOCRUZ for the monitoring POPs in the environmental and biota samples. CETESB continued monitoring in air and other environmental samples but the limitation is only one sampling site for air monitoring and need human resources to increase the monitoring sites and analytical capacity.

The Latin American Passive Atmospheric Sampling Network (LAPAN) is the only national monitoring network existing in the country, but need improvements for analytical infrastructure to attend the network for sample analysis.

Infrastructure and human resources are crucial to create a network for sampling and analytical activities in the country in a continuous and organized way to generate data to contribute more effectively to the GMP.

The lessons learnt and experiences gained from participating in the UNEP/GEF GMP-1 and GMP-2 projects and other related activities in the country made it possible to draw up some plans and strategies for the future monitoring activities in the country.

The National Implementation Plan for the Stockholm Convention has established measures to improve POPs monitoring and analytical capacity, research, development and innovation as one of action plan including the activities related to the POPs monitoring capacity such as (1) Strengthen the working groups to discuss the creation of a monitoring network in Brazil and measurement protocols; (2) Support the analytical capacity building in national laboratories for the new POPs analysis; (3) Include mandatory analysis/monitoring of new POPs by companies that use them in their industrial processes or that recycle articles that contain, in the licensing processes.

On the other hand, there is a need to improve and develop new legislation on POPs in Brazil. Resolutions on the levels of POPs in environmental compartments, such as drinking water, reservoirs, sediments, air and food, must be created and complied with. This is especially

relevant for those POPs that are still in use in the country for specific exceptions or acceptable purposes.

The private laboratories informed that they have capacity to attend the reviewed regulations with new POPs and currently is possible to find national laboratories accredited (ISO 17025/2017) for POPs/new POPs analysis in environmental, biota and material samples.

For the future GMP activities, will be necessary to join all national capacities from universities and governmental institutions for the creation of a national sampling and analytical network to generate consistent monitoring data that allow the evaluation of POPs trends over the time. The Ministry of the Environment and Climate Change, focal point of the Stockholm Convention, will join forces with the Ministry of the Health, Stockholm Convention Regional Centre/CETESB, governmental institutions and universities researchers for the future POPs monitoring activities in the country.

For the activities development it is necessary to find financial resources like FINEP (Studies and Projects Funding Agency); Ministry of Health, Environment, Agriculture and Education; BNDES (National Bank for the Development); CNPQ (National Counsel of Technological and Scientific Development); CAPES (Coordination of Improving Higher Education Personnel); State Development Agencies; INMETRO (National Institute of Metrology); JICA (Japan International Cooperation Agency); GEF (Global Environmental Facility)

For the effective implementation of the SC, it is necessary dealing with POPs in an integrated manner, as part of the country's macro framework (political, economic, environmental and health; as well as within the management plans for chemicals, plastics, waste and contaminated areas)

7 Results and Achievements

The project strengthened the capacity building for PBDE/PBB and PFAS analysis in Brazil and all the passive air and water samples collected were analysed. The PBDEs/PBB analysis methodology were implemented, passive air samples and some national sediment samples were analysed. The PFAS analysis methodology was implemented, passive air and water samples were analysed. All planned activities in the project were completed.

The passive air sampling will continue at least at GMP site in São Paulo city and the PBDE/PBB monitoring will continue in air samples and sediment monitoring program. The PFAS analysis in air samples need to be improved with additional clean-up step and the PFAS analysis will be continued in the monitoring of surface and groundwater in São Paulo State.

It was clearly evidenced the decline of the pesticide endosulfan from the GMP period phase 1 period to phase 2 period. A progressive ban of endosulfan was established in Brazil from 2010 to 2014 and this is the reason of the decline of endosulfan to the levels lower than quantitation levels in the past years. In this case, it is possible to say that the Brazilian government's action plan regarding to endosulfan was effective.

The conclusions of the national workshops demonstrate that there are some analytical and monitoring capacities in the country, requiring better structuring and financial resources to allow continuous POPs monitoring.

The lessons learned and the experience gained from the UNEP/GEF GMP-1 and GMP-2 projects will help Brazilian group to continue and improve the POPs monitoring in the country in a continuous and more organized way, in order to generate data and contribute more effectively to the GMP. But considering the complexity of POPs analysis, the need of the laboratory infrastructure for the development of the monitoring activities and the dimension of the country, greater GMP investments will be necessary in Brazil.

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ANNEXES

ANNEX 1 – NATIONAL LAB RESULTS

Table A1 – Dioxin like (dl) POPs – 2017 Passive Air Sample Results from CETESB

Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6
Sampling year	2017	2017	2017	2017	2017
Start day	02/01/2017	31/03/2017	30/06/2017	29/09/2017	02/01/2017
End day	31/03/2017	30/06/2017	29/09/2017	29/12/2017	29/12/2017
Exposure days	88	91	91	91	361
Season code	I	II	III	IV	I+II+III+IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2017-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8(2017-I)	BRA-8 (2017-II)	BRA-8 (2017-III)	BRA-8 (2017-IV)	BRA-6+6+6+6 (2017-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2017-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg4PUF ⁻¹
PCDD/PCDF					
2378-Cl ₄ DD	<5,15	<2,15	<7,77	<1,02	2,56
12378-Cl ₅ DD	<5,37	<3,59	<9,63	<2,50	5,59
123478-Cl ₆ DD	<5,65	<2,81	<6,33	<2,50	<3,87
123678-Cl ₆ DD	<5,92	<2,62	<6,17	<2,50	7,27
123789-Cl ₆ DD	<6,38	<3,07	<7,37	<2,50	5,51
1234678-Cl ₇ DD	9,87	8,27	14,6	8,65	48,7
Cl ₈ DD	27,6	31,4	43,1	24,8	158,0
2378-Cl ₄ DF	8,05	5,95	<13,7	7,61	30,0
12378-Cl ₅ DF	7,47	4,95	8,97	5,52	22,6
23478-Cl ₅ DF	6,68	5,61	10,0	5,43	21,3
123478-Cl ₆ DF	6,84	4,20	8,00	4,46	20,1
123678-Cl ₆ DF	6,60	3,35	7,24	3,40	16,5
123789-Cl ₆ DF	<4,83	<2,79	<11,3	<2,50	4,45
234678-Cl ₆ DF	4,35	2,92	<7,64	2,73	14,9
1234678-Cl ₇ DF	12,9	8,03	15,4	9,67	43,7
1234789-Cl ₇ DF	<4,32	<2,50	<7,40	<2,50	4,54
Cl ₈ DF	6,53	3,94	<9,45	5,37	16,6
WHO₂₀₀₅-TEQ_{PCDD}*	0,11	0,09	0,16	0,09	10,0
WHO₂₀₀₅-TEQ_{PCDF}*	4,94	3,55	4,95	3,71	16,2

WHO₂₀₀₅-TEQ_{PCDD/PCDF}*	5,05	3,65	5,11	3,81	26,1
dl-PCB					
PCB 77	220,0	118,0	179,0	169,0	721,0
PCB 81	<75,7	18,6	36,0	21,6	93,2
PCB 126	<162	<23,8	<31,6	<20,8	85,8
PCB 169	<65,2	<5,90	<9,43	<10,0	<20,8
PCB 105	602,0	322,0	625,0	494,0	1960,0
PCB 114	<779	32,1	63,4	46,7	191,0
PCB 118	1600,0	870,0	1630,0	1260,0	4880,0
PCB 123	<976	22,6	<25,3	29,3	111,0
PCB 156	<286	70,6	153,0	108,0	440,0
PCB 157	<221	16,6	38,0	25,6	105,0
PCB 167	<746	37,2	68,5	50,7	213,0
PCB 189	<641	<12,8	<17,0	9,16	46,1
WHO₂₀₀₅-TEQ_{no-PCB}*	0,02	0,02	0,03	0,02	8,68
WHO₂₀₀₅-TEQ_{mo-PCB}*	0,07	0,04	0,08	0,06	0,24
WHO₂₀₀₅-TEQ_{PCB}*	0,09	0,06	0,11	0,08	8,92
WHO₂₀₀₅-TEQ_{total}*	5,14	3,71	5,21	3,89	35,0
Number of PUFs	1	1	1	1	4
WHO₂₀₀₅-TEQ_{PCDD/PCDF}*	5,05	3,65	5,11	3,81	6,53
WHO₂₀₀₅-TEQ_{PCB}*	0,09	0,06	0,11	0,08	2,23
WHO₂₀₀₅-TEQ_{total}*	5,14	3,71	5,21	3,89	8,76

*Lower Bound

Table A2 – Dioxin like (dl) POPs – 2018 Passive Air Sample Results from CETESB

Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6
Sampling year	2018	2018	2018	2018	2018
Start day	29/12/2017	29/03/2018	29/06/2018	28/09/2018	29/12/2017
End day	29/03/2018	29/06/2018	28/09/2018	28/12/2018	28/12/2018
Exposure days	90	92	91	91	364
Season code	I	II	III	IV	I+II+III+IV
Year-season	2018-I	2018-II	2018-III	2018-IV	2018-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8(2018-I)	BRA-8 (2018-II)	BRA-8 (2018-III)	BRA-8 (2018-IV)	BRA-6+6+6+6 (2018-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)	BRA (2018-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg4PUF ⁻¹
PCDD/PCDF					
2378-Cl ₄ DD	<1,86	<2,15	<1,51	<2,20	2,85
12378-Cl ₅ DD	<2,50	<3,87	<2,50	<3,11	6,06
123478-Cl ₆ DD	<2,50	<2,98	<2,50	<3,24	2,71
123678-Cl ₆ DD	<2,50	<2,64	<2,50	<3,12	6,64

123789-Cl ₆ DD	<2,52	<3,48	<2,50	<3,68	5,02
1234678-Cl ₇ DD	7,22	10,5	14,6	10,8	46,0
Cl ₈ DD	20,8	28,7	40,1	34,3	155,0
2378-Cl ₄ DF	4,65	9,51	9,82	9,18	31,0
12378-Cl ₅ DF	3,26	7,08	8,68	8,53	26,9
23478-Cl ₅ DF	3,31	7,15	8,57	8,01	27,3
123478-Cl ₆ DF	3,18	6,25	7,10	10,00	25,6
123678-Cl ₆ DF	2,71	4,72	6,53	7,24	20,6
123789-Cl ₆ DF	<2,50	<3,52	<2,50	<7,46	5,68
234678-Cl ₆ DF	<2,50	4,26	5,7	6,23	18,6
1234678-Cl ₇ DF	6,85	12,6	14,8	16,10	46,2
1234789-Cl ₇ DF	<2,50	<3,29	<2,50	<4,29	4,30
Cl ₈ DF	<5,00	6,87	7,6	<5,00	22,3
WHO₂₀₀₅-TEQ_{PCDD}	0,08	0,11	0,16	0,12	10,9
WHO₂₀₀₅-TEQ_{PCDF}	2,21	4,96	5,89	6,08	19,7
WHO₂₀₀₅-TEQ_{PCDD/PCDF}*	2,29	5,07	6,05	6,20	30,5
dl-PCB					
PCB 77	148,0	149	144,0	167,0	507,0
PCB 81	16,5	24,1	18,6	20,6	108,0
PCB 126	<16,3	21,3	24,6	20,6	92,6
PCB 169	<10,6	<9,70	<3,93	<4,57	<21,4
PCB 105	403,0	614	392,0	410,0	1940,0
PCB 114	36,0	54,4	38,5	48,6	195,0
PCB 118	1030,0	1490	1000,0	1060,0	4840,0
PCB 123	21,3	32,4	22,7	22,7	109,0
PCB 156	79,5	126	92,3	96,5	436,0
PCB 157	19,7	31,5	24,1	23,1	103,0
PCB 167	40,7	56,0	45,1	47,5	207,0
PCB 189	6,75	<12,0	10,1	13,60	40,7
WHO₂₀₀₅-TEQ_{no-PCB}*	0,02	2,15	2,5	2,1	9,3
WHO₂₀₀₅-TEQ_{mo-PCB}*	0,05	0,07	0,05	0,05	0,24
WHO₂₀₀₅-TEQ_{PCB}*	0,07	2,22	2,53	2,13	9,58
WHO₂₀₀₅-TEQ_{total}*	2,36	7,30	8,58	8,34	40,1
Number of PUFs	1	1	1	1	4
WHO₂₀₀₅-TEQ_{PCDD/PCDF}*	2,29	5,07	6,05	6,20	7,63
WHO₂₀₀₅-TEQ_{PCB}*	0,07	2,22	2,53	2,13	2,4
WHO₂₀₀₅-TEQ_{total}*	2,36	7,30	8,58	8,34	10,0

*Lower Bound

Table A3 – Indicator PCB – 2017 Passive Air Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6

Sampling year	2017	2017	2017	2017	2017
Start day	02/01/2017	31/03/2017	30/06/2017	29/09/2017	02/01/2017
End day	31/03/2017	30/06/2017	29/09/2017	29/12/2017	29/12/2017
Exposure days	88	91	91	91	361
Season code	I	II	III	IV	I+II+III+IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2017-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8 (2017-I)	BRA-8 (2017-II)	BRA-8 (2017-III)	BRA-8 (2017-IV)	BRA-6+6+6+6 (2017-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2017-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg (4PUF) ⁻¹
PCB #28	618,0	3369	4092,0	3076,0	13810,0
PCB #52	228,0	2938	4475,0	4520,0	20017,0
PCB #101	<1417	1795	3124,0	2644,0	10037,0
PCB #138	<2810	666,0	1338,0	1063,0	4254,0
PCB #153	<2579	871,0	1694,0	1344,0	5586,0
PCB #180	<678	255,0	418,0	395,0	1725,0
Sum PCB ₆	846,0	9894,0	15141,0	13042,0	55429,0

Table A4 – Indicator PCB – 2018 Passive Air Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6
Sampling year	2018	2018	2018	2018	2018
Start day	29/12/2017	29/03/2018	29/06/2018	28/09/2018	29/12/2017
End day	29/03/2018	29/06/2018	28/09/2018	28/12/2018	28/12/2018
Exposure days	90	92	91	91	364
Season code	I	II	III	IV	I+II+III+IV
Year-season	2018-I	2018-II	2018-III	2018-IV	2018-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8 (2018-I)	BRA-8 (2018-II)	BRA-8 (2018-III)	BRA-8 (2018-IV)	BRA-6+6+6+6 (2018-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)	BRA (2018-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg (4PUF) ⁻¹
PCB #28	2668,0	9740,0	2770,0	2640,0	11000,0
PCB #52	3871,0	17700,0	3240,0	3260,0	14300,0
PCB #101	2172,0	8740,0	1560,0	1900,0	8170,0
PCB #138	901,0	4020,0	928,0	932,0	4710,0
PCB #153	1201,0	5590,0	901,0	1050,0	5520,0
PCB #180	346,0	1400,0	287,0	332,0	1480,0

Sum PCB ₆	11159,0	47190,0	9686,0	10114,0	45180,0
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Table A5 – OCP – 2017 Passive Air Sample Results from CETESB

Matrix	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sample from samplers	2+4	2+4	2+4	2+4
Sampling year	2017	2017	2017	2017
Start day	02/01/2017	31/03/2017	30/06/2017	29/09/2017
End day	31/03/2017	30/06/2017	29/09/2017	29/12/2017
Exposure days	88	91	91	91
Season code	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV
Exposure months	3 months	3 months	3 months	3 months
Original Sample-ID	BRA-2+4 (2017-I)	BRA-2+4 (2017-II)	BRA-2+4 (2017-III)	BRA-2+4 (2017-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)
Unit	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹
Aldrin	<1,00	<1,00	<1,00	<1,00
Dieldrin	2,23	2,29	1,56	1,87
Endrin	<2,00	<2,00	<2,00	<2,00
Sum drins	2,23	2,29	1,56	1,87
a-Chlordane	<10,0	<10,0	<10,0	<10,0
g-Chlordane	<10,0	<10,0	<10,0	<10,0
Oxychlordane				
cis-Nonachlor				
trans-Nonachlor				
Sum chlordanes	0,0	0,0	0,0	0,0
o,p'-DDT				
p,p'-DDT	4,06	<3,00	<3,00	3,07
o,p'-DDD				
p,p'-DDD	<1,00	<1,00	<1,00	<1,00
o,p'-DDE				
p,p'-DDE	6,33	5,23	3,45	3,92
Sum DDTs	10,4	5,2	3,5	7,0
Heptachlor	<2,50	<2,50	<2,50	<2,50
cis-Heptachlorepoxide	<2,50	<2,50	<2,50	<2,50
trans-Heptachlorepoxide	NA	NA	NA	
Sum heptachlors	0,0	0,0	0,0	0,0
Parlar 26	<5,00	<5,00	<5,00	<5,00
Parlar 50	<5,00	<5,00	<5,00	<5,00
Parlar 62	<5,00	<5,00	<5,00	<5,00
Sum toxaphenes	0,0	0,0	0,0	0,0
HCB	1,70	5,48	5,08	1,87
Mirex	<1,00	<1,00	<1,00	<1,00
a-HCH	<5,00	<5,00	<5,00	<5,00
b-HCH	<5,00	<5,00	<5,00	<5,00
g-HCH	5,41	3,83	3,99	4,86

Sum HCH	5,4	3,83	4,0	4,9
sum Chlordecone	0,0	0,0	0,0	0,0
α-endosulfan	<10,0	<10,0	<10,0	<10,0
β-endosulfan	<10,0	<10,0	<10,0	<10,0
Endosulfan sulfate	<10,0	<10,0	<10,0	<10,0
Sum endosulfans	0,0	0,0	0,0	0,0
Pentachlorobenzene	<5,00	<5,00	<5,00	<5,00
Chlordecone				
HCBD				

Table A6 – OCP – 2018 Passive Air Sample Results from CETESB

Matrix	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sample from samplers	2+4	2+4	2+4	2+4
Sampling year	2018	2018	2018	2018
Start day	29/12/2017	29/03/2018	29/06/2018	28/09/2018
End day	29/03/2018	29/06/2018	28/09/2018	28/12/2018
Exposure days	90	92	91	91
Season code	I	II	III	IV
Year-season	2018-I	2018-II	2018-III	2018-IV
Exposure months	3 months	3 months	3 months	3 months
Original Sample-ID	BRA-2+4 (2018-I)	BRA-2+4 (2018-II)	BRA-2+4 (2018-III)	BRA-2+4 (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹	ng PUF ⁻¹
Aldrin	<1,00	<1,00	<1,00	<1,00
Dieldrin	2,22	1,76	1,83	2,57
Endrin	<2,00	<2,00	<2,00	<2,00
Sum drins	2,2	1,8	1,8	2,57
a-Chlordane	<10,0	<10,0	<10,0	<10,0
g-Chlordane	<10,0	<10,0	<10,0	<10,0
Oxychlordane				
cis-Nonachlor				
trans-Nonachlor				
Sum chlordanes	0,0	0,0	0,0	0,0
o,p'-DDT				
p,p'-DDT	3,38	<3,00	<3,00	3,33
o,p'-DDD				
p,p'-DDD	<1,00	<1,00	<1,00	<1,00
o,p'-DDE				
p,p'-DDE	6,73	4,82	4,74	6,43
Sum DDTs	10,1	4,8	4,7	9,8
Heptachlor	<2,50	<2,50	<2,50	<2,50
cis-Heptachlorepoxide	<2,50	<2,50	<2,50	<2,50
trans-Heptachlorepoxide				
Sum heptachlors	0,0	0,0	0,0	0,0
Parlar 26	<5,00	<5,00	<5,00	<5,00
Parlar 50	<5,00	<5,00	<5,00	<5,00
Parlar 62	<5,00	<5,00	<5,00	<5,00
Sum toxaphenes	0,0	0,0	0,0	0,0

HCB	2,58	3,29	3,79	2,11
Mirex	<1,00	<1,00	<1,00	<1,00
a-HCH	<5,00	<5,00	<5,00	<5,00
b-HCH	6,57	<5,00	<5,00	<5,00
g-HCH	6,46	4,57	5,03	5,91
Sum HCH	13,0	4,6	5,0	5,9
sum Chlordecone	0,0	0,0	0,0	0,0
α-endosulfan	<10,0	<10,0	<10,0	<10,0
β-endosulfan	<10,0	<10,0	<10,0	<10,0
Endosulfan sulfate	<10,0	<10,0	<10,0	<10,0
Sum endosulfans	0,0	0,0	0,0	0,0
Pentachlorobenzene	<5,00	<5,00	<5,00	<5,00
Chlordecone				
HCBD				

Table A7 – PBDE/PBB – 2017 Passive Air Sample Results from CETESB

Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6
Sampling year	2017	2017	2017	2017	2017
Start day	02/01/2017	31/03/2017	30/06/2017	29/09/2017	02/01/2017
End day	31/03/2017	30/06/2017	29/09/2017	29/12/2017	29/12/2017
Exposure days	88	91	91	91	361
Season code	I	II	III	IV	I+II+III+IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2017-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8 (2017-I)	BRA-8 (2017-II)	BRA-8 (2017-III)	BRA-8 (2017-IV)	BRA-6+6+6+6 (2017-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2017-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg 4PUF ⁻¹
PBDE-17	42,7	28,7	51,8	81,0	393,0
PBDE-28	137,0	145,0	149,0	124,0	541,0
PBDE-47	1.250,0	85,6	792,0	164,0	2.460,0
PBDE-99	561,0	322,0	496,0	335,0	1.400,0
PBDE-100	141,0	78,4	116,0	79,1	324,0
PBDE-153	60,8	36,5	58,0	53,1	<1150
PBDE-154	<47,0	63,0	55,9	PI	PI
PBDE-183	<103	47,0	99,5	92,9	904,0
Sum PBDE(8)	2.192,5	806,2	1.818,2	929,1	6.022,0
PBB 153	NA	NA	NA	NA	NA
PBDE 209	NA	25.550,0	50.016,0	10.603,0	104.202,0
PBDE-119	<63,0	<100	<100	<100	<185
PBDE-126	<25,7	<100	<100	<100	<195

PBDE-138	<62,5	<100	<100	<100	<1320
PBDE-156	<116	<100	<100	<100	<2290
PBDE-184	<80,2	<100	<100	<100	<255
PBDE-191	<219	<100	<100	<100	<585
PBDE-49	143	125	153	129	657
PBDE-66	148	<100	105	<100	213
PBDE-71	<14,9	128	138	<100	<173
PBDE-77	30,7	<100	<100	<100	<105
PBDE-85	<39,3	<100	<100	<100	<302

Table A8 – PBDE/PBB – 2018 Passive Air Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB	CETESB
Sample from samplers	8	8	8	8	6+6+6+6
Sampling year	2018	2018	2018	2018	2018
Start day	29/12/2017	29/03/2018	29/06/2018	28/09/2018	29/12/2017
End day	29/03/2018	29/06/2018	28/09/2018	28/12/2018	28/12/2018
Exposure days	90	92	91	91	364
Season code	I	II	III	IV	I+II+III+IV
Year-season	2018-I	2018-II	2018-III	2018-IV	2018-I+II+III+IV
Exposure months	3 months	3 months	3 months	3 months	12 months
Original Sample-ID	BRA-8 (2018-I)	BRA-8 (2018-II)	BRA-8 (2018-III)	BRA-8 (2018-IV)	BRA-6+6+6+6 (2018-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)	BRA (2018-I+II+III+IV)
Unit	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg PUF ⁻¹	pg 4PUF ⁻¹
PBDE-17	69,4	278,0	92,4	17,6	315,0
PBDE-28	103,0	433,0	108,0	60,5	356,0
PBDE-47	358,0	3.220,0	561,0	420,0	2.280,0
PBDE-99	291,0	2.500,0	435,0	248,0	1.440,0
PBDE-100	72,1	486,0	97,7	70,8	338,0
PBDE-153	46,4	258,0	67,9	48,7	308,0
PBDE-154	PI	PI	44,1	33,6	184,0
PBDE-183	60,9	180,0	120,0	170,0	674,0
Sum PBDE(8)	1.000,8	7.355,0	1.526,1	1.069,2	5.895,0
PBB 153	NA	PI	<20,0	<20,0	<20,0
PBDE 209	6.648,0	65.100,0	22.700,0	23.900,0	101.000,0
PBDE-119	<100	116	<10,0	<10,0	52,8
PBDE-126	<100	<14,3	<10,0	<10,0	<15,2
PBDE-138	<100	<28,5	<20,0	<20,0	30,9
PBDE-156	<100	<49,4	<20,0	<20,0	<20,0
PBDE-184	<100	<20,0	<20,0	<20,0	36,3
PBDE-191	<100	<29,9	<43,3	<20,0	41,7
PBDE-49	114	612	121	78,6	366
PBDE-66	<100	294	70,5	44,8	208
PBDE-71	<100	26,9	26,7	20,0	74,3

PBDE-77	<100	66,9	22,0	12,7	65,0
PBDE-85	<100	93,8	15,0	<10,0	48,2

Table A9 – PFAS – 2017 Passive Air Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sample for samplers	12	12	12	12
Sampling year	2017	2017	2017	2017
Start day	02/01/2017	31/03/2017	30/06/2017	29/09/2017
End day	31/03/2017	30/06/2017	29/09/2017	29/12/2017
Exposure days	88	91	91	91
Season code	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV
Exposure months	3 months	3 months	3 months	3 months
Original Sample-ID	BRA- (2017-I)	BRA- (2017-II)	BRA- (2017-III)	BRA- (2017-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)
Unit	pg 1PUF ⁻¹	pg 1PUF ⁻¹	pg 1PUF ⁻¹	pg 1PUF ⁻¹
L-PFOS	<2727	<4712	<4410	NR
br-PFOS	<4821	<8330	<7797	NR
Sum PFOS lower bound (ND=0)	<7548	<13042	<12207	NR
Sum PFOS upper bound (ND=LOD)	<7548	<13042	<12207	NR
PFOA	NR	NR	NR	NR
PFHxS	NR	NR	NR	NR
FOSA	NR	NR	NR	NR
NMeFOSA	NR	NR	NR	NR
NEtFOSA	NR	NR	NR	NR
NMeFOSE	NR	NR	NR	NR
NEtFOSE	NR	NR	NR	NR
Sum PFOS precursors lower bound (ND=0)	NR	NR	NR	NR
Sum PFOS precursors upper bound (ND=LOD)	NR	NR	NR	NR
PFBS	NR	NR	NR	NR
PFDS	<5159	<6537	<7310	NR
PFBA	NR	NR	NR	NR
PFPeA	NR	NR	NR	NR
PFHxA	NR	NR	NR	NR
PFHpA	NR	NR	NR	NR
PFNA	NR	NR	NR	NR
PFDA	NR	NR	NR	NR
PFUnDA	NR	NR	NR	NR
PFDoDA	NR	NR	NR	NR
PFTTrDA	NR	NR	NR	NR
PFTeDA	NR	NR	NR	NR
6:2 FTSA	NR	NR	NR	NR
PFCAs + PFSAs Lower Bound (ND=0)	NR	NR	NR	NR
PFCAs + PFSAs Upper Bound (ND=LOD)	NR	NR	NR	NR

NR – not reported – low recovery of labered internal standards and/or interferences

Table A10 – PFAS – 2018 Passive Air Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sample for samplers	12	12	12	12
Sampling year	2018	2018	2018	2018
Start day	29/12/2017	29/03/2018	29/06/2018	28/09/2018
End day	29/03/2018	29/06/2018	28/09/2018	28/12/2018
Exposure days	90	92	91	91
Season code	I	II	III	IV
Year-season	2018-I	2018-II	2018-III	2018-IV
Exposure months	3 months	3 months	3 months	3 months
Original Sample-ID	BRA- (2018-I)	BRA- (2018-II)	BRA- (2018-III)	BRA- (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	pg 1PUF ⁻¹	pg 1PUF ⁻¹	pg 1PUF ⁻¹	pg 1PUF ⁻¹
L-PFOS	NR	NR	NR	NR
br-PFOS	NR	NR	NR	NR
Sum PFOS lower bound (ND=0)	NR	NR	NR	NR
Sum PFOS upper bound (ND=LOD)	NR	NR	NR	NR
PFOA	NR	NR	NR	NR
PFHxS	NR	NR	NR	NR
FOSA	NR	NR	NR	NR
NMeFOSA	NR	NR	NR	NR
NEtFOSA	NR	NR	NR	NR
NMeFOSE	NR	NR	NR	NR
NEtFOSE	NR	NR	NR	NR
Sum PFOS precursors lower bound (ND=0)	NR	NR	NR	NR
Sum PFOS precursors upper bound (ND=LOD)	NR	NR	NR	NR
PFBS	NR	NR	NR	NR
PFDS	NR	NR	NR	NR
PFBA	NR	NR	NR	NR
PFPeA	NR	NR	NR	NR
PFHxA	NR	NR	NR	NR
PFHpA	NR	NR	NR	NR
PFNA	NR	NR	NR	NR
PFDA	NR	NR	NR	NR
PFUnDA	NR	NR	NR	NR
PFDoDA	NR	NR	NR	NR
PFTTrDA	NR	NR	NR	NR
PFTeDA	NR	NR	NR	NR
6:2 FTSA	NR	NR	NR	NR
PFCAs + PFSAs Lower Bound (ND=0)	NR	NR	NR	NR
PFCAs + PFSAs Upper Bound (ND=LOD)	NR	NR	NR	NR

NR – not reported – low recovery of labered internal standards and/or interferences

Table – A11 – PFAS – 2017 Water Sample Results from CETESB

Region	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	Water	Water	Water	Water
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sampling year	2017	2017	2017	2017
Season code	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV
Original Sample-ID	BRA- (2017-I)	BRA- (2017-II)	BRA- (2017-III)	BRA- (2017-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)
Unit	ng/L	ng/L	ng/L	ng/L
L-PFOS	0,04	0,03	0,02	0,03
br-PFOS	0,01	0,01	0,01	0,01
Sum PFOS lower bound (ND=0)	0,05	0,04	0,03	0,04
Sum PFOS upper bound (ND=LOD)	0,05	0,04	0,03	0,04
PFOA	0,55	NR	0,28	NR
PFHxS	0,03	0,02	0,02	0,02
FOSA	0,05	0,01	0,07	<0.01
Sum PFOS precursors lower bound (ND=0)	0,63	NR	0,37	NR
Sum PFOS precursors upper bound (ND=LOD)	0,63	NR	0,37	NR

NR: not reported, presence of interference

Table – A12 – PFAS – 2018 Water Sample Results from CETESB

Matrix	Water	Water	Water	Water
Analytical lab	CETESB	CETESB	CETESB	CETESB
Sampling year	2018	2018	2018	2018
Season code	I	II	III	IV
Year-season	2018-I	2018-II	2018-III	2018-IV
Original Sample-ID	BRA- (2018-I)	BRA- (2018-II)	BRA- (2018-III)	BRA- (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA
Sample ID	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	ng/L	ng/L	ng/L	ng/L
L-PFOS	1,65	1,05	1,20	1,57
br-PFOS	0,34	<0.50	0,36	<0.63
Sum PFOS lower bound (ND=0)	1,99	1,05	1,56	1,57
Sum PFOS upper bound (ND=LOD)	1,99	1,55	1,56	2,20
PFOA	0,91	<12.05	<3.61	<18.6
PFHxS	0,65	1,53	0,92	1,79
FOSA	0,03	<0.92	<0.48	<0.25
Sum PFOS precursors lower bound (ND=0)	1,59	1,53	0,92	1,79
Sum PFOS precursors upper bound (ND=LOD)	1,59	14,50	5,01	20,61

**ANNEX 2 – EXPERT LAB RESULTS – Basic POPs and dl-POPs in Passive Air Samples
(CSIC)**

Report of Results

UN Environment/GEF Project “Continuing Regional Support for the POPs Global Monitoring Plan under the Stockholm Convention in the Latin American and Caribbean Region”

Results of POP Analyses in Ambient Air Samples (PUFs) from **BRASIL**

Barcelona, Wednesday, 30 September 2020

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HOLGADO
ESTEBAN -
DNI
38441611D

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Dr. Esteban Abad
Head of the Laboratory

Dear Participant,

Below you will find the results of the analysis of: Basic POPs, polychlorodibenzo-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (dl-PCBs), indicator polychlorinated biphenyl (PCBs Ind.), polybrominated biphenyl ethers (PBDEs), as well as polybrominated biphenyl (PBB # 153), within the framework of the UN Environment / GEF Project "Continuing regional Support for the POPs Global Monitoring Plan under the Stockholm Convention in the Latin American and Caribbean Region".

For a better understanding and interpretation of the data, the following aspects must be taken into consideration:

- In all the analyzed samples we report the results expressed in nanograms per PUF (ng/PUF) for all compounds, except for dioxins, furans and dl-PCBs, which are expressed in picogram per PUF (pg/PUF). In addition, the results of dioxins, furans and dl-PCBs of the annual samples refer to the concentrations determined in the total of PUFs indicated in each case (e.g.: 4 PUFs), so that they must be divided by the corresponding number of PUFs in order to normalize the data to pg / PUF.
- The analytical methodology is based on analysis by gas chromatography coupled to high resolution mass spectrometry (GC-HRMS) and using isotopic dilution as the quantification method. Prior to this instrumental analysis, Soxhlet extraction and subsequent purification of the extract were carried out. The purification was based on solid-liquid adsorption chromatography, using open columns eluted by gravity, with different adsorbents, such as modified silica, alumina, Florisil or activated carbon.
- For those substances not detected or whose concentrations are below the limit of quantification (LOQ), the LOQ value is included.
- Sum values are included for the different families of compounds following the "lowerbound" (LB) approach, that is, considering the contribution of those compounds with values lower than the LOQ equal to 0. In particular:
 - In the case of basic POPs, the sum of some families of substances is shown (e.g. DDTs, etc.). The identification of the compounds belonging to the different families is done by using different colours for the cells.

- In the case of PBDEs, the sum of 8 or 10 PBDEs is added. The 2 compounds added to the 8 PBDEs that are normally documented in the literature are indicated in red.
 - For dioxins, furans and dl-PCBs, the results expressed in WHO-TEQ are included, also in “lowerbound”.
- As complementary information, the identification of the sample is attached according to the harmonized SOP in the Project protocols, the sampling period and the analyzed PUF.

Table 1. Results of Basic POP in ambient air samples in the 8 campaigns carried out between 2017 and 2018.

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Sampler	1	1	1	1	1	1	1	1
Lab	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC
Sampling year	2017	2017	2017	2017	2018	2018	2018	2018
Season code	I	II	III	IV	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2018-I	2018-II	2018-III	2018-IV
Exposure time	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly
Original Sample-ID	BRA-1 (2017-I)	BRA-1 (2017-II)	BRA-1 (2017-III)	BRA-1 (2017-IV)	BRA-1 (2018-I)	BRA-1 (2018-II)	BRA-1 (2018-III)	BRA-1 (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF
OCPs								
Pentachlorobenzene	<1,00	40	4,9	<1,00	10	12	7,5	11
a-HCH	3,0	2,7	3,5	3,1	4,1	2,5	2,9	3,8
Hexachlorobenzene	3,9	8,4	9,2	3,6	5,2	4,8	4,8	3,7
g-HCH (lindane)	7,3	5,3	8,8	11	10	6,7	7,3	8,8
b-HCH	1,4	0,79	0,81	1,7	1,3	0,51	0,89	2,1
d-HCH	0,34	<0,20	<0,20	0,31	0,23	<0,20	<0,20	<0,20
Heptachlor	3,2	2,7	3,0	3,1	3,5	2,3	2,3	4,7
Endrin (achlorobenzene peak)	0,93	<0,20	<0,20	0,30	<0,20	<0,20	<0,20	<0,20
Oxychlorodane	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40
cis-Heptachlor Epoxide	0,91	0,64	0,49	0,95	0,93	0,49	0,53	0,92
trans-Heptachlor Epoxide	<1,00	<1,00	<1,00	<1,00	<1,00	<1,00	<1,00	<1,00
o,p'-DDE	1,3	1,00	1,2	1,2	1,4	0,88	0,93	1,7
p,p'-DDE	11	7,7	8,5	10	14	7,5	7,9	13
trans-Chlordane	3,5	2,4	2,8	3,4	3,6	2,0	2,2	3,7
cis-Chlordane	0,79	0,58	0,47	0,75	0,78	0,57	0,49	1,1
a-Endosulfan	9,5	2,0	1,3	2,3	6,1	1,4	1,0	3,4
trans-Nonachlor	0,63	0,44	0,5	0,60	0,66	<0,40	0,47	0,76
Dieldrin	5,4	3,8	3,7	5,1	5,2	3,4	3,6	6,1
Endrin	0,85	0,74	0,95	0,90	1,0	0,65	0,67	1,2
o,p'-DDD	0,28	0,17	0,20	0,31	0,26	0,18	0,17	0,31
o,p'-DDT	3,1	2,1	2,1	2,7	3,0	1,7	1,9	3,5
p,p'-DDD	0,38	0,24	0,36	0,55	0,44	0,30	0,22	0,33
p,p'-DDT	5,2	3,4	6,0	5,0	5,0	2,8	3,3	5,8
cis-Nonachlor + Chlordecone	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40	<0,40
b-Endosulfan	n.q.	<1,00	n.q.	n.q.	1,1	<1,00	n.q.	1,3
Endosulfan sulfate	n.q.	<0,20	n.q.	n.q.	<0,20	<0,20	n.q.	0,27
Mirex	0,43	0,17	0,16	0,43	0,40	0,16	0,21	0,41
Sum HCHs (α, β, γ, δ)	12	8,8	13	17	16	10	11	15
Sum Heptachlors	4,2	3,3	3,5	4,1	4,4	2,8	2,9	5,6
Sum Chlordanes	4,9	3,4	3,7	4,7	5,0	2,6	3,2	5,6
Sum Drins	7,2	4,5	4,7	6,3	6,2	4,1	4,2	7,3
Sum DDTs	22	15	18	20	24	13	14	25

Table 2. Results of indicator PCBs in ambient air samples in the 8 campaigns carried out between 2017 and 2018.

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Sampler	3	3	3	3	3	3	3	3
Lab	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC
Sampling year	2017	2017	2017	2017	2018	2018	2018	2018
Season code	I	II	III	IV	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2018-I	2018-II	2018-III	2018-IV
Exposure time	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly
Original Sample-ID	BRA-3 (2017-I)	BRA-3 (2017-II)	BRA-3 (2017-III)	BRA-3 (2017-IV)	BRA-3 (2018-I)	BRA-3 (2018-II)	BRA-3 (2018-III)	BRA-3 (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF
Indicator PCB								
PCB 28	3,9	3,2	2,9	2,1	3,2	2,8	3,2	2,5
PCB 52	3,4	2,9	4,2	3,8	3,2	3,7	2,9	3,3
PCB 101	2,6	1,9	3,4	3,2	2,5	3,0	2,4	2,4
PCB 153	1,6	1,1	1,8	1,9	1,5	1,7	1,4	1,5
PCB 138	1,3	0,81	1,7	1,9	1,2	1,6	1,1	1,2
PCB 180	0,52	0,34	0,57	0,50	0,42	0,54	0,48	0,53
Sum Indicator PCB (LB)	13	10	15	13	12	13	12	11

Table 3. Results of PCDD / PCDFs in ambient air samples in the 8 campaigns carried out between 2017 and 2018, as well as in the annual samples corresponding to 2017 and 2018.

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Sampler and nº of PUFs	7 (1 PUF)	7 (1 PUF)	7 (1 PUF)	7 (1 PUF)	5 (4 PUFs)	7 (1 PUF)	7 (1 PUF)	7 (1 PUF)	7 (1 PUF)	5 (4 PUFs)
Lab	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC
Sampling year	2017	2017	2017	2017	2017	2018	2018	2018	2018	2018
Season code	I	II	III	IV	I+II+III+IV	I	II	III	IV	I+II+III+IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2017-I+II+III+IV	2018-I	2018-II	2018-III	2018-IV	2018-I+II+III+IV
Exposure time	quarterly	quarterly	quarterly	quarterly	quarterly x 4	quarterly	quarterly	quarterly	quarterly	quarterly x 4
Original Sample-ID	BRA-7 (1 PUF) (2017-I)	BRA-7 (1 PUF) (2017-II)	BRA-7 (1 PUF) (2017-III)	BRA-7 (1 PUF) (2017-IV)	BRA-5 (4 PUFs) (2017-I+II+III+IV)	BRA-7 (1 PUF) (2018-I)	BRA-7 (1 PUF) (2018-II)	BRA-7 (1 PUF) (2018-III)	BRA-7 (1 PUF) (2018-IV)	BRA-5 (4 PUFs) (2018-I+II+III+IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2017-I+II+III+IV)	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)	BRA (2018-I+II+III+IV)
	pg / PUF	pg / PUF	pg / PUF	pg / PUF	pg / 4 PUF	pg / PUF	pg / PUF	pg / PUF	pg / PUF	pg / 4 PUF
PCDD/PCDF										
2378-Cl ₂ DD	0,5	<1.8841	0,6	0,7	<1.2052	<1.0867	<0,6638	<1,0004	1,5	4,2
12378-Cl ₂ DD	1,6	<1.7274	2,5	1,6	5,8	1,0	1,7	3,1	2,7	7,1
123478-Cl ₂ DD	1,3	<2.8721	1,0	0,7	3,3	<1,1966	0,8	<2,2569	1,5	3,0
123678-Cl ₂ DD	2,2	<1.7918	3,1	1,6	7,2	1,8	1,1	<2,0375	1,7	8,6
123789-Cl ₂ DD	2,4	<3.1647	1,8	0,7	2,2	<1,4078	1,3	<2,2243	3,3	6,8
1234678-Cl ₂ DD	11,9	12,9	18,8	11,7	50,8	10,3	13,3	22,7	14,3	59,7
Cl ₄ DD	33,5	43,3	57,0	32,2	147,4	30,8	43,5	65,0	39,9	184,8
2378-Cl ₂ DF	5,1	6,8	11,8	8,7	33,5	5,9	6,0	6,7	11,1	34,6
12378-Cl ₂ DF	3,9	2,8	9,4	5,9	30,4	4,6	6,7	7,8	18,8	26,7
23478-Cl ₂ DF	4,9	4,7	9,9	6,7	29,7	5,2	7,8	10,1	10,6	27,7
123478-Cl ₂ DF	5,1	3,1	7,7	5,0	20,4	2,4	3,6	5,8	12,8	24,9
123678-Cl ₂ DF	5,2	2,7	7,5	4,1	19,6	2,0	5,3	7,4	8,9	21,6
123789-Cl ₂ DF	<1.0671	<2.0434	<0.8196	<0.4512	<3.6072	0,9	<2,068	<3,6424	<1,1561	2,4
234678-Cl ₂ DF	4,8	3,6	7,9	2,8	19,6	3,6	5,3	3,5	7,8	20,8
1234678-Cl ₂ DF	12,3	9,5	18,7	10,2	42,2	8,1	13,9	24,2	21,1	52,5
1234789-Cl ₂ DF	2,7	<1.693	2,6	1,1	3,7	1,5	<0,985	<1,7578	3,0	5,5
Cl ₄ DF	7,6	3,2	8,1	4,1	17,2	5,8	4,8	18,4	12,9	22,2
WHO₂₀₀₅-TEQ_{PCDD/PCDF}	6,6	3,4	11	7,1	27	4,5	6,9	9,2	13	34
dl-PCB										
PCB 77	157,2	118,2	174,7	155,1	624,1	128,4	148,6	138,7	147,2	635,9
PCB 81	20,1	14,6	23,2	16,9	72,9	12,2	20,6	28,4	22,2	78,1
PCB 126	25,0	18,8	31,5	23,7	86,6	18,9	26,4	34,0	28,9	119,0
PCB 169	9,4	3,3	5,7	2,5	<32.3852	3,1	3,9	15,2	7,4	18,6
PCB 105	446,1	384,9	698,0	638,4	2290,2	476,7	763,0	506,2	499,0	2407,6
PCB 114	45,0	33,7	53,8	46,2	166,6	36,7	33,6	45,5	45,9	193,5
PCB 118	1378,4	995,0	1649,2	1533,5	5850,1	1254,9	1942,5	1246,1	1243,7	5697,5
PCB 123	19,2	19,7	35,4	28,1	132,1	17,3	42,8	24,6	28,1	45,5
PCB 156	101,2	82,7	159,2	119,3	461,7	90,8	154,6	119,8	112,8	520,9
PCB 157	25,3	17,9	34,1	27,2	104,4	20,5	36,2	33,0	27,2	124,5
PCB 167	53,1	40,2	69,6	60,8	231,1	44,9	66,2	59,2	47,9	229,6
PCB 189	15,5	9,5	15,4	10,6	46,7	8,6	13,8	23,8	18,4	55,8
WHO₂₀₀₅-TEQ_{PCB}	2,9	2,0	3,4	2,5	9,0	2,1	2,9	3,9	3,2	13
WHO₂₀₀₅-TEQ_{total}	9,4	5,4	14	9,6	36	6,6	9,7	13	16	47

Table 4. Results of PBDEs and polybrominated biphenyl (PBB # 153) in ambient air samples in the 8 campaigns carried out between 2017 and 2018.

Region	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC	GRULAC
Matrix	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Sampler	9	9	9	9	9	9	9	9
Lab	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC	CSIC
Sampling year	2017	2017	2017	2017	2018	2018	2018	2018
Season code	I	II	III	IV	I	II	III	IV
Year-season	2017-I	2017-II	2017-III	2017-IV	2018-I	2018-II	2018-III	2018-IV
Exposure time	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly	quarterly
Original Sample-ID	BRA-9 (2017-I)	BRA-9 (2017-II)	BRA-9 (2017-III)	BRA-9 (2017-IV)	BRA-9 (2018-I)	BRA-9 (2018-II)	BRA-9 (2018-III)	BRA-9 (2018-IV)
Full country name	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil	Brazil
Country ISO-3	BRA	BRA	BRA	BRA	BRA	BRA	BRA	BRA
Sample ID	BRA (2017-I)	BRA (2017-II)	BRA (2017-III)	BRA (2017-IV)	BRA (2018-I)	BRA (2018-II)	BRA (2018-III)	BRA (2018-IV)
Unit	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF	ng / PUF
PBDEs								
BDE-17	0,06	<0,03	<0,03	0,03	<0,03	0,05	0,04	0,04
BDE-28	0,11	0,06	0,11	0,08	0,08	0,11	0,14	0,09
BDE-47	0,65	0,56	0,67	0,56	0,53	0,64	0,75	0,56
BDE-66	0,05	0,05	0,07	0,05	0,04	0,06	0,08	0,05
BDE-100	0,07	0,06	0,08	0,06	0,06	0,07	0,09	0,07
BDE-99	0,34	0,30	0,40	0,27	0,24	0,34	0,46	0,30
BDE-85	<0,07	<0,07	<0,07	<0,07	<0,07	<0,07	<0,07	<0,07
BDE-154	<0,16	<0,16	<0,16	<0,16	<0,16	<0,16	<0,16	<0,16
BDE-153	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
BDE-183	<1,00	<1,00	<1,00	<1,00	2,41	<1,00	<1,00	<1,00
Sum 10 PBDEs (LB)	1,3	1	1	1,1	3,4	1,3	1,6	1,1
Sum 8 PBDEs (LB)	1,2	1,0	1,3	1,0	3,3	1,2	1,5	1,0
PBB 153 (ng / PUF)	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03	<0,03

ANNEX 3 – EXPERT LAB RESULTS – PFAS in Passive Air Samples (Orebro University)



August 31, 2020

Subject: Results for analysis of PFOS, PFOA, PFHxS, and PFOS precursors in samples from passive samplers (PAS/PUF) under the UNEP/GMP2 project

Dear Participant,

Please find below the results from the analysis of PFAS in PUFs from passive air samplers under the UNEP/GEF GMP2 project.

For understanding the values and when interpreting the results, please note the following:

- We report the results as picogram per PUF (from PUF-11) for the all the samples received; these are denominated in the unit “pg/PUF”;
- Since we found many values below the limit of quantification, we combined the PUFs from one year into one new sample consisting of mostly four PUFs (denominated as “pg/4 PUF”). We did so to receive more quantitative results.
- However, sometimes the blanks or the recoveries were higher.
- Occasionally, we did not receive four PUFs for the respective year; then, the number of PUFs can be read from the unit;
- For comparison, we recommend that each country “reduces” the result to 1 PUF and the period of 3 months (note: some countries had shorter or longer exposure times; then, roughly these should be taken into account as well – although science would imply that PFASs are not “collected for more than 3 months as the dioxins are);
- We report the data for linear PFOS (L-PFOS), branched PFOS (br-PFOS) and the sum of the two (Σ PFOS) as well as the PFOS precursors;
- The LOQs are as follows: L-PFOS: 12 pg/PUF; br-PFOS: 5 pg/PUF; Σ PFOS: 12 pg/PUF; PFOA: 13 pg/PUF; PFHxS: 12 pg/PUF; FOSA: 25 pg/PUF; NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, each: 200 pg/PUF
- In addition, we report the values for the new or possible future PFAS, namely PFOA and PFHxS. Value below the LOQ are indicated as “<LOQ” and “NR” indicates samples, where PFASs could not be quantified due to too low recoveries of the labeled internal standards (NR = not reported).

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Results table:

Sample ID	Unit	L-PFOS	br-PFOS	ΣPFOS	PFOA	PFHxS	FOSA	NMeFOSA	NEtFOSA	NMeFOSE	NEtFOSE
BRA (2017-I)	pg/1 PUF	224	139	363	409	12	NR	NR	NR	NR	NR
BRA (2017-I+II+III+IV)	pg/4 PUF	1677	700	2377	1462	12	3142.2	NR	NR	NR	<200
BRA (2017-II)	pg/1 PUF	1168	453	1621	334	12	NR	NR	NR	NR	NR
BRA (2017-III)	pg/1 PUF	866	456	1322	649	12	NR	NR	NR	NR	NR
BRA (2017-IV)	pg/1 PUF	172	114	286	0	12	NR	NR	NR	NR	NR
BRA (2018-I)	pg/1 PUF	146	82	228	207	32	NR	NR	NR	NR	<200
BRA (2018-I+II+III+IV)	pg/4 PUF	499	150	649	1304	NR	3856.4	NR	3316.5	<200	NR
BRA (2018-II)	pg/1 PUF	127	53	180	341	17	610.5	NR	693.8	NR	<200
BRA (2018-III)	pg/1 PUF	138	55	192	386	26	NR	NR	NR	NR	NR
BRA (2018-IV)	pg/1 PUF	NR	NR	NR	260	37	NR	NR	NR	<200	NR

ANNEX 4 – EXPERT LAB RESULTS – PFAS in Water Samples (Orebro University)

August 29, 2020

Subject: Results for analysis of PFOS, PFOA and PFHxS in water samples under the UNEP/GMP2 project

Dear Participant,

Please find below the results from the analysis of PFASs in surface water samples under the UNEP/GEF GMP2 project.

We have validated all PFASs data, have included recoveries and established a limit of quantification for the PFASs using our optimized method. Therefore, the data shown below are slightly different from the data reported in April. The values shown below are those that we report to UNEP and subsequently to the GMP data warehouse.

In brief:

- We used 500 mL of water, did solid phase extraction (SPE) and separated the PFASs using UPLC/MS-MS instrumentation. The values are in ng/L.
- We report the data for linear PFOS (L-PFOS), branched PFOS (br-PFOS) and the sum of the two (Σ PFOS).
- The limits of quantification (LOQs) were as follows: L-PFOS: 0.025 ng/L; br-PFOS: 0.025 ng/L; Σ PFOS: 0.025 ng/L; PFOA: 0.05 ng/L; PFHxS: 0.025 ng/L
- In addition, we report the values for the new or possible future PFAS, namely PFOA and PFHxS; only the linear isomers. We did not find quantifiable branched isomers.
- In the column "Sample ID", the ISO-3 alpha codes are used for the country, followed by Arabic number for the year the sample was taken, the Roman numbers refer to the end of each quarter with I = 31 March, II = 30 June, III = 30 September, and IV = 31 December.

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Sample ID	Unit	L-PFOS	br-PFOS	Σ PFOS	PFOA	PFHxS
BRA (2017-I)	ng/L	0.33	0.02	0.35	0.08	<0.025
BRA (2017-II)	ng/L	0.16	0.03	0.20	0.13	0.05
BRA (2017-III)	ng/L	0.04	<0.025	0.04	0.05	<0.025
BRA (2017-IV)	ng/L	0.05	<0.025	0.05	0.15	<0.025
BRA (2018-I)	ng/L	2.14	0.85	2.98	0.71	0.79
BRA (2018-II)	ng/L	1.51	0.79	2.30	0.65	0.56
BRA (2018-III)	ng/L	2.64	1.44	4.08	0.86	0.81
BRA (2018-IV)	ng/L	2.07	0.99	3.06	0.71	0.60