Spatial assessment of dioxin-like POPs in samples collected with passive air sampling using polyurethane foam disks

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1 Introduction

A global monitoring plan (GMP) was established under the Stockholm Convention on Persistent Organic Pollutants (POPs) to follow changes in POPs concentrations regionally and with time and to periodically evaluate the effectiveness of measures taken under the Convention (UNEP, 2007). The GMP has defined ambient air and water as core matrices for environmental occurrence and transport and human milk or human blood for human exposure (UNEP, 2021). Passive air samplers (PAS) equipped with polyurethane foam (PUF) disks were recommended as simple and cost-effective tool to measure and assess atmospheric concentrations of POPs. PAS/PUFs have been widely applied and have the capacity to retain POPs at low cost and ease of handling (Herkert et al., 2016; Shoeib and Harner, 2002). Regional projects coordinated by the United Nations Environment Programme (UNEP) and financed by the Global Environment Facility (GEF) in four regions used these PAS/PUF combinations to undertake comparative measurements for the POPs listed in either Annex A, B, or C of the Convention (UNEP, 2015a; b; c; d).

Here we assess 195 ambient air samples analyzed for PCDD/PCDF and dl-PCB for spatial distribution during two years of sampling in 42 countries.

2 Materials and Methods

The setup of the PAS/PUFs followed the previous UNEP/GEF GMP1 projects (Bogdal et al., 2013; Fiedler et al., 2013) and are described in a recent publication (Abad et al., 2022). In brief, for dl-POPs, one or two air samples were taken during a 3-months period at each site. The PAS consisted of two bowls as protective chamber and were equipped with pre-cleaned (toluene) PUF disks. The sampling sites were designated to not having direct POPs impact (UNEP, 2017; 2021). For dl-POPs, since analysis is complex and expensive and concentrations were expected to be low, four PUFs should be combined for one annual sample. After exposure, PUFs were shipped with express mail to the expert laboratory at CSIC in Barcelona for dioxin analysis.

The samples included 15 countries in Africa, 7 in Asia, 9 in the Pacific Islands (PAC), and 11 in GRULAC, a total of 42 countries (see Table 1). Most samples were collected in 2017 (N=107) and 2018 (N=73), and only 15 in 2019.

Table 1: Number of samples/results in each region and list of countries within each region
* PAC = Pacific Islands countries; ** GRULAC = Group of Latin American and Caribbean countries

Region	Africa	Asia	PAC*	GRULAC**	Overall
#samples	89 (45.6%)	30 (15.4%)	23 (11.8%)	53 (27.2%)	195 (100%)
Countries	N=15 COD, EGY, ETH, GHA, KEN, MAR, MLI, MUS, NGA, SEN, TGO, TUN, TZA, UGA, ZMB	N=7 IDN, KHM, LAO, MNG, PHL, THA, VNM	N=9 FJI, KIR, MHL, NIU, PLW, SLB, TUV, VUT, WSM	N=11 ARG, ATG, BRA, BRB, CHL, COL, ECU, JAM, MEX, PER, URY	N=42

Analysis was accomplished by a high-resolution gas chromatograph (Agilent 6890NT, Agilent, Palo Alto, CA, USA) equipped with a DB5-MS (J&W Scientific, CA, USA) fused-silica capillary column (60 m × 0.25 mm i. d., 0.25 µm film thickness) and helium as the carrier gas (1 mL/min) and coupled to a high-resolution mass spectrometer sector-field instrument (HRGC–HRMS, Micromass UltimaNT, Waters, Manchester, UK) at 10,000 resolving power (10% valley definition). The results were expressed as toxic equivalents (TEQ) using the World Health Organization's toxicity equivalency factors (TEFs) as established in 2005 (van den Berg et al., 2006). Since PCDD, PCDF, and dl-PCB were listed as three POPs, results are reported for 7 PCDD and expressed as TEQ_PCDD), for 10 PCDF as TEQ_PCDF), and 12 dl-PCB as TEQ_PCB. Values for dl-POPs were reported in picogram per PUF (pg TEQ/PUF); all results were normalized to 1 PUF and 2 months exposure time. No conversion to volume was done.

The original coordinates for latitudes were grouped from north to south with "-" indicating location on southern hemisphere; the altitudes (in meter above sea level), and the temperatures (in °C) as shown in Table 2

Table 2: Description and denominations used for latitude, altitude, and temperature

Range	Latitude	Altitude (ranges in m)	Temperature (ranges in °C)
North of 23.5 °	N_23+	A_0-50	T<10
From 10 ° to 23.5 °	N_10-23	A_60-200	T_10-20
From-10 ° to 10 °	Eq	A_300-1000	T_20-25
From -10 ° to -23.5 °	S_10-23	A_1000-1999	T_25-30
South of 23.5 °	S_23+	A_2000+	T_30+

All data were maintained in Microsoft Office 365 Excel®; statistical evaluations were made using R packages with R-Studio. The Kruskal-Wallis H test was used to determine if there are statistically significant differences between the independent variables and dependent variables. Post-hoc analysis was performed using the pairwise Wilcoxon test with adjustment of the p-value using the Benjamini-Hochberg method. Significance level was set to p=0.05.

3 Results

The regional distribution of samples is shown in Table 1 and the number of samples within the various latitude, altitude, and temperature ranges in Table 3. It can be seen that the majority f the samples is located in the tropical region, *i.e.*, from 23 ° northern latitude to 23 ° southern latitude (N=130, corresponding to 67% of all samples). The most northern sampling station was in Ulaanbaatar, Mongolia, at 47.9 ° northern latitude, which is about the same as Vienna, Austria or Victoria, BC, Canada.

The majority of the sampling locations were located at quite low altitudes with 110 below 200 m. The PAC had only one country (Samoa, WSM) with two measurements in the range A_300-1000 (728 m). Ecuador (at 2742 m) and Ethiopia (at 2376 m) were above 2000 m; in addition, both were in the equator definition (Eq).

With respect to temperature, Africa was the hottest region. Temperatures below 10 °C and even below freezing point during the three months of exposures were found in Mongolia only.

Table 3: Number of samples/results by region and latitude (from north to south), altitude (increasing), and temperature (increasing)

	Latitude					Temperature				
Region	N_23+	N_10-23	Eq	S_10-23	S_23+	T<10	T_10-20	T_20-25	T_25-30	T_30+
Africa	25	12	40	12			17	21	34	17
Asia	6	22	2			4	4	1	20	1
PAC			14	9				3	20	
GRULAC	10	14	4	1	24		20	24	9	
Total	41	48	60	22	24	4	41	49	83	18

	Altitude					
Region	A_0-50	A_60-200	A_300-1000	A_1000-1999	A_2000+	Subtotal
Africa	16	10	37	21	5	89
Asia	4	20		6		30
PAC	14	7	2			23
GRULAC	24	15	10	2	2	53
Total	58	52	49	29	7	195

The main findings for dioxin-like POPs have been presented in a recent publication (Abad *et al.*, 2022). Here we report the results according to the listing of the dl-POPs in Annex C of the Convention, namely as TEQs for PCDD, PCDF, and dl-PCB. The overall median values for the 195 PUFs were 2.39 pg TEQ/PUF [min=0.000495 pg TEQ/PUF, max=22.8 pg TEQ/PUF] for TEQ_PCDD, 3.40 pg TEQ/PUF [<LOQ, max=56.1 pg TEQ/PUF] for TEQ_PCDF and 2.34 pg TEQ/PUF [min=0.0004 pg TEQ/PUF, max=16.4 pg TEQ/PUF] for TEQ_PCB. With respect to regional distribution, GRULAC had the highest median values for TEQ_PCDD and TEQ_PCB (5.0 pg TEQ/PUF and 2.62 pg TEQ/PUF) whereas TEQ_PCDF were highest in Asia (6.37 pg TEQ/PUF) (Figure 1). On a regional basis, the concentrations in the PUFs were significantly different with a p-value of 8.457×10^{-9} and pairwise significant differences for PAC (lowest median values for all three TEQs) with all other regions. No significant differences were found for Africa-Asia (p=0.12) and Asia-GRULAC (p=0.75).

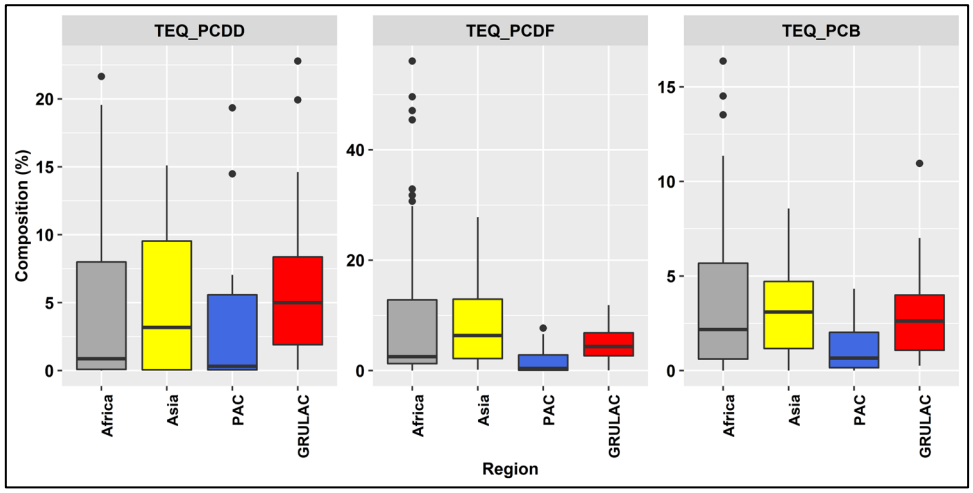

Figure 1: Box plot according to region
The whiskers represent the minimum and maximum concentrations without the outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper border is the third quartile (75%). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller the interquartile range multiplied by 1.5

Assessment of results according to latitude showed that for PCDD and PCDF, higher values were found on the northern hemisphere (Figure 2). In general, the values for locations at the equator were lower than at higher latitudes. The data generated for results at Eq were significantly different to all other temperature ranges (p-values between 0.022 and 1.2×10^{-10}). Great similarity was found for N:23+ with N_10-23 (p=0.70). Especially for TEQ_PCDF and TEQ_PCB, many outliers towards higher values were observed.

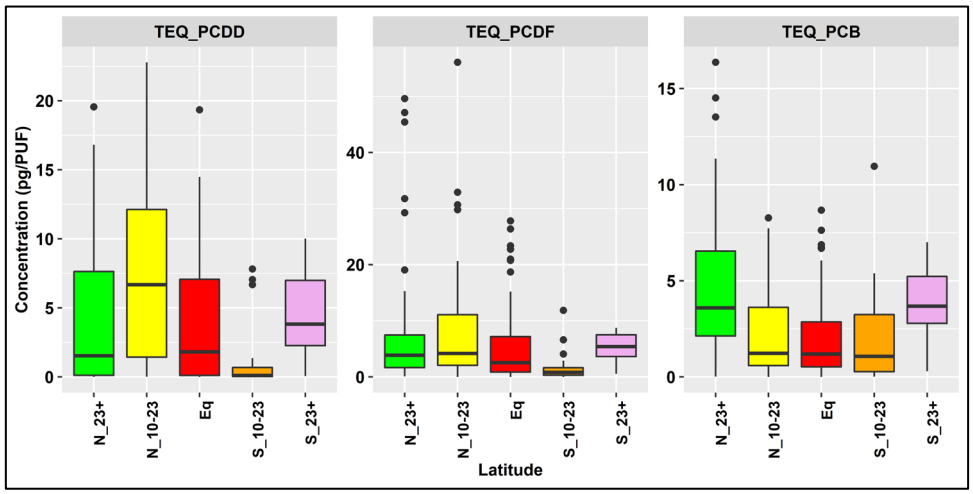

Figure 2: Box plot according to latitude

The concentrations found at the different altitudes did not confirm general assumptions that dioxin concentration increase with increasing altitudes. The median values at the higher temperature ranges were lower than those at the lower altitudes (below 1000 m) (Figure 3). With respect to altitude, the data were significantly different across all results ($p=9.347\times10^{-11}$; also, pairwise significant differences for all altitudes with exception of A_60-200 with A_300-1000 (p=0.217).
The distribution of results according to temperature is shown in Figure 4. The highest median values for all three TEQs were found at the highest temperatures, which were African countries (Ghana, Mali) but also one sample from Vietnam. The samples at T_30+ were statistically significantly different from all other (p-values <0.03 and lower). All other were statistically not significantly different with the exception of T_10-20 with T_25-30 (p=0.005).

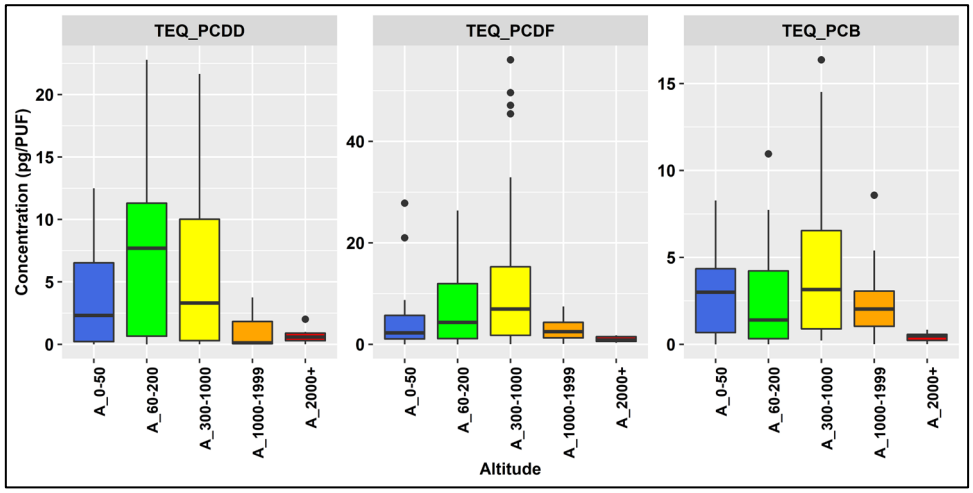

Figure 3: Box plot according to altitude

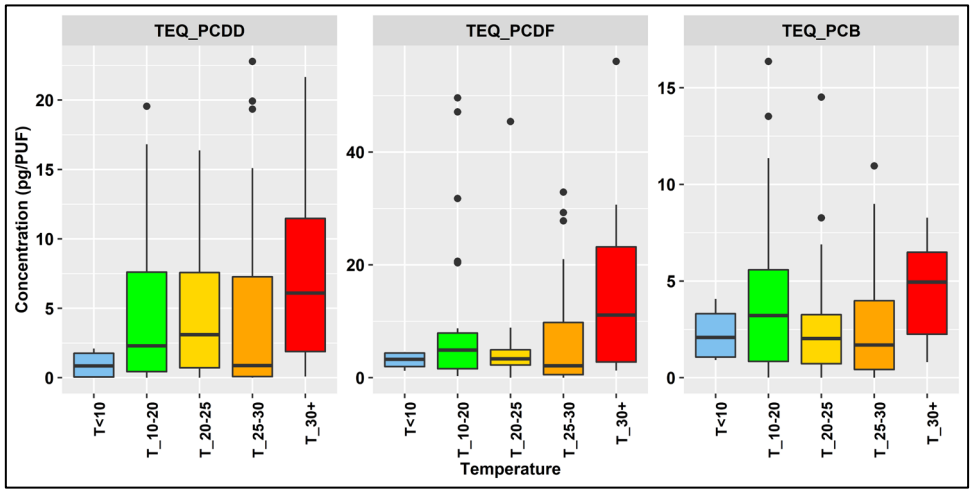

Figure 4: Box plot according to temperature

4 Discussion

The data generated in this project have been generated using a harmonized protocol that was applied in 42 countries including pre-cleaned PUFs in expert laboratories (UNEP, 2017) and one analytical chemical laboratory; thus, minimizing differences due to different suppliers of materials and interlaboratory variation. Our data from 42 developing countries confirm earlier results from the GMP1 project (Bogdal *et al.*, 2013; Fiedler *et al.*, 2013) but differ in so far, that the assessment of metadata did not confirm rough estimates such as that higher concentrations of PCDD/PCDF are associated with higher latitudes, higher altitudes or lower temperatures. Our data showed significant differences for all these parameters, indicating that nowadays global transport and partition process may be superseded by orography and local sources of PCDD, PCDF, and PCB.

5 Conclusions

The use of simple and cost-effective sampling equipment and approaches has shown to be a useful tool to assess ambient air concentrations. We advocate for comparison of mass concentrations in the sorbent and minimize manipulation of the data. With the reduction to a defined sampling period (3 months exposure but combination of four PUFs to an annual sample), countries would be able to monitor the PCDD, PCDF, and dl-PCB in ambient air. With the approach, it would not be possible to make predictions for other locations or years but a robust approach is provided to follow national trends.

6 Acknowledgments

This work was financed with UNEP grants and funds by the Global Environment Facility (GEF) to Örebro University and CSIC.

7 References

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