Assessing Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans in Air across Latin American Countries Using Polyurethane Foam Disk Passive Air Samplers

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S *Supporting Information*

ABSTRACT: A passive air sampling network has been established to investigate polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at Global Atmospheric Passive Sampling (GAPS) sites and six additional sites in the Group of Latin American and Caribbean Countries (GRULAC) region. The air sampling network covers background, agricultural, rural, and urban sites. Samples have been collected over four consecutive periods of 6 months, which started in January 2011 [period 1 (January to June 2011), period 2 (July to December 2011), period 3 (January to June 2012), and period 4 (July 2012 to January 2013)]. Results show that (i) the GAPS passive samplers (PUF disk type) and analytical methodology are adequate for measuring PCDD/F burdens in air and (ii) PCDD/F concentrations in air across the GRULAC region are widely variable by almost 2 orders of magnitude. The highest concentrations in air of Σ_{4-8}PCDD/Fs were found at the urban site São Luis (Brazil, UR) (i.e., 2560 fg/m^3) followed by the sites in São Paulo (Brazil, UR), Mendoza (Argentina, RU), and Sonora (Mexico, AG) with values of 1690, 1660, and 1610 fg/m^3, respectively. Very low concentrations of PCDD/Fs in air were observed at the background site Tapanti (Costa Rica, BA), 10.8 fg/m^3. This variability is attributed to differences in site characteristics and potential local/regional sources as well as meteorological influences. The measurements of PCDD/Fs in air agree well with model-predicted concentrations performed using the Global EMEP Multimedia Modeling System (GLEMOS) and emission scenario constructed on the basis of the UNEP Stockholm Convention inventory of dioxin and furan emissions.

■ INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are recognized as persistent organic pollutants (POPs) because of their properties of persistence, potential to bioaccumulate, and inherent toxicity to wildlife and humans.[1] Although PCDDs and PCDFs are restricted under the Stockholm Convention on POPs, they are still emitted unintentionally from numerous sources as by-products of chemical manufacturing, incineration, and other combustion-related activities.[2] This makes the estimate of PCDD and PCDF inventories and burdens more challenging compared to those of other chemicals. The unintentional production of PCDD/Fs as byproducts during the production of other chemicals (i.e., polychlorinated biphenyls, pentachlorophenol, and trichlorobenzene) and in industrial processes involving chloro-organic compounds (i.e., pulp and paper industry) was a major source in the past, leading to PCDD and PCDF emissions via contamination products (i.e., pentachlorophenol-treated wood, leather, and textiles) and emissions directly to water and soil. Stricter legislation and the introduction of new processes reduced these sources significantly in most countries.[1] Today, thermal processes are the major sources of PCDDs and PCDFs in the air, e.g., municipal solid waste incineration (MSWI) with PCDDs and PCDFs associated with fly and bottom ash. While the PCDD and PCDF emissions from MSWI have been reduced in recent years through optimizing incineration conditions, this still provides the major contribution to the total PCDD and PCDF emissions in most countries.[1]

Under Article 16 of the Stockholm Convention, dealing with its Effectiveness Evaluation, there is a need to measure PCDDs and PCDFs in air under a regionally based Global Monitoring Plan (GMP). Air is one of two core media targeted under the GMP (human tissues being the other). The measurements in air should include both temporal and spatial resolution to evaluate the effectiveness of control measures and to provide information about the long-range transport of PCDDs and PCDFs. Air monitoring data for PCDDs and PCDFs from national networks are available for Northern America from the Canadian National Air Pollution Surveillance network (NAPS), the U.S. National Dioxin Air Monitoring Network (NDAMN), and the Mexican Dioxin Air Monitoring Network (MDAMN).[3]

In the first GMP report submitted in 2009, it was recognized that information about PCDDs and PCDFs in air in the Group of Latin American and Caribbean States (GRULAC) was lacking. Fiedler recently published a review of PCDD and PCDF emission estimates provided to United Nations Environment Programme (UNEP) by participating countries.[4] The review highlighted MSWI as the main source of PCDDs and PCDFs to air, followed by open burning processes and heat and power generation. The UNEP global emission inventory for PCDDs and PCDFs was used to link emissions to a country's economic status[5] and in the Global European Monitoring and Evaluation Programme (EMEP) Multimedia Modeling System (GLEMOS) to estimate global PCDD and PCDF concentrations in air.[6]

Thus, the objective of this project was to further assess the suitability of the polyurethane foam (PUF) disk passive air sampler for PCDDs and PCDFs and to address this gap in data and implement an air monitoring network for PCDDs and PCDFs that can deliver baseline information about PCDDs and PCDFs in air. It will also serve as a baseline against which future concentrations in air can be compared so as to inform on the "effectiveness" of the Stockholm Convention on POPs on reducing levels of PCDDs and PCDFs in air in the GRULAC region.

■ METHOD

Study Design. The compounds targeted in this study are the tetra-chlorinated (TCDD/Fs), penta-chlorinated (PeCDD/Fs), hexa-chlorinated (HxCDD/Fs), hepta-chlorinated (HpCDD/Fs), and octa-chlorinated (OCDD/Fs) dibenzo-p-dioxins/furans. Results are reported as the sums of the homologue groups as well as the 17 individual 2,3,7,8 chloro-substituted PCDDs and PCDFs (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,23,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD).

Passive air samples were collected during the period from January 2011 to March 2013 at 13 sites in six South American countries (Mexico, Costa Rica, Ecuador, Colombia, Brazil, and Argentina). The sampling sites spanned a longitude of 44−110°W and a latitude of 52°S−27°N. The average temperatures at the sites during the deployment period ranged from 7.6 °C at the most southern site to 25.8 °C at the northern sites. The sampling sites were classified as "background" (BA; $n = 6$), "agricultural" (AG; $n = 1$), "rural" (RU; $n = 3$), and "urban" (UR; $n = 3$) depending on land use and population density. The sampling periods were ∼6 months, and the consecutive samples collected per site vary ($n = 1−4$) [period 1 (January to June 2011), period 2 (July to December 2011), period 3 (January to June 2012), and period 4 (July 2012 to January 2013)]. The sampling period of 6 months ensures a higher effective sampling volume for PCDDs and PCDFs and allows for a higher level of accumulation of the target chemicals on the sampling medium in background areas. Figure 1 and Tables 1 and 2 of the Supporting Information summarize information about the sites that comprise the PCDD and PCDF passive air monitoring network.

Precleaning Procedure for Passive Sampling Media. PUF disks were precleaned using an Accelerated Solvent Extractor (ASE) (one cycle of 200 mL of acetone and two cycles of 200 mL of hexane) and dried under ultra-high-purity (UHP) grade nitrogen in a vacuum oven at 30−40 °C. PUF disks were stored in 1 L amber jars for shipping.

Sample Collection. A sampling kit including a sampling protocol, precleaned PUF disks, and a passive sampler housing was shipped from Environment Canada to the participating partners on site. Details of the sampling process can be found in the sampling protocol in Text 1 of the Supporting Information. In short, the sampler housing was installed at a minimum of 2 m from the ground in an unobstructed air flow. PUF disks were installed and removed from the sampler housing using clean forceps. Sampling media were stored in a dark and cool place prior to and after deployment. Field blanks ($n = 14$) were collected by following the same steps as for the air samples but without actual deployment. The field blanks are used to assess possible contamination associated with the methodology and sample treatment. Samples were returned to Environment Canada for analysis.

Extraction and Analysis. PUF disks were spiked with a known amount of isotopically labeled surrogate standards ($[^{13}C_{12}]$TCDD, $[^{13}C_{12}]$TCDF, $[^{13}C_{12}]$PeCDD, $[^{13}C_{12}]$PeCDF, $[^{13}C_{12}]$HxCDD, $[^{13}C_{12}]$HxCDF, $[^{13}C_{12}]$HpCDD, $[^{13}C_{12}]$-HpCDF, and $[^{13}C_{12}]$OCDD; all standards were supplied by Wellington Laboratories Inc., Guelph, ON) and then extracted with toluene by a Soxhlet apparatus for 16−20 h. After extraction, samples were cleaned up using column chromatography with an

Table 1. Information about the 13 Sampling Sites, Average Concentrations, and Minimum and Maximum Values[a]

site	country	land use	n	T [°C]	latitude (deg)	longitude (deg)	Σ_{4-8}PCDD/Fs (fg/m³)			Σ_{17}TEQ PCDD/Fs (fg of TEQ/m³)		
							mean	minimum	maximum	mean	minimum	maximum
Sonora	Mexico	AG	4	24.5	27.1	−109.9	1310	893	1610	19.8	16.5	24.1
Yucatan	Mexico	BA	4	25.8	20.9	−90.4	546	513	606	7.29	5.69	8.16
Tapanti	CostaRica	BA	2	14.1	9.8	−83.9	14.4	10.8	18.1	<MDL	<MDL	<MDL
Quito	Ecuador	UR	2	15.9	−0.1	−78.5	213	208	218	3.58	2.78	4.38
Manizales	Columbia	BA	4	13.6	5.1	−75.4	286	223	444	4.63	3.54	7.37
Arauca	Columbia	RU	4	27.3	7.1	−70.8	167	128	195	2.98	2.36	3.46
São Paulo	Brazil	UR	2	20.5	−23.6	−46.7	1580	1470	1690	24.9	20.2	29.5
São Luis	Brazil	UR	2	27.9	−2.4	−44.1	1630	701	2560	29.6	16.7	42.5
São Jose dos Ausentes	Brazil	BA	2	15.1	−28.6	−49.8	46.2	34.5	57.7	1.23	1.15	1.31
Salta	Argentina	BA	2	18.4	−25.1	−66.1	25.7	21.0	30.3	0.852	0.699	1.005
Malargüe	Argentina	BA	1	12.6	−35.5	−69.6	71.9	NA	NA	1.65	NA	NA
Mendoza	Argentina	RU	1	14.7	−33.9	−69.1	1660	NA	NA	24.1	NA	NA
Rio Gallegos	Argentina	RU	2	7.6	−51.6	−69.2	757	655	859	9.12	8.27	10.0

[a]Abbreviations: *n*, number of collected samples; *T*, average temperature during the sampling period; MDL, method detection limit; NA, not available; Σ_{4-8}PCDD/Fs, sum of all homologue groups; Σ_{17}TEQ PCDD/Fs, sum of TEQ of 17 2,3,7,8-chloro-substituted PCDD/Fs; BA, background; AG, agricultural; RU, rural; UR, urban.

acid/base column followed by an activated alumina column. The fraction containing the PCDDs and PCDFs was eluted with a dichloromethane (DCM)/hexane mixture [50/50 (v/v)] and blown down to dryness. A known concentration of internal standard ($[^{13}C_{12}]$-1,2,3,4-TCDD and $[^{13}C_{12}]$-1,2,3,7,8, 9-HxCDD) was added prior to analysis by gas chromatography (GC) and high-resolution mass spectrometry (Agilent 6890 and Waters MicromassAutoSpecUltima HRMS). Samples were analyzed via electron impact ionization in selective ion mode on a 60 m DB-5 column (0.25 mm inside diameter, 0.25 μm film thickness). Samples were injected in splitless mode (injector temperature of 290 °C) with helium as the carrier gas. The GC oven temperature program began at 100 °C for 1 min and was increased at a rate of 35 °C/min to 200 °C, then at a rate of 4 °C/min to 280 °C, where it was held for 15 min, and then at a rate of 10 °C/min to 300 °C, where it was held for 5 min.[3,7]

Quality Assurance (QA) and Quality Control (QC). Results for field blanks and method recoveries are presented in Tables 3 and 4 of the Supporting Information. Average recoveries of surrogates ranged from 93 to 103%, and analysis of field blanks showed no major contamination issues, with most PCDDs and PCDFs falling below the instrumental detection limit in field blanks. The method detection limit (MDL) was calculated as the average concentration of the field blanks plus 3 times the standard deviation of the field blanks. The MDL is reported in Table 3 of the Supporting Information. For data interpretation, values below the MDL were replaced by $^2/_3 \times$ MDL.

Global EMEP Multimedia Modeling System (GLEMOS). PCDD and PCDF air concentrations for the sampling sites were estimated using GLEMOS and the UNEP Stockholm Convention emission inventory of dioxins and furans. Details of GLEMOS and the emission inventory are discussed by Gusev et al.[6,8]

RESULTS AND DISCUSSION

Passive Air Sampling Basics for PCDDs and PCDFs. PCDDs and PCDFs are semivolatile compounds, and at ambient temperatures, most of the PCDDs and PCDFs are associated with the particle phase rather than the gas phase because of their low volatility.[9] At the temperatures observed during the study, only the lighter homologue groups (TCDFs, PeCDFs, and

TCDDs) will be found predominately in the gas phase.[10] A recent analysis of PUF disk samplers for the uptake of the mostly particle-bound polycyclic aromatic hydrocarbons indicates that particle-phase compounds are captured at rates similar to those of the gas-phase compounds.[11,12] Mari et al. published data on PCDDs and PCDFs acquired simultaneously by passive and active air sampling. Average PCDD and PCDF sampling rates estimated from concentrations in the combined gas and particle phase were more realistic (2.0 m³/day) than values estimated solely from the gas-phase concentration (25 m³/day).[13]

The conversion of an amount accumulated in the sampler to a concentration in air basis involves the derivation of effective air sample volumes as is done under the GAPS Network.[14,15] Linear uptake can be assumed for the PCDDs and PCDFs for the entire sampling period because of their low volatility. Therefore, the equivalent air volume is simply the product of the linear gas-phase sampling rate of the PUF disk sampler (i.e., ~4 m³/day) and the deployment time (e.g., 180 days for a 6 month deployment). This results in an effective air sample volume of ~720 m³.

Monitored PCDD and PCDF Concentrations in Air. Σ_{4-8}PCDD/F concentrations (average, minimum, and maximum) in air are summarized in Table 1. Concentrations in air observed during the 6 month deployment periods are reported in Table 5 of the Supporting Information. The highest concentrations in air of Σ_{4-8}PCDD/Fs were at the urban site, São Luis (Brazil, UR) (i.e., 2560 fg/m³), while the lowest concentrations were at the background site, Tapanti (Costa Rica, BA) (10.8 fg/m³). Correlations were determined between the observed PCDD and PCDF concentrations in air and site-specific properties such as land use, latitude, and average temperature. No significant trends were observed. This suggests that PCDD and PCDF concentrations in air are more likely associated with local sources.

At the majority of sites, two consecutive 6 month samples were collected. There was no substantial difference between the timing and duration of sampling periods at the individual sites. The PCDD and PCDF data from the sites Sonora (Mexico, AG), Yucatan (Mexico, BA), Manizales (Colombia, BA), and Arauca (Colombia, RU) are available for all four sampling intervals between January 2011 and December 2012. No substantial differences or seasonal trends were observed between the PCDD
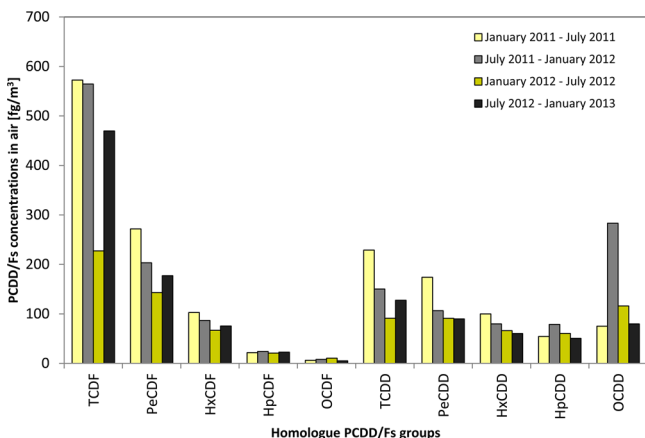
Figure 1. Concentrations in air of the sums of the individual PCDD and PCDF homologue groups for four consecutive sampling periods at Sonora (Mexico, AG).

and PCDF concentrations in air for the different 6 month sampling periods at the individual sites (Figure 1 for Sonora and Figure 2 of the Supporting Information for Yucatan, Manizales, and Arauca). Other studies have reported seasonal variations for PCDD and PCDF concentrations in air between winter and

summer seasons.[10,16,17] However, the 6 month sampling periods in this study span both winter and summer months, so no seasonal variations are expected.

The toxic equivalent (TEQ) values were calculated for the 17 most toxic 2,3,7,8-chloro-substituted PCDDs and PCDFs using international toxic equivalency factors (TEFs).[1] The highest monitored TEQ values were found for 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF with average values of 3.2 fg of TEQ/m^3 (0.10−12 fg of TEQ/m^3) and 3.0 fg of TEQ/m^3 (0.13−14 fg of TEQ/m^3) respectively. The values for Σ_{17}TEQ PCDD/Fs ranged from 0.7 to 43 fg of TEQ/m^3 with the highest concentrations observed at São Luis (Brazil, UR) and the lowest quantifiable data at Salta (Argentina, BA). Average values for Σ_{4-8}PCDD/Fs are listed in Table 1.

Values monitored at Tapanti for the individual 2,3,7,8-chloro-substituted forms were all below the MDL. The concentration trends for the Σ_{17}TEQ PCDD/Fs values mirror the trends observed for the total Σ_{4-8}PCDD/F concentrations in air with the higher values of 30, 24, and 24 fg of TEQ/m^3 monitored at São Paulo (Brazil, UR), Mendoza (Argentina, RU), and Sonora (Mexico, AG), respectively. Figure 2 shows the distribution of the average TEQ concentrations in air for the individual congeners at all sites.
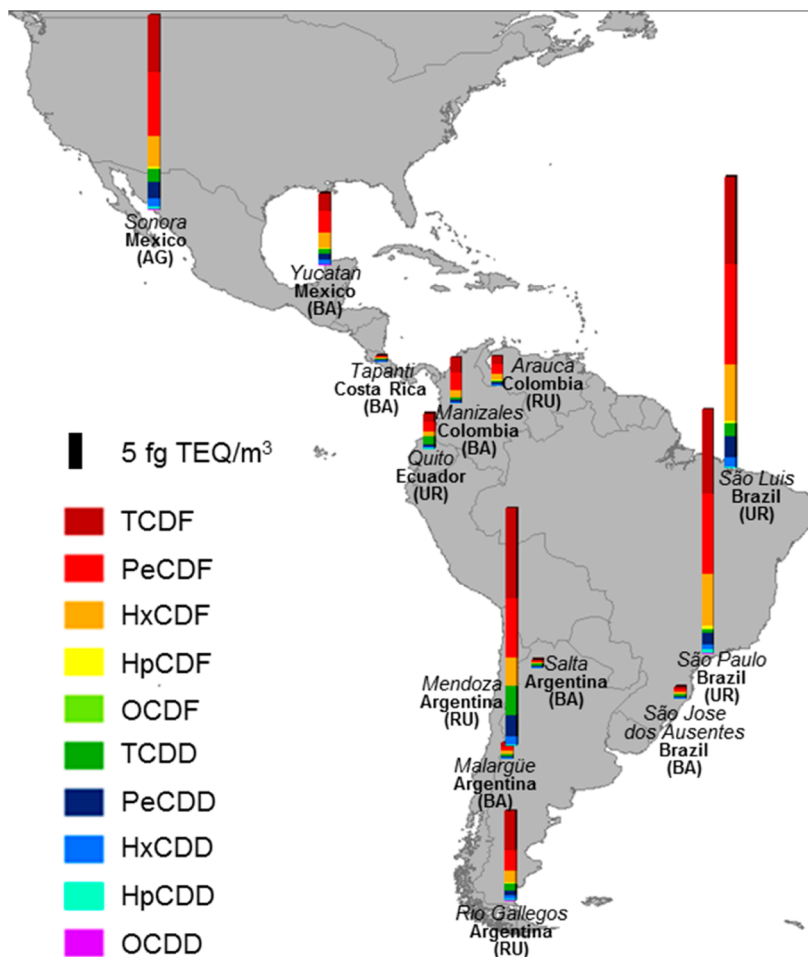

Figure 2. Concentrations of 2,3,7,8-substituted PCDDs and PCDFs in air in the GRULAC region (femtograms of TEQ per cubic meter of air). The individual homologues represented are as follows: TCDF = 2,3,7,8-TCDF, PeCDF = $\sum$(1,2,3,7,8-PeCDF; 2,3,4,7,8-PeCDF), HxCDF = $\sum$(1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF), HpCDF = $\sum$(1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF), OCDF, TCDD = 2,3,7,8-TCDD, PeCDD = 1,2,3,7,8-PeCDD, HxCDD = $\sum$(1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD), HpCDD = 1,2,3,4,6,7,8-HpCDD, OCDD.

Comparison to PCDD and PCDF Levels Published in Other Studies. The TEQ values observed for the GRULAC region in this study are on the same order of magnitude as other concentrations in air reported in recent studies. Bogdal et al. reported concentrations derived from passive samplers deployed between 2010 and 2011 in the GRULAC region, ranging from 9 to 678 fg of TEQ/m^3.[18,19] As two sites that were monitored in the 2010−2011 study were also used in this study, a direct comparison of the observed concentrations in air is possible. Bogdal et al. published monitoring results as sample loads (picograms per PUF), which were here converted to concentrations in air for the purpose of comparison by applying the sampling rate of 4 m^3/day resulting in derived average TEQ concentrations for São Paulo (Brazil, UR) and Quito (Ecuador, UR) of 34 and 5.3 fg of TEQ/m^3, respectively. These are within a factor of 2 of results from this study of 25 fg of TEQ/m^3 (January to December 2012) and 3.6 fg of TEQ/m^3 (January to December 2011), respectively. This study observed an average concentration in air of 4.6 fg of TEQ/m^3 between January 2011 and December 2012 at the background site Manizales (Colombia, BA) in a nature reserve 11 km from the city limits, whereas Aristizábal et al. reported values between 1 and 52 fg of TEQ/m^3 for 2009−2010 at an urban site in Manizales.[20] The MDAMN study site Celestún at Yucatan is identical with the site in this study. MDAMN applied active air samplers, and results from 2011−2012 show a PCDD and PCDF concentration in air for four 6 day samples ranging from 5.6 to 26 fg of TEQ/m^3. With the exception of one unusually high value reported by MDAMN for February 2012, the 6 month integrated PCDD and PCDF concentrations from this study that range from 5.7 to 8.2 fg of TEQ/m^3 are in the same range as the MDAMN values.[3]

Other studies reported a wide range of PCDD and PCDF concentrations in air for other areas around the world. Bogdal et al. reported concentrations in air ranging from 18 to 532 fg of TEQ/m^3 and from 1 to 87 fg of TEQ/m^3 for Africa and the Pacific Islands, respectively.[19] For Europe, recent values were reported for Catalonia, Spain, 17−348 fg of TEQ/m^3 (for 1994−2002 for 28 sites[21]), for Barcelona, Spain, 11−39 fg of TEQ/m^3 (2005[13]), for Italy, 2.9−65 fg of TEQ/m^3 (2000−2001[22]), for Zurich, Switzerland, 11−190 fg of TEQ/m^3 (2010−2011[16]), and for the United Kingdom, <50 fg of TEQ/m^3 (2005−2008[23]). Li et al. reported concentrations in air of 1−145 fg of TEQ/m^3 in Anshan, Northeast China, for 2008−2009.[17]

Comparison to Modeled PCDD and PCDF Levels. Measured PCDD and PCDF air concentrations in the GRULAC region were compared with the results of a pilot modeling study, performed using the Global EMEP Multimedia Modeling System (GLEMOS) and emission scenario constructed on the basis of the UNEP Stockholm Convention inventory of dioxin and furan emissions.[6,8] Model predictions obtained for 2012 were in reasonable agreement with measured air concentrations. For more than half of the sites, modeled values were within a factor of 2 of measurements and found to correlate with observed levels (Figure 3). Some sites showed concentrations higher than those predicted by the model, especially for some of the rural and urban sites (e.g., São Luis and Mendoza). The largest difference was obtained for the site Rio Gallegos (more than 1 order of magnitude), which is likely caused by the uncertainties in the spatial distribution of PCDD and PCDF emissions. The model used population densities for the estimations of the PCDD and PCDF emissions grid and possibly underestimated local PCDD and PCDF sources.
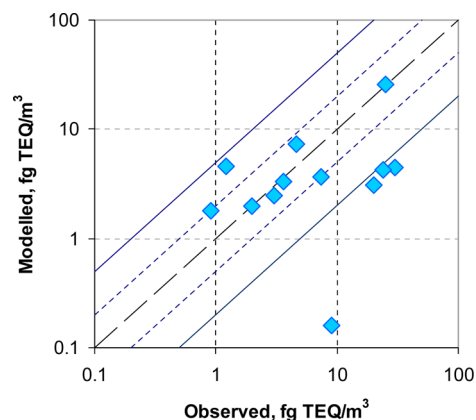

Figure 3. Comparison of modeled annual mean PCDD and PCDF air concentrations for 2012 (femtograms of TEQ per cubic meter) with measurements performed in the GRULAC region. The black large dashed line is the 1:1 ratio. Blue dashed lines denote the area of agreement within a factor of 2 and solid lines the area of agreement within a factor of 5.

PCDD and PCDF Homologue Distribution. The PCDD and PCDF homologue contributions to Σ_{4-8}PCDD/F can be an indication of the origin of the emissions and/or reflect weathering after emission. In general, the most dominant PCDDs and PCDFs in this study were OCDD and 2,3,7,8-TCDF, with average concentrations of 35 and 30 fg/m^3, respectively. This agrees with the general pattern reported for the 2,3,7,8-substituted PCDDs and PCDFs in air.[10,13] Higher OCDD concentrations in air were previously explained by an atmospheric removal rate lower than those of other PCDDs.[24] Gullett and Tuoati also reported OCDD and TCDFs as the dominant PCDD and PCDF homologues that are released during biomass burning.[25] This differs from more industrial emission profiles and might be related to ongoing deforestation processes in some countries of the GRULAC region. The PCDF congeners show decreasing concentrations in air with an increasing degree of chlorination, whereas PCDDs show increasing concentrations in air with an increasing degree of chlorination (Figure 4). This
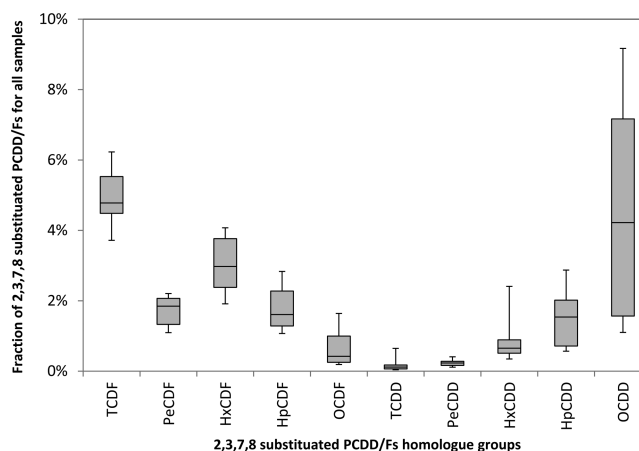

Figure 4. Box-whisker plots for the fractions of 2,3,7,8-substituted PCDD and PCDF homologue groups of the Σ_{4-8}PCDD/Fs plotted for all samples to show the variations found in this study. The boxes show median concentrations and the 25th and 75th percentiles, and 10th and 90th percentiles are indicated by the whiskers.

pattern was observed in PCDD and PCDF air sampling campaigns conducted with both passive and active samplers,

which is further evidence that the PUF disk sampler is suitable for monitoring both gas- and particle-phase PCDDs and PCDFs.[10]

In general, the relative contributions of the individual PCDD/F congeners to Σ_{4-8}PCDD/F were consistent for most sites in this study. However, the three sites, Manizales (Colombia, BA), Arauca (Colombia, RU), and São Luis (Brazil, UR), exhibited consistently mass%(2,3,7,8-TCDF) > mass %(OCDD), which sets their congener pattern apart from those of the other sites in this study. This likely reflects a different dominant PCDD and PCDF emission source for these three sites compared to those of the other sites in this study.

Overall, there was no shift in the PCDD and PCDF contributions between the different sampling periods at the individual sites. The ΣPCDDs/ΣPCDFs ratio ranged from 0.18 to 1.2, which is within the reported range of 0.13−21.[10]

■ IMPLICATIONS

This study is among the first to report concentrations of PCDDs and PCDFs in air in South America. In addition to establishing baseline data for air across the region, the study establishes a suitable monitoring network for PCDDs and PCDFs that is based on the GAPS Network and the PUF disk passive air sampler. This cost-effective approach is a model that can be used in other regions to assess spatial and temporal trends of PCDDs and PCDFs for reporting under the Global Monitoring Plan of the Stockholm Convention on POPs. Furthermore, the study demonstrates how the results from passive samplers can be integrated with emission inventories and models to better assess the effectiveness of control measures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Individual PCDD and PCDF data observed in this study, information about the sampling sites, and the sampling protocol provided to the participants of this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Fiedler, H. Dioxins and furans (PCDD/PCDF). In *Persistent Organic Pollutants*; Springer: Berlin, 2003; pp 123−201.

(2) Lee, W.-S.; Chang-Chien, G.-P.; Wang, L.-C.; Lee, W.-J.; Tsai, P.-J.; Wu, K.-Y.; Lin, C. Source identification of PCDD/Fs for various atmospheric environments in a highly industrialized city. *Environ. Sci. Technol.* **2004**, *38* (19), 4937−4944.

(3) Wöhrnschimmel, H.; Yao, Y. Assessing Comparability of Atmospheric PCDD, PCDF and Coplanar PCB Data from North American Ambient Air Monitoring Networks. 2014.

(4) Fiedler, H. National PCDD/PCDF release inventories under the Stockholm Convention on Persistent Organic Pollutants. *Chemosphere* **2007**, *67* (9), S96−S108.

(5) Cao, Z.; Fiedler, H.; Wang, B.; Zhang, T.; Yu, G.; Huang, J.; Deng, S. Economic status as a determinant of national PCDD/PCDF releases and implications for PCDD/PCDF reduction. *Chemosphere* **2013**, *91* (3), 328−335.

(6) Gusev, A.; Rozovskaya, O.; Shatalov, V.; Aas, W.; Nizzetto, P. Persistent Organic Pollutants in the Environment; Norwegian Institute for Air Research (NILU): Kjeller, Norway, 2014.

(7) Dann, T. Ambient Air Measurements of Polycyclic Aromatic Hydrocarbons (PAH), Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans in Canada (1987−1997); Environment Canada: Ottawa, ON, 1998.

(8) Gusev, A.; Shatalov, V.; Rozovskaya, O. Pilot Modelling of PCDD/F Transport and Fate on Global Scale and within the European Region. *Organohalogen Compounds*, in press.

(9) Harner, T.; Green, N. J.; Jones, K. C. Measurements of octanol-air partition coefficients for PCDD/Fs: A tool in assessing air-soil equilibrium status. *Environ. Sci. Technol.* **2000**, *34* (15), 3109−3114.

(10) Lohmann, R.; Jones, K. C. Dioxins and furans in air and deposition: A review of levels, behaviour and processes. *Sci. Total Environ.* **1998**, *219* (1), 53−81.

(11) Harner, T.; Su, K.; Genualdi, S.; Karpowicz, J.; Ahrens, L.; Mihele, C.; Schuster, J.; Charland, J.-P.; Narayan, J. Calibration and application of PUF disk passive air samplers for tracking polycyclic aromatic compounds (PACs). *Atmos. Environ.* **2013**, *75*, 123−128.

(12) Eng, A.; Harner, T.; Pozo, K. A Prototype Passive Air Sampler for Measuring Dry Deposition of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 77−81.

(13) Mari, M.; Schuhmacher, M.; Feliubadaló, J.; Domingo, J. L. Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers. *Chemosphere* **2008**, *70* (9), 1637−1643.

(14) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C.; Jones, K. C. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environ. Sci. Technol.* **2009**, *43* (3), 796−803.

(15) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36* (19), 4142−4151.

(16) Bogdal, C.; Müller, C. E.; Buser, A. M.; Wang, Z.; Scheringer, M.; Gerecke, A. C.; Schmid, P.; Zennegg, M.; MacLeod, M.; Hungerbühler, K. Emissions of Polychlorinated Biphenyls, Polychlorinated Dibenzo-p-dioxins, and Polychlorinated Dibenzofurans during 2010 and 2011 in Zurich, Switzerland. *Environ. Sci. Technol.* **2014**, *48* (1), 482−490.

(17) Li, X.; Li, Y.; Zhang, Q.; Wang, P.; Yang, H.; Jiang, G.; Wei, F. Evaluation of atmospheric sources of PCDD/Fs, PCBs and PBDEs around a steel industrial complex in northeast China using passive air samplers. *Chemosphere* **2011**, *84* (7), 957−963.

(18) Bogdal, C. Report on Passive Air Sampling under the Global Monitoring Plan for Persistent Organic Pollutants: GMP Projects 2010−2011; United Nations Environment Programme/DTIE: Nairobi, Kenya, 2012.

(19) Bogdal, C.; Scheringer, M.; Abad, E.; Abalos, M.; van Bavel, B.; Hagberg, J.; Fiedler, H. Worldwide distribution of persistent organic pollutants in air, including results of air monitoring by passive air sampling in five continents. *TrAC, Trends Anal. Chem.* **2013**, *46*, 150−161.

(20) Aristizábal, B. H.; Gonzalez, C. M.; Morales, L.; Abalos, M.; Abad, E. Polychlorinated dibenzo-p-dioxin and dibenzofuran in urban air of an Andean city. *Chemosphere* **2011**, *85* (2), 170−178.

(21) Abad, E.; Caixach, J.; Rivera, J.; Gustems, L.; Massagué, G.; Puig, O. Temporal trends of PCDDs/PCDFs in ambient air in Catalonia (Spain). *Sci. Total Environ.* **2004**, *334*−*335*, 279−285.

(22) Menichini, E.; Iacovella, N.; Monfredini, F.; Turrio-Baldassarri, L. Atmospheric pollution by PAHs, PCDD/Fs and PCBs simultaneously collected at a regional background site in central Italy and at an urban site in Rome. *Chemosphere* **2007**, *69* (3), 422−434.

(23) Katsoyiannis, A.; Gioia, R.; Sweetman, A. J.; Jones, K. C. Continuous Monitoring of PCDD/Fs in the UK Atmosphere: 1991−2008. *Environ. Sci. Technol.* **2010**, *44* (15), 5735−5740.

(24) Brubaker, W. W.; Hites, R. A. Polychlorinated Dibenzo-p-dioxins and Dibenzofurans: Gas-Phase Hydroxyl Radical Reactions and Related Atmospheric Removal. *Environ. Sci. Technol.* **1997**, *31* (6), 1805−1810.

(25) Gullett, B. K.; Touati, A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003**, *37* (6), 803−813.