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CALCULATION OF PASSIVE AIR SAMPLING RATES OF DIOXINS AND FURANS USING SIMPLE LINEAR REGRESSION

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Introduction

Passive air sampling of Polyurethane Foam (PAS-PUF) disk is widely used for measurements of Persistent Organic Pollutants (POPs). Several field-based calibration studies of the PUF disk have shown that sampling rates are typically around 4 m³ day-1 relative to gas- and particle-phase compounds. Nonetheless, there are discrepancies regarding compound specific sampling rate (R_s)[1–4]; Rs may vary significantly according to classes and individual compounds within each class. This seems an unlikely behaviour since the accumulation of chemical by a passive sampling medium is driven by the mass-transfer across the PAS-PUF-air interface[5]. In order to effectively calculate the passive sampling rates, a simple linear regression model was tested to determine the specific air sampling rates of PCDD/F homologue groups.

Materials and methods

Study design

Concentrations of seventeen 2,3,7,8-chloro-substituted PCDDs and PCDFs from a field-based calibration study conducted previously were used for the calculation of Rs. Details about the air sampling and analysis procedures have been presented elsewhere[4,6,7]. In summary, passive and active samplers were deployed at urban, urban/industrial and background sites in São Paulo, SP - Brazil, over two consecutive 4-month periods: September to December 2014 (period 1) and May to August 2015 (period 2). Active samples were collected during 120h each around 10 days, representing between 15 – 30% of the 4-month integration period of PUF disk passive sampling.

Sampling rates (Rs)

Specific sampling rate were obtained using two methods as follows:

Method 1: this procedure is commonly used in the literature for PUF-PAS, and it consists of dividing the amount of a given compound (pg) accumulated in the PUF-PAS at a given exposure time ($C_{PUF\text{-}PAS}$) by the average air concentration (pg m³), gas + particle phase, measured by the active sampler (C_{act}), according to equation (1).

$R_s = C_{PUF\text{-}PAS}/C_{act} \times t$ (1)

Where R_s is the specific sampling rate (m³ day-1).

Method 2: performing a linear regression analysis. The accumulated PCDD/F levels (pg/sampler/day) from passive air samplers were assumed as the dependent variable (Y) while the exposure time (day) as the independent variable (X). PCDD/F concentrations, when analysed by Kolmogorov-Smirnov test, returned normal distribution. Scatter plots were used to display Y and X values and the simple linear regression model assumed for each class of compound ($Y=\beta_0+\beta_1X$) according to Figure 1. The slope of the linear regression (β_1) represents the sampling rate of PCDD/Fs, m³/day. The regression analysis was performed for both periods (1 and 2) and sampling sites (urban, urban/industrial and background). The accuracy and significance of the model were tested, respectively, by coefficient of determination (r^2) and p-value (<0.05). Statistical analyses were carried out using the free software RStudio, version 3.1.2 (2014-10-31).

Results and discussion:

The corresponding regression lines for PCDDs and PCDFs are shown in Figure 1 and Table 1 shows the regression coefficients and statistical significance for the PCDD/F trends. These results represent the data from urban, urban/industrial and background sites in period 1 and 2. Poor linear relationship was found for some congeners, and there was no statistical significance for few compound trends (p-value

>0.05). A possible explanation for this may be the low PCDD/F levels (<LOQ - limit of quantification) and missing data.

The low p-value ($p<0.05$) showed high statistical significance for the linear regression and the high coefficient of determination ($r^2>0.6$) ensures that the model is accurate (Table 1). The coefficient β_1 represents the sampling rate. Figure 3 shows the comparison of R between methods 1 and 2. It was not observed seasonality of the sampling rate for both methods. Sampling rate obtained by Method 2, ranged from 1.17 to 5.17 m^3/day with only a few outliers. These values seem more realistic compared to the typical sampling rate (4 m^3/day). Method 1 showed lower sampling rates (from 0.50 to 2.64 m^3/day). Figure 2 shows linear trend considering all PCDD/F congeners, in this case passive sampling rate is 2.99 m^3/day. Previous studies have indicated low PCDD/F sampling rates[1-4], however; there are various uncertainties in the methods to derive sampling rates, such as sampling artifacts associated with active and passive samplers, meteorological conditions, averaging errors of C_{act}, etc.

When using PUF-PAS, a linear uptake can be assumed for the PCDDs and PCDFs for the entire the 4-month integration period because of their high Koa (values greater than about 10^9), since the uptake phase of equilibrium has been shown to be proportional to the PUF-air partition coefficient, which also is correlated to the octanol-air partition coefficient (Koa) of the compound[5].

Future studies should include temperature, wind speed, and ozone concentration in a multiple linear regression that could explore the potential artifacts in passive air sampling and derive more accurate coefficients for the estimative of R using method 2.

Linear regression analysis showed more realistic sampling rates compared to method 1 wich is commonly used in the literature for PUF-PAS. The passive sampling rate (Method 2) was around two times higher than Rs (method 1), which shows that PUF disk sampling rates are similar for PCDD/Fs, and averaged 4 m^3/day. The estimate of the sampling rate can be further improved by taking into account for artifacts in active and passive air sampling, meterological conditions and ozone concentrations, using multiple linear regression.

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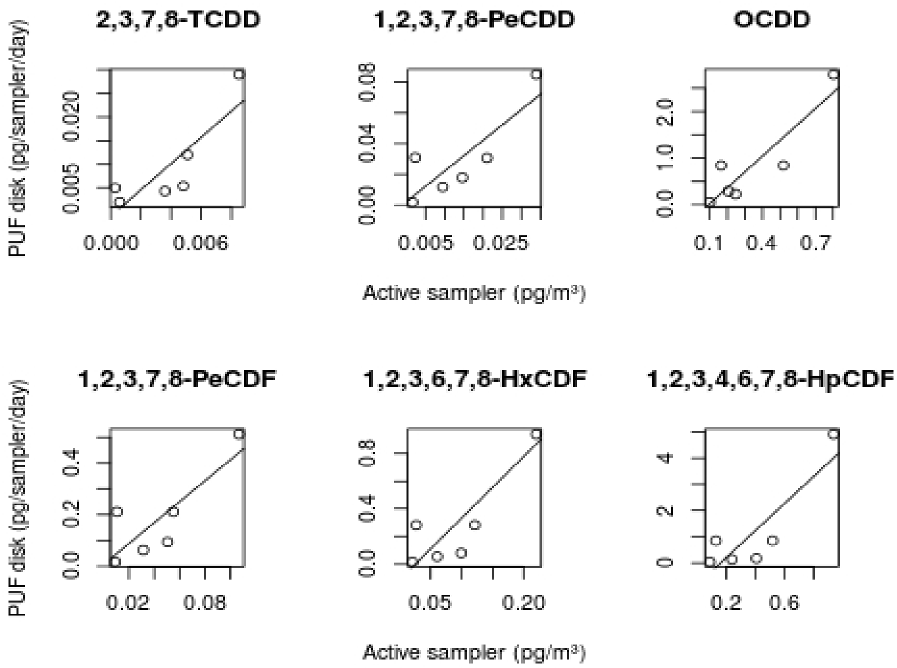
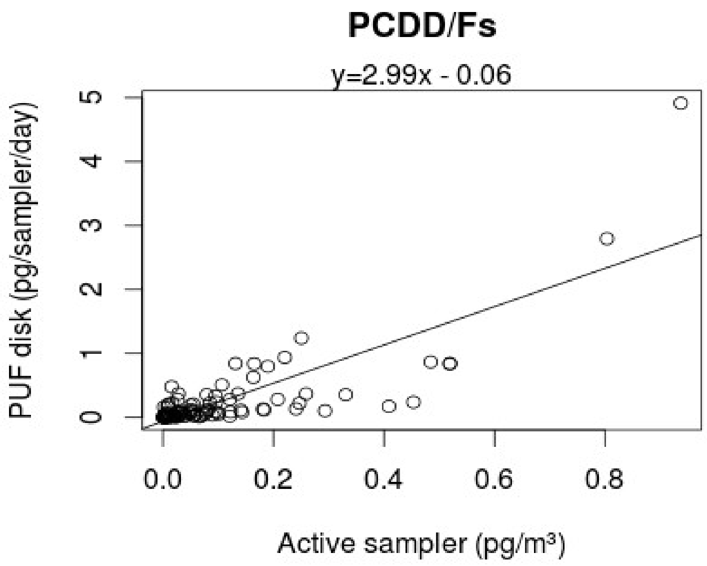


Figure 1. Illustration of linear relantionship between passive and active sampler concentrations.

Table 1: Regression coefficients and statistical significance of PCDD/F trends.

Congeners	**β_1**	**p**	**r^2**
	Dioxin		
2,3,7,8-TCDD	2.78	0.03	0.72
1,2,3,7,8-PeCDD	2.00	0.04	0.70
OCDD	3.40	0.01	0.81
	Furan		
1,2,3,7,8-PeCDF	4.06	0.04	0.68
1,2,3,6,7,8-HxCDF	3.94	0.03	0.72
1,2,3,4,6,7,8-HpCDF	4.34	0.01	0.82



igure 2. Linear relantionship between PCDD/F congeners from passive and active samplers.

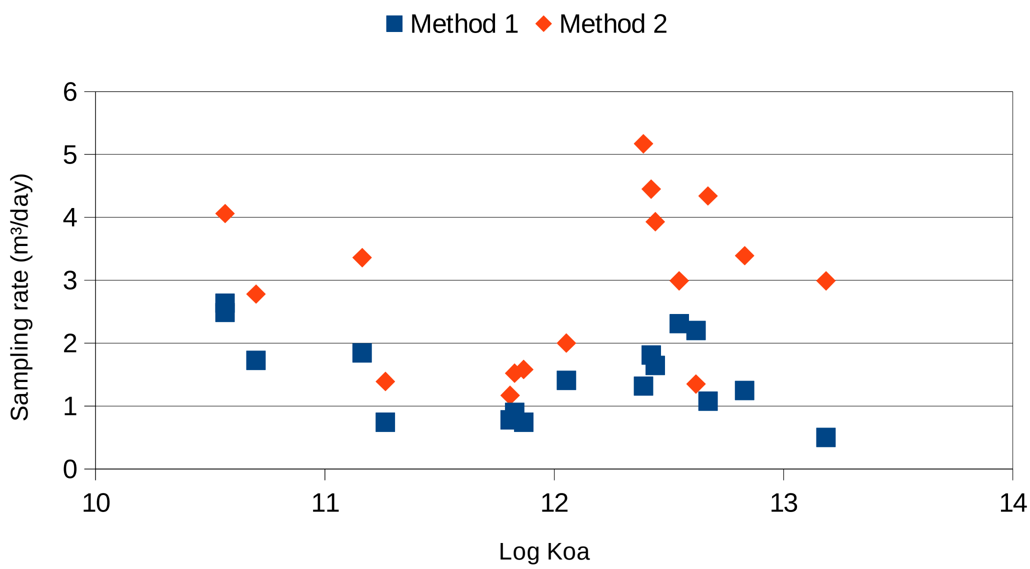


Figure 3. Comparison of sampling rates from methods 1 and 2.