UPTAKE RATES OF PCDD/PCDF AND dl-PCB FROM PASSIVE AND ACTIVE AIR SAMPLERS

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Introduction

Linear sampling rates (or uptake rates), R, are useful parameters for explaining and evaluating transport mechanisms and gas-particle partitioning differences among POPs. Sampling rates are obtained from passive samplers calibration with respect an accurate determination of air concentration, using high volume air samplers as function of air-side mass transfer coefficients[1]. Passive air sampling techniques have been performed in different zones of the world determining levels of POPs in ambient air. In comparison to active sampling, passive sampling overcomes limitations often encountered in developing nations, with no electrical requirements, and low equipment costs. The use of passive samplers requires knowledge of the uptake rate of POPs in polyurethane foam disk (PUFs).

Passive sampler calibration consists in a correlation of total POPs concentrations in passive samplers (for both gas and particular phases) with those measured by active devices. Different studies have published concentration levels and sampling rates for different POPs such as PACs, PCBs and PCNs[1,2,3], but little information has been published for particle-associated POPs like PCDD/Fs and some dl-PCBs. Moreover, this work offers the available sampling rate data and flow calibration between passive and active air samplers regarding sampling rates, and flow calibration procedures between active and passive samplers.

POPs partitioning between different media depends on octanol-air partition coefficients (K_{OA}). For air matrixes, K_{OA} is the tendency for POPs to distribute in either the gaseous or particle fraction. Some POPs are almost exclusively in the gas phase (those with low Koa), whereas other POPs could be exclusively associated with particles (those with high K_{OA})[4]. Reported values of K_{OA} for POPs compounds allow estimation of their theoretical phases, as a tool to calculate total concentration values in active samplers equipped only with filter media for particulate sampling. This approximation is a key factor for calibrating passive samplers in zones with limited information, and for explaining sources, differences and gas to particle mechanisms in terms of POPs levels.

This study analyzes sampling rates, R (m^3/day), of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs) for passive and active samplers, in order to explain differences between level concentrations collected by these devices in an Andean ecosystem, and how particulate and gaseous phases are also captured by passive devices for both PCDD/F and dl-PCB.

Materials and methods

Sampling rates were calculated from PCDD/PCDFs and dl-PCBs concentrations using active and passive samplers in the city of Manizales, Colombia, located on the western slope of the Cordillera Central in the Colombian Andes at 2150 m.a.s.l. The urban area of the city is bordered by pronounced slopes, as a result, the area available for development is limited and there is a relatively high urban density. Three air quality monitoring stations were distributed equidistant along a 7 km line in Manizales, which is oriented perpendicular to the Cordillera Central. These sampling stations represent an industrial zone (La Nubia) closest to the Cordillera Central, a central area (Palogrande) in a mostly residential zone, and a downtown high density area (Liceo) located furthest from the Cordillera Central summit. Passive sampling (PAS) was carried out from June 2012 to October 2012, obtaining one sample per station. Polyurethane foam (PUF) was used as adsorbent medium. Active sampling was carried out collecting a total of 8 samples during June 2012 (2 samples in Liceo, 3 in Palogrande and 3 in Nubia). Hi-Vol samplers were used with quartz fiber filters, volumes ranged from 1226 m^3 to 1400 m^3 for a period of 24 h. Active sampling was limited to collect particulate material.

Collection and analysis procedures followed the methodologies described in U.S. EPA 40[5] and US EPA 1613[6] protocols. Samples were subject to soxhlet extraction, clean-up and instrumental analysis by HRGC/MS to determine the concentrations of PCDD/PCDF and dl-PCBs, according to the isotope dilution method.

Sampling rates were calculated assuming most PCDD/F and dl-PCB were accumulated in the linear (kinetic phase) of the PUF-disk. These rates were determined as the ratio of the passive sampling concentration of congener i, C_{PAS} (ng/sampler day), to high volume concentration of the same congener, C_{ACT} (ng/m^3)[1], following equation 1.

$$R = \frac{C_{PAS}}{C_{ACT}} \qquad (1)$$

This calculation was derived by first obtaining the total concentration (gas and particle) in active samplers. Theoretical gas fractions for active data were calculated using the model proposed by Harner[7], assessing the gas-phase fraction, 1-ϕ, as a function of particulate matter concentration, PM_{10} (µg/m^3) and the particle-gas partition coefficient, Kp (m^3/µg), according to equation 2. Values of this coefficient were obtained as a function of octanol–air partition coefficients, K_{OA}, and the fraction of organic matter on the particle, f_{om}, following equation 3. Harner[7] reported a typical value of organic matter fraction on particles (f_{om}) equivalent to 0.2, for particulate matter concentration around 30 µg/m^3.

$$1 - \emptyset = 1 - \left[\frac{K_p * PM_{10}}{K_p * PM_{10} + 1}\right] \qquad (2)$$

$$\log K_p = \log K_{OA} + \log f_{om} - 11.91 \qquad (3)$$

Results and discussion

PCDD/Fs and dl-PCBs 81, 77, 126 exhibited higher affinity in the particle-phase mainly; while dl-PCBs 169, 123, 118, 104, 105, 167, 156, 157 and 189 exhibited higher affinity in the gas-phase mainly. These two behaviors were observable analyzing congener profiles in terms of R data (Figure 1a-b).

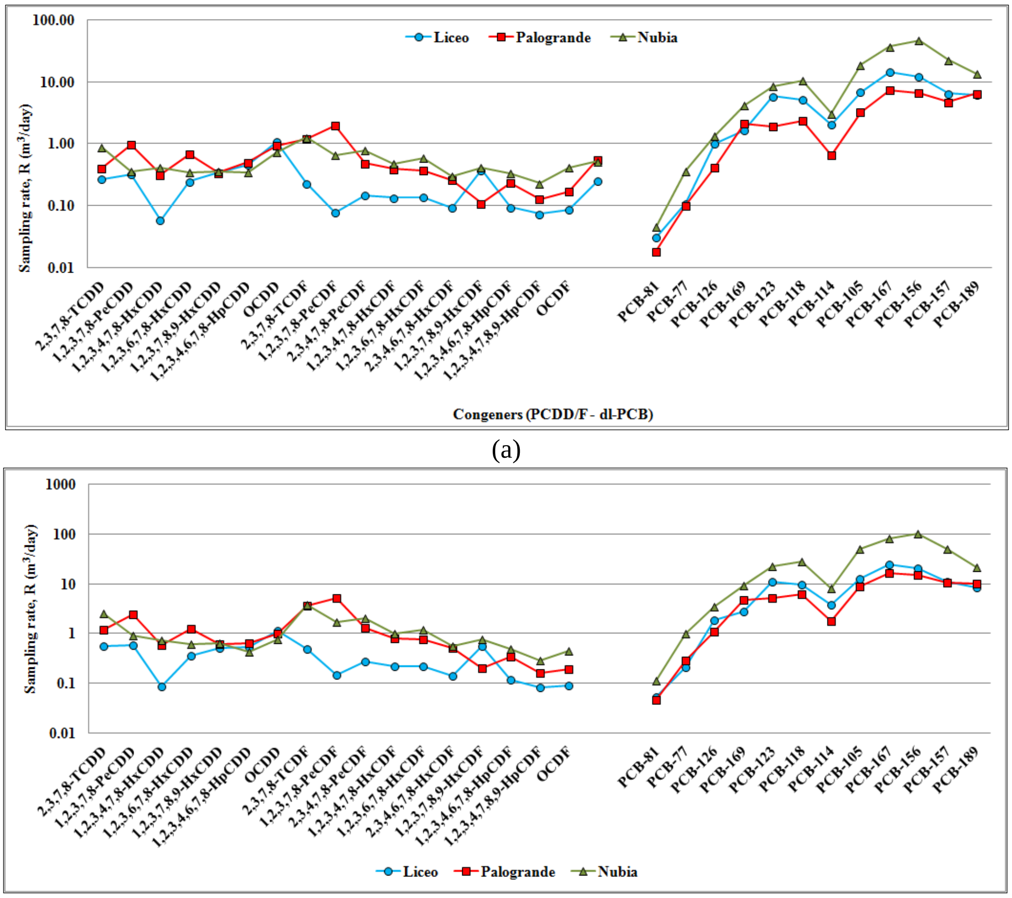
Mean sampling rate for PCDD/Fs in all stations was 0.4 m^3/day (±0.3 std.) and log K_{OA} ranged between 10 and 12 (Figure 1a). This uptake rate was lower than similar studies in Barcelona, Spain[3] (1.7 m^3/day) and Gyeonggi-do in South of Korea[8] (1.4 m^3/day). Low R values are typical for particle-associated chemicals that are not captured well by PUF-disk and high log K_{OA} values[3,8].

Sampling rate mean value of dl-PCBs for all stations was 7.35 m^3/day (± 5.8 std.) and log K_{OA} ranged between 9 and 12 (Figure 1a). This R average value was similar to data reported by Chaemfa[9] for compounds with intermediate log K_{OA} (~7-11 m^3/day), and those reported by Shoeib and Harner[2] for PCBs, which can vary from 2 to 8 m^3/day for indoor conditions. However, lower R value was reported by Heo[8] for dl-PCBs in Gyeonggi-do in South of Korea (2.0 m^3/day). Typical uptake rates for most non-polar hydrophobic chemicals are on the order of 4 m^3/day[1].

Selective trend of target POPs to be in particles of active or passive samplers was observed in uptake rate profiles only for particle-phase (Figure 1b). Lower R values for PCDD/Fs and non-ortho dl-PCBs in comparison with those obtained for mono-ortho dl-PCBs, suggest higher affinity of PCDD/Fs to be adsorbed in particles of active samplers and higher affinity of major dl-PCBs in particles captured by passive samplers. This pattern suggests that PUF disk samplers captured particle and gas phases at a similar rate, characterized by high and low molecular congeners respectively.

The combined effect of environmental conditions, the influence of emission sources and physicochemical properties of analyzed compounds (e.g. gas-particle partitioning) could be attributed to variations in uptake rates between PCDD/Fs and dl-PCBs[8]. However, temperature is probably the main driver of gas phase concentrations of dioxin-like pollutants[8]. In the case of PCBs, temperature exerts a dominant effect by controlling the volatilization rates, while PCDD/Fs are controlled by gas-particle partitioning. Although Manizales experiences bi-modal distribution of rainfall, there is a little temperature difference throughout the year (ranging from 15 °C to 27 °C) and little mean difference month to month. These conditions could contribute to major levels of dl-PCB in the passive monitoring campaigns[10].

Sampling rates for PCDD/Fs in downtown Liceo showed the lowest values, suggesting a majority presence of these compounds in particulate matter, associated with the highest concentration of ambient air particles around this station (PM_{10}=42 µg/m^3). On the other hand, Palogrande and Nubia stations had similar PCDD/Fs sampling rates and similar particle concentrations (PM_{10} ~29 µg/m^3). Previous studies carried out in the city exhibited higher values of PCDD/Fs concentrations associated with the highest concentration of particulate matter[10,11]. Higher values were observed in dl-PCB profiles for the industrialized station (Nubia), probably associated with industrial PCB precursors[10]. Variability of entrapping airborne particles in PUF-disk among stations is a function of particulate matter concentrations, size distribution of particles and some representative meteorological factors of each monitoring zone[1].



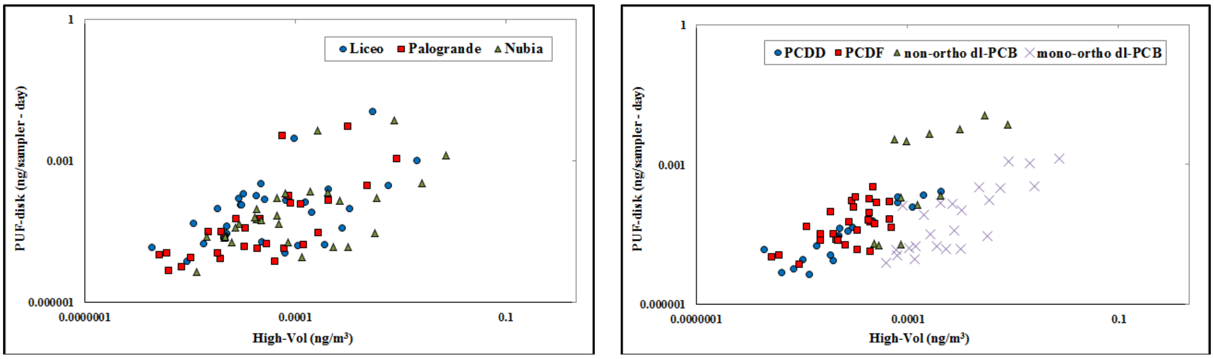
(a)

(b)

Figure 1. R profiles for PCDD/Fs and dl-PCBs congeners for all sampling stations a) Global uptake rates for PUF-disk concentrations (gas + particle phase) and active air sampler concentrations (gas + particle phase). b) Uptake rates in particulate phase only for both passive and active samplers.

Sampling rate trends were compared with specific data between passive and active samplers (Figures 2a-b). In general, the results did not differ substantially among stations, and sampling rates were similar for all congeners. This trend is consistent with results from previous studies published by Harner[1]. Adsorption of POP groups in particulate or gaseous phase was also observed in Figure 2b, where PCDD/Fs and some dl-PCB (non-ortho PCB mainly) were clustered in the same region, unlike mono-ortho PCB. This clustering is consistent with the greater affinity of PCDD/Fs mainly in particle phase and dl-PCB (except 81, 77 and 126) mainly in gaseous phase.

Few studies have estimated uptake rates of particle associated chemicals such as PCDD/Fs. Further studies which explore differences in sampling rates for different periods, using field measurements of particle and gas active concentrations, could contribute to a better understanding of how particle and gas phases are captured by PAS and more scientific information about trends in the fate and transport of POPs and levels of these data.



(a) (b)

Figure 2. Comparison between levels of passive samplers (PUF disk) and active samplers (HiVol). (a) Agreement between site sampling and (b) Agreement for different congeners.

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