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PCDD/FS VAPOUR-PARTICLE PARTITIONING IN A WORKPLACE ATMOSPHERE AFTER A FIRE

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Introduction

PCDD/Fs are semivolatile organic compounds (SVOC); they are defined by the World Health Organization as organic compounds with a boiling point ranging between 240 and 400°C and vapour pressures approximately between 10^{-4} and 10^{-11} atm at ambient temperatures (WHO, 1989). Vapour to particle ratio is controlled by the SVOC vapour pressure and the suspended particle concentration.

Active, high-volume (HiVol) samplers are usually used; they have a sampling module which consists of two compartments: a filter (quartz fiber filter, QFF) which collects particle associated compounds and a solid adsorbent (usually polyurethane foam, PUF) which is located on line downstream from the filter to collect gas phase components that pass through the filter. The adsorbent can also retain those compounds that volatilize from the filter during sampling (ISO 16000-13, 2008; Li et al., 2015; Rahman et al., 2014; Saral et al., 2015).

For HiVol air sampling, gas and particulate phases are operationally defined as the compounds trapped by the PUF and retained by the QFF, respectively. Known HiVol sampling artifacts include particle blow-off from the QFF, adsorption to the QFF, “stripping” of compounds from the particle phase onto the PUF, and breakthrough of compounds in the adsorbent. In a previous work (Mosca et al., 2010) the system filter+adsorbent has been validated for sampling time up to 10 days, without loss of analytes. Even if the sampling of PCDD/Fs requires a filter followed by a PUF, several studies for the characterization of PM10 analyzes only particle fraction (Khedidji et al., 2015; Galletti M. et al., 2015).

This study will focus on the partitioning of PCDD/Fs sampled after a large fire occurred in an industrial building where large amounts of PVC, cables, sealing materials and plastics caught on fire.

The exposure to chemicals at work is often greater than the exposure in non-working situations but the duration for the exposure is often longer in non-working situations than the occupational. Therefore, also long time low level exposure may be important.

The distribution of PCDD/Fs in the air is a sensitive issue: the concentrations which generally are found in ambient air are close to the LOD and the study of the distribution is difficult, unless sampling for long periods - resulting in possible artifacts. In this case, however, the experimental measurements were carried out in a confined environment (industrial building) in which the concentrations of PCDD/F were sufficiently high.

Materials and methods

Three sampling sites, at reduced distance from the fire location were monitored (A the farthest, B and C the nearest) for a sampling time of 48 or 72h. The temperature inside the building was at about $20 \pm 2^\circ\text{C}$ in each sampling site; the sampling campaign was conducted in a period between June and December.

Gas and particle phase samples were collected simultaneously using high volume PM10 samplers, operating at $0.225 \text{ m}^3/\text{min}$ flow rate (Echo HiVol, Tecora). Quartz fiber filters (QFF) and polyurethane foam (PUF) cylindrical filters were used for particle and gas-phase samplings, respectively. The analytical procedure was previously reported (Rossetti et al., 2012). Briefly, each sample was Soxhlet extracted with toluene and then cleaned-up by a GPC column and fractionated by an inline alumina SPE column (Preplinc, J2 Scientific). The instrumental determination was carried out by GC/MS and the samples were quantified with the isotope dilution procedure.

Results and discussion

First of all, the contribution of vapour and particle-bound PCDD/Fs on the total WHO-TEQ concentration (filter + PUF) was analyzed. The partitioning seems to be independent from the concentration (blue dots in figure 1), and from the sampled volume, signed in figure 1. The average particle-bound PCDD/Fs are only about 30% of the total concentration: it means that a severe underestimation is done when the gaseous phase is not considered.

The partitioning is controlled by the vapour pressure: it means that the higher degree of chlorination, the lower the volatility. Thus, the next step, was the evaluation of the vapour-to-particle ratio of each 2,3,7,8-chlorine substituted compound. The evaluation was done on pg/m^3 concentrations, not taking into account the toxicity equivalence factors. Figure 2 shows the average distribution in each site, and

the relative WHO-TEF in green. The distribution is similar in all the sampling sites, even with different concentrations and sampled volumes (see figure 1).

It is important to underline that the most volatile congeners (tetra and penta chlorine substituted) trapped by the PUF: they are also the most toxic, which means that a health assessment performed only on PCDD/Fs bonded to particulate matter is underestimated. Figure 3 shows the concentrations of each sample considering only the particle-bound fraction (blue lines) and the total filter + PUF (red dots): the underestimation is more evident at higher concentrations.

Conclusions

In this work, the partitioning of PCDD/Fs between vapour- and particle phase has been investigated. The fact that the experimental campaign was carried out in a "naturally" contaminated environment, with high concentrations almost constant for a relatively long time (months) and not affected by very low concentration often found in the environment and by meteorological conditions, allowed an in-depth study of the distribution.

In all three sites similar partitioning has been observed; the contribution of particle-bonded PCDD/Fs on the total concentration (expressed in pg WHO-TEQ/m³) is only about 30%. In detail, tetra and penta congeners are retained mostly on vapour phase (PUF). All these findings seems to be unaffected by air concentration or sampled volume.

It means that when PCDD/Fs are collected only on filters, the toxic equivalent concentration of the samples is underestimated.

References

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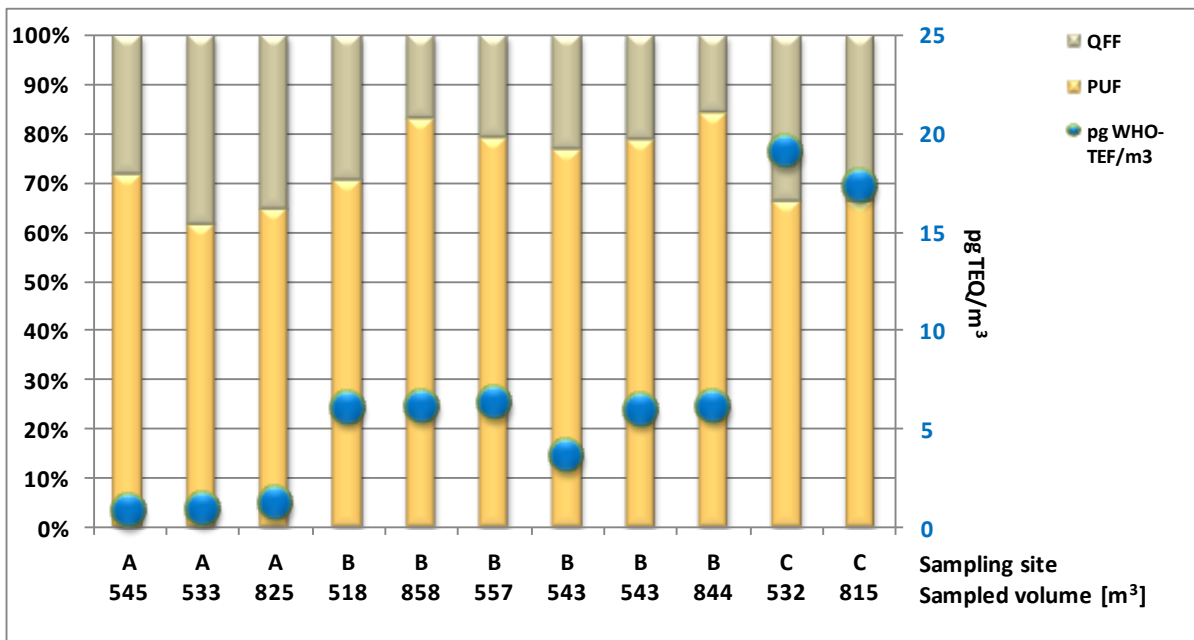


Figure 1 - Vapour- and particle-phase partitioning (grey and yellow, respectively) The blue dots represents the concentration in pgWHO-TEQ/m³.

Figure 2 – Average partitioning of PCDD/F between particle and gaseous phase

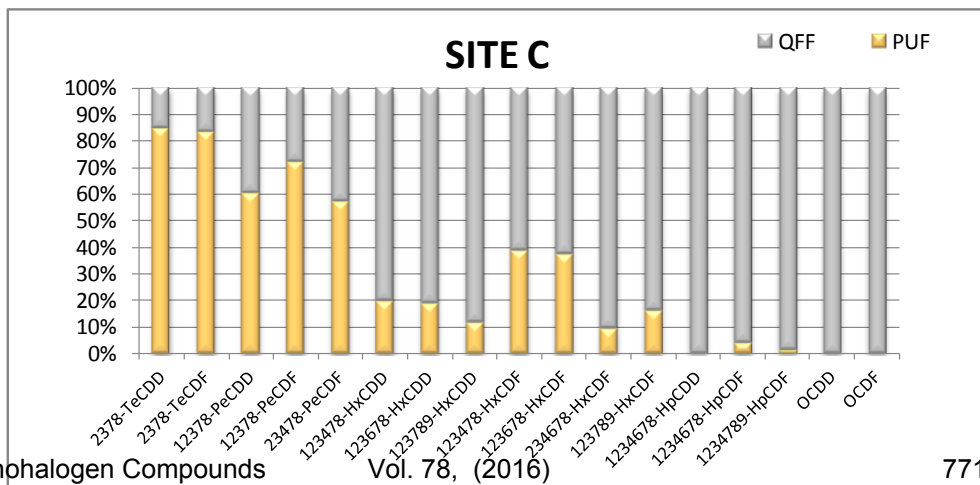
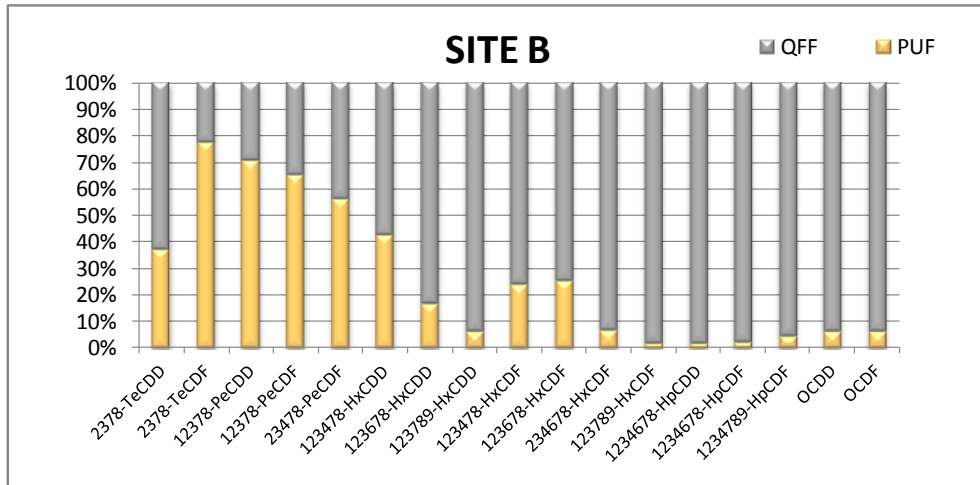
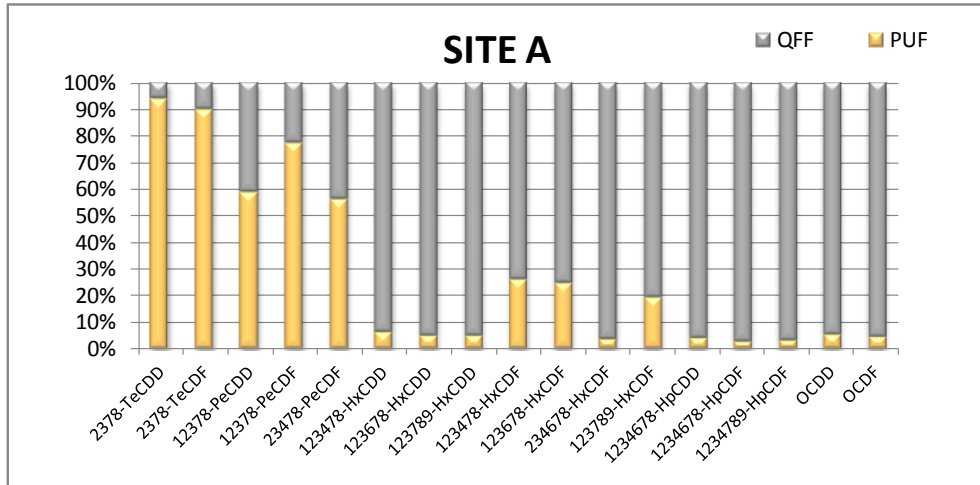


Figure 3 – toxic equivalent concentration of PCDD/Fs

