AIR-PLANT TRANSFERS OF PCDD/Fs FIELD DATA AND IMPLICATIONS FOR MODELLING

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Introduction

Due to the highly toxic properties of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), in recent years these persistent organic pollutants (POPs) have received a great attention by the scientific community and environmental agencies [1]. Vegetation receives inputs of airborne organic contaminants via gas-phase deposition, articulate dry deposition, and wet deposition. The concentration of compounds associated with the plant tissue is therefore affected by the rate at which compounds are supplied by the atmosphere, the diluting effect of the plant growth, environmental variables (temperature, precipitation), and characteristics of the plant [2,3].

However, there are still some uncertainties on the precise role of vegetation in influencing the fate of POPs, and more specifically about the mechanisms of vegetation contamination by PCDD/Fs. To date, investigations have been mainly focused on acute exposure in the laboratory, as well as studies in controlled growth chambers that might not adequately mimic the processes of deposition in the field[4]. In areas with industrial activities, the process transfer can be changed. It is important to understand the principal processes that take part in the accumulation of POPs in grass in order to develop reliable food chain transfer model and to evaluate human a wildlife exposure via the terrestrial food chain[5]. It is also of great interest to know the processes of vegetation transfer in order to be used as biomonitor of spatial and temporal variations in monitoring programs.

The main goal of the present study was to investigate the transfer processes of PCDD/Fs to grass by means of field studies. Soil and air (gas and particle) transfer to vegetation were evaluated in residential and industrial areas.

Material and Methods

PCDD/F concentrations measured in 24 herbage samples collected during 2001 and 2002 in the proximity of a Municipal Solid Waste Incinerator (MSWI) (Montcada, Barcelona, Spain) and in a residential area at 8 km from the MSWI were used [6-9]. Seven high volume air samples collected from January 2001 to March 2002 (provided by the Environment Department of the Regional Government of Catalonia) were measured for PCDD/F concentrations. The receptor site was

located at 1.5 km from the MSWI. Similarities and differences of the congener profiles were evaluated.

For air vapor measures, 7 passive samplers were used. Passive samplers were placed at 5 different points in the surrounding of the MSWI and at 2 points in the residential area. The samplers were deployed during 2 months (November/December 2002) at the same points where herbage and soil samples had been taken. The average temperature during the deployment period was 16.4ºC (range 5.2-29.5ºC). The average wind velocity was 1.2 m/s to the north. Total suspended particle (TSP) in the area of study was 60 µg/m³. Details about extraction, clean-up and analytical determination of PCDD/Fs were previously goven[6-9].

Results and Discussion

The percentages of the geometric mean PCDD/F congener profile for grass and air samples are depicted in Figure 1. The congener profile air-vegetation is quite similar. However, a general increase in the percentages of the lower substituted PCDF congeners in air in relation to those in vegetation can be noted. Coefficient factors (scavenging coefficients, m^3/g d.m.) ranged from 1.9 m^3/g to 11.3 m^3/g. The highest coefficient factors corresponded to OCDF (11.3 m^3/g) followed by 1,2,3,7,8,9-HxCDF (7.5 m^3/g), 1,2,3,7,8 PeCDF (7.4 m^3/g) and OCDD (7.3 m^3/g), while the lowest coefficient factors corresponded to 1,2,3,4,7,8-HxCDF (1.9 m^3/g) and 2,3,7,8-TCDF (2.1 m^3/g), 2,3,4,7,8 PeCDF (2.6 m^3/g) and 1,2,3,4,7,8,9-HpCDF (3.0 m^3/g). With the exception of OCDF, scavenging coefficients were higher for PCDDs than for PCDFs. A good trend with K_{OA} was observed for PCDDs (R = 0.82). Notwithstanding, it was lower for PCDFs (R = 0.55). It would mean that the chemical structure of the molecule can play an important role in diffusing processes of PCDD/Fs.

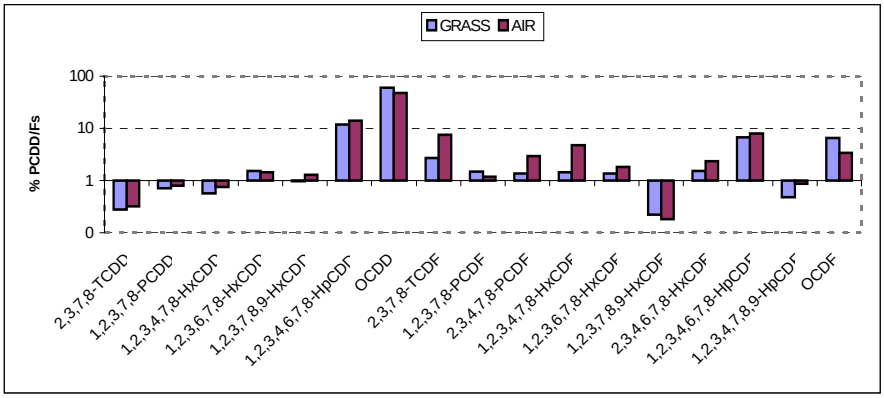

Figure 1. PCDD/F air-grass congener profile from monitoring program.

Welsch-Pausch and McLachlan[4] reported a larger overall scavenging coefficient for the lower chlorinated congeners. In turn, McLachlan[10] observed scavenging ratios ($C_{hay}/C_{total\ air}$) between 6 and 12. However, he did not find any trend with Koa. Lorber and Pinsky[11] reported that the

scavenging ratio decreased from the tetra to the hepta degrees of chlorination, with an increase at the octa degree of chlorination. Barber et al[12] observed that POPs air uptake rate constants in plants increased with the increasing level of chlorination (and hence K_{OA}), since diffusion rates in air decrease with molecular weight (and hence K_{OA}). These investigators suggested that although a greater contribution of particle bound POPs may contribute to it, the most probable explanation would be that permeability cuticles increases with increasing K_{OA} of the diffusing chemical.

The results shown in Figure 1 confirm the hypothesis raised by other authors[4,13] that PCDD/F concentrations in vegetation are associated with atmospheric deposition. Because OCDD is mainly bound to air particle phase, the process of particle deposition and absorption (or adsorption) by plants could be of a great relevance. Consequently, in the current study the vapor-particle partitioning of the PCDD/Fs in air was subsequently calculated.

Vapor-particles partitioning

Atmospheric deposition of PCDD/Fs can be classified into three different forms: dry gaseous deposition, dry particle bound deposition and wet deposition. The relative importance of these pathways depends on the air/particle partitioning of the PCDD/Fs in the atmosphere. Wet deposition contains primarily particle bound chemicals. Vapor-particle partitioning of each congener varies with temperature, amount and size of particles in the atmosphere, and with the physical-chemical properties of the individual congeners. In zones with temperate climate, the gas/particle partitioning during the growing season varies over a wide range for the different PCDD/F congeners, going from almost completely gaseous for the TCDD/F to completely particle bound for the OCDD/F[14].

Plant uptake of organic contaminants from wet and dry particle bound deposition is a complex phenomenon, which not only depends on the rate of deposition to the plant surface, but also on the degree of retention of the contaminant on the plant surface. This is a function of the degree of particle retention on the plant surface and those particles not being retained, as well as on the degree of transfer of the chemical from the particles to the plant cuticle. The lipid content of the plant, the roughness of the leaves, and the orientation of the vegetation to the atmosphere (i.e., horizontal or vertical) may also influence the ability of vegetation to collect and retain PCDD/Fs from both the gas and particle phases[15].

In order to evaluate the principal air pathways of PCDD/Fs in herbage samples, we calculated the gas and particle concentrations in the air of the area of study using the equation by Harner and Bidleman[16]. Figure 2(A,B) shows the PCDD/F congener profiles of the geometric mean values for the 24 herbage samples and the air vapor and air particle, respectively (geometric mean values of the 7 samples of air measured during the monitoring program).

It could be noted that for the highest substituted PCDD/F congeners, the air-particle uptake from plants is the principal pathway. However, it is not clear if accumulation of the lowest substituted congeners come from gas, particle air deposition, or both. Although initially, it was thought that dry particle-bound deposition was the dominant atmospheric pathway to plants, studies by Welsch-Pausch and McLachlan[4] showed that dry gaseous deposition was the dominant pathway of the tetra-hexaCDD/F to the typical grass (ryegrass), while wet deposition and/or dry deposition of large particles might have been primarily responsible for the uptake of the Hepta-OCDD/F. Harrad and

Smith[17] also reported that the vapor-phase transfer was the most significant uptake pathway for all PCDD/F toxic congeners. Uptake from particle deposition (dry and wet) was predicted to play a minor role.

In order to evaluate individual air vapor uptake, in the current study 7 air passive samplers were deployed representing 4 different zones for two months, and grass samples were collected at the same points in which passive samplers had been placed. One sampling point was established at 100 m from the MSWI at the flowing wind direction. This point should be mainly impacted by wet deposition and for the congeners bounded to the most weighted particles. A second sampling point was placed at 500 m from the MSWI at the blowing wind direction. A higher quantity of particles due to the plume of the MSWI emission was here expected. The third sampling point was established at 500 m from the MSWI, but opposite to the flowing wind direction. Therefore, no special plume effect from the incinerator was there expected. The fourth sampling point was placed at 8000 m from the MSWI, in a residential area with no known PCDD/F emission sources. In the passive samplers, total concentrations of PCDD/Fs for these four samples were the following: 7.7, 17.3, 4.2 and 2.8 pg I-TEQ/sampler, respectively. In grass, PCDD/F concentrations were: 0.45, 0.34, 0.37 and 0.21 ng I-TEQ/kg d.m., respectively. Figure 3 shows the profiles corresponding to each sampling point.

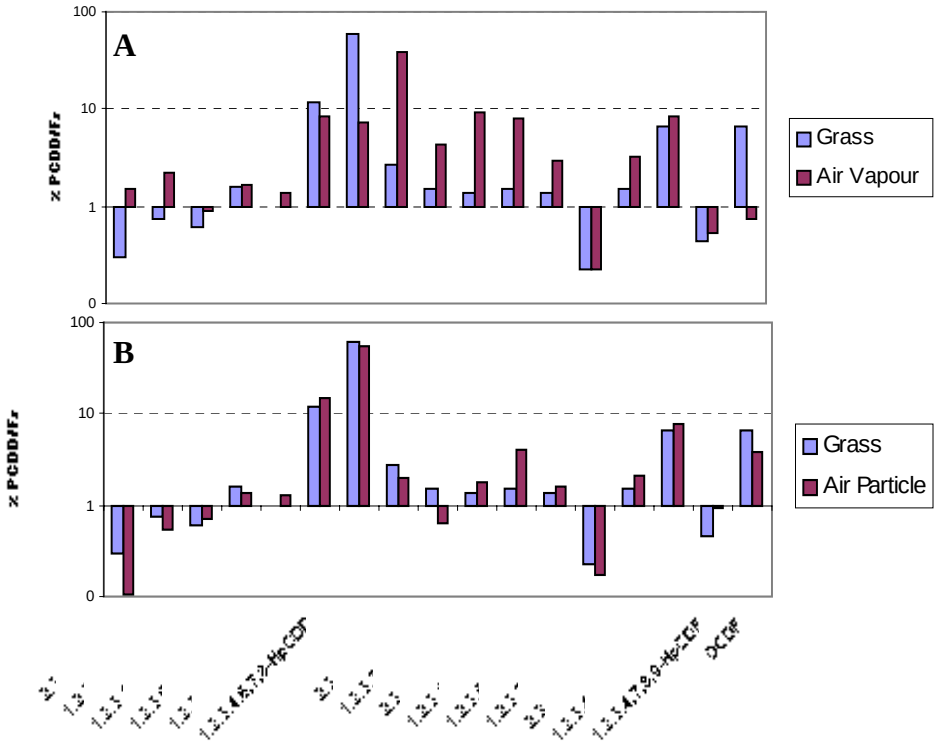

Figure 2. PCDD/F congener profiles for grass samples and air in the area of study.
A: Grass-Air Vapor; B: Grass-Air Particle

In the passive samplers, concentrations of the OCDD congener were higher than those expected taking into account the vapor-particle partitioning. Although the sampler was protected to avoid the inclusion of particles, the inclusion of some small quantity of particles can not be discarded.

Anyhow, special attention is given to the lowest PCDD/F substituted congeners. In Figure 3, it can be observed that profiles for grass and air vapor are quite similar. The profile gas-grass fits quite well, especially for the lowest substituted PCDFs, which are expected to be bounded to the vapor phase. In Figure 3B, (sample collected at 500 m from the MSWI at the flowing wind direction), the correlation for the lowest PCDD and PCDF congeners is very bad. The transference grass-air vapor of these congeners is modified with respect to the other areas of study. The highest concentration of PCDD/Fs in air in the impacted area (17.3 pg I-TEQ/sampler) is not correlated with an increase in grass concentrations (0.34 pg I-TEQ/kg d.m). A potential explanation could be that the presence of a higher quantity of particles in the emission plume modifies the partitioning gas-particle in air. In contrast, the particle deposition would be the principal grass-air process transfer. However, in places where not important air emission exists, the vapor absorption would be the principal way of grass budget.

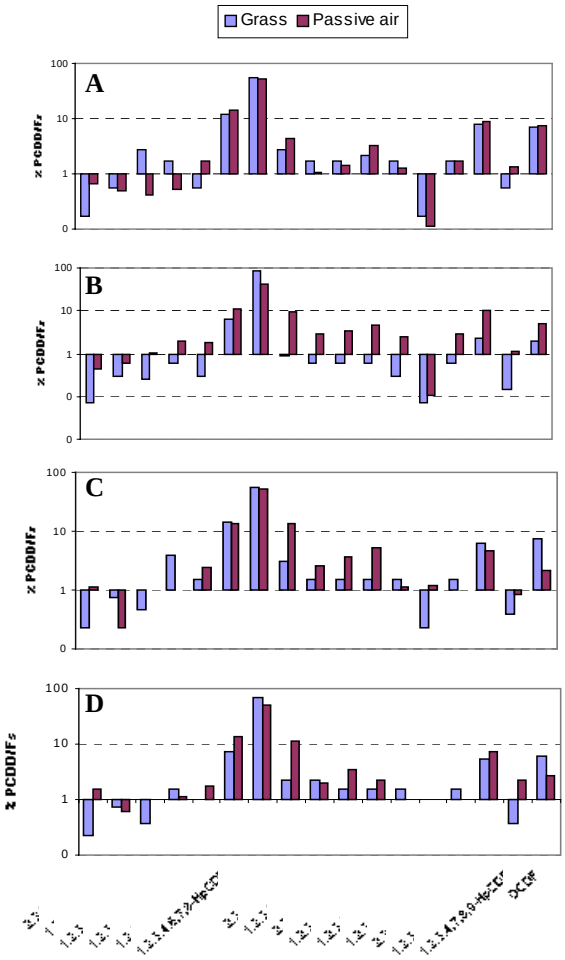

Figure 3.- PCDD/F congeners profile for a vegetation sample and air vapor passive sample
A: Sample collected at 100 m from the MSWI at the flowing wind direction. Vapor conc. = 7.7 pg I-TEQ/sampler; grass conc. = 0.45 ng I-TEQ/kg d.m
B: Sample collected at 500 m from the MSWI at the flowing wind direction. Vapor conc.=17.3 pg I-TEQ/sampler; grass conc. = 0.34 ng I-TEQ/kg d.m
C: Sample collected at 500 m from the MSWI at the opposite direction of the flowing wind direction. Vapor conc. = 4.2 pg I-TEQ/sampler; grass conc. = 0.37 ng I-TEQ/kg d.m.
D: Sample collected in a residential area 8000 m from the MSWI. Vapor conc = 2.8 pg I-TEQ/sampler; grass conc. = 0.21 ng I-TEQ/kg d.m

The above results suggest that the accumulation of PCDD/Fs in grass can depend on the presence of source emissions. In these cases, the particle phase would be the most important way of PCDD/Fs transfer in plants. However, in areas where not defined emission sources exist the air gas phase deposition would be the principal way of transfer in plants. McLachlan[10] supported that

particle bound deposition plays a more important role for the lower chlorinated congeners at locations close to source where very high levels of atmospheric particles are detected. Dry gaseous deposition would appear to be dominant uptake mechanism for the lower chlorinated PCDD/F congeners in rural areas. These results can have potential implications for risk assessment studies and environmental fate models.

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