

Interpreting the Accumulation of Dioxins and Related Compounds in Plants

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Introduction

Plant uptake of persistent, lipophilic, semivolatile compounds such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from the atmosphere is the major pathway of these compounds into the agricultural food chain. Plants also play an important role in environmental fate, modulating the transfer from the atmosphere to the terrestrial environment and hence influencing the long range transport and environment half lives of these substances. Furthermore, plants are employed as passive biomonitors of atmospheric contamination.

Organic chemicals can be deposited on plant surfaces via wet deposition, via dry deposition of chemical bound to atmospheric particles, or via diffusive transport of gaseous chemical in the air to the plant surface. Each of these processes is governed by a different set of plant properties, environmental parameters, and atmospheric concentrations. In order to understand the uptake in plants, it is essential that the process making the dominant contribution to the accumulation be known. This has often been neglected in the past, resulting in misinterpretation and misleading conclusions that arise when, for instance, a substance which is taken up by particle-bound deposition is treated as if it had been deposited via the gaseous phase.

To address this problem, a simple framework for identifying the dominant uptake process from field data is developed. The framework is then employed in interpret the data from a study of plant uptake of PCDD/Fs and other related compounds in 10 different grassland species and agricultural crops.

Theory

The theoretical basis of the interpretive framework is presented in ref. 1. It is applicable to hydrophobic chemicals for which deposition in dissolved form in precipitation is not an important process. The underlying premise is that the dominant uptake process is determined largely by a single physical-chemical property, the octanol-air partition coefficient K_{OA} . Compounds with low K_{OA} values are relatively volatile. They do not sorb to atmospheric particles to a meaningful extent and are hence deposited primarily via gaseous diffusion. Compounds with low K_{OA} values also have comparatively low vegetation/air partition coefficients (K_{VA}), and hence tend to approach a partitioning equilibrium rapidly. In this case the relationship between the concentration in the vegetation CV (mol/m³) and in the gaseous phase CG (mol/m³) can be expressed as follows:

$$CV/CG = mK_{OA}^n \quad (1)$$

where m and n are constants that are specific for a given plant.

For compounds with somewhat higher K_{OA} values, there is still little tendency to partition out of the gas phase onto particles, but the vegetation/air partition coefficient becomes so large that a partitioning equilibrium between the vegetation and the gas phase is not approached during the lifetime of the vegetation. In this case the following equation can be used:

$$CV/CG = AvGGt/V \quad (2)$$

where A is the surface area of the vegetation (m²), V is the volume of the vegetation (m³), vGG is the mass transfer coefficient describing transport from the atmosphere to the vegetation surface (m/h), and t is time (h). vGG can be viewed as an averaged gaseous deposition velocity to the vegetation surface.

For compounds with high KOA values, there is a strong tendency to partition out of the gas phase onto particles, and particle-bound deposition (both wet and dry) becomes the dominant process. The plant concentration is then determined by the particle-bound concentration in the atmosphere CP (mol/m³), and the relationship can be expressed as follows:

$$CV/CP = AvP/(V kE) \quad (3)$$

where vP is the mass transfer coefficient of the particle-bound chemical to the vegetation surface, and kE is the time constant describing erosion of particle-bound chemical from the plant surface. Assuming a linear relationship between the particle/gas partition coefficient KPG and KOA as proposed in ref 2:

$$KPG = CP/CG = B TSP KOA \quad (4)$$

where TSP is the concentration of total suspended particles in the air (g/m³) and B is a constant (m³/g). Substituting eq 4 into eq 3 yields:

$$CV/CG = A B vP TSP KOA/(V kE) \quad (5)$$

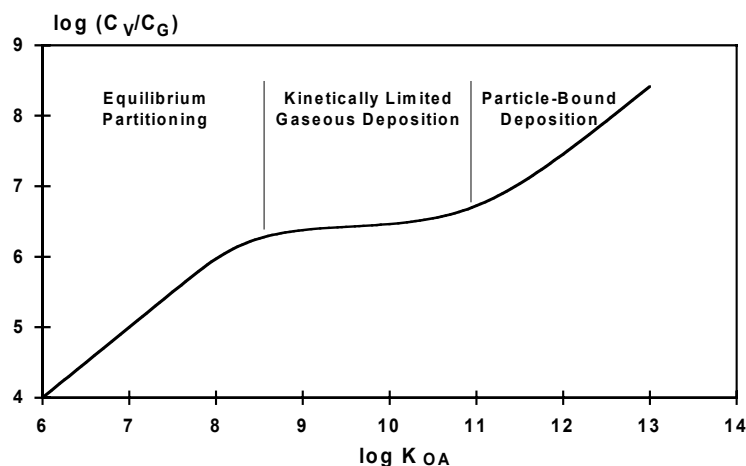


Figure 1: Illustrative plot for identifying the primary process of plant uptake of organic chemicals

We now have a family of 3 equations (1, 2, and 5) that describe CV/CG as a function of a single physical-chemical property, KOA. When these equations are combined and plotted for the full range of KOA, a graph of the form given in Fig. 1 is obtained. Three separate segments are present on the graph corresponding to the three processes described above and described by the three equations 1, 2, and 5.

We now have a tool for identifying the dominant process determining the uptake of PCDD/Fs and related compounds in plant samples. The quotient of the concentration measured in the vegetation and the average concentration measured in the gas phase are plotted against KOA for a wide range of compounds. This yields a graph of the form in Figure 1. The dominant uptake process of a

given compound is then given by the segment of the graph in which the compound lies. The utility of this interpretive framework was tested with the following field study.

Methods

Vegetation samples were collected from a farm to the south of the city of Bayreuth. The samples were collected on Sept. 15-16, 1995. Ten different species were sampled including eight grassland species from a meadow as well as corn and sunflower. The vegetation had developed over a 15-18 week period. The plants were cut with scissors, sorted, packed in aluminium foil, and stored at -18°C .

Air samples were collected continuously in one month intervals during May, June and July, and in two week intervals during August and September. The particle-bound contaminants were collected on a glass fibre filter and the gaseous contaminants on XAD-2 resin (3).

Four parallel samples were analysed for each plant species. The vegetation was freeze-dried, ground, and soxhlet extracted in toluene for 16-18 h. The filters and XAD resin were also soxhlet extracted. A cocktail of 35 isotope labelled internal standards was added to the extraction solvent prior to extraction. The extracts were cleaned up using H_2SO_4 -silica gel, NaOH -silica gel, aluminium oxide, and gel permeation chromatography. The HRGC/HRMS analyses were performed on a VG Autospec Ultima. The compounds analysed were pentachlorobenzene, hexachlorobenzene, 15 PCB congeners, 12 PAHs and the tetra- through octachlorinated PCDD/F homologue sums. The methods are described in detail elsewhere (3).

Results and Discussion

With a few exceptions, the standard recoveries were good and no evidence of interferences or chromatographic problems was observed. The laboratory blanks were low; only in two cases did the blank exceed one-third of the quantity in the sample, and these two data points were discarded. For almost all chemicals in all plant species the coefficient of variation for the 4 parallel analyses was <0.15 .

The framework presented above was used to examine the data. Figure 2 shows the graph of CV/CG vs. $\log \text{KOA}$ for ryegrass (*Lolium multiflorum*). The three segments illustrated in Figure 1 are clearly visible. For compounds with $\log \text{KOA} < 8.8$ (the chlorobenzenes, most of the PCBs, phenanthrene, fluoranthene, and pyrene), equilibrium partitioning was the dominant process determining plant uptake. For compounds with $8.8 < \log \text{KOA} < 11$ (the higher chlorinated PCBs, lower chlorinated PCDD/Fs, and triphenylene/chrysene), plant uptake was determined by kinetically limited gaseous deposition. Finally, for compounds with $\log \text{KOA} > 11$ (the higher chlorinated PCDD/Fs and the 5-6 ring PAHs (not shown)), particle-bound deposition dominated. A similarly clear picture was obtained for the other 9 species.

The interpretative framework allowed compounds to be identified for which a given process dominated in all of the plant species studied. For instance, the chlorinated benzenes and trichlorinated biphenyls were taken up via equilibrium partitioning in all 10 species. This allowed the interspecies variability of plant uptake to be examined in a systematic way. It was found that $\text{AvP}/(\text{V kE})$, the parameters governing, particle-bound deposition, varied by only a factor of 3 between the 10 species, and much of this variability could be explained by the differences in A/V .

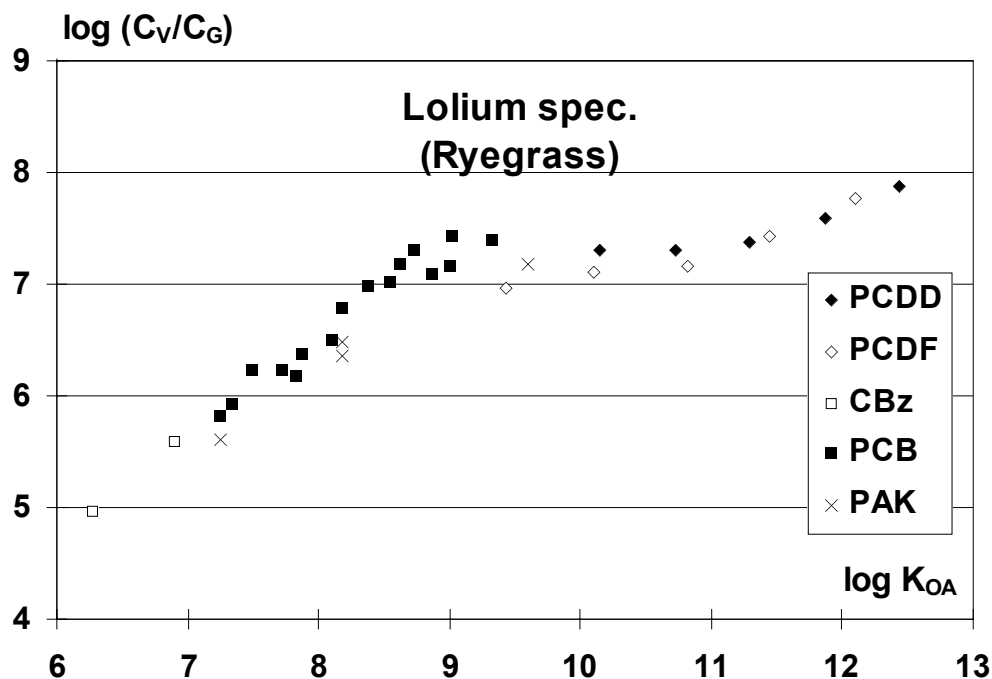


Figure 2: Plot of the quotient of the vegetation and gaseous concentrations of a range of SOCs in ryegrass (*Lolium multiflorum*) vs. log K_{OA}

The parameters governing kinetically limited gaseous deposition, A_vGG/V , also varied by only a factor of 3, and in this case much of the variability was also due to A/V . However, in the case of equilibrium partitioning the interspecies variability ranged up to a factor of 20. Good agreement was found between the partition coefficients estimated from the field measurements and vegetation/gas phase partition coefficients measured in the laboratory (3).

The results indicate that the interspecies variability in the gaseous and particle-bound deposition velocities is relatively minor compared to the variability in K_{VG} . Hence the interspecies variability in plant concentrations can be expected to be high for compounds with low K_{OA} values such as the chlorinated benzenes, while the variability should be lower for less volatile compounds such as the PCDD/Fs. This case study clearly demonstrates the utility of the interpretive framework.

References

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