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Chlorinated Dioxins: Volatilization from Soils and Bioconcentration in Plant Leaves

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Polychlorinated dibenzodioxins (PCDDs) are a group of xenobiotics of extreme environmental interest, by virtue of their high toxic potential, coupled with high bioaffinity and resistance to degradation. One in particular (2,3,7,8- tetrachloro dibenzo-*p*-dioxin, 2,3,7,8-TCDD), is probably the most poisonous substance ever introduced into the environment. PCDDs are not intentionally produced, but mainly arise from combustion processes and certain industrial activities; all the sources of these substances are not yet completely known (Hutzinger and Fiedler 1989). However, loads to the environment are certainly significant as PCDD residues may be found in many different environmental matrices (Jones and Bennet 1989).

In terrestrial systems non-polar and low-volatile compounds tend to partition in soil compartments, which constitute the main environmental reservoir of these chemicals. From the soil, vapor movements of trace contaminants are expected to be significant when the vapor pressure of the chemical is in the order of 10^{-6} Pa, or more (Bacci and Gaggi 1987). In the air, the partition between gaseous and particulate phases is regulated by the subcooled liquid vapor pressure of the chemical (Bidleman et al. 1986, Mackay et al. 1986, Foreman and Bidleman 1987): substances with a liquid vapor pressure of 3×10^{-5} Pa (25 °C), can be expected to be equally distributed between air and particulate in rural environments (3×10^{-4} Pa is the vapor pressure value for equipartitioning in urban environments). Higher vapor pressure values will lead to an increase of the fraction in the vapor phase.

From the data reported by Shiu et al. (1988) it can be seen that vapor pressure of PCDDs, as subcooled liquids, is roughly 10^{-a} Pa (25 °C), where "a" is the number of chlorine atoms. So, dioxins having from 1 to 4 chlorine atoms can move from soil to the air. In the air these chemicals are likely to partition mostly in the vapor phase, with higher chlorinated homologs distributed mainly, but not exclusively, in the airborne particulate. Recent measurements indicate that a significant proportion can be found in the vapor phase, even for the more chlorinated homologs (i.e. 6-8 Cl atoms; Eitzer and Hites 1989), indicating that vapor movements play an essential role in the environmental transport of PCDDs.

The air-to-leaf transfer of gaseous organics can be considered as a key process

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for plant uptake, particularly for less water-soluble compounds, which are characterized by low mobility in water and consequently negligible translocation via roots from contaminated soils. As recently pointed out (Reischl et al. 1989a, Reischl et al. 1989b), it is rather unlikely that PCDDs undergo significant translocation, even over a long period.

Recent studies have developed new correlations to predict the plant leaf-to-air equilibrium bioconcentration factor (BCF) for undissociated chemical substances, based on the influence of the n-octanol/water partition coefficient, K_{OW}, and the air/water partition coefficient, K_{aw}, or on Henry's Law constant, H (Reischl et al. 1989a, Reischl et al. 1989b, Bacci and Calamari 1990, Bacci et al. 1990a, Bacci et al. 1990b).

The aims of present study were:
1) to evaluate the volatilization potential of PCDDs from contaminated soils;
2) to provide an experimental support for the calculation of the leaf/air BCF for one tetrachlorodioxin;
3) to apply a new correlation with K_{aw} and K_{OW} for the calculation of BCF of PCDDs in plant leaves, using azalea as a model.

MATERIALS AND METHODS

The chemical selected for studying accumulation and release kinetics, to calculate the BCF, was 1,2,3,4-tetrachloro dibenzo-*p*-dioxin (1,2,3,4-TCDD). This substance has very similar partition properties to the most toxic 2,3,7,8- isomer (Shiu et al. 1988) but a significantly lower toxic potential (Olson et al. 1989).

The test plant was the azalea, *Azalea indica*, using as bioconcentrators only the old leaves, whose growth during the experiment was negligible.

During the uptake phase, two plants in pots, with their original soil were placed in a 200-L glass greenhouse kept at 20-22 °C by a warm-water system in the bottom and continuously illuminated by 3x20 W True-Lite fluorescent tubes. The greenhouse was located in a deserted fenced building to avoid unintentional exposure of humans and animals. The pots with azalea plants were arranged on a glass tray to reduce the impact of air flowing in through a 3 cm diameter hole near the bottom of the greenhouse. Two similar holes near the top and slight gaps between the cover and the walls guaranteed sufficient air turnover. The turnover time of the air inside the system was 70-90 min, and the mixing of the air was enough to obtain similar mean levels of contamination both near the corners and in the middle (Bacci and Gaggi 1987).

As 1,2,3,4-TCDD vapor source, two 100 g aliquots of dried (80 °C) Pliocene sand, pH 7.6, 0.2 % organic carbon, with the texture of a "fine sandy medium sand" (Doeglas 1968), were each fortified with 5 mg of 1,2,3,4-TCDD. Before the addition of the chemical, the sand was flooded with 200 mL n-hexane; after fortification, the solvent was removed by vacuum rotary evaporator.

The plants were watered daily, as were the vessels containing the contaminated sand, to maintain a constant volatilization potential.

In the release phase, the vessels containing the contaminated sand and the cover of the greenhouse were removed, and the walls were lifted (4 cm), to increase air turnover.

At different times, 10–15 old leaves were taken at random from the two azalea plants, by means of a small noose introduced through one of the lateral aeration holes. Uptake was studied for 370 h, and elimination was followed for 500 h.

Air samples (about 1 m^3 each) were taken by means of Florisil traps, prepared by filling disposable Pasteur pipets with 700 mg of Florisil, as suggested by Giam et al. (1975), with minor modifications. Apparent sample volume was measured by soap–bubble flowmeter, connected in series with the air trap and a tap–water vacuum pump. These volumes were corrected only for internal pressure (~50 kPa), measured by a vacuometer on the suction line.

The vapors adsorbed onto the Florisil were then eluted with 50 ml 4% acetone in n–hexane in glass chromatography columns. After appropriate concentration, the samples were ready for GLC analysis.

Plant foliage samples (1–1.5 g, wet weight) were separated into two homogeneous aliquots, the first for the measurement of water content (105 °C, 5 h), the second for the analysis of 1,2,3,4–TCDD. Extraction was carried out by means of an Ultra–Turrax homogenizer, after the addition of 5 mL distilled water, 10 mL acetone and 15 mL n–hexane (all solvents for pesticide residue analysis). After centrifugation, the green upper layer was recovered and the aqueous phase reextracted with a further 15 mL n–hexane, as before, recovering a second green phase. The volume of the extract was then reduced to 2–4 mL, eliminating the acetone. After the addition of 20 mL n–hexane, 5 mL 96% H_2SO_4 were used to destroy interfering materials. After centrifugation, to eliminate the acid layer, the clean–up procedure was continued by a Florisil column chromatography (2 g Florisil, height 4 cm), eluting first with 50 mL n–hexane (discarded), and then with 50 mL 4% acetone in n–hexane, recovering 75% of the 1,2,3,4–TCDD.

For air samples the recovery was assumed to be 100%.

The detection of 1,2,3,4–TCDD in foliage and air samples was carried out by high resolution gas chromatography. The following equipment was used: a Perkin–Elmer Sigma 3B gas chromatograph equipped with ^{63}Ni electron capture detector (ECD), and a Supelco SPB–5 bonded phase (0.25 μm film thickness) fused silica capillary column, 30 m x 0.2 mm i.d.; carrier gas: argon–methane, 95/5%, regulated at 100 kPa. Injector and detector temperatures were 220 and 280 °C respectively; oven temperature program: 100 °C for 10 min, then to 250 °C at 3 °C/min, hold 40 min.

RESULTS AND DISCUSSION

The concentration of 1,2,3,4–TCDD vapors in the air of the greenhouse, C_a, during the uptake phase of the experiments was relatively constant (Table 1). This indicates that a constant air turnover was coupled with a constant vapor flux from the dioxin–fortified soil. The vapor flux of a chemical from a contaminated soil can be described by the following relationship (Hartley 1969):

$$J = \text{const}\ P\ (mw)^{1/2} \qquad (1)$$

Table 1. Concentration of 1,2,3,4-TCDD vapor in the greenhouse air (C_a, ng/L), at different times during uptake.

t (h)		C_a (ng/L)
42		0.0050
165		0.0065
200		0.0075
250		0.0055
300		0.0065
	mean	0.0062
	%C.V.*	15.7

* Per cent coefficient of variation = (standard deviation/mean) x 100.

where J indicates the vapor flux from the soil (considered as an inert surface); P is the vapor pressure and mw is the molecular weight; "const" indicates a proportionality constant. In a given system, characterized by constant temperature, constant air turnover and turbulence, constant "inert" surface and load of contaminant, the eq 1 could be rearranged as follows:

$$C_a = K\,P_s\,(mw)^{1/2} \qquad (2)$$

where C_a is the concentration of the chemical in the air (mol/m^3), K is a proportionality constant, mol/(m^3 Pa), mw the molecular weight and P_s the vapor pressure (Pa) of the chemical in the solid state (if the melting point is higher than 20 °C). The use of P_s for solids, instead of the subcooled liquid vapor pressure (P_l), is justified when there is the possibility of crystal formation, as is the case in the fortified soils used in this and similar experiments (Bacci et al. 1990a, Bacci et al. 1990b).

In Figure 1 data obtained under the same or very similar conditions indicates that eq 2 can be used to predict the concentration of a chemical as vapor in our experimental systems, where the value of K (eq 2) is $\approx 10^{-7}$ mol/(m^3 Pa). This assuming that the slope of the Log/Log correlation, shown in Figure 1, is 1. In principle, the same approach could be used in other similar semi-closed systems. Moreover, under the same environmental conditions, the relative volatility of different chemicals can be related either to the product $P_s(mw)^{1/2}$ in the case of high contaminant load, where the formation of crystals is likely, or to the product $P_l(mw)^{1/2}$ when the formation of crystals is unlikely.

The data for the uptake and clearance kinetics of 1,2,3,4-TCDD in azalea leaves was treated according to a single compartment first-order model:

$$dC_l/dt = k_1\,C_a - k_2\,C_l \qquad (3)$$

where C_l and C_a indicate the concentration of the chemical in the leaf and in the air, respectively, t is the time, k_1 and k_2 the uptake- and release-rate constants.

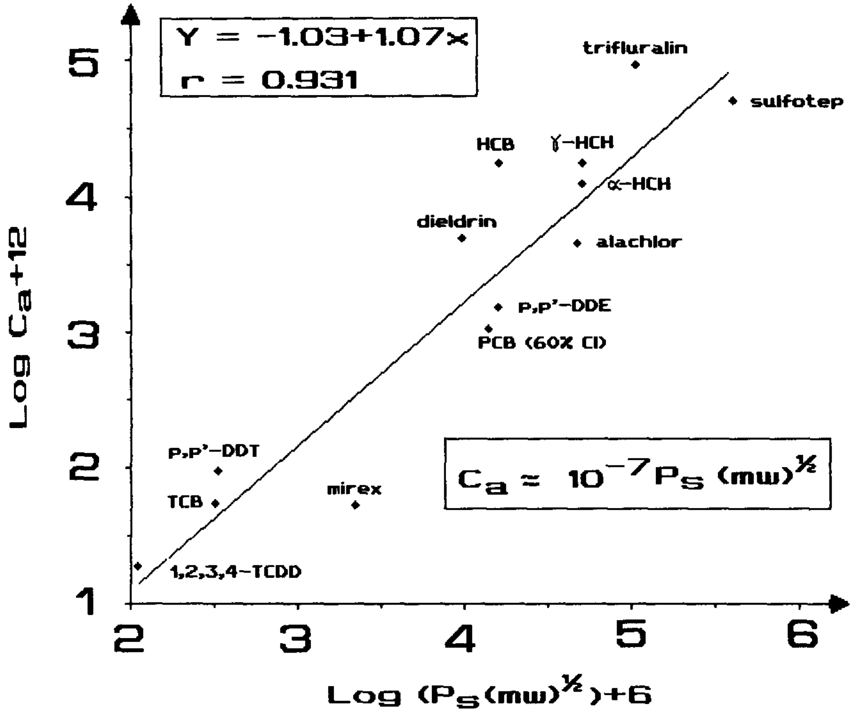

Figure 1. Log/Log correlation between the concentration of the vapors of different chemicals in the air of experimental greenhouses, the solid vapor pressure, P_s, and the square root of molecular weight, $(mw)^{1/2}$. Levels in air, C_a, are in mol/m^3, and P_s is Pa; data from Bacci et al. 1990a,b. The constants 12 and 6 were added to simplify the graphic illustration.

During uptake, the concentration, $C_l(t)$, of the dioxin in the leaves (ng/L wet weight; 70% water content; density 890 g/l), varies as a function of time t (h) according to the following equation:

$$C_l(t) = C_a\, k_1/k_2\, (1-e^{-k_2 t}) \qquad (4)$$

where C_a is the constant concentration of the chemical, as vapor, in the air (ng/L), and k_1 and k_2 are input- and output-rate constants (h^{-1}).

At equilibrium, $C_l = C_a\, k_1/k_2$, and the leaf/air bioconcentration factor, BCF, (ng/L wet leaf)/(ng/L air) is equal to the ratio k_1/k_2.

The input rate constant, k_1, can be calculated from the initial accumulation rate, taken to be constant in the first 90 h of intake (low C_l values, elimination assumed to be negligible), divided by C_a. To a first approximation, the initial accumulation rate is the level of 1,2,3,4-TCDD at t = 90 h, divided by the time elapsed (90 h), the concentration of dioxin in the azalea leaves at t = 0 being negligible. To calculate the output rate constant k_2, the C_a value in eq 3 was taken to be zero, and the following clearance function was used:

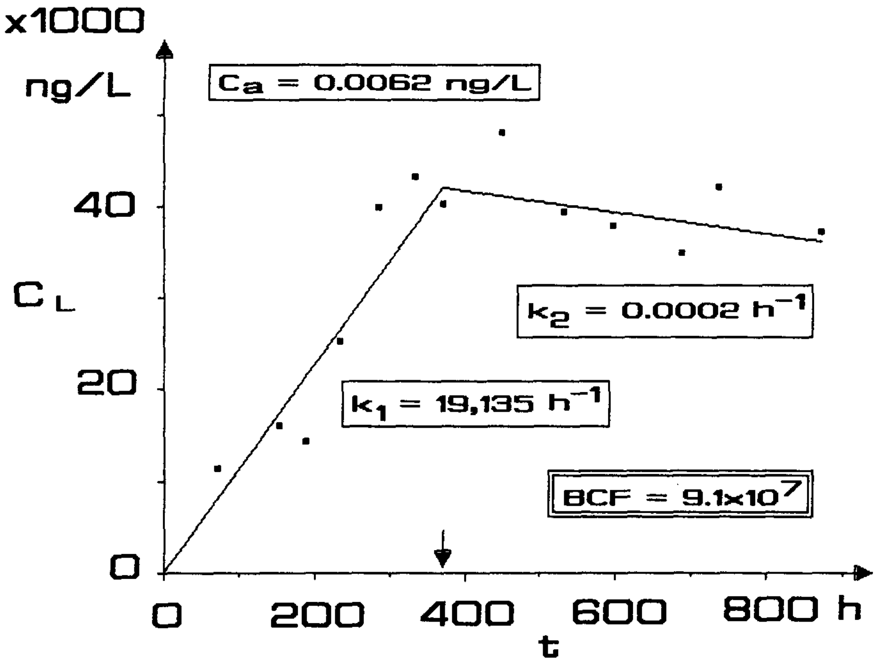

Figure 2. Uptake and clearance kinetics of 1,2,3,4-TCDD vapors in azalea leaves. Level of exposure C_a = 0.0062 ng/L; concentration in the leaf, C_l, in ng/L wet weight (70% water content, density = 890 g/L). BCF is dimensionless (mass/volume)/(mass/volume).

$$C_l(t) = C_{l0}\, e^{-k_2 t} \qquad (5)$$

and after logarithmic transformation:

$$\ln C_l(t) = \ln C_{l0} - k_2 t \qquad (6)$$

Equation 6 is a straight line and the slope k_2 can be calculated by the method of least-squares.

As illustrated in Figure 2, k_1 is 19,135 h^{-1}, k_2 is 0.00021 h^{-1}, and BCF (ng/L)/(ng/L) is 9.1×10^7. The half-life $t_{1/2} = \ln 2/k_2$, is 3,300 h.

The leaf/air BCF obtained for 1,2,3,4-TCDD was included in a series of 14 different chemicals to develop a correlation with n-octanol/water (K_{ow}) and air/water (K_{aw}) equilibrium partition coefficients (Bacci et al. 1990a, Bacci et al. 1990b):

$$\text{Log}\,(\text{BCF}\,K_{aw}) = -\,1.654 + 1.065\ \text{Log}\,K_{ow} \quad r = 0.957 \ (7)$$

where BCF, K_{aw} and K_{ow} are in (mol/m^3)/(mol/m^3). BCF is referred to the wet leaf, density 890 g/L, 70% water content. The air/water partition coefficient, K_{aw}, is obtained dividing the Henry's Law constant, H, by RT, where R is the gas constant, 8.314 Pa m^3/ (mol K), and T the temperature (293 K); H is calculated from the ratios P_l/C_l or P_s/C_s, where P and C indicate the vapor pressure (Pa) and the water solubility (mol/m^3), and the subscripts l and s the liquid (or subcooled liquid) or solid state of the chemical.

Since the coefficient of Log K_{ow} is very near to 1, from eq 7:

$$BCF\ K_{aw} = 0.022\ K_{ow} \qquad (8)$$

and, to a first approximation:

$$BCF = 0.022\ K_{ow}/K_{aw} \qquad (9)$$

where the constant 0.022 is close to the measured value of the lipidic fraction of *Azalea indica* leaves: 0.015 (as weight of lipids/weight of wet leaf).

Equation 9 was used to calculate BCF values for some PCDDs (Table 2). The calculated value for the 1,2,3,4-TCDD BCF, 5.76×10^7, is very near to the value obtained in present work (9.11×10^7).

Table 2. Calculated leaf/air equilibrium bioconcentration factors, BCF as (mass/volume wet leaf)/(mass/volume air), 20–25 °C, for some PCDDs. The leaf density is 890 g/L and the water content is 70%.

PCDDs	K_{ow}*	K_{aw}*	BCF
1-chloro-	5.62×10^{4}	3.38×10^{-3}	3.66×10^{5}
2,7-dichloro-	5.62×10^{5}	3.27×10^{-3}	3.79×10^{6}
1,2,4-trichloro-	2.24×10^{6}	1.55×10^{-3}	3.18×10^{7}
1,2,3,4-tetrachloro-	3.98×10^{6}	1.52×10^{-3}	5.76×10^{7}
2,3,7,8-tetrachloro-	6.31×10^{6}	1.35×10^{-3}	1.03×10^{8}
1,2,3,4,7-pentachloro-	2.51×10^{7}	1.07×10^{-4}	5.16×10^{9}
1,2,3,4,7,8-hexachl.-	6.31×10^{7}	1.82×10^{-3}	7.68×10^{8}
1,2,3,4,6,7,8-hept.-	1.00×10^{8}	5.37×10^{-5}	4.10×10^{10}
octachloro-	1.58×10^{8}	2.74×10^{-4}	1.26×10^{10}

*From Shiu et al. (1988).

These data indicate that "low-volatile" chemicals can significantly move from soil to the air. When conservative and non-polar, as in the case of the majority of the PCDDs, strong leaf/air bioconcentration is expected.

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