Kale Uptake of PCDD/PCDF, PCB and PAH under Field Conditions: Importance of Gaseous Dry Deposition

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Abstract

Field measurements on polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in corresponding soil and kale samples show a clear increase of plant-to-soil concentration ratios with decreasing molecular mass: Lower chlorinated homologs are enriched in the plants. The same behavior was found for series of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH). It is concluded that gas-phase dry deposition from air onto/into the plant is the responsible transfer mechanism. Lower 2,3,7,8-chlorinated PCDD are favored by kale accumulation compared to the corresponding PCDF congeners.

1. Introduction

Food is the major source of human intake of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). In recent years, some effort has been devoted to discover the main pathway(s) of these environmental pollutants into vegetables and other plants, and thereby into the food chain.
It is now accepted that PCDD/F may be taken up by plant roots and transported into the upper part of the plant only in some exceptional cases. More likely is the uptake from polluted air by adsorption and possibly incorporation into the inner parts of the leaves. This deposition can take place either by rain or snowfall ("wet deposition"), by settling of dust particles ("dry particle deposition") or by scavenging gaseous PCDD/F on the plant surface ("gas-phase dry deposition")[1].
Usually only the first two deposition processes are discussed and treated analytically[2], while the gas-phase to solid transport is neglected. As only 70 % of the airborne toxicity equivalents are particle-related in ambient air, some 30 % are thus neglected[2,3].

2. Results and Discussion

Field experiments at 10 sampling sites of a large German city showed that the concentrations in soil and green kale (unwashed leaves) are not correlated. Furthermore, the concentration ratios between plant and soil samples increase with decreasing molecular mass, i.e. the lower chlorinated PCDD and PCDF homologues are found in the leaves at relatively higher concentrations than the higher chlorinated ones (see Table 1). This observation is in contrast to the common belief that airborne PCDD/F are deposited on plants and soil in a similar manner, both via wet and dry particle deposition. Since the lower (Cl_4- and Cl_5-) chlorinated homologues occur above all in the gas phase and are only partly adsorbed on particles, we propose that they reach the plants mainly by means of gas-phase dry deposition. Table 1 shows also that the concentration ratios between kale and soil are also (about 3fold) higher for the Cl_5 to Cl_7 dibenzo-p-dioxin homologues compared to the corresponding dibenzofurans.

Simultaneous measurements of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) in soils and kale leaves also showed the same behaviour for these groups of substances: Those with lower molecular mass, which in ambient air are found mainly in the gas-phase[4], were preferentially accumulated in the kale leaves rather than in the soil (see Table 1).

The homologue and congener specific distribution between air, soil and plants is further complicated by plant-specific accumulation differences, by temperature changes which may shift the gas-to-particle ratio and thereby the fraction of airborne PCDD/F available to plants, and by photochemical degradation of higher chlorinated PCDD/F on soil (and possibly also on plant surfaces?), which favors the 2,3,7,8-chlorinated dibenzo-p-dioxins and unfavors the corresponding dibenzofurans[5].

In summer at high temperatures, e.g., the PCDD/F distribution may be effected as follows:

1. The gas-phase concentrations of lower chlorinated PCDD and PCDF (probably with higher TE) will increase by evaporation from airborne particles and from soil[6].
2. Photochemical transformation of higher chlorinated PCDD and PCDF on soil and possibly particle and plant surfaces can produce additional lower chlorinated congeners, preferentially lower-toxic PCDF and higher-toxic 2,3,7,8-PCDD[5], which may again evaporate to enhance the gas-phase concentration of toxic congeners.
3. Photochemical reactions, on the other hand, may reduce specifically the concentration of gaseous congeners.
4. Plant absorption favors the incorporation of specific congeners and probably that of the lower chlorinated gaseous PCDD, especially the most toxic 2,3,7,8-TCDD (see table 1).

Our results are in accordance with laboratory studies performed by KRAUSE[6] on the accumulation of PCDD/F in grass: He also found homologue-specific plant-to-soil concentration ratios, although in contrast to our field experiments on kale the grass accumulated relatively more PCDF than PCDD. The kale-to-soil ratios are roughly 10fold higher than that of the grass for single isomers and in terms of toxicity equivalents Therefore our results emphasize the importance of the evaporation of PCDD/F from soil which has been clearly demonstrated by the laboratory experiments of KRAUSE[6]. This evaporation may also be a reason why HAGENMAIER et al.[7] could not observe significant homologue or isomer pattern changes in polluted soils over several years. Even transformation rates of 0.1-1 percent, which are well within the analytical accuracy of the soil measurements(± 20 %), would increase the overall toxicity equivalents drastically, if 2,3,7,8-congeners are photochemically formed from "non-toxic" PCDD/F[6,8].

3. References

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Table 1: Ratios of green kale and soil concentrations for PCDD/F, PCB and PAH at 10 sites (μg/kg dry matter/μg/kg dry matter)

Congener/Substance	Range	Average	Median
2,3,7,8-TCDD	0.27 - 1.38	0.61	0.52
1,2,3,7,8-PentaCDD	0.15 - 0.97	0.46	0.37
1,2,3,6,7,8-HexaCDD	0.036 - 0.52	0.27	0.24
1,2,3,4,6,7,8-HeptaCDD	0.033 - 2.6	0.42	0,13
OCDD	0.07 - 7.3	1.1**	0.11
2,3,7,8-TCDF	0.19 - 0.72	0.44	0.39
1,2,3,7,8-PentaCDF	0.038 - 0.25	0.14	0.11
1,2,3,4,7,8-HexaCDF	0.030 - 017	0.097	0.067
1,2,3,4,6,7,8-HeptaCDF	0.012 - 0.12	0.037	0.031
1,2,3,4,7,8,9-HeptaCDF	0.020 - 0.28	0.10	0.033
OCDF	0.004 - 0.097	0.031	0.018
Sum of PCDD/F, TE (BGA)	0.12 - 0.84	0.30	0.22
Sum of PCDD/F, I-TE	0.11 - 0.76	0.27	0.18
PCB No.			
28	0.6 - 8.5	3.6	2.8
52	0.3 - 4.3	1.6	0.8
101	0.13 - 0.86	0.41	0.39
138	0.09 - 0.60	0.23	0.18
153	0.08 - 0.42	0.20	0.14
180	0.03 - 0.22	0.10	0.08
PAH			
Fluorene	(0.09)*	-	-
Anthracene	0.06 - 0.56	0.25	0.17
Phenanthrene	0.09 - 0.47	0.19	0.12
Fluoranthene	0.05 - 0.36	0.14	0.10
Pyrene	0.03 - 0.22	0.08	0.06
Benzo[a]anthracene	0.02 - 0.16	0.06	0.04
Chrysene	0.005 - 0.03	0.01	0.01

* single value
** high value caused by two outliers (1.43 and 7.3)