MEASUREMENT OF THE SPEED OF DIOXIN TRANSFER FROM CROP PLANTS TO THE ATMOSPHERE

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Abstract

The speeds at which dioxins in plants are transferred from crop plant to the atmosphere were measured used ^{13}C-labeled dichlorinated, tetrachlorinated, and hexachlorinated dioxins. The dichlorinated dioxin was transferred the fastest and graphs of the transfer speeds showed that the dioxins were transferred in two stages. All isomers were almost dissapered after 24 hours, after that transfer speeds became slow.

Introduction

It has clearly been shown that dioxins in plants originate from gas-phase dioxins in the atmosphere.[1,2] In addition, the relationship between dioxin concentrations and profiles in plants and in the atmosphere depends on the octanol–air partition coefficients of the dioxins (K_{OA}).1) Therefore, dioxin concentrations and profiles in plants can be predicted from dioxin concentrations and profiles in the atmosphere.[1,2] Moreover, dioxin concentrations and profiles in plants strongly depend on dioxin concentrations and profiles in the atmospheric gas phase at the time when the plant sample is gathered.[3] That is, dioxins in plants do not accumulate over the entire exposure period but instead are continuously transferred in and out of the plants. Do the deposition of the dioxin that entered the plant to the plant inside of the body of how much time once or the time of which extent is required though it is discharged is not cleared. How long the transfer of dioxins between plants and the atmospheric gas phase takes is an interesting question because researchers would like to be able to use plants as an index for environmental monitoring of dioxins in the atmosphere and to be able to reliably predict dioxin concentrations and profiles in plants from dioxin concentrations and profiles in the atmosphere. Then, atmospheric sampling becomes important.

If a method for accomplishing these goals could be developed, it could, of course, also be applied to other persistent organic pollutants. In this study, the time required for transfer of dioxins between plants and the atmospheric gas phase were mesuered. We used ^{13}C-labbled dioxins to achieve the purpose more clearly. It contributes to the prediction of dioxin concentration and profiles.

Materials and Methods

Cultivation of Plants

Corn (*Zea mays* L.) 'Dea' (Pioneer Hi-Bred Japan Co., Tokyo, Japan) and komatsuna (*Brassica rapa* var. *peruviridis*) 'Yokattana' (Kaneko Seeds Co., Maebashi, Japan) were used in these experiments. Seeds of both crops plants were sown in plastic pots (400 × 700 × 150 mm; corn, 2 pots; komatsuna, 1 pot), allowed to grow for 40 days (May 19–June 29, 2004) in a greenhouse, and then used in the following experiments.

Dioxin deposition in the crop plants

The pots of plants were arranged in the growth chamber as shown in Fig. 1 (720 × 1310 × 1015 mm; Yunion-Ace Co., Tsukuba, Japan). The following ^{13}C-labeled dioxins were purchased from Wellington Laboratories Inc. (Ontario, Canada) and used in the experiments: [$^{13}C_{12}$]-2,3-dichloro-dibenzo-*p*-dioxin (Cl_2-dioxin), [$^{13}C_{12}$]-1,3,6,8-tetrachloro-dibenzo-*p*-dioxin (Cl_4-dioxin), [$^{13}C_{12}$]-1,2,3,4,6,7-hexachloro-dibenzo-*p*-dioxin (Cl_6-dioxin). The dioxins (50 μg each) were allowed to soak into silica gel, and then the dioxin-containing silica gel was placed in the chamber with the plants. The door of the chamber was closed, and the chamber was sealed, placed in the greenhouse, and maintained at 25 °C under natural illumination for 7 days. Irrigation was controlled from the outside.

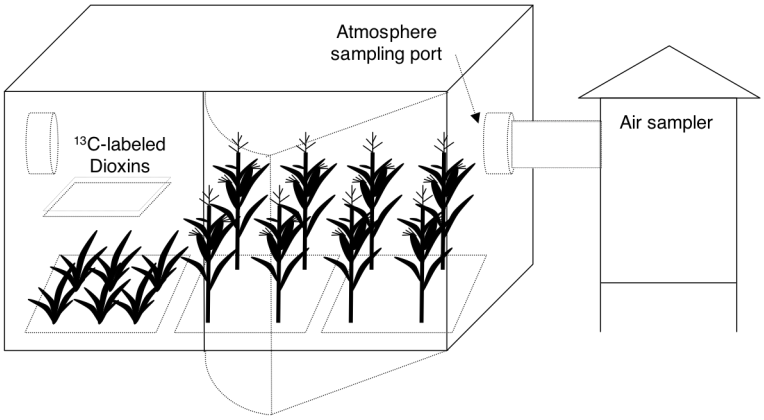

Figure 1. Schematic diagram of the growth chamber

Transfer of dioxins from the crop plants to the atmosphere

After 7 days (on July 5), the door of the chamber was opened (time = 0 h), and the silica gel containing the ^{13}C-labeled dioxins was removed from the chamber. Then the air in the chamber was sampled with a high-volume air sampler (HV-100F, Sibata Scientific Technology, Tokyo, Japan) equipped with polyurethane foam (20 mL/min). Corn was sampled in the order of 5 times (at 0, 4, 24, 72, and 168 h; n = 3), and komatsuna was sampled in the order of 3 times (at 0, 24, and 168 h; n = 1). Then, the air was sampled continuously. The dioxins in the gas phase were adsorbed in the polyurethane foam.

Dioxin analysis

Atmospheric deposition: Dioxins in the polyurethane foam were Soxhlet-extracted with toluene. We purified and fractionated the extracts by means of column chromatography, using silica-gel and activated-carbon columns.

Plant samples: We crushed leaf samples (corn, 80 g fresh weight [FW]; komatsuna, 20 gFW) in dry ice and then added *n*-hexane and acetone (150 mL each) and passed the slurry through a glass-fiber filter (Kiriyama Glass Works, Tokyo, Japan). We washed the filtrate with water, treated it with conc. sulfuric acid, and evaporated, purified, and fractionated the organic layer. Purification and fractionation were carried out as described above.

All samples were analyzed by means of high-resolution gas chromatography combined with high-resolution

mass spectrometry (HRGC/HRMS; HP6890/VG Autospec Ultima, Micromass Technologies, Manchester, UK). The HRGC/HRMS instrument was equipped with a DB-5 column (J&W Scientific, Folsom, CA, USA). [$^{13}C_{12}$]-2,8-Dichloro-dibenzofuran, [$^{13}C_{12}$]-2,3,7,8-tetrachloro-dibenzo-*p*-dioxin, [$^{13}C_{12}$]-1,2,3,4,6,7-hexachloro-dibenzo-*p*-dioxin, and [$^{13}C_{12}$]-1,2,3,6,7,8-hexachloro-dibenzo-*p*-dioxin were used as internal standards. [$^{13}C_{12}$]-1,2,3,4-Tetrachloro-dibenzo-*p*-dioxin was used as an injection spike. Detection limits were as follows: atmosphere: Cl_2, 0.15 pg/m^3; Cl_4, 0.15 pg/m^3; Cl_6, 0.2 pg/m^3 (distribution volume ≒ 1 m^3); corn: Cl_2, 2 pg/g dry weight (DW); Cl_4, 2 pg/g DW; Cl_6, 4 pg/g DW (sampling weight = 80 g FW); komatsuna: Cl_2, 10 pg/g DW; Cl_4, 10 pg/g DW; Cl_6, 20 pg/g DW (sampling weight = 20 g FW). The following log K_{OA} values[1] were used: Cl_2, 8.90; Cl_4, 9.95; Cl_6, 11.0.

Results and Discussion

Dioxin concentrations in the plants and in the atmosphere at t = 0 h are shown in Fig. 2. The Cl_6 isomer was not detected in komatsuna. In both crop plants, the concentration of the dichlorinated dioxin was the highest of the three isomers. The log of the ratio of the dioxin concentrations in the plants and in the atmospheric gas phase is plotted against log K_{OA} for the three isomers in Fig. 3. Straight lines (R^2 = 0.981) were obtained for all three isomers in corn, as reported by Harner et al.[1] The data was a little, a feature difference was not admitted in both crops

The results for the experiments on the disappearance of the dioxins from the crop plants are shown in Fig. 4. The lines were fitted 2 dimention models of the corn experiment. After 24 h, more than half of all three isomers had disappeared

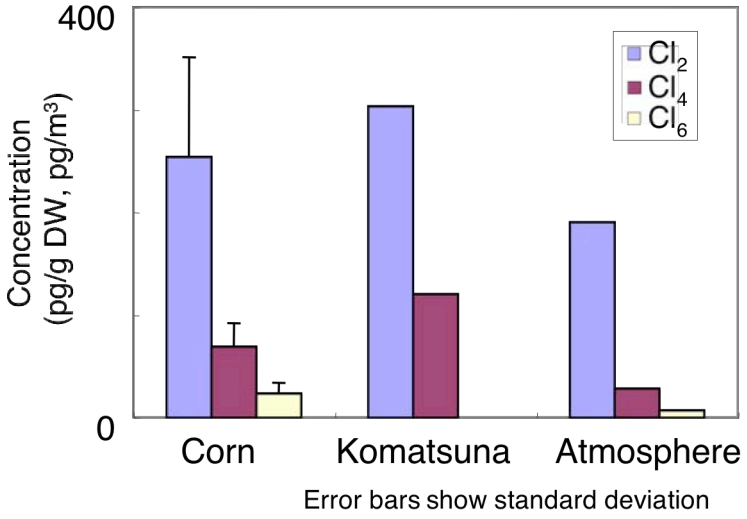

Figure 2. Dioxin concentrations in the crop plants and the chamber atmosphere

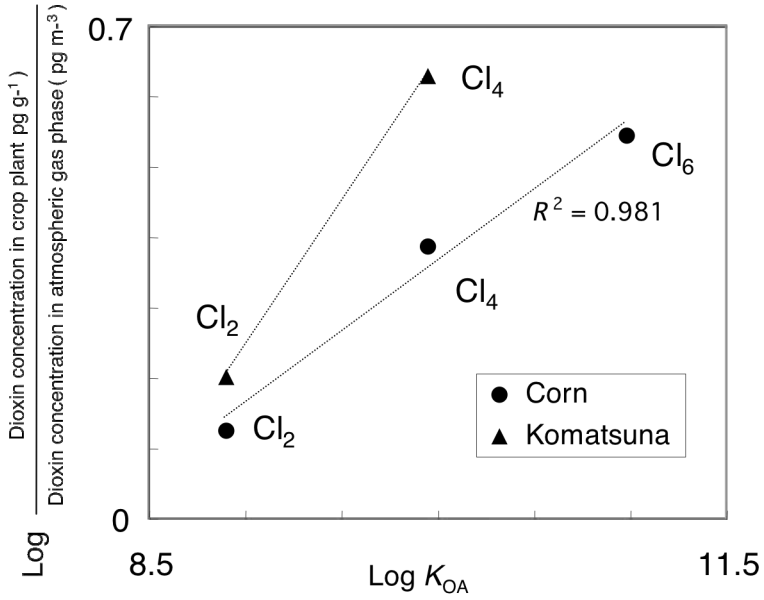

Figure 3. Log plots of (dioxin concentration in crop plant) / (dioxin concentration in atmospheric gas phase) vs. K_{OA}

from both crops. However, in both crops, transfer the three isomers slowed considerably after 24 h. The order of the transfer speeds was $Cl_2 > Cl_4 > Cl_6$. The obvious difference was not admitted in both crops. The reason for the two stages is not clear. There are two possible explanations for this two-stage transfer of the dioxins from the corn: (1) it only took time by the time that reaching stability, or (2) the behavior we observed reflects the distribution of the dioxins in the plants. For example, dioxins on the plant surface may have been transferred rapidly (first stage), and then dioxins inside the plant were transferred (second stage). Dioxins distributed deep inside the plants may be transferred to the atmosphere by means of gas exchange due to photosynthesis and respiration. This hypothesis seems to agree with results indicating that dioxin concentrations in crop plants do not change substantially after harvest. Barber et al.[4] carried out experiments on competitive PCB uptake by *Hemerocallis x hybida* under light conditions and dark conditions and found that PCB uptake differed under the two conditions.

Our results indicate that nearly all the dioxins in the crop plants we tested had disappeared after 1 week. Therefore, if plant was used as the atmospheric environmental monitoring about POPs, it was at about one week to reflect. And if to predict concentration and profiles of dioxins in plant, from several days to one week is preferable for the sampling period of the atmosphere.

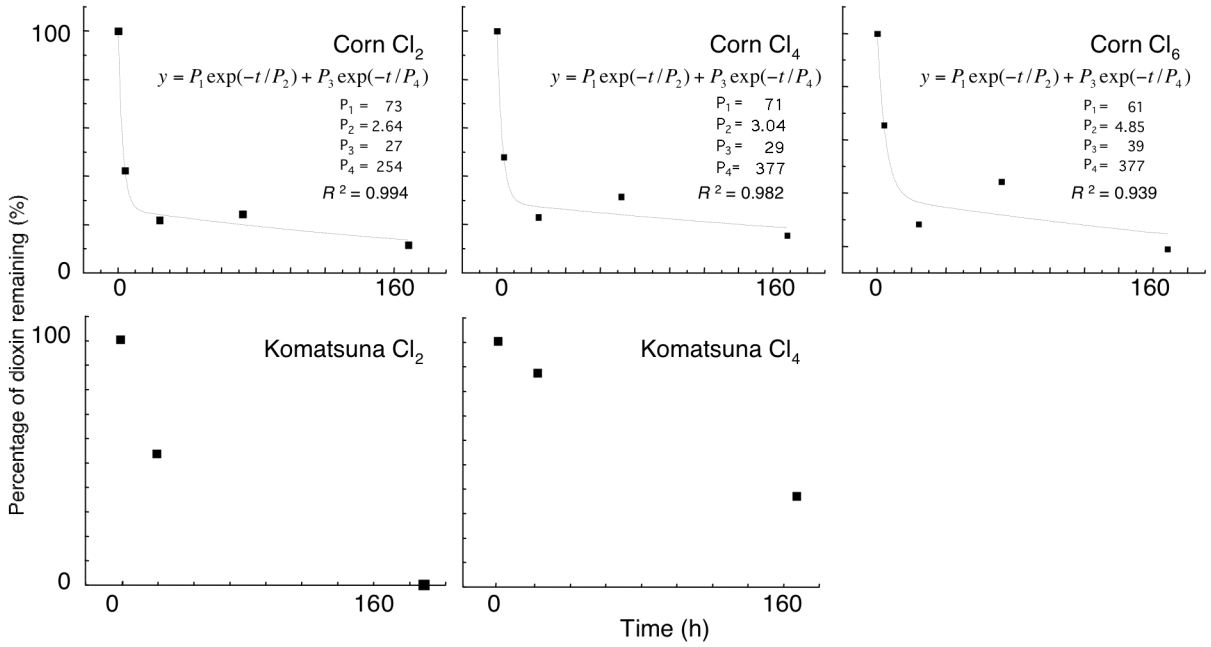

Figure 4. Disappearence of dioxins from the crop plants

References

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4. Barber, J.L., Kurt, P.B., Thomas, G.O., Kerstiens, G., Jones, K.C., 2002. *Environ. Sci. Technol*. 36, 4282-4287.