Photodegradation of PCDD/Fs on Pasture Grass

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Abstract

The effect of UV-B radiation on the uptake of PCDD/F in pasture grass was studied under near natural conditions. While the initial results of this study are not conclusive, they do indicate that if photodegradation of PCDD/F on the leaf surfaces is occurring, it has only a minor influence on the uptake of these compounds in the pasture grass.

Introduction

McCrady and Maggard reported that 2,3,7,8-Cl_4DD is photolytically degraded on the surfaces of reed canarygrass (*Phalaris arundinacea L.*) [1]. Their work suggests that photodegradation could have a significant influence on the accumulation of PCDD/Fs in plants. In contrast to this, we could not find any differences in the chlorine substitution pattern between grass samples (*Lolium multiflorum*) grown on an outdoor plot and grass samples cultivated in greenhouses [2]. As photodegradation would not be expected to affect all PCDD/F isomers equally, this study indicates that photodegradation does not measurably influence the uptake of PCDD/F in this species. In an attempt to clarify this discrepancy, we designed an experiment to examine the effect of photodegradation on the uptake of PCDD/F in plants under near natural conditions. The experiment was carried out using genuine pasture grass due to its importance in the agricultural food chain [3].

Experimental Design

The experiment was conducted during the 1994 growing season on the campus of the University of Bayreuth. The air concentrations of PCDD/F at this site, situated to the south of the city, are low and represent a typical background situation for this area.

The greenhouses

The two greenhouses employed were made of an aluminium profile frame that measured 202 x 222 x 150 cm (H x L x D). One of the greenhouses (G I) was glassed in with normal window glass (4 mm) with an UV cutoff at 320 nm (Fig. 1). For the second greenhouse (G II) we used plexiglass (4 mm) with an UV-light transmission of > 50 % in the 280-320-nm range (Fig. 2) which is relevant for photolytic reactions of PCDD/F [4].

The glass transmission was checked repeatedly throughout the experiment using a photometer (UVIKON 930, Kontron Instruments).

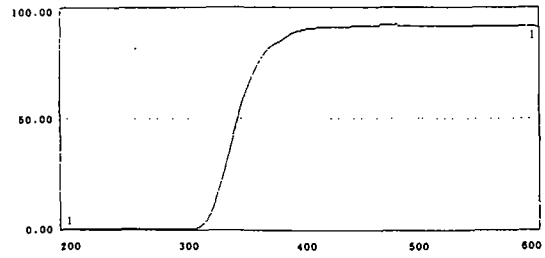

Fig. 1: UV transmission of window glass / percent transmission versus wavelength (nm)

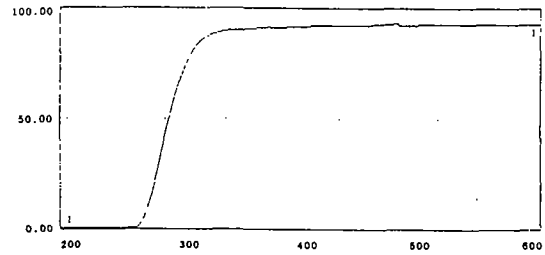

Fig. 2: UV transmission of plexiglass / percent transmission versus wavelength (nm)

There was a roof window (70 x 63 cm) in each greenhouse and at the bottom 30 cm of the walls were not glassed in to allow for ventilation.

The grass cultures

The experiment was conducted employing genuine grass cultures from a pasture located to the south of Bayreuth. This pasture was classified as *Arrhenatherion elatioris*, a typical representative of German grassland. The grass sod was transplanted into containers (78 x 46 x 30 cm; L x W x H). Six containers were placed in each greenhouse, thus providing a vegetation surface of about 2 m^2 per greenhouse. Water was supplied from below through a layer of gravel and a second layer of clay pellets at the bottom of the containers. A fertilizer solution was added to this water reservoir following the first harvest (see below).

Harvest

The experiment started on June 15, 1994. On August 18 the first harvest was conducted whereby the grass in the greenhouses was cut back to about 4 cm and weighed in order to determine the biomass production of each plot. Afterwards the plant material was packed in aluminium foil and stored at -18 ° C. A second exposure ran from August 19 to October 11.

Analytical Methods

The grass samples were freeze-dried and pulverized in a blender. Extraction was carried out in a soxhlet device using toluene for 16 h. An internal standard mixture containing 12 $^{13}C_{12}$ labelled 2,3,7,8-substituded PCDD/F congeners representing all 10 homologue groups was added prior to extraction. After rotary evaporation the extracts were first passed through a combined Na_2SO_4, H_2SO_4/silica gel, silica gel, NaOH/silica gel column that was eluated with n-hexane. The purified extract was then fractionated on a basic alumina column. The PCDD/F fraction was concentrated almost to dryness, a labelled recovery standard was added, the samples were again reduced almost to dryness and taken up in 20 µl of toluene. Analytical blanks were run regularly.

The samples were analysed using an HP-5890 II gas chromatograph coupled to a VG Autospec Ultima mass spectrometer operating in EI mode at 34 eV with a resolution of 10,000. A DB-5-MS capillary column (J&W), 0.25 mm x 0.10µm, was employed.

Results

For the summer as well as for the autumn exposure 4 parallel samples were analysed for each grass plot i. e. greenhouse. The agreement between the parallels was in all cases satisfactory as is shown in Fig. 3 for G I and the summer exposure.

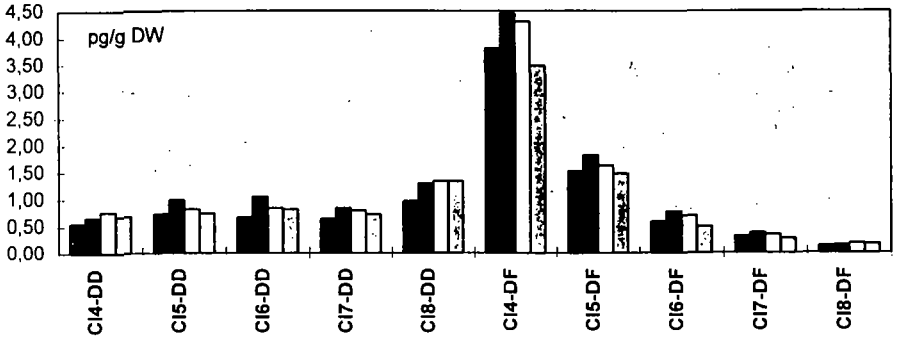

Fig 3.: Comparison of the PCDD/F concentrations in 4 parallel grass samples

The recovery of the internal standards was 86 % (mean).

The average concentrations of the PCDD/F homologues in the grass from the two greenhouses following the summer exposure are plotted in Fig. 4. The results for the autumn exposure are plotted in Fig. 5. In both cases the concentrations of the PCDD/F are similar in the grass exposed to UV-light and in the grass that was not exposed. There is some indication in Fig. 4 that the levels of several homologues in the grass exposed to UV-light are lower than in the non-exposed control. Further investigation of the isomer patterns and possible chamber effects should yield more information as to whether photolytic degradation did indeed lead to different concentrations. However, from the results now available it is clear that if there is indeed an effect, it is a relatively insignificant factor in the accumulation of PCDD/F in the pasture grass studied here.

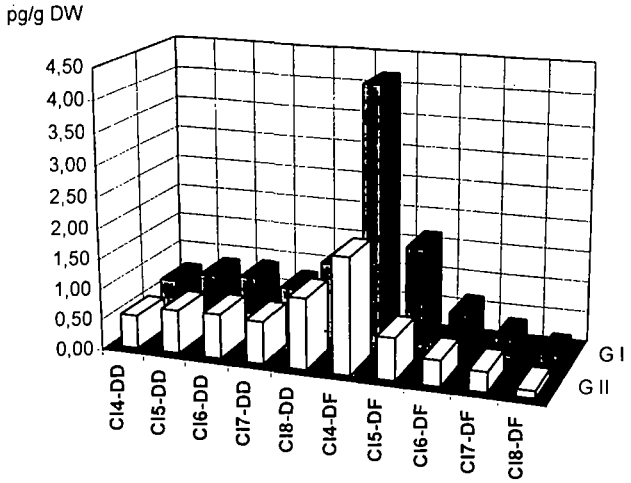

Fig. 4: Comparison of PCDD/F concentrations in grass samples of G I and G II / summer '94

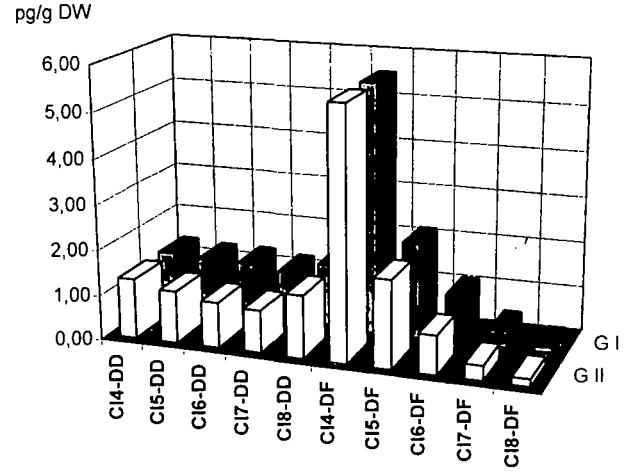

Fig. 5: Comparison of PCDD/F concentrations in grass samples of G I and G II / autumn '94

Acknowledgement

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