

# DIOXIN PREVENTION & REDUCTION

## PRELIMINARY STUDIES ON PHOTOLYSIS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS ON SOILS SURFACE

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### Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are ubiquitous environmental contaminants, and widely distributed in air, water and soil. They are persistent in the environment and accumulate in living organisms. Some of these compounds are extremely toxic and carcinogenic to animals and possibly humans<sup>1</sup>. The Occurrence of PCDDs/PCDFs in the environment originated from both natural and anthropogenic sources. Anthropogenic sources are not manufactured for commercial purposes. These toxic compounds, however, are formed as unintentional by-products from chemical impurities in various industrial processes involving chlorine or by burning organic matter in the presence of chlorine molecules<sup>2,3</sup>. A significant portion of PCDDs accumulated in soils in Japanese paddy fields was shown to have originated from agrochemicals, especially pentachlorophenol (PCP) and chloronitrofen (2,4,6-trichlorophenyl-4'-nitrophenyl ether, CNP)<sup>4,5</sup>. Their impurities of PCP were mostly highly chlorinated congeners, especially OCDD that currently remains to the level of 20,000 pg/g in paddy soils.

Compounds such as PCDDs/PCDFs that absorbed UV/Vis light can react photochemically by reaching excited state through the direct absorption of light (direct photolysis) or by accepting energy from an excited donor molecule (sensitized photolysis). Reactions can also occur with reactive oxygen species such as singlet oxygen, hydroxyl radicals, etc., formed from photochemical interactions with other organic molecules such as humic acids. Direct photolysis is the only mechanism for photolysis of organic chemicals in pure water and hydrocarbon solutions. However, PCDDs/PCDFs solubilities are extremely low in pure water. The low solubilities of these compounds in aqueous solution make photolysis experiments difficult. Therefore, in most previous studies of photolysis in aqueous solutions an acetonitrile/water mixture was used, furthermore, photolysis experiments were conducted through exposing samples to UV light emitted by Hg-lamps<sup>6,7,8,9</sup>. The photocharacteristics of these lamps were not similar to sunlight. So, it is difficult to predict photolysis of PCDDs/PCDFs in the environment.

Photolysis by sunlight is potentially an important process for transformation of higher chlorinated compounds, especially OCDD (relatively lower toxic) to lower chlorinated compounds (relatively higher toxic) or to the other degradation products. However, little data are available concerning the photolysis of PCDDs on soil surfaces by sunlight. Therefore, the objective of this study is to design the photochemical apparatus for equipped with the solar simulator to evaluate the photolysis of PCDDs/PCDFs on soil surfaces. The apparatus is similar to the spectral characteristics of solar radiation, especially the wavelength region of about 280 to 400 nm.

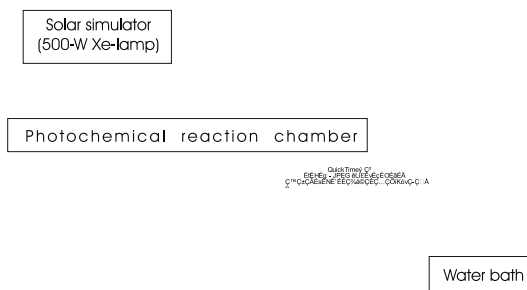
### Methods and Materials

#### *Photolysis equipments*

The photolysis experiments were performed using a 500-W Xe-lamp (xenon arc lamp, Model: WXS-105C-5, AM1.5GUV, WACOM) and photochemical reaction chambers (borosilicate glass) with

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top quartz plates as irradiation window for soil samples (Fig.1). The Xe-lamp was approximated to especially near-ultraviolet region (280 to 400 nm) of standard solar radiation (AM1.5G: Air Mass filter) by modifying optical filters. The irradiation intensity of this Xe-lamp was 85 to 120 mw/cm<sup>2</sup>, and the spectral characteristic was evaluated by measuring with a UV-VIS-NIR (ultraviolet-visible-near infrared) spectrophotometer (V-570: JASCO) over a wavelength range of 280-2000 nm. The photochemical reaction chamber with a size of 10 cm diameter is separable (effective irradiation diameter: 10 cm, the upper and lower chamber volumes ca. 400 ml and ca. 280 ml, respectively).



**Figure 1.** Experimental apparatus the photolysis experiments of PCDDs/PCDFs on soil surfaces

## *Reagents and soil samples*

OCDD were obtained from Cambridge Isotope Laboratories, Inc. Soil used for this study was collected from 0 to 5 cm depth increment at the experimental field of National Institute of Agro-Environmental Sciences, Tsukuba, Japan. The soil type is Hydric Hapludand. Furthermore, reference samples of clay were obtained from the Clay Science Society of Japan. The physical chemical properties of the clay reference sample (montmorillonite, Tukifu, JCSS-3101) were presented in Table 1. These samples were air-dried, homogenized, and sieved (<2 mm). Fortified samples were prepared by adding a large excess volume of benzene and standard solution of OCDD to the samples to obtain ca. 5000 pg OCDD/g soil samples. After fortification, the samples were homogenized and kept at room temperature for 2 days to allow evaporation of solvent.

## *Irradiation experiments*

Photolysis experiments were conducted through exposing soil samples to light emitted by a Xe-lamp by immersion in a water bath. (25 °C). A contribution depth of photolysis was evaluated by measuring penetration light through soil samples on a quartz plate. These soil layers were divided by placing a stainless steel mesh disk (diameter: 10 cm, wire diameter: 0.274 mm, voidage: 40 %).

## *Analytical Procedures*

PCDDs/PCDFs concentrations in soil samples were measured according to the standard method of Ministry of the Environment, Japan.

## **Results and Discussion**

Figure 2 shows photocharacteristics of the solar simulator and standard solar radiation (AM1.5G). Near-ultraviolet region of solar radiation is important in photolysis of compounds such as PCDDs/PCDFs on soil surfaces. The solar simulator well reproduced especially near-ultraviolet region (280 to

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**Table 1.** The characteristics\* of the reference

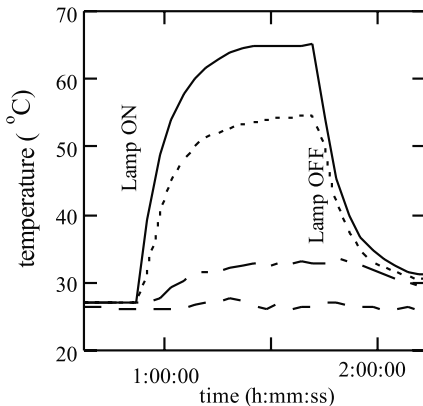
used in photolysis experiments		
SiO	61.3 CaO	0.46 (%)
Al O	21.9 Na O	4.06
TiO	0.15 K O	0.12
Fe O	1.9 P O	0.02
FeO	0.31 Ignition Loss	6.24
MnO	0.01 Total	99.9
MgO	3.43	

C	0.1228
H	1.6913
N	0.0289

\*The Standard Clay Committee, The Clay

Science Society of Japan.

- air space in the photochemical reaction chamber
- soil below a stainless steel mesh disk
- soil surface
- water



**Figure 3.** Changes of temperature conditions in the photochemical reaction chamber

**Table 2.** Changes of TEQ by photolysis of OCDD on reference clay samples

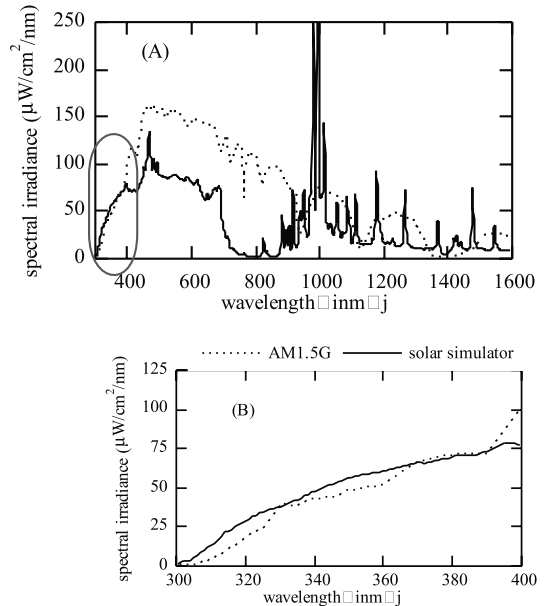
	original	fortified by OCDD	the lowerlayer irradiated <sup>a</sup>	the upper layer irradiated <sup>b</sup>	dark
TEQ	0.039	0.310	1.050	5.375	1.000

\*TEQ for only OCDDs (pg-TEQ/g)

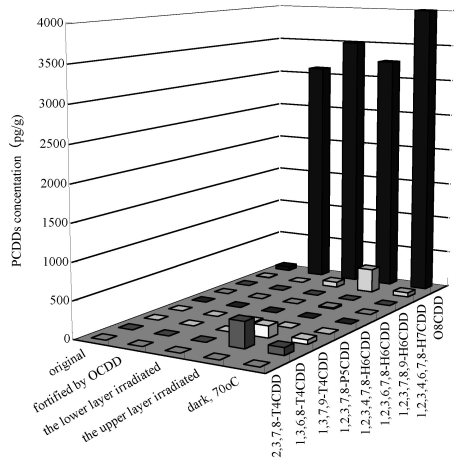
TEQ were calculated concentration of less than quantitative limits as "0".

<sup>a</sup>below the stainless mesh disk

<sup>b</sup>on the stainless mesh disk



**Figure 2.** Photocharacteristics of the solar simulator (a 500-W Xe-lamp) approximated to especially near-ultraviolet region (280 to 400 nm) of standard solar radiation (AM1.5G)



**Figure 4.** Photolysis of OCDD on the clay reference sample (montmorillonite, Tukifu, JCSS-3101) by the solar simulator

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400 nm) of standard solar radiation. Furthermore, the effective irradiation area of the solar simulator was  $\varnothing$  105 mm, the homogeneity within the irradiation area was less than  $\pm 3\%$ , and the parallelism of the light was less than  $\pm 3^\circ$ .

The penetration light through a soil layer of 2.0 mm thickness on a quartz plate was not detectable, and almost zero. The contribution of photolysis was judged to the 2 mm depth of soil surface. These soil layers were divided by placing a stainless steel mesh disk in depth of 2mm from the soil surface.

Figure 3 shows temperature changes of the photochemical reaction chamber under irradiation by the solar simulator. The temperature in the chamber was controlled below  $65^\circ\text{C}$  by immersion in water to cut heat ray with water of some mm depth.

After fortification by OCDD, montmorillonite clay samples were irradiated with the solar simulator for 168 hrs. Further, control samples were kept in a dark place at  $70^\circ\text{C}$ . The dechlorinated compounds of OCDD were generated by photolysis on the soil surfaces, and the TEQ (Toxicity Equivalency Quantity) limited to PCDDs increased in about 5 times at this time point. This new technique with the solar simulator can be applied easily to predict the fate of PCDDs/PCDFs by sunlight under the environmental condition.

## Acknowledgments

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