

## PHOTOLYSIS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND ENHANCED DETOXICATION BY TITANIUM DIOXIDE PHOTOCATALYST ON SOILS SURFACE

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### *Introduction*

The occurrence of PCDDs/PCDFs in the environment originates from both natural and anthropogenic sources. Anthropogenic sources 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>1,2,3</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.

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. Increase of montmorillonite clays' TEQs (Toxicity Equivalency Quantity), by irradiation with the solar simulator, was reported by Kobara<sup>6</sup>. Therefore, the objective of this study is to enhance detoxication by applying titanium dioxide (TiO<sub>2</sub>) photocatalyst to clay samples contaminated with OCDD.

### *Methods and Materials*

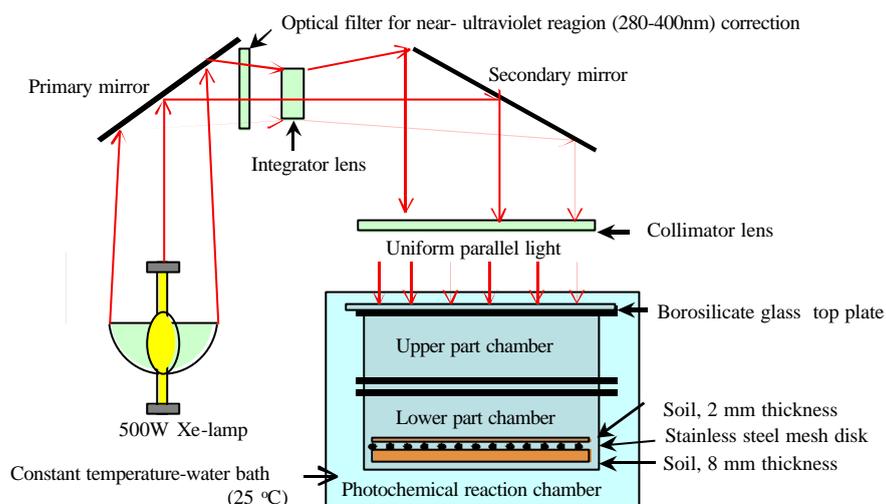
#### *Photolysis equipments*

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 top quartz or borosilicate 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 280-2000nm. The photochemical reaction chamber with a size of 10 cm diameter is separable (effective irradiation diameter: 10cm, the upper and lower chamber volumes ca. 400 ml and ca. 280 ml, respectively).

#### *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 for Agro-Environmental Sciences, Tsukuba, Japan. The soil type is Hydric Hapludand. Further,

reference samples of clay were obtained from the Clay Science Society of Japan. The physical chemical properties of clay reference samples (montmorillonite, Tukifu, JCSS-3101 and kaolinite, Kanpaku, JCSS-1101) 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. 10,000 pg OCDD/g soil samples. After fortification, the samples were homogenized and kept at room temperature for 2 days to allow evaporation of solvent. TiO<sub>2</sub> photocatalyst, ST-01 was obtained from Ishihara Sangyo Kaisha, Ltd.



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

#### ***Irradiation experiments***

Photolysis experiments were conducted through exposing soil samples to light emitted from a Xe-lamp by immersion of photochemical reaction chambers to 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%) in Fig. 1.

#### ***Analytical Procedures***

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

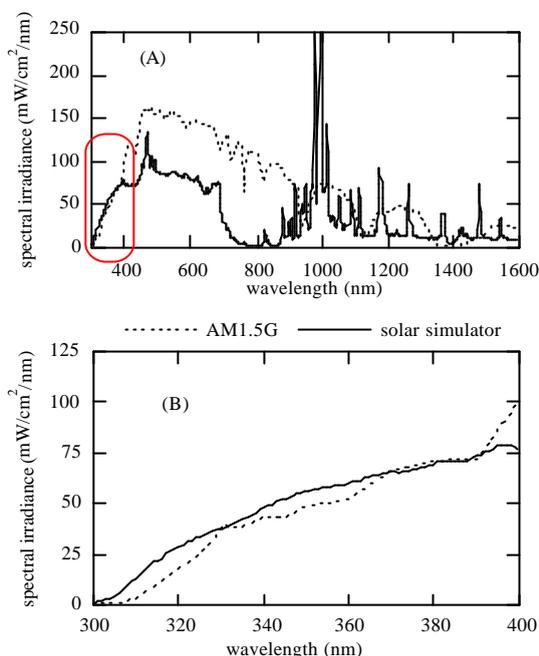
#### ***Results and Discussion***

Near-ultraviolet region of solar radiation is important in photolysis of compounds such as PCDDs/PCDFs on soil surfaces. Photocharacteristics of the solar simulator and standard solar radiation (AM1.5G) is shown in Fig. 2. The solar simulator well reproduced especially near-ultraviolet region (280 to 400 nm) of standard solar radiation (AM 1.5G). The penetration light through a soil layer of 2.0 mm thickness on a quartz plate was not detectable, and almost zero. The

**Table 1.** The characteristics\* of the reference clay samples in photolysis experiments

	montmorillonite, Tukifu, JCSS-3101	kaolinite, Kanpaku, JCSS-1101
SiO <sub>2</sub>	61.3	46.45
Al <sub>2</sub> O <sub>3</sub>	21.9	39.52
TiO <sub>2</sub>	0.15	0.17
Fe <sub>2</sub> O <sub>3</sub>	1.90	0.04
FeO	0.31	0.01
MnO	0.01	n.d.
MgO	3.43	0.06
CaO	0.46	0.04
Na <sub>2</sub> O	4.06	0.05
K <sub>2</sub> O	0.12	0.01
P <sub>2</sub> O <sub>5</sub>	0.02	0.19
Ig. Loss	6.24	14.2
Total	99.9	100.74
CHN content (%)		
C	0.1228	0.0583
H	1.6913	1.7191
N	0.0289	0.0182

\*The Standard Clay Committee, The Clay Science Society of Japan  
n.d.: not detected



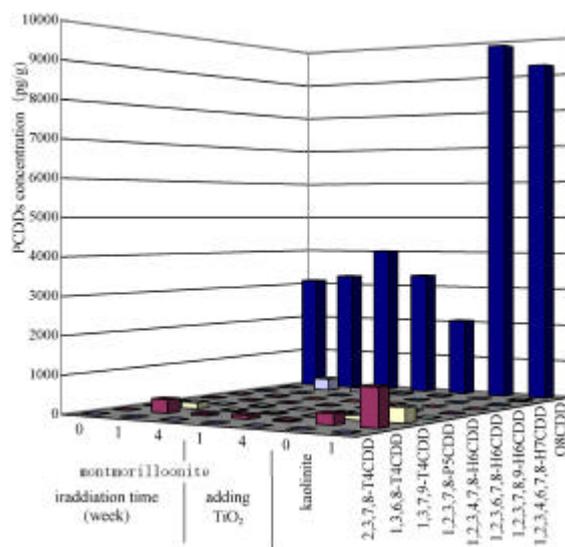
**Figure 2.** Photocharacteristics of the solar simulator (a 500-W Xe-lamp) approximated to especially near-ultraviolet region (280 to 400 nm) of standard solar radiation (AM1.5G)

contribution of photolysis was judged to the 2mm depth of soil surface. These soil layers were divided by placing a stainless steel mesh disk in depth of 2mm from the soil surface.

Fortified samples were prepared by adding a large excess volume of benzene and standard solution of OCDD to the clay samples to obtain ca. 10,000 pg OCDD/g soil samples. After fortification, the analysis values of initial OCDD concentration in montmorillonite and in kaolinite were 3,100 pg/g and 9800 pg/g, respectively (Fig. 3), and their recoveries were values to be different more than 3 times. Montmorillonite typically forms microscopic or at least very small platy micaceous crystals, and has a high specific surface area (600-800 m<sup>2</sup> g<sup>-1</sup>). On the other hand, Kaolinite's structure is composed of silicate sheets (Si<sub>2</sub>O<sub>5</sub>) bonded to aluminum oxide/hydroxide layers (Al<sub>2</sub>(OH)<sub>4</sub>) called gibbsite layers, and has a relatively small specific surface area (10-55 m<sup>2</sup> g<sup>-1</sup>). The decrease of initial OCDD concentrations was related to the specific surface area of montmorillonite. OCDD adsorption in clays strongly depends on the specific surface area of the material.

Montmorillonite and kaolinite clay samples were irradiated with the solar simulator. The dechlorinated compounds of OCDD were generated by photolysis on the soil surfaces (2 mm thickness), and the TEQ limited to PCDDs increased in about 87 times after 4 weeks in montmorillonite, and 1.3 times after 1 week in kaolinite, respectively. The scatter in OCDD measurement values of only montmorillonite was within the measurement errors. The applying of TiO<sub>2</sub> photocatalyst into the soil (2 mm depth, soil: TiO<sub>2</sub>= 20:1) prevented TEQ's increase by enhanced decomposition. Tendencies of photolysis were not observed in these experiments, and

photolysis appeared to occur on only clay crystal surfaces. These techniques with the solar simulator and TiO<sub>2</sub> photocatalyst can be applied easily to predict the fate of OCDD, and enhance photolysis by sunlight under the environmental condition.



**Figure 3.** Photolysis of OCDD on the clay reference samples by the solar simulator

**Table 2.** Changes of TEQ by photolysis of OCDD on reference clay samples and by the addition of TiO<sub>2</sub> photocatalyst

	montmorillonite, Tukifu, JCSS-3101			adding TiO <sub>2</sub> (0.5g) to clay samples (10g)		kaolinite, Kanpaku, JCSS-1101	
	0	1	4	1	4	0	1
irradiation time (week)	0	1	4	1	4	0	1
TEQ*	0.31	1.1	27	0.60	0.43	0.98	1.3

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

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

#### Acknowledgments

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