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Transformation of triclosan to 2,8-dichlorodibenzo-*p*-dioxin by iron and manganese oxides under near dry conditions

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HIGHLIGHTS

- Fe and Mn oxides catalyzed the transformation of triclosan.
- Triclosan was converted to 2,8-DCDD under near dry conditions.
- Water inhibited the formation of 2,8-DCDD.

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ABSTRACT

Triclosan (TCS) is a broad-spectrum antibacterial agent widely used in household and personal care products and is frequently detected in the environment. Previous studies have shown that TCS could be converted to the more toxic compound 2,8-dichlorodibenzo-*p*-dioxins (2,8-DCDD) in photochemical reactions and incineration processes. In this study, we demonstrated the formation of 2,8-DCDD from the oxidation of TCS by α-FeOOH and a natural manganese oxides (MnO_x) sand. Experiments at room temperature and under near dry conditions showed that Fe and Mn oxides readily catalyzed the conversion of TCS to 2,8-DCDD and other products. Approximately 5.5% of TCS was transformed to 2,8-DCDD by α-FeOOH in 45 d and a higher conversion percentage (6.7%) was observed for MnO_x sand in 16 d. However, the presence of water in the samples significantly inhibited the formation of 2,8-DCDD. Besides 2,8-DCDD, 2,4-dichlorphenol (2,4-DCP), 4-chlorobenzene-1,2-diol, 2-chloro-5-(2,4-dichlorophenoxy)-benzene-1,4-diol, and 2-chloro-5-(2,4-dichlorophenoxy)-1,4-benzoquinone were identified in the reactions. The possible pathways for the formation of reaction products were proposed. This study suggests that Fe and Mn oxides-mediated transformation of TCS under near dry conditions might be another potential pathway for the formation of 2,8-DCDD in the natural environment.

1. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol, TCS) is commonly used as an antibacterial agent in many personal care (e.g., cosmetics, deodorants, toothpaste, soaps, and shampoos) and consumer products (e.g., plastic kitchenware, knickknack, and garbage bags) (Bedoux et al., 2012). It was estimated that TCS is present in more than 200 kinds of daily chemical products and other new emerging products which are currently being used in over 50 countries (SCCS, 2010). TCS is frequently detected in the influent of wastewater treatment plant (Suarez et al., 2007). Owing to the high hydrophobicity ($\log K_{ow} = 3.5–4.8$), more than 90% of TCS can be removed in conventional activated sludge wastewater treatment via the sorption to biosolids (Heidler and Halden, 2007). Davis et al. (2012) found that TCS concentrations in municipal sewage sludge and biosolids ranged from 4.9×10^2 to 1.4×10^4 ng g^{-1} (dry weight). TCS tends to bioaccumulate in organisms and the frequent detection of this contaminant in biosolids is of emerging concern. The high concentration of TCS in biosolids raises a controversy on its fate after the land application of biosolids.

One of the biggest concerns on the fate of TCS in the environment is its conversion to the more toxic compound 2,8-dichlorodibenzo-*p*-dioxins (2,8-DCDD) (Suarez et al., 2007). For example, 2,8-DCDD was readily formed in the photochemical transformation of TCS (Mezcua et al., 2004; Chen et al., 2008; Buth et al., 2009, 2010). Chen et al. (2008) demonstrated the formation of 2,8-DCDD and dimers in the photodegradation of TCS

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in an aqueous medium with a relatively high TCS concentration >30 mg L^{-1}. In view of the prevalence and photochemical conversion of TCS, Buth et al. (2009) suggested that TCS and its chlorinated derivatives may be an important source of dioxins (i.e., di-, tri-, and tetrachlorinated dibenzo-*p*-dioxins) in sediment cores. In addition, TCS may be transformed to chlorodioxins during heating and incineration processes (Kanetoshi et al., 1988; Wiater-Protas and Louw, 2001). For instance, Kanetoshi et al. (1988) showed the formation of polychlorinated dibenzo-*p*-dioxins upon the combustion of commercial textile products containing TCS at 600 °C.

Once entering into the environment via biosolids application, TCS may react with soil components such as clay minerals. Metal oxides (e.g., Fe and Mn oxides) are commonly found in soils and sediment and play an important role in the transformation of organic contaminants in the natural environment (Borch et al., 2010; Liu et al., 2014). For example, goethite (hydrous ferric oxide, α-FeOOH), a pure crystalline iron oxide with a redox potential of 0.67 V, is widely present in soils, subsoils, sediments, and prehistoric clay deposits (Stone and Morgan, 1987). Manganese oxides are another important naturally occurring oxidant in soils and sediments with a higher redox potential of 1.23 V (McBride, 1994). Many previous studies have shown that Fe and Mn oxides mediated the abiotic transformation of organic contaminates (Stone and Morgan, 1984; Kriegman-King and Rheinhard, 1992; Torrents and Stone, 1993; McBride, 1994; Post, 1999; Lin et al., 2009, 2012, 2014). The oxidation of organic contaminants by the oxides generally involves an electron transfer process from the organics to the oxides, forming radical intermediates which may undergo reactions such as radical coupling, bond cleavage (Stone and Morgan, 1984; Kriegman-King and Rheinhard, 1992; Torrents and Stone, 1993; McBride, 1994; Post, 1999; Lin et al., 2009, 2012, 2014). Although the transformation TCS by Fe(III)-montmorillonite and MnO_2 has been previously studied (Zhang and Huang, 2003; Liyanapatirana et al., 2010), the identified products mainly included 2,4-dichlorophenol, 2-chloro-5-(2,4-cichlorophenoxy)-[1,4] benzoquinone and 2-chloro-5-(2,4-cichlorophenoxy)benzene-1,4-diol, and dimmers, likely as a result of the reaction of the forming TCS radical. However, it is unclear whether 2,8-DCDD can be formed from the oxidative transformation of TCS by Fe and Mn oxides.

The aim of this study is to test whether 2,8-DCDD can be formed from TCS via the oxidation of Fe and Mn oxides. Specifically, a natural manganese oxides sand and α-FeOOH were used as the model oxides. The formation products were indentified and possible reaction pathways were proposed. In addition, the effect of water content on the formation of products was also evaluated.

2. Materials and methods

2.1. Chemicals

Triclosan (purity > 97%) and 2,4-dichlorophenol (2,4-DCP) (purity > 99%) were purchased from Sigma–Aldrich (St. Louis, MO). Standard of 2,8-DCDD (purity > 99%) was purchased from Accustandard (New Haven, CT). Acetone and *n*-hexane were high performance liquid chromatography grade. Other chemicals and solvents used in this study were of analytical grade. Ultrapure water (18.2 MΩ-cm resistivity) was prepared using a Millipore purification system (Millipore S.A.S, Molsheim, France). Stock solution of 1000 mg L^{-1} TCS was prepared in acetone.

Three oxides were used to evaluate the transformation of TCS. Goethite I [iron (III) oxide, α-FeOOH, catalyst grade, 30–50 mesh] was purchased from Sigma–Aldrich and specified as Sig-FeOOH. Goethite II was synthesized in our laboratory as described by Lin et al. (2012) and specified as Syn-FeOOH. Both Sig- and Syn-FeOOH displayed all the typical diffraction peaks of goethite (standard XRD spectrum PDF # 29-0713) in the analysis of X-ray powder diffraction (XRD). However, scanning electron microscopy (SEM) analysis suggested that Sig-FeOOH exhibited a smaller and consistent particle size and a more uniform distribution. The surface area was 177 $m^2\,g^{-1}$ for Syn-FeOOH and 75 $m^2\,g^{-1}$ for Sig-FeOOH. The natural manganese oxides (MnO_x, contains 33% of MnO_2) sand was purchased from Kaiyuan Ceramic Materials (Dengfeng, Henan, China) and was sieved through 60-mesh prior to use. The surface area of the MnO_x sand was 28 $m^2\,g^{-1}$.

2.2. Reaction setup

All reactions were carried out in 10-mL amber glass centrifuge tubes. The reaction was prepared by mixing 1 μg TCS (dissolved in 0.5 mL acetone) with 1.0 g Sig-FeOOH, Syn-FeOOH or natural MnO_x sand and the acetone was allowed to evaporate in a fume hood. The use of solvent ensured TCS to homogeneously spread on the surface of the oxides. The nominal initial concentration of TCS was 6.94 μmol kg^{-1} oxides. The treated samples were incubated at room temperature (25 ± 1 °C) and in the absence of light. For the reaction under near-dry conditions, samples were maintained in a desiccator with a relative humidity less than 8%. To investigate the effect of water on reaction, a suite of samples was reacted under humid conditions with 50% (wt%) of water. The water content in samples was maintained by weighing the samples daily and deionized water was added to compensate water loss when necessary. At given time intervals, triplicate samples were withdrawn and extracted twice with 10 mL of 1:1 (v/v) acetone/hexane. For extraction, the mixtures were shaken on a shaker for 20 min and then centrifuged at 5346 g for 5 min. The supernatant was collected using a pipette to determine the residual TCS and the formation of reaction products.

2.3. Chemical analysis

The analysis of TCS and reaction products was carried out on an Agilent 7890A gas chromatograph (GC) coupled with an Agilent 5975C mass spectrometer (MS) (Agilent Technologies, Wilmington, DE, USA) operated on a full scan mode (50–600 amu). An HP-5MS column (30 m × 0.25 mm × 0.25 mm; Agilent) was used for the separation. The inlet temperature was 280 °C, and the detector temperature was 300 °C. The oven temperature was initiated from 80 °C and held for 2 min, then increased to 300 °C at 10 °C min and held for 10 min. The flow rate of the carrier gas (helium) was 1.0 mL min^{-1}. The injection of 2 μL sample was carried out by an Agilent 7693 autosampler in a pulsed splitless mode. The temperatures of transfer line, ion source, and MS detector were 280 °C, 230 °C, and 150 °C, respectively. For the identification of reaction products, the MS detector was operated in the electron impact mode at 70 eV and the mass spectra were acquired in a full scan mode with m/z ranging from 50 to 700 amu. The residual TCS was quantified based on the ion m/z 252.

To quantify the formation of Fe^{2+} and Mn^{2+} during reaction, an additional set of samples was also included. At designated time intervals, samples were withdrawn and 5 mL of water was immediately added into the samples. The samples were then shaken on a shaker for 5 min and centrifuged at 5346 g for 5 min. The supernatant was collected to determine the formation of Fe^{2+} or Mn^{2+}. The concentration of Fe^{2+} was measured according to the ferrozine colorimetric method (Viollier et al., 2000), which is based on a spectrophotometric method via the stoichiometric reaction of Fe^{2+} with ferrozine and hydroxylamine hydrochloride. The formation Mn^{2+} was determined using an AAanalyst 800 flame atomic absorption spectrometer (Perkin–Elmer, Waltham, MA). A deuterium lamp was used as background correction and the