

EFFECT OF OXYGEN CONTENT ON THE THERMAL DESORPTION OF POLYCHLORINATED BIPHENYLS CONTAMINATED SOIL

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1. Introduction

Soil contamination by polychlorinated biphenyls (PCBs) has become a big issue in China because of the leakage of PCB-containing oil from waste capacitors and transformers at their storage sites¹. With the contamination of PCBs spreading in large areas, effective and proven remediation technologies for PCBs decontamination in soil or sediments are needed, such as biodegradation, solvent extraction, chemical oxidation, and thermal treatment². Thermal desorption is a most operative method³ and many studies were devoted to the effect of temperature, heating time, particle size, pressure and flow rate of carrier gas on the thermal desorption of PCBs contaminated soil⁴⁻⁷. However, the formation of PCDD/Fs during thermal desorption of PCBs contaminated soil are not involved in these studies.

Under anaerobic conditions, thermal desorption of PCBs is accompanied by dechlorination and decomposition. While in the presence of oxygen PCBs may act as precursors of the polychlorinated dibenzofurans (PCDFs)⁸. Weber⁹ and Zhao et al.¹⁰ investigated the formation pathways of PCDFs in the presence of oxygen, including the loss of ortho-Cl, ortho-H, or HCl, involving a 2,3-chlorine shift and dechlorination of PCBs. It is necessary to study the behaviour of PCDD/Fs in carrier gas containing oxygen, and to investigate the effect of oxygen content on the formation of PCDD/Fs. Therefore, thermal desorption with several carrier gases with different oxygen content were conducted to study the concentrations of PCBs and PCDD/Fs in evolved gas and treated soil after thermal desorption of PCBs contaminated soil.

2. Materials and methods

2.1 Pretreatment and properties of soil samples

Soil samples were collected from the vicinity of one capacitor storage site in Zhejiang Province, China. This site was heavily contaminated by PCBs because of oil leakage from waste PCB capacitors. The soil samples were shattered and screened through a 60 mesh sieve; the particle size of the soil is less than 250 μ m.

Physicochemical properties of contaminated soil are shown in Table 1. The moisture content of soil sample is 11.3% and the organic matter content is 3.02%. All the heavy metal content values are below the limits of national soil standards in China.

Table 1. Physicochemical properties of contaminated soil

Properties	Value
Soil texture	Sand (32.6%); silt (38.8%); clay (28.6%)
pH	6.83
Chlorine content, %	0.898
Organic matter content, %	3.02
Bulk density, g/cm ³	1.65
Porosity, %	59.1
Water content, %	11.3%

2.2 Experimental apparatus and conditions

The experiment system, consisting of the supply of carrier gas, a tubular furnace, a quartz cylindrical tube and a flue gas collection system, is shown in Fig. 1. Four carrier gases with different oxygen content were tested, including pure O₂, air (21 % O₂), 5% O₂ and 95% N₂, and pure N₂. Soil (2.00g) was heated for 1 h at 500 $^{\circ}$ C with a carrier gas flow rate of 400 ml/min. After thermal desorption, the treated soil, the toluene from the absorption bottles and the XAD-2 resin were collected and both the PCBs and PCDD/Fs were analysed.

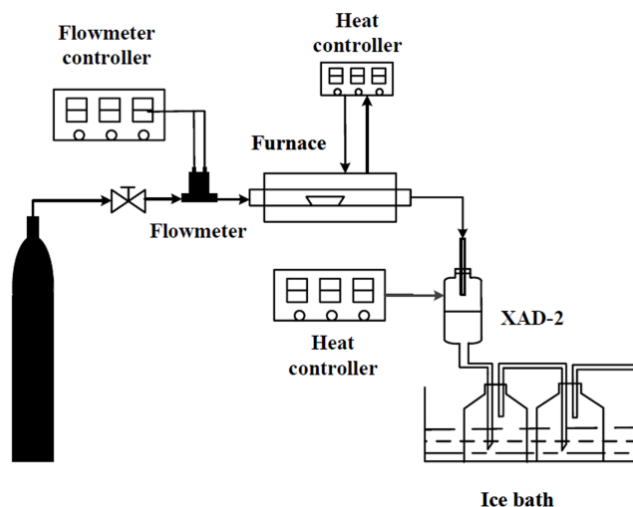


Fig 1. Experimental system

2.3 Samples pretreatment and analysis

In the pretreatment process, the solid phase samples (s) and the gas phase samples (g) were collected (from the treated soil, the toluene and XAD-2 resin, respectively) and pretreated by Soxhlet extraction, solvent exchange and purification before analysing with HRGC/HGMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan). All operation refers to the USEPA method 1668 and 1613¹¹⁻¹³.

All 209 PCBs isomers from mono- to deca-PCBs and 136 PCDD/Fs isomers from tri- to octa- PCDD/Fs isomers were detected. The PCBs and PCDD/Fs toxic equivalency quantities (TEQ) of samples were calculated by using the WHO 2005 toxic equivalency factors (TEFs)¹⁴.

The removal efficiency (RE) is defined and calculated by

$$\text{Removal efficiency} = \frac{\text{PCBs}(\text{raw soil}) - \text{PCBs}(\text{treated soil})}{\text{PCBs}(\text{raw soil})} \times 100\%$$

The destruction efficiency (DE) is calculated as

$$\text{Destruction efficiency} = \frac{\text{PCBs}(\text{raw soil}) - \text{PCBs}(\text{treated soil}) - \text{PCBs}(\text{in gas})}{\text{PCBs}(\text{raw soil})} \times 100\%$$

3. Results and discussion

3.1 PCBs concentration and TEQ

Mass units. The raw soil is heavily polluted by PCBs with a total PCBs concentration of 6466 $\mu\text{g/g}$. TrCBs and TeCBs dominate the homologues of PCBs, accounting for 52.2% and 36.2% of the total PCBs. Fig. 2 presents the concentration and TEQ of PCBs in soil and gas with different carrier gases. After thermal desorption in nitrogen and oxygen, the residual concentrations of PCBs in soil were 326.1 $\mu\text{g/g}$ and 399.6 $\mu\text{g/g}$, corresponding to removal efficiencies (RE) of 95.0% and 93.8%, respectively. Also, the destruction efficiency (DE) of PCBs was between 83.0-85.0% for these carrier gases. There are only slight differences between the results with different carrier gases. Oxygen content has little effect on PCBs removal and destruction.

The composition of PCBs isomer groups in soil and gas are shown in Fig 3. Compared with the composition in raw soil, the ratio of the lower chlorinated PCBs isomers (MoCB, DiCB) increased while the ratio of higher chlorinated PCBs (TeCB, PeCB) decreased in treated soil. No obvious differences were found between the isomers composition in raw soil and in gas phase.

TEQ units. The TEQ-load for PCBs was 26.2 ng TEQ in raw soil. After thermal treated, the TEQ decreased to 3.65-3.88 ng TEQ in treated soil. The total TEQ in soil and gas varied from 5.12 ng TEQ to 5.62 ng TEQ under various carrier gases, with the DE of 78.5-80.4%. Thermal desorption is effective to detoxify PCBs. With decreasing oxygen amount, no observable differences of TEQ in soil and gas are observed.

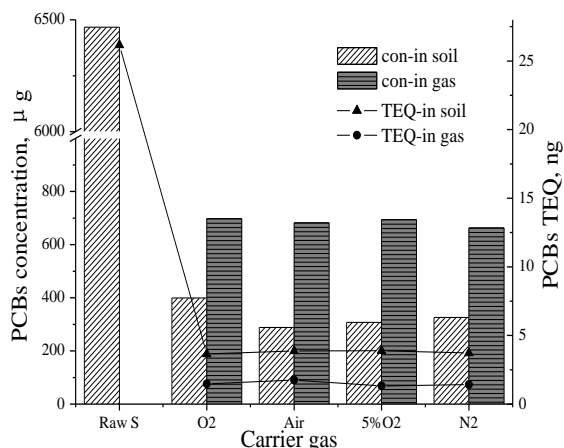


Fig 2. The concentration and TEQ of PCBs in soil and gas. Basis=1.00g raw soil

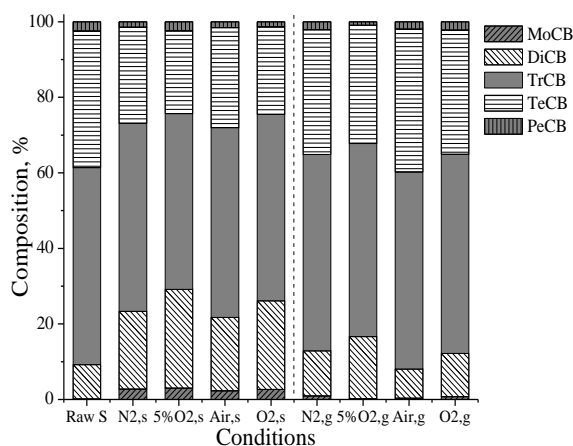


Fig 3. The composition of PCBs isomers in soil and gas

3.2 PCDD/Fs concentration and TEQ in soil

Fig. 4 shows the concentration and TEQ of PCDD/Fs in soil. The concentration of PCDDs and PCDFs in raw soil was 1.57 ng/g and 21.9 ng/g. After thermal treatment, both PCDDs and PCDFs in soil decreased. The amount of PCDDs in soil decreased to 230 pg/g in 5%O₂ and 143 pg/g in nitrogen with a RE of 85.3% and 90.9%, much higher than a RE of 65.3% in pure oxygen. Compared with PCDDs, PCDFs in soil were not effectively removed under oxidative conditions. PCDFs concentration dropped to 2.16 ng/g under nitrogen, corresponding to 10% of the original load. When the oxygen content was 5%, the RE of PCDFs was 69.2%. With the increasing oxygen content, RE of PCDFs decreased to 27.2% for air and 15.9% for oxygen.

Sato et al.¹⁵ investigated the behavior of PCDDs, PCDFs in oxygen/nitrogen (10%/90%) as carrier gas after 5min of thermal desorption. The concentration ratio of PCDFs to PCDDs in sediments was 35.5 with the 60 mg/kg KC-300 addition. In our result the ratio was a little lower (29.4).

The TEQ of PCDDs and PCDFs were 41.5 pg TEQ and 538.3 pg TEQ in raw soil, both of which decreased with declining oxygen content. The total RE of TEQ for PCDDs and PCDFs reached 88.8% and 82.6% in oxygen, 89.8% and 91.2% in 5% oxygen, 92.0% and 97.9% in nitrogen. Inert atmosphere is more beneficial to toxicity removal.

The total TEQ, containing the TEQ of PCBs, PCDDs and PCDFs, was 26.7ng TEQ in raw soil and it decreased to 3.74-3.94 ng TEQ in thermal treated soil. Because the PCBs concentration in soil are almost four orders of magnitude higher than PCDD/Fs, the effect of oxygen content in carrier gas is insignificant on total TEQ.

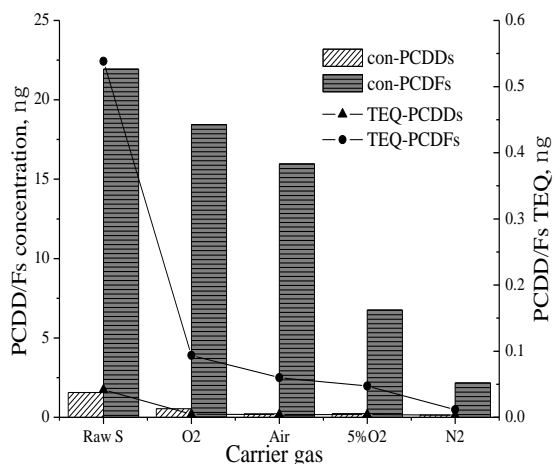


Fig 4. The concentration and TEQ of PCDDs and PCDFs in soil. Basis=1.00g raw soil

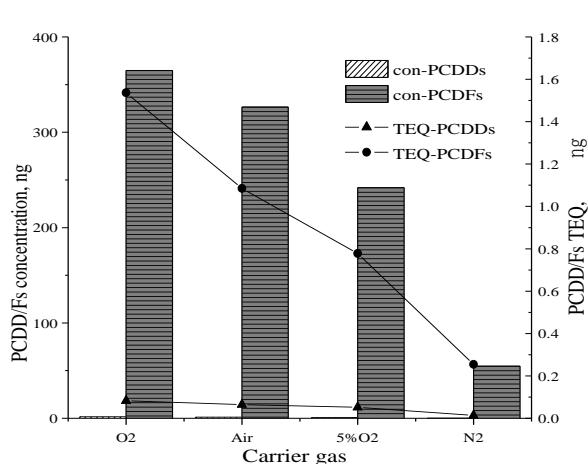


Fig 5. The concentration and TEQ of PCDD/Fs in gas. Basis=1.00g raw soil

3.3 PCDD/Fs concentration and TEQ in gas

The concentrations of PCDFs were 364.8, 326.5, 242.0 and 54.7 ng in oxygen, air, 5% O₂ and nitrogen, about 200 times higher than of PCDDs (Fig. 6). With the increasing of oxygen content in carrier gases, the PCDD/Fs in gas increased. The total concentration of PCDFs in soil and gas was 17.5, 15.6, 11.3 and 2.6 times of the initial PCDFs concentration (21.9 ng/g) in raw soil with decreasing oxygen content. Large amounts of PCDFs generated in the presence of oxygen. In comparison, the concentration of PCDDs in soil and gas was 1.35, 0.87, 0.69 and 0.27 times of the initial PCDDs concentration (1.57 ng/g) in raw soil, which indicates PCBs are the precursors of PCDFs and not of PCDDs.

When the oxygen content was low, the TEQ of PCDD/Fs increased quickly, yet it climbed slowly with the incremental oxygen content. Compared with PCDDs, the TEQ levels of PCDFs were markedly higher, and the ratio of PCDF to PCDDs was 14.9-19.1 in gas. With decreasing oxygen content, the TEQ of PCDFs in gas decreased from 1536.6 pg TEQ in oxygen to 254.7 pg TEQ in nitrogen.

Moreover, there was a linear relationship between the concentration of PCDDs and PCDFs, also the TEQ of PCDDs and PCDFs without reference to the oxygen content, as demonstrated in Fig. 6 and Fig. 7. These results are mainly due to the identical effect of promotion and destruction to PCDDs and PCDFs during thermal desorption.

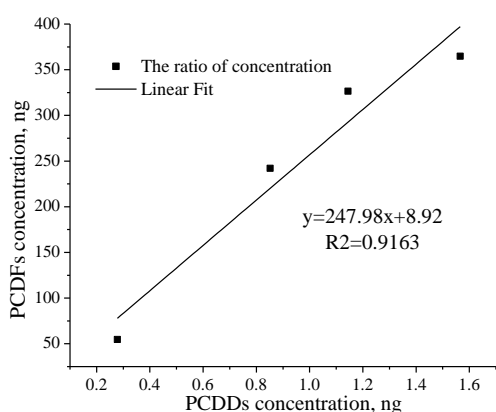


Fig 6. The relationship of concentration between PCDDs and PCDFs in gas.

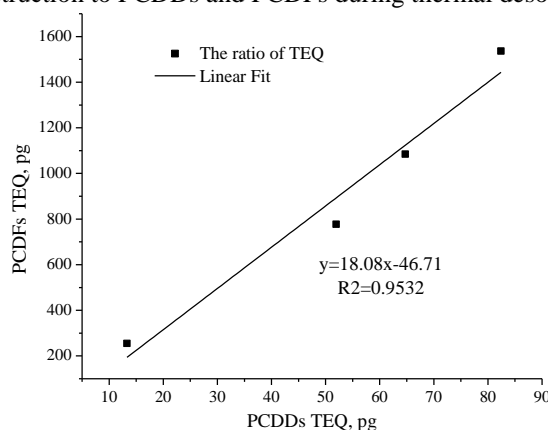


Fig 7. The relationship of TEQ between PCDDs and PCDFs in gas.

Acknowledgements

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