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Research paper

Immobilization of polychlorinated biphenyls in contaminated soils using organoclays

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ABSTRACT

Background: Clay minerals especially organoclays modified by the introduction of organic molecules into the mineral structure show much promise for environmental remediation applications. Application of organic attapulgite (O-APG) and organic montmorillonite (O-MMT) as soil amendments to bind polychlorinated biphenyl (PCB) in contaminated soils and observe PCBs accumulated in the ryegrass shoots and roots was investigated.
Results: Pot experiments in greenhouse indicated that organoclays could significantly fix the PCB in soils and reduce its contents in ryegrass shoots and roots. Compared with the control, the migration of concentrations of PCB into the environment in contaminated soils is reduced by about 28.5 and 44.1%, and concentrations of PCB in ryegrass roots and shoots were reduced within the range from 57.0 to 63.0% and 49.6 to 56.5%, respectively, through addition of 6% organic attapulgite and montmorillonite. There was a negative correlation between the accumulation of PCB in ryegrass and the amount of organoclay addition. The accumulations of PCB in ryegrass roots were significantly higher than those in the ryegrass shoots.
Conclusions: The two organoclays had been proved effective as environmental amendments for reducing the mobility and bioavailability of PCB in contaminated soils. The results of this study provided an efficient method for the remediation of PCB contaminated soils.

1. Introduction

Since chemical products had been used in numerous applications, more chemical contaminants had entered into the soil systems. Especially the toxic substances spilled from poisonous and hazardous solid waste landfills had heavily polluted the soils and ground water. Dang et al. (2010) and Ounnas et al. (2010) reported that the persistent organic pollutants would make a direct threat to the human health because of enrichment in the human body through the food chain.

As one kind of typical persistent organic pollutants, polychlorinated biphenyls (PCBs) were highly persistent, toxic, bioaccumulative and widespread (Halsall et al., 1995). They were semi-volatile, inert, thermally stable, low water solubility, highly lipophilic, resistant to degradation (Edgar et al., 2003). Soils acted as source and sink of PCBs in the environment, where they could be retained with reported half lives ranging from 3 months to 47 years (Erickson, 1997). Furthermore, their chemical stability had also caused the accumulation of PCBs in higher organisms of the food chain. Due to their toxic effects in humans and wildlife (Stewart et al., 1999; Xing et al., 2009), the levels and distributions of PCBs had aroused great concerns of people on environmental health.

Taking effective treatments to prevent the PCBs of contaminated soils from migrating to the air, water, plant and wildlife became the research focus of environmental science. There were many techniques developed for remediating organic contaminated soils, including physical–chemical remediation methods (He et al., 2009), phytoremediation and microbial remediation methods (Chekol and Cough, 2004; Adebusoye et al., 2008). Among these techniques, the use of physical–chemical methods (e.g., adsorption, chemical oxidation and biological process) for organic pollutants removal had been paid more and more attention by the whole society because of its high removal capacities (Javorska et al., 2009).

Previous studies showed that organic modified clay minerals had shown significant affinity to some organic compounds (Gullick and Weber, 2001; Upson and Burns, 2006), and they were widely used as adsorbents for organic pollutants in soils and water (Zhu et al., 2008; Changchaivong and Khaodhiar, 2009). PCBs were lipophilic (Dang et al., 2010) and could be strongly attracted onto organic modified clays, which minimized the volatilization and migration loss in the environment. Using organoclays as soil amendments to immobilize PCBs in contaminated soils could effectively prevent PCBs from migrating into the groundwater and accumulating in the food chain, and furthermore protect the quality of agricultural products and human health.

This study aimed to demonstrate the technical feasibility of organic modified clays to bind priority organic pollutants in contaminated

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soils. Organic attapulgite and montmorillonite were added to PCBs in contaminated soils with various amounts in a pot experiment of ryegrass. The specific objectives of this study were to: (1) observe the effects of type and dose of the amendments on PCBs in contaminated soils as well as PCBs accumulated in the ryegrass shoots and roots, (2) investigate the PCB enrichment mechanism in ryegrass roots and shoots, and (3) determine the effects of amendments on ryegrass growth in terms of fresh weight.

2. Materials and methods

2.1. Soils and amendments

Clean soils were cultivated yellow brown soil (i.e., 0–20 cm), supplied by a vegetable field in Nanjing, Jiangsu Province, China (118°49′ E, 32°5N). Soil pH was 7.10 with water to soil ratio of 5:1. Organic matter and total nitrogen contents were 14.70 and 1.18 g kg^{-1}, respectively. PCBs contaminated soils were obtained from a certain field in Zhejiang Province, China. Its pH was 6.68 with the same ratio of water to soil and the overall content of PCBs was 238.4 μg g^{-1}. Annual ryegrass seeds were obtained from Changzhou Weihua Lawn Company Limited (Co., Ltd.). Attapulgite (APG) was purchased from Nanjing Yadong Aotu Mining Company Limited (Co., Ltd.), organic attapulgite (O-APG) was obtained by sonication-surfactant-modified with hexadecyl trimethyl ammonium bromide (HDTMA-Br) according to previous report (Huang et al., 2007). Organic montmorillonite (O-MMT) were also modified by hexadecyl trimethyl ammonium bromide were purchased from Zhejiang Fenghong New Material Company Limited (Co., Ltd.). Organic substance content was determined by dichromate oxidation using the Tiurin method (Jackson, 1960), the cation exchange capacity (CEC) was determined with $BaCl_2$-triethanolamine following the usual international methods (Li et al., 2009). Basic properties of inorganoclays and organoclays were listed in Table 1.

2.2. Chemicals

All PCBs used (IUPAC Nos. 28, 52, 77, 101,105, 114, 118, 123, 126, 138, 153, 156, 167, 169, 180 and 189) had a declared purity of ≥98% and were obtained from Dr. Ehrenstorfer GmbH (Germany), the selected properties of all PCBs including numbers of the substituted chlorinate (N_{Cl}), log K_{ow} and Electrophilic Index (EI) were listed in Table 2 (Brodsky and Ballschmiter, 1988). The hexane, acetone, concentrated sulfuric acid, silica gel (200–300 mesh), anhydrous sodium sulfate chemicals were supplied by Nanjing Chemical Reagent Co. Ltd., China, with analytical grade. Prior to use, silica gel was activated at 180 °C for 16 h and anhydrous sodium sulfate was activated at 450 °C.

2.3. Pot experiments

Clean soil (CK) samples were air-dried, ground and sieved (2 mm) after collection, then mixed with PCBs contaminated soils to make the total PCB concentration as 2384 ng g^{-1} except CK. Contents of PCB congeners in soil samples were listed in Table 3. After two weeks of culture in a greenhouse, inorganoclays (APG or MMT) and organoclays (O-APG or O-MMT) were added into above soil samples according to doses shown in Table 4. The soils were also thoroughly mixed to ensure uniform distribution of clays. Each pot had 1000 g soil samples and irrigated with 120 mL basic fertilizer solution (0.4 g N (urea), 1.2 g P_2O_5 (superphosphate) and 1.6 g K_2O (potassium sulfate)). The mixture was systematically saturated with double deionized water (DDW) to hold the soil at 80% of the maximum water retention capacity. Pot experiments were carried out after two weeks with photoperiod 10 h. Sixty granule seeds except CK1 were sowed in each pot. 10 d after seedling emergence, 50 seedlings were grown in each pot. Ryegrass shoots were harvested in 40 d (the first growth period, 40 d) and their shoots and roots were harvested simultaneously in 80 d (the second growth period, another 40 d). Ryegrass shoots and roots were washed with DDW, with their fresh weight recorded, broken by plant disintegrator and then frozen preservation for PCB congener extraction. Air-dried contaminated soils were got rid of impurity, sieved (0.25 mm) and saved at 4 °C before analysis. Nitrogen fertilizer was applied at 20 and 45 d after planting. Pot experiments with a completely random design of five treatments with three replications were carried out in a greenhouse under controlled conditions (20 °C/25 °C for day/night, relative humidity 60%, photoperiod 10 h).

Table 1
Basic properties of inorganoclays and organoclays.

Clay	pH	Organic substance content (g 100 g^{-1})	CEC (cmol kg^{-1})
APG	6.28	0.598	45.81
Na-MMT	6.54	1.46	77.73
O-APG	6.35	15.3[a]	55.02
O-MMT	6.67	43.6[a]	156.2

[a] Indicated that the organic substance content in the organoclays was given in meq of $HDTMA^+$ per 100 g clay.

Table 2
The selected properties of sixteen kinds of PCBs.

PCB Nos.	Compounds	N_{Cl}	log K_{ow}	EI
28	2,4,4′-Trichlorobiphenyl	3	5.63	0.124
52	2,2′,5,5′-Tetrachlorobiphenyl	4	5.81	0.120
77	3,3′,4,4′-Tetrachlorobiphenyl	4	6.37	0.145
101	2,2′,4,5,5′-Tetrachlorobiphenyl	5	6.35	0.130
105	2,3,3′,4,4′-Pentachlorobiphenyl	5	6.93	0.140
114	2,3,4,4′,5-Pentachlorobiphenyl	5	6.59	0.141
118	2,3′,4,4′,5-Pentachlorobiphenyl	5	6.68	0.145
123	2′,3,4,4′,5-Pentachlorobiphenyl	5	6.64	0.143
126	3,3′,4,4′,5-Pentachlorobiphenyl	5	6.90	0.155
138	2,2′,3,4,4′,5′-Hexachlorobiphenyl	6	6.74	0.135
153	2,2′,4,4′,5,5′-Hexachlorobiphenyl	6	6.74	0.139
156	2,3,3′,4,4′,5-Hexachlorobiphenyl	6	7.53	0.150
167	2,3′,4,4′,5,5′-Hexachlorobiphenyl	6	7.16	0.153
169	3,3′,4,4′,5,5′-Hexachlorobiphenyl	6	7.61	0.165
180	2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	7	7.21	0.143
189	2,3,3′,4,4′,5,5′-Heptachlorobiphenyl	7	7.56	0.158

2.4. Analytical methods

2.4.1. PCB congener extraction procedures

5.0 g samples (soils or ryegrasses) were placed into a 150 mL Erlenmeyer flask with stopper, containing 15.0 mL n-hexane-acetone (1/1, V/V) and soaked overnight. Then, the mixture in the flask was ultrasonically extracted for 15 min. The acetone/hexane solution was

Table 3
Contents (mean ± SE, $n = 3$) of PCB congeners in soil samples.

PCB congeners	Content (ng g^{-1})
PCB-28	1632 ± 96.9
PCB-52	354.5 ± 19.7
PCB-77	71.68 ± 2.04
PCB-101	52.37 ± 3.26
PCB-105	51.40 ± 3.14
PCB-114	5.949 ± 0.13
PCB-118	84.87 ± 7.23
PCB-123	23.63 ± 5.63
PCB-126	13.30 ± 0.09
PCB-138	19.87 ± 0.07
PCB-153	22.57 ± 3.99
PCB-156	3.640 ± 0.74
PCB-167	22.86 ± 9.55
PCB-169	16.57 ± 0.31
PCB-180	8.492 ± 0.58
PCB-189	ND[a]

[a] Indicated that this PCB congener had not been detected in polluted soils.