Effects of nature organic matters and hydrated metal oxides on the anaerobic degradation of lindane, p, p'-DDT and HCB in sediments

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Abstract: Effects of natural organic matters(NOM) and hydrated metal oxides(HMO) in sediments on the anaerobic degradation of γ-666, p, p'-DDT and HCB were investigated by means of removing NOM and HMO in Liaohe River sediments sequentially. The results showed that the anaerobic degradation of γ-666, p, p'-DDT and HCB followed pseudo-first-order kinetics in different sediments. But, the extents and rates of degradation were different, even the other conditions remained the same. Anaerobic degradation rates of γ-666, p, p'-DDT and HCB were 0.020 d^{-1}, 0.009 d^{-1} and 0.035 month^{-1} respectively for the sediments without additional carbon resources. However, with addition of carbon resources, the anaerobic degradation rates of γ-666, p, p'-DDT and HCB were 0.071 d^{-1}, 0.054 d^{-1} and 0.088 month^{-1} in the original sediments respectively. After removing NOM, the rates were decreased to 0.047 d^{-1}, 0.037 d^{-1} and 0.066 month^{-1}; in the sediments removed NOM and HMO, the rates were increased to 0.067 d^{-1}, 0.059 d^{-1} and 0.086 month^{-1}. These results indicated that NOM in the sediments accelerated the anaerobic degradation of γ-666, p, p'-DDT and HCB; the HMO inhibited the anaerobic degradation of γ-666, p, p'-DDT and HCB.

Keywords: lindane; p, p'-DDT; HCB; anaerobic degradation; sediments; natural organic matters

Introduction

Lindane, p, p'-DDT and HCB are semivolatile and lipophilic, and they fall into the class of compounds described as persistent organic pollutants. Moreover, these compounds have been identified as potent endocrine disrupters(Smith, 2002; Willett, 1998; Robert, 2001). It has been reported chlorinated organic compounds can be decomposed very slowly in sediments through various reactions(Niesl, 1990). Factors influencing the biodegradation of compounds are various. Among them, it was reported that the effects of natural organic matters (NOM) in sediments on biodegradation of organic pollutants are contradictory(Hoi-ying, 2002). Some researches showed that NOM might enhance the biodegradation of compounds; some indicated that NOM may inhibit biodegradation, and others showed it did not play effect. Few studies have investigated the effect of hydrated metal oxides (HMO) on the anaerobic degradation of lindane, p, p'-DDT and HCB. The purpose of this paper was to explore the influence of NOM and HMO on the biodegradation of the three compounds.

1   Materials and methods

Sediment samples were 1—10 cm surface sediments collected from Liao River at Shashanjie areas. The samples were air-dried, sieved through a 60 mm mesh. Then the samples were stored hermetically. Some characteristics of the sediments are listed in Table 1. According to the procedure(Irene, 1998), NOM and HMO in the original sediments were removed. NOM were removed by H_2O_2, and $NH_2OH \cdot HCl$ and HOAc eliminated HMO. In order to increase the degradation rate, additional carbon sources(solution of sodium acetate) were added into the system. Thus, four series of samples were obtained: (1) original sediment without additional carbon sources, (2) original sediment with additional carbon sources, (3) NOM removed sediments with additional carbon sources, and (4) sediments removed NOM and HMO with

additional carbon sources.

The source microorganisms were collected from a swine waste septic tank in Dalian countryside, and stored in an anaerobic bottle. Before being used, the source microorganisms were diluted with water in a mass ratio of 10 : 1 and put aside for 0.5 h. Anaerobic experiments were performed with a cone shaped flacon(100 ml). 2 ml of experimental medium(in mg/L: $K_2HPO_4 \cdot 3H_2O$, 500; KH_2PO_4, 300) and 10 ml of deionized water were added to each of the bottles. The initial concentration of lindane, p, p'-DDT or HCB in each sample bottles was about 1000 μg per kg sediment. The bottles were shaken(200 r/min) for 2 h; each bottle was continuously sparged with N_2 for five minutes in order to remove oxygen in the bottle. Then the bottle was capped immediately and incubated stationary at 22 ± 1℃. The samples were periodically taken for analysis. Using ultrasound, the samples were extracted by 40 ml mixed solution (acetone: petroleum ether = 1 : 1). Then the extracts were concentrated to 25 ml and analyzed by GC (HP6890) equipped with a Ni^{63} ECD and a HP-5 fused silica capillary column. The operating temperatures of the injector and detector were 250℃ and 350℃, respectively. The injection was splitless. The recoveries of lindane, p, p'-DDT and HCB were determined to be higher than 85%.

2   Results and discussion

The components of the sediments are listed in Table 1 and Table 2. The anaerobic degradations of lindane, p, p'-DDT and HCB are shown in Fig.1, Fig. 2 and Fig.3, respectively.

Table 1   The physico-chemical properties of the original sediments

Water content, %	pH	Carbonate, %	Organic matters, %	Hydrated, mg/kg
2.21	7.82	4.87	2.83	65.60
Hydrated ferric oxide, %	Hydrated alumna, %	Total nitrogen, %	Total phosphorus, %	Sulphide, %
0.10	0.29	0.17	0.14	1.65

Table 2   The removal efficiencies of NOM and HMO

Sediment components	Original sample	Treated sample	Removal efficiency, %
Organic matters, %	2.83	0.92	67.5
Hydrated oxide manganese, mg/kg	65.60	4.26	93.5
Hydrated ferric oxide, %	0.10	0.02	80.0
Hydrated alumna, %	0.29	0.03	89.7

Meantime, we investigated the kinetics of anaerobic degradation of lindane, p, p'-DDT and HCB in sediments under different conditions. Generally, the biodegradation rate constants were calculated using pseudo first-order kinetics by plotting $\ln(C_t/C_0)$ against time where C_0 was the initial concentration and C_t was the concentration of the compounds at time t. Linear regression coefficients, r^2, were typically not less than 0.9 in all cases. The results are presented in Table 3.
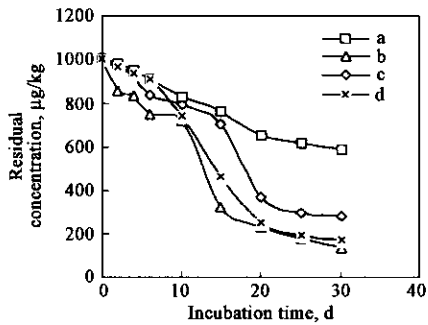

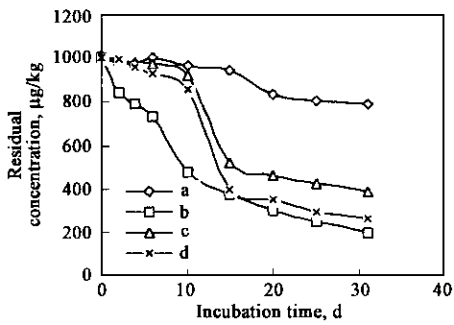Fig. 1   The degeneration of HCH in different sediments

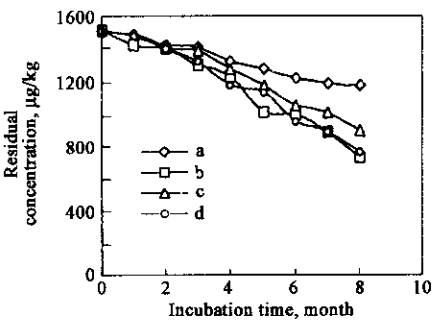Fig.2   The degeneration of p, p'-DDT in different sediments

Fig.3   The degeneration of HCB in different sediments

The results indicated that anaerobic degradations of lindane, p, p'-DDT and HCB in the original sediments without additional carbon sources were slow, and the degradation kinetics rate constants were 0.020 d^{-1}, 0.009 d^{-1} and 0.035 $month^{-1}$, respectively. However, with the addition of carbon sources, the degradation rate constants increased to 0.071 d^{-1}, 0.054 d^{-1} and 0.088 $month^{-1}$, separately. However, under the condition of NOM being removed, the degradation rate constants decreased to 0.047 d^{-1}, 0.037 d^{-1} and 0.066 $month^{-1}$, respectively. These results showed that the NOM in the sediments enhanced anaerobic degradation rates of lindane, p, p'-DDT and HCB.

The NOM in the sediments consists of a complex mixture of organic substances, which is mainly divided into humus and other organic compounds. Humus includes humin, fulvic acid, humic acid mainly. Other compounds are mainly composed by all kinds of carbohydrate, protein, and amino acid compounds (Stevenson, 1994). Previous research indicated humus in the sediments could be used by cell for growth and propagation(Schnitzer, 1972). Other compounds can provide microbe carbon sources and energy for their growth indirectly. The research work of Meredith and others showed that soluble NOM in sediments could provide energy sources for the metabolism of microbe(Meredith, 1998). Samantha also reported the role of NOM in enhancing biodegradability of sodium sulfate(Samantha, 2000). C. M. Kao's research indicated that peat can serve as the diffusion source of primary substrate, and enhance the PCE/TCE biodegradation under aerobic cometabolism and reductive dechlorination (Kao, 2000). As mentioned above, lindane, p, p'-DDT and HCB could be decomposed slowly by anaerobic microbe without additional carbon sources, these results showed NOM in the sediments could be used by microbe as growth substrate to decompose lindane, p, p'-DDT and HCB. However, under the condition of adding carbon sources, the degradation of lindane, p, p'-DDT or HCB in the sediments removed NOM was slower than its degradation in original sediments, respectively. These results indicated that NOM might interact with additional carbon sources, and take part in the activities of microbe metabolism. Thus, the biodegradations of lindane, p, p'-DDT and HCB were enhanced.

Fig. 1, 2, 3 and Table 3 also showed that the degradations of lindane, p, p'-DDT and HCB in the NOM and HMO removed sediment were faster than those in the NOM removed sediment, respectively. The degradation rate constants of lindane, p, p'-DDT and HCB increased to 0.067 d^{-1}, 0.059 d^{-1} and 0.086 $month^{-1}$. These results showed the HMO in the sediments inhibited anaerobic degradation of lindane, p, p'-DDT and HCB. The HMO in the sediments is important inorganic nature colloids. After metal oxides were removed, the redox potential decreased from 196 mV to 101 mV, thus enhanced reductive dechlorination of these compounds

Table 3   The kinetic equations of the degradation of lindane, p, p'-DDT and HCB under different conditions

Compounds	Sediment samples	K	Correlation coefficient, R^2
Lindane	(a)	0.020, d^{-1}	0.98
	(b)	0.071, d^{-1}	0.97
	(c)	0.047, d^{-1}	0.94
	(d)	0.067, d^{-1}	0.96
p,p'-DDT	(a)	0.009, d^{-1}	0.92
	(b)	0.054, d^{-1}	0.98
	(c)	0.037, d^{-1}	0.91
	(d)	0.059, d^{-1}	0.92
HCB	(a)	0.035, $month^{-1}$	0.98
	(b)	0.088, $month^{-1}$	0.94
	(c)	0.066, $month^{-1}$	0.96
	(d)	0.086, $month^{-1}$	0.96

Notes: (a) Original sediment without additional carbon sources; (b) original sediment with additional carbon sources; (c) NOM removed sediments with additional carbon sources; and (d) sediments removed NOM and HMO with additional carbon sources

(Gantzer, 1991).

3   Conclusions

Anaerobic biodegradation of lindane, p, p'-DDT and HCB could take place in natural sediments. The natural organic matters could be used by microbe as growth substrate to decompose these compounds and enhanced the biodegradation of these compounds in sediments. Hydrated metal oxides inhibited the degradation of these compounds. More experiments should be carried out in order to elucidate the mechanisms operating in such systems and interpret the decomposition pathway of these compounds.

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