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Biodegradation of chlordane and hexachlorobenzenes in river sediment

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Abstract

Contamination of river sediments by persistent organic pollutants (POPs) is a worldwide concern, and microbial degradation is regarded as an important process for removal of POPs from river sediments. To date, there is still a lack of systematic study on chlordane biodegradation in river sediments, and the information on hexachlorobenzene (HCB) biodegradation in river sediments is very limited in Japan. We investigated the anaerobic biodegradation potential of *trans*-chlordane (TC), *cis*-chlordane (CC), and HCB in sediment samples collected at three sites along the Kamogawa River in Saitama Prefecture, Japan. Lag period and biodegradation rates of TC and CC in the three sediments varied greatly with their properties and contamination by TC and CC. In contrast, biodegradation of HCB in all three sediments started immediately with the start of the experiment without lag period, and major differences in biodegradation rates among the sediments were not observed. At the end of 20-week anaerobic incubation in the dark at 30 °C temperature, degradation rates ranged from 0.0% to 33.0% for TC, 0.0% to 12.0% for CC, and 47.6% to 59.4% for HCB. Results showed that the high-to-low order of biodegradation in the river sediments was HCB > TC > CC. Although the sediments were collected in the same river, their biodegradation potential varied with properties. Sediment with rich organic content and contamination by TC and CC or HCB was observed to have high biodegradation rates for these pollutants. In addition, biodegradation of TC, CC and HCB was companied by obvious methane generation and drop of oxidation–reduction potential (ORP).

Keywords: Persistent organic pollutants; Chlordane; Hexachlorobenzene; Anaerobic biodegradation; Sediment; Japan

1. Introduction

Persistent organic pollutants (POPs) are organic compounds that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. They are highly hydrophobic and persist in sediments of rivers and lakes long after their release. Sediments are usually recognized as both the carrier and potential source of POPs in aquatic environments, and removal of POPs from the sediment is therefore of high importance.

The toxicity and persistence of chlordane and hexachlorobenzene (HCB) in the environment have led to their being included as one of the 12 POPs whose use is curtailed by the Stockholm Convention. This is a global treaty to protect human health and the environment from POPs, which entered into force in May 2004 (Wong et al., 2005).

Chlordane is a ubiquitous and persistent pesticide, which was once widely used in the United States and other countries for both agricultural and residential applications from the time of its introduction in the 1940s to its banning in the late 1980s (Eitzer et al., 2001; Ouyang et al., 2005). Chlordane was a mixture of over 140 different related compounds known as technical chlordane, of which the three most abundant components are *cis*-chlordane (CC), *trans*-chlordane (TC), and *trans*-nonachlor (Dearth and Hites, 1990).

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In Japan, chlordane was also heavily and widely used for household termite control, especially during the early 1980s (Taguchi and Yakushiji, 1988). Although the use and manufacture of chlordane was banned from the late 1980s, it is still commonly found in biota, humans and environment (Taguchi and Yakushiji, 1988; Hirai and Tomokuni, 1995; Murayama et al., 2003; Ouyang et al., 2005).

HCB had several uses in agriculture and industry. The peak of HCB production was from the late 1970s to the early 1980s, when the annual production in the world was about 10000 tons/year from 1978 to 1981 (Barber et al., 2005). In Japan, HCB was mainly used as a precursor of herbicide (pentachlorophenyl), a flame retardant processing chemical, and a plasticizer for polyvinyl. Japan also has banned the manufacture, use, or import of HCB since 1979. Although the commercial production of HCB has been banned in most countries, it continues to be produced as a byproduct during manufacture of some solvents and pesticides, and incineration of municipal waste (Bailey, 2001; Barber et al., 2005). It is estimated that about 23000 kg of HCB has been introduced into the environment every year, of which 6500 kg is from pesticide application, 9500 kg from manufacturing, and 7000 kg from waste combustion (Bailey, 2001).

In aquatic environment, chlordane and HCB are highly hydrophobic, and strongly associated with the organic carbon, clay and silt that comprise the anaerobic regions of sediments. Both chlordane and HCB can still be often detected extensively in river sediments in Japan (Nakano et al., 2004).

Microbial degradation is regarded as an important process for POPs removal from sediments, and many researchers have so far reported studies on biodegradation of POPs in sediments (Chang et al., 2001; Yuan et al., 2001; Fava et al., 2003; Miyoshi et al., 2004). However, there is a surprising lack of data on chlordane biodegradation in sediments. It is still not known whether much breakdown of chlordane occurs in sediments (ATSDR, 1994). For HCB, some reports documented its microbial degradation in sediments (Pavlostathis and Prytula, 2000; Chen et al., 2002, 2004), however, information from Japan is still limited.

In this study, anaerobic biodegradation of TC, CC and HCB in river sediments was investigated.

2. Materials and methods

2.1. Sampling and Sediment

Fig. 1 shows the collection sites for the sediment samples along the Kamogawa River, one of the most heavily contaminated rivers in Saitama prefecture, Japan. As a large number of industries discharge their treated wastewaters into the river, contamination of the water and sediment with various organic pollutants, such as chlordane, DDT, hexachlorobenzene and nonylphenol, has been noted in this river. Using an Ekman-Barge sampler, we collected the surface sediment samples from three sites along the Kamogawa River in August 2004. The sediment was sieved through a 5 mm screen to remove debris, centrifuged for 20 min at 3000 rpm to remove the supernatant, and stored in the dark at 4 °C for further use. The labels used in the present study represent the part of the river from which individual samples were collected. Sample K7 was collected upstream, K9 was collected in the midstream portion, and K11 was collected downstream. Some selected properties of the sediment are shown in Table 1. As shown, K7 and K9 were higher in water content than K11, but much lower in ignition loss, and contents of SO_4-S, total organic carbon (TOC) and total nitrogen (TN). HCB was detected in all three sediments with a concentration range of 0.30–0.92 ng/g.d.w., but TC and CC were detected only in the K11 sample with concentrations of 10.86 and 7.84 ng/g.d.w., respectively.

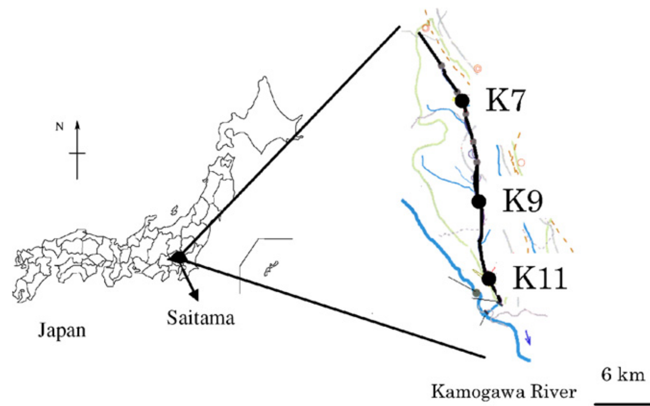

Fig. 1. Map of the sampling sites. K7 (upstream), K9 (midstream), and K11 (downstream) indicate the sampling points along the Kamogawa River.

2.2. Experimental design

TC, CC and HCB incubation experiments were performed using 50 ml serum vials containing 3.0 g (dry weight) sediment and 40 ml cultural medium, to which 1000 ng of TC, 1000 ng of CC, or 500 ng of HCB was added. The cultural medium was a modification according to Kohring et al. (1989), with addition of vitamins and

Table 1
Selected properties of the sediment

Sample	K7	K9	K11
Water content (%)	72.2	76.0	59.1
Ignition loss (%)	2.92	1.20	9.32
SO_4-S (mg/l)	5.61	1.37	12.2
Total carbon (%)	0.56	0.05	4.46
Total nitrogen (%)	0.05	0.01	0.35
trans-Chlordane (ng/g.d.w.)	n.d.[a]	n.d.[a]	10.86
cis-Chlordane (ng/g.d.w.)	n.d.[a]	n.d.[a]	7.84
HCB (ng/g.d.w.)	0.92	0.30	0.70

[a] Not detectable.