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Hexachlorobenzene dechlorination in constructed wetland mesocosms

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A B S T R A C T

We studied the dechlorination of hexachlorobenzene (HCB) in wetland mesocosm (MC) trials filled with sediment (well mineralized homogenized peat mixed with mud) from a wastewater treatment wetland located in a floodplain: three MCs were planted with common reed (*Phragmites australis*) and another three with broad-leaved cattail (*Typha latifolia*). According to the rootzone development we distinguished between the upper (0–10 cm from the soil surface) and lower layers (20–30 cm). Over 36 days, the initial measured concentration of HCB was reduced to 61%, 51%, 42% and 40% in the lower layer without roots of *Phragmites*, in the lower layer with roots of *Typha*, in the upper layer with roots of *Typha*, and in the upper layer with roots of *Phragmites* respectively. The 90% degradation time (DT_{90}) of the initial measured HCB can be calculated as 192, 121, 110 and 92 days (d) respectively. PeCB, 1, 2, 3, 4-, 1, 2, 3, 5- and 1, 2, 4, 5-TeCB, and 1, 2, 3-, 1, 2, 4- and 1, 3, 5-TCB were the main dechlorination products detected in MC sediment samples. The dechlorination rates of HCB were higher in sediment layers with well-developed root zones. According to the DT_{50} of 28–58 days and DT_{90} of 92–192 days, HCB can be considered to be a less persistent organic pollutant in constructed wetlands.

1. Introduction

Constructed wetlands (CWs) have traditionally been used for the treatment of domestic and municipal sewage from both separate and combined sewerage (Vymazal et al., 1998). However, CWs have proven to different extents, to be an interesting option for several types of pesticide pollution that need to be treated by biological means (Moore et al., 2000; Schulz et al., 2003; Elsaesser et al., 2011). Constructed wetlands have many advantages over other technologies (powdered activated carbon and granulated activated carbon filtration, and reverse osmosis etc.), and are relatively inexpensive to build, operate and maintain (Vymazal, 2009). There are several examples on the successful use of CWs for treatment of water polluted by pesticides from agricultural watersheds (Schulz and Peall, 2001; Braskerud and Haarstad, 2003; Matamoros et al., 2008).

It has been widely accepted that the active reaction zone of CWs is the rhizosphere (Stottmeister et al., 2003). This is where the physicochemical and biological processes induced by the interaction between plants, microorganisms, the soil and pollutants take place (Nielsen, 2005; Pauly et al., 2006). The plant roots enhance microbial density and activity by providing a surface for microbial growth, a source of carbon compound through root exudates and a micro-aerobic environment via root oxygen release (Gersberg et al., 1986; Brix, 1997).

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Furthermore, plant species-specific morphology can influence microbial density through higher root surface (Kyambadde et al., 2004). Root growth can also affect the hydraulic quality of soils (Cooper and Boon, 1987). For wastewater treatment CWs, common reed (*Phragmites australis*) and broad-leaved cattail (*Typha latifolia*) are the most common species applied in respect to total nitrogen removal (Brisson and Chazarenc, 2009), reducing biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Calheiros et al., 2009) as well as breaking down micro-pollutants (Janzen et al., 2009). Peat has been used as an activated soil filter for the elimination of xenobiotics from wastewater because its high organic carbon content and large surfaces can help to assemble microbial communities that are able to degrade the compounds (Bester and Schäfer, 2009). However, whether CWs are suitable for the degradation of hexachlorobenzene (HCB) was not fully elucidated before the commencement of this study.

HCB is of great concern as a typical anthropogenic hydrophobic organic compound (HOC) due to its long half-life, bioaccumulative nature and chronic adverse effects on humans and animals. HOCs have been detected in air, soil, fish, birds and even human milk (Qiu et al., 2004). This finding is comprehensible because HCB is still being unintentionally generated as a by-product of the manufacture of chlorinated pesticides such as atrazine and simazine (Bailey, 2001), although the use has been ceased in most countries in the 1970s (US EPA, 2002).

HCB has low vapour pressure at 20 °C (1.1×10^{-5} mm Hg) and low water solubility at 25 °C (6.0×10^{-3} mg/L). Its high octanol–water partition coefficient ($K_{ow} = 5.7$) and soil organic matter–water partitioning coefficient ($K_{oc} = 6.1$) imply that HCB is hydrophobic and sorption is the main process of elimination in the peat of CW mesocosms (MC) (Wilken and Wirth, 1986).

This project was conducted to study whether constructed wetland mesocosms filled with floodplain sediment (well mineralized homogenized peat) are suited to the reductive dechlorination of HCB.

2. Materials and methods

2.1. Experimental setup and sampling

The wetland sediment (well mineralized peat mixed with mud) and first-year seedlings of common reed (*P. australis*) and broad-leaved cattail (*T. latifolia*) from the Tänassilma seminatural wetland (58°22′W, 25°31′N) in Viljandi County, Estonia, a wastewater treatment wetland located in a floodplain, were used in this project. This wetland sediment was chosen because it is plant-compatible and has been investigated in earlier studies (Maddison et al., 2005, 2009). *Phragmites* and *Typha* seedlings were planted in peat-filled MCs in a roof-covered environment at the University of Tartu Botany Department for 30 days prior to HCB exposure.

The contaminated sediment was prepared as follows: 250 mg of HCB with a 99.5% purity (Dr. Ehrenstorfer, Germany) was dissolved in 400 ml analytical grade hexane (Sigma–Aldrich, Germany), added to 1000 g quartz sand powder (Sigma–Aldrich, Germany), then mixed thoroughly until the solvent evaporated completely. Individual portions of 1000 g of contaminated quartz sand powder and 120 kg of sediment (water content 54.5%) were thoroughly homogenized using a concrete mixer and then transferred to a polypropylene container ($60 \times 60 \times 80$ cm, length–width–height). The calculated concentration of HCB in the sediment added to each container was 3825 μg/kg dry matter (dm, wetland sediment + sand). Considering literature values, this concentration is at medium level (see high initial concentrations of 15,000 and 30,000 μg/kg HCB in Zhou et al., 2012, and low initial concentration of 1980 μg/kg according to Liu et al., 2010) and is optimal regarding the relatively short-term dynamics of dechlorination process. Six MC containers were filled with a 10 cm layer of gravel (15–25 mm) at the bottom followed by 50 cm layer of sediment and an HCB–quartz–sand mixture as an active filter, and finally filled with tap so that 10 cm water layer stayed in the top of the filter (Fig. 1) and placed outdoors under a roof. Each MC was watered with a water faucet to maintain the same water level during the experiments. Three MCs were planted with *Typha* and three with *Phragmites* at a density of 10 plants per MC to study the effects of the different species on the dechlorination process of HCB. This type of “steady flow” system mimics the zero-outlet wetlands (depressions in landscape with no outflow) from which the water losses occur only via evapotranspiration. The flow direction was upwards, guaranteeing the best contact with sediment. Thus the soil was always water-saturated, which was beneficial for the anaerobic conditions necessary for dechlorination. To compensate water losses and to keep the water table constant, we manually added about 8 L tap water twice a week. The water was added to the drainage layer in the bottom using a garden pipe (measuring 95 cm and perforated in the lower part).

The seedlings were transplanted to the MC on July 19th. During the plants’ growing period, sediment was sampled in the 1st, 3rd, 7th, 14th, 22nd and 36th days. Composite samples (each sediment sample: 100 g homogenate of 10 randomly chosen points) were taken from two different layers (0–10 cm and 20–30 cm from the sediment surface) of each MC using a stainless steel tube (diameter 25 mm) with a cutting edge for easy core removal. Altogether 72 plant samplings were done over the period.

During each sampling session in MCs and water temperature, pH, redox potential (eH; mV), dissolved oxygen content (mg/L), and conductivity (μS/cm) was measured from water levels of MCs vegetated with cattail and reed using the Cyberscan PC 510 Ph/mV/Conductivity/TDS °C/°F Bench Meter by Eutech Instruments Pte Ltd., Ayer Rajah Crescent, Singapore and the YSI Professional Plus Handheld Multiparameter Water Quality Meter by YSI Incorporated, Yellow Springs, OH, USA.

2.2. Analysis of plant growth

Plant height (a mean of all plants in MC) was monitored on a weekly basis and recorded. In July 2011, initial aboveground and belowground plant biomass was measured as a mean of all plants weights of each MC. Before the weight determination the roots were carefully removed from the sediment, washed with tap water and dried with absorbent paper. After the experiment was finished, plant biomass was weighed as a whole and then separately as aboveground biomass and belowground biomass.