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Fate Processes of Chlorobenzenes in Soil and Potential Remediation Strategies: A Review

Ferdi BRAHUSHI[1,2], Fredrick Orori KENGARA[3], SONG Yang[1], JIANG Xin[1], Jean Charles MUNCH[4] and WANG Fang[1,*]

[1] *Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008 (China)*
[2] *Department of Agroenvironment and Ecology, Agricultural University of Tirana, Tirana 1029 (Albania)*
[3] *Department of Chemistry, Maseno University, Private Bag Maseno 40105 (Kenya)*
[4] *Center of Life and Food Sciences, Technical University Munich, Fresing 85354 (Germany)*

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ABSTRACT

Chlorobenzenes (CBs) are a group of organic pollutants that pose a high environmental risk due to their toxicity, persistence and possible transfer in the food chain. Available data in literature show that CBs are detected in different environmental compartments such as soil, water, air and sediment. The widespread presence of CBs in the environment is related to their former extensive use in agriculture and industry. Some CBs are ranked in the list of priority pollutants by the Stockholm Convention, and their reduction or elimination from the environment is therefore of high importance. Environmental risk assessment of CBs requires knowledge on the role and importance of the main environmental fate processes, especially in soil. Furthermore, development of remediation strategies for reduction or elimination of CBs from the environment is related to the enhancement of fate processes that increase their dissipation in various environmental compartments. The main objectives of the current review were to present up-to-date data on fate processes of CBs in the soil environment and to explore possible remediation strategies for soils contaminated with CBs. Dechlorination of highly-chlorinated benzenes is the main degradation pathway under anaerobic conditions, leading to the formation of lower-chlorinated benzenes. Biodegradation of lower-chlorinated benzenes is well documented, especially by strains of adapted or specialized microorganisms. Development of techniques that combine dechlorination of highly-chlorinated benzenes with biodegradation or biomineralization of lower-chlorinated benzenes can result in useful tools for remediation of soils contaminated with CBs. In addition, immobilization of CBs in soil by use of different amendments is a useful method for reducing the environmental risk of CBs.

Key Words: biodegradation, chlorinated benzenes, environmental risk, immobilization, mineralization, organic pollutant, reductive dechlorination

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INTRODUCTION

Chlorobenzenes (CBs) or chlorinated benzenes are a group of substituted benzene compounds with only chlorine and hydrogen atoms on the benzene ring; the number of chlorine atoms can vary from 1 to 6. Chlorobenzenes are chemically unreactive and generally stable under environmental conditions. Due to the high electronegativity of the chlorine atom, CBs are resistant to different degradation reactions such as oxidation, hydrolysis, dechlorination, *etc.* The differences in structure between CBs include the number of chlorine atoms they possess and their position on the benzene ring. The position of the chlorine atoms leads to different isomers with different properties.

Chlorobenzens are listed as toxic compounds and their toxicity generally increases with the number of chlorine atoms. They can be very irritating to the eyes, skin and respiratory system, and react readily with liver and kidney tissues (IPCS, 1991; WHO, 2004). The potential health hazard of a xenobiotic compound is a function of its persistence in the environment as well as its toxicity. Hexachlorobenzene (HCB) is classified as a probable human carcinogen by the US Environmental Protection Agency (ATSDR, 1999, 2002). Due to their toxicity and persistence, some CBs are ranked in the priority list of organic pollutants.

The main properties of CBs such as potential for long-range atmospheric transport, persistence in the environment, bioaccumulation and ecotoxicity are con-

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[*] Corresponding author. E-mail: wangfang@issas.ac.cn.

sistent with the properties of persistent organic pollutants (POPs) (UNEP, 2001; Lerche *et al.*, 2002). Indeed, HCB and pentachlorobenzene (PeCB) are listed as priority compounds in the Stockholm Convention on POPs (UNEP, 2001).

Chlorobenzenes are mainly used as solvents, odorizers, herbicides, insecticides, fungicides, fire retardants, degreasers, heat transmitters and chemical intermediates for the production of several other compounds, such as dyes and pharmaceutical products (IPCS, 1991; WHO, 2004). In particular, mono- and dichlorobenzenes are produced in large volumes. Monochlorobenzene (MCB) constitutes approximately 70% of the total world production of all CBs. They are usually produced by direct chlorination of benzene or a lower-chlorinated benzene in the presence of a Lewis acid or an aluminum catalyst (IPCS, 1991). The HCB has been widely employed as a fungicide on seeds, especially against the fungal disease "bunt" that affects some cereal crops. The marketing and use of HCB as a plant protection product was banned in Europe, Canada and USA in the 1970s and in China in 2004 because of concerns about its adverse effects on the environment and on human health (US EPA, 1986; Canadian Environmental Protection Act, 1993; IPCS, 1997; Wei *et al.*, 2007).

CHLOROBENZENS EMISSION INTO ENVIRONMENT

Chlorobenzenes are released into the environment through their extensive use as industrial effluents and wastes or by the incineration of wastes that contain organochlorine compounds (Ahling *et al.*, 1978). They may also enter ecosystems due to biodegradation of chlorinated compounds (IPCS, 1991). Since there is no more HCB production, the only anthropogenic releases of HCB are as unintentional by-products in the chemical and metal industries, as well as in combustion processes. The HCB could also be present as a contaminant in several chlorinated pesticides and solvents (Bailey, 2001). The estimated potential sources of global HCB emission according to Bailey (2001) are from pesticide application (6 500 kg year^{-1}), manufacturing (9 500 kg year^{-1}) and combustion (7 000 kg year^{-1}, including 500 kg year^{-1} from biomass burning). This adds up to the total current HCB emission of approximately 23 000 kg year^{-1}, with an estimated range of 12 000–92 000 kg year^{-1}. Thus, the cumulative world production of HCB, since the first date of its initial use in 1945, is about 1–2 million tons (Häggblom and Bossert, 2003). Gusev *et al.* (2015) reported that levels of HCB in air decreased substantially from 1990 to 2013 and, by using modeling, showed that major sources of HCB pollution included Southeast Asia, Europe, Central Asia and North America. Thus, in 2013, elevated air concentrations could be seen in Southeast Asia and Eastern Europe (30–100 pg m^{-3}), while the other regions were characterized by relatively lower concentrations (5–30 pg m^{-3}).

The extensive use and potential long-range transport of CBs lead to potential occurrence in different environmental compartments, and CBs are detected in soil samples from different areas. The occurrence of CBs is also observed in sewage sludge (Rogers *et al.*, 1989; IPCS, 1991), which can be transported into soils *via* sewage sludge application (Wang *et al.*, 1992; Wang and Jones, 1994b, c). Wang *et al.* (1995) reported that the levels were less than 0.4 mg kg^{-1} for dichlorobenzene (DCB) congeners and less than 0.1 mg kg^{-1} for other CBs in uncontaminated soils. The total CB concentrations in soil samples from a former pesticide factory in Germany ranged from 1.5 to 18 400 mg kg^{-1} (Feidieker *et al.*, 1994). The concentrations of HCB in soil samples that originated from Leipzig-Halle region were between 0.57 and 3.75 μg kg^{-1} dry weight (DW) (Manz *et al.*, 2001). In Switzerland, agricultural soil had HCB levels of only 0.15–5.0 μg kg^{-1} DW (Streit, 1994), while considerably higher values of approximately 40 μg kg^{-1} DW were encountered in Italy (Leoni and D'Arca, 1976). Nakata *et al.* (2005) detected HCB concentrations of up to 3.2 μg kg^{-1} DW in soil samples from the vicinity of Shanghai City in China. Meijer *et al.* (2003) determined background HCB concentrations in nearly 200 surface soil samples and found an average value of 680 ng kg^{-1} DW, clearly demonstrating the ubiquitous presence of HCB in the environment. The total CB concentrations in a vegetable field near an industrial site in China ranged from 71.06 to 716.57 μg kg^{-1} DW (Song *et al.*, 2012b).

CHLOROBENZENES DEGRADATION IN SOIL

The degradation process of an organic compound is defined as the abiotic or biologically mediated structural alteration, resulting in the formation of new compounds or metabolites. Both the extent and rate of degradation are important and dependent on numerous factors, including chemical structure of the compound, the concentration of the chemical in environment, the density of microbial population, the availability of nutrients, the presence of other compounds which can either enhance or decrease the rate of degradation, the soil temperature, the oxygen content in the soil, *etc.* (Scheunert, 1992; Alexander, 1994).

Chlorobenzenes are considered to be very persis-