

## Occurrence and distribution of hexachlorocyclohexane isomers in vegetation samples from a contaminated area

P.C. Abhilash<sup>a</sup>, Sarah Jamil<sup>a</sup>, Vandana Singh<sup>a</sup>, Amita Singh<sup>a</sup>,  
Nandita Singh<sup>a,\*</sup>, S.C. Srivastava<sup>b</sup>

<sup>a</sup> Eco-auditing Group, National Botanical Research Institute, Council of Scientific and Industrial Research, Rana Pratap Marg, Lucknow 226 001, Uttar Pradesh, India

<sup>b</sup> Department of Botany, University of Lucknow, Lucknow 226 007, Uttar Pradesh, India

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### Abstract

The occurrence and distribution of four major hexachlorocyclohexane (HCH) isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -) were studied in vegetation samples of a highly contaminated area close to a small-scale industrial belt in Lucknow (North India). Eight species of plants were collected at different points of the contaminated area and different parts of the plants were separated in order to study the difference in uptake and accumulation. The samples were extracted by matrix solid-phase dispersion (MSPD) extraction and finally determined by a gas-chromatograph equipped with <sup>63</sup>Ni electron capture detector (ECD). HCH isomers were present in almost all samples and the concentration of total HCH in the plant sample analyzed varied between 13 and 44 mg kg<sup>-1</sup>, being the main isomer of  $\beta$ -HCH (8–22 mg kg<sup>-1</sup>). Lindane ( $\gamma$ -HCH) was present in all samples (1–9 mg kg<sup>-1</sup>). *Solanum torvum* Sw., and *Erianthus munja* shows the highest and lowest capacity for accumulation of HCH, respectively with a significant difference at  $p < 0.01$  level. The highest concentration of HCH residue in root samples indicates the most likely mechanism of HCH accumulation in these plants was sorption of soil HCH on roots. *Solanum torvum* Sw., and *Withania somnifera* (L.) Dunal could accumulate considerable levels of HCH isomers (44 and 34 mg kg<sup>-1</sup>, respectively). The results reflect the importance of plants in monitoring purposes and their potential for phytoremediation of HCH contaminated soils.

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### 1. Introduction

Hexachlorocyclohexane (HCH), also known as benzene hexachloride (BHC), is an organochlorine insecticide that is available in two formulations, technical grade HCH (CAS No. 608-73-1) and lindane (CAS No. 58-89-9) (Van Velsen, 1986; WHO, 1991; WWF, 1999). Generally, technical HCH contains the isomers in the following percentages:  $\alpha$ -HCH (60–70%),  $\beta$ -HCH (5–12%),  $\gamma$ -HCH (10–15%),  $\delta$ -HCH (6–10%) and  $\epsilon$ -HCH (3–4%) (Willet et al., 1998;

Walker et al., 1999). Lindane, technically  $\gamma$ -HCH is a broad spectrum organochlorine pesticide that has been extensively used for the control of agricultural and medical pests (Rigas et al., 2005). It is refined from technical grade HCH (13–26% of  $\gamma$ -HCH) resulting in a significant quantity of waste HCH consisting primarily of  $\alpha$ -HCH and  $\beta$ -HCH isomers, which in addition to lindane becomes an environmental liability due to its highly persistent nature and toxicity (Willet et al., 1998).

Because of their widespread use, the isomers of HCH have penetrated in to almost all ecosystems (Walker et al., 1999; Meijer et al., 2003). It is a persistent organic pollutant (POP), potent carcinogen and teratogen and classified by WHO as ‘moderately hazardous’ (WHO, 1991). Once

\* Corresponding author. Tel.: +91 522 2205835x302; fax: +91 522 2205847.

E-mail address: [nanditasp@hotmail.com](mailto:nanditasp@hotmail.com) (N. Singh).

present in an environment, these compounds redistribute and partition into the different systems (such as soil, soil biota, water, plants, air) by different process, such as adsorption onto soil particles, adsorption onto plant root tissues, volatilization, microbial degradation, leaching, etc. which over time leads to thorough contamination of the whole ecosystem (Calvelo Pereira et al., in press; Gouin and Wania, 2007). Most countries have prohibited the use of this persistent compound, but some are still using  $\gamma$ -HCH for economic reasons and new sites are consequently being contaminated. Indiscriminate use of lindane coupled with its extreme persistence and slow degradation has led to a global environmental problem. Therefore the determination of lindane and other active HCH isomers in vegetation is of major importance for assessing the risk of transfer to the trophic chain and for the development of phytoremediation techniques that can be applied to HCH contaminated soils.

The cycling of lindane and other HCH isomers through the environment must be comprehensively elucidated to assess adequately the human health risks posed from such POPs and their potential long-range transport. The uptake and accumulation of toxic contaminants by green plants is an important process in determining the transfer of pollutants along the lines of food chain and food web (Bacci et al., 1990). Several plants have been used to indicate ubiquitous pollutant contamination levels (Holoubek et al., 2000). Vegetation integrates contamination over times, and it has been used to identify point sources of organic pollutants and to determine the global contamination of organic pollutants. The uptake of organic pollutants in plants is governed by the chemical and physical properties of pollutants, environmental conditions and plant species (Schnoor, 2002; Calvelo-Pereira et al., 2006). There are several pathways through which organic pollutants enter in vegetation: (i) the soil–plant pathway; and (ii) the air–plant pathway. In the soil–plant route, the organic pollutants present in the soil close to the roots can either (i) be absorbed by the plants and, in some instances, translocated into the aerial parts through the xylem; and/or become adsorbed onto the root tissues. The air–plant route on the other hand involves the air–plant partitioning of POPs through volatilization from the soil surface and further adsorption on plant leaves, but may also include the partitioning of pollutants between air-suspended particles contaminated with POPs and plant surfaces. (Patterson et al., 1991; Holoubek et al., 2000; Calvelo Pereira et al., in press). The soil–plant route is important in the case of hydrophilic or moderately hydrophobic compounds ( $\log K_{ow}$ : 0.5–3; Briggs et al., 1982; Burken and Schnoor, 1998) and air–plant route is for volatile or relatively hydrophobic compounds ( $\log K_{ow}$ : > 3; Simonich and Hites, 1994). The accumulation of pesticides by air–plant route increases with the lipid content of the plant tissues and with the leaf surface area (Bakker, 2000; Barber et al., 2004). Deposition is again controlled by environmental factors such as temperature and wind speed (Patterson et al.,

1991; Simonich and Hites, 1995a). Gradually, these compounds tend to concentrate in the soil surface as a result of the decay of HCH contaminated plant litter into the soils (Horstman and McLachlan, 1996; Calvelo-Pereira et al., 2006). However, with time, the bioavailability of these compounds reduces due to an “aging” effect and the formation of “Bound-residues”, which takes place during processes of decomposition and humification of organic matter (Alexander, 2000).

Several plants have been recently recognized to serve as an environmental counterbalance to POPs. Plants can indeed be considered as green livers, acting as a sink for environmental contaminants. Phytoremediation is a nascent technology that aims to provide a cheap, soft and safe treatment applicable to contaminated sites. Further, it is accepted worldwide that remediation techniques, which are economically and ecologically safe, should be developed. In this respect phytoremediation techniques present a potential scope. However, very few plants are reported for phytoremediation of pesticides in general because pesticides are meant for killing living organisms. Monitoring of plants which are growing in and around the contaminated sites will provide a general outlook on the distribution of pollutants in plant species and their ability to uptake the pollutants. The aim of the present study was to check the accumulation of HCH isomers in vegetation samples growing in an industrial premise. In future, the selected species will be tested against their ability to clean HCH contamination from the above sites.

## 2. Materials and methods

### 2.1. Study area and sample locations

The plant samples were collected from the campus and nearby areas of India Pesticides Limited (IPL), a lindane producing factory situated at Chinhath industrial estate, around 20 km from the Lucknow city in Uttar Pradesh. The study area is located between 27° 55' North latitude and 89° 3' East longitude. The industry has started during 1993 and apart from the lindane production, the industry has also in house formulation facility for producing various lindane formulations; lindane EC, carbaryl lindane 4.4 granules, lindane 6% granules, lindane 6.5 WDP, lindane 1.3%. Eight species of the most abundant growing plants were collected (in triplicate) from the industry, (Table 1) and samples were washed, separated into different matrices like root, stem and leaves, air-dried and stored at 4 °C for posterior analysis. We tested only the mature plant parts for HCH occurrence. A brief description of the plant species studied is given below.

### 2.2. Plant characteristics

*Lantana camara* is a profusely branching, scrambling shrub 2–4 (up to 8) m tall and wide, with square-sectioned, often prickly cane-like stems. The leaves are opposite,

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