ENVIRONMENTAL FATE AND BEHAVIOR OF HCH ISOMERS IN A SOIL-PLANT SYSTEM IN A CONTAMINATED SITE

M. Carmen Monterroso[1], Marta Camps Arbestain[1], Roberto Calvelo Pereira[1], Beatriz Gomez Garrido[1], Soledad Muniategui Lorenzo[2], Purificación López Mahía[2], Darío Prada[2] and Felipe Macías[1]

[1]Dpt. Edafoloxía e Q. Agrícola, Universidade de Santiago, Campus Sur, 15706-Santiago de Compostela, Spain

[2]Dpt. Química Analítica, Facultad de Ciencias, Universidade de A Coruña, Campus A Zapateira, 15701-A Coruña, Spain

Introduction

During the last few decades, technical-grade hexachlorocyclohexane (HCH), containing 55-80 %, α-HCH, 5-14 %. ß-HCH, and 8-15 % γ-HCH, has been used in large quantities as an insecticide, γ-HCH (lindane) being the only insecticidal component in the mixture. Although its application has been restricted, lindane is still used in several parts of the world. During many years, the waste products from the synthesis of lindane (85 % of HCH isomers produced) were disposed of on areas surrounding the production centres, causing a serious worldwide contamination problem.

Once HCH isomers enter the soil they are subject to various physical (evaporation, leaching, adsorption, irreversible sorption) and biological processes (plant accumulation, biodegradation). Residual HCH can persist for long time, and both HCH isomers and their metabolites can contaminate the groundwater. Plants can absorb and sequester organic pollutants directly or indirectly, thus allowing their entry into the trophic chain. Degradation of these pollutants can be enhanced in the immediate vicinity of plant roots - the rhizosphere soil - which is characterized by a high degree of both chemical and biological activity. Dissipation of contaminants in the rhizosphere has been reported for insecticides[1], herbicides[2], trichloroethylene[3], PAHs[4], and fuel oil hydrocarbons[5].

The aims of this study were i) to evaluate the bioaccumulation of HCH isomers in the vegetation developed on a heavily contaminated area, and ii) to investigate the effect of the rhizosphere on these compounds.

Materials and Methods

The study site is a contaminated area (3500 m^2) located in Porriño (Galicia, Spain), where HCH residues from lindane synthesis were dumped in the past. Topsoil samples were collected from 18 points, dried at room temperature, passed through a 2-mm sieve, and ground to <50 µm. Soil samples were extracted with hexane:acetone and sonication, then analyzed for HCH isomers by GC/ECD.

Five plant species were harvested and separated into roots, stems and leaves. Plant tissues were washed, dried at room temperature, and ground to a fine powder. HCH isomers in plant tissues were extracted with hexane:acetone in a microwave oven; the extracts were purified with florisil and alumine, and thereafter eluted with hexane:ethyl acetate. HCH isomers in the purified extracts were quantified by GC/ECD.

Two plant species were selected for the rhizosphere studies: *Cytisus striatus* and *Avena sativa.* The former is a wild species, common in the area, whereas the latter is important in agriculture. Rhizosphere soil was separated from the bulk soil using a modified version of the shaking method of Chung and Zazoski[6]. Bulk soil, rhizosphere soil, and roots were analyzed for HCH isomers as above.

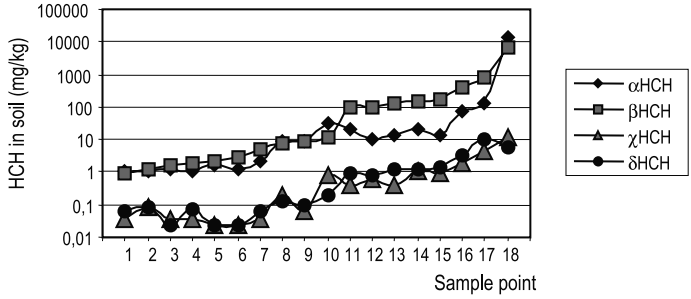

Fig. 1 Concentration of HCH isomers in topsoil samples from the contaminated site.

Results and Discussion

Concentration and distribution of HCH isomers in soil

The soil samples was very variable in terms of both concentration and distribution of HCH isomers, typical of contaminated industrial sites. Chemical analysis indicated the presence of four HCH isomers (α, ß, γ, and δ), a and b being dominant (Fig. 1). Concentrations of total HCH, calculated as the sum of concentrations of the four isomers, ranged between 2 and 20000 mg kg^{-1}, displaying a large standard deviation.

Concentration and distribution of HCH isomers in plant tissues

All five species tested were able to accumulate the four isomers in their tissues, and concentrations of HCHs in leaves were closely related to those found in soils (Fig. 2). Concentrations of total HCH in plant tissues ranged between 1.7 and 62.5 mg kg^{-1}, there being differences among species and among plant organs. *Cytisus striatus* and *Chenopodium vulgare* were the highest and the lowest HCH accumulators, respectively. Within each plant species, the distribution of HCHs among the different plant organs studied generally showed a similar pattern: leaves > stems > roots (examples of these trends are shown in Fig. 3 for two selected sites with medium and very high contamination, respectively).

Volatilization of HCH isomers from the soil surface and subsequent sorption by leaves may be the main accumulation pathway in aerial biomass. Schroll et al[7] reported no translocation of lipophilic compounds from root to shoot. Moreover, bioaccumulation of HCH isomers in plant tissues seems to

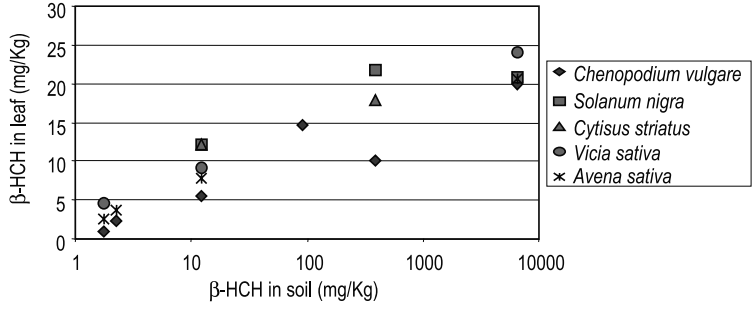

Fig. 2. Concentration of β-HCH in soil and leaves from five species grown in contaminated soil.

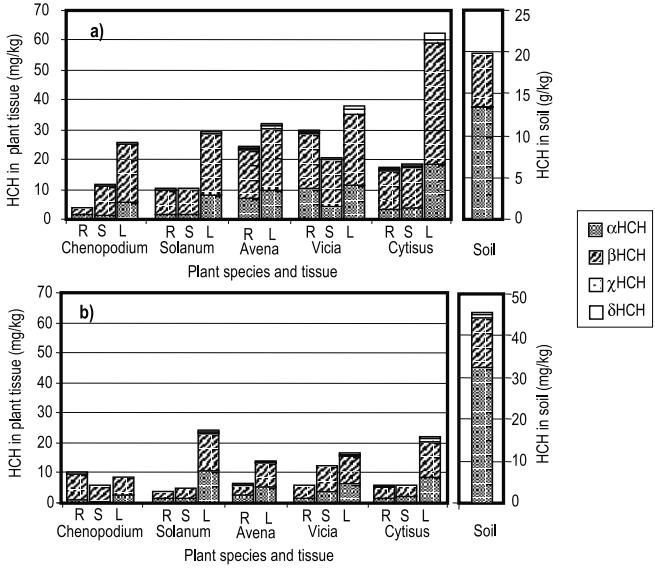

Fig 3. Concentration of HCH isomers in plant tissues of five species and soil from two selected sites with a) very high contamination, and b) medium contamination (R=roots, S=stem, L=leaves).

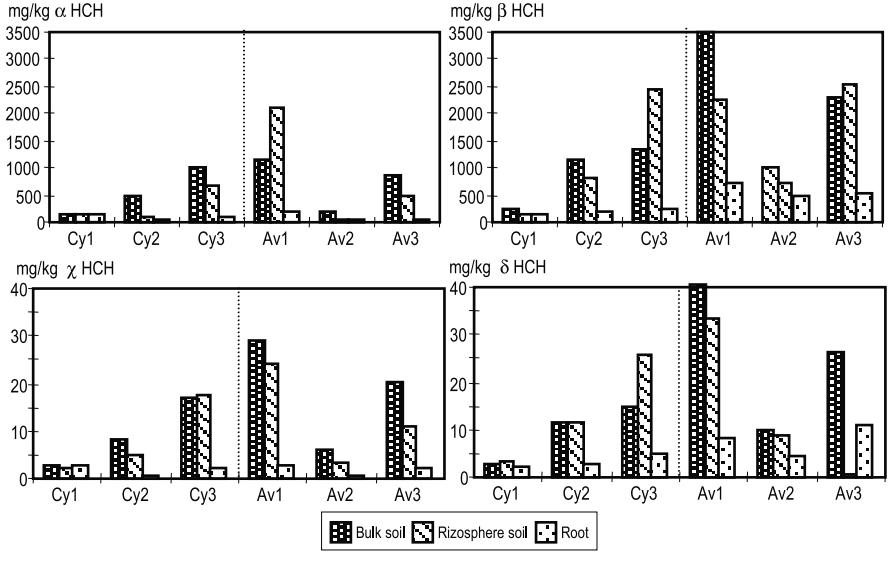

Fig. 4. Concentration of HCH isomers in bulk soil, rhizosphere soil and roots of *Cytisus striatus* (Cy) and *Avena sativa* (Av).

be isomer-selective, as ß-HCH, the most lipophilic isomer, was always the most abundant isomer found in the plant tissue (60-80 % from total HCH), even in those areas where αHCH was dominant (Fig. 3).

Rhizhosphere study

Data obtained from the bulk and rhizosphere soils of the two plant species selected suggest that both species tend to reduce the levels of the four HCH isomers in the rhizosphere (Fig. 4). This reduction was relatively more important for α-HCH than for ß-HCH, resulting in a change in the relative distribution of these two isomers from the bulk soil to the rhizosphere soil. Concentrations of HCH isomers in roots were found to be relatively constant whitin each plant species. *Avena sativa* was able to accumulate more HCHs, in particular ß-HCH, than *Cytisus striatus*.

The lower levels of HCHs in the rhizosphere than in the bulk soils was probably the result of several factors: a) sequestration by partitioning to the lipophilic pant tissues and/or uptake by the roots (as indicated above), b) root exudation of enzymes, such deshalogenase, which may be able to dechlorinate organochlorated compounds[8, 9], and c) enhanced biodegradation by a rhizospheric effect[10]. The capacity of these plants to dissipate HCH in the rhizosphere soil can be used for phytorremediation purposes.

Acknowledgments

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