# Persistence of lindane and heptachlor in a representative soil from Balcarce, Argentina, under natural environmental conditions.

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**Abstract :** Lindane and heptachlor persistences were studied in a composite loam soil obtained from Balcarce, Argentina. Soil treated with either pesticide was distributed in drilled pots inserted into slightly larger ones, where percolating water could be collected after rainfall. Pots were placed at the field and analysed every five weeks by gas chromatography, upto a total of fifty five weeks. Lindane half-lives were 9.4 and 8.6 weeks for 2.0 and 4.0 kg active ingredient/ha applied to the soil, respectively. A total loss of 96.5% of the initial single lindane dose disappeared after fifty-five weeks. One the contrary, 73.9% of extractable heptachlor remained in the soil at the end of the study. Both pesticides were absent in water percolating through the soil, suggesting a strong adsorption by soil particles.
**Key Words :** Heptachlor - Lindane - Organochlorine pesticides - Persistence - Soil.

## Introduction

Balcarce's region in the Province of Buenos Aires, Argentina, has ca. 313,000 ha of productive soils, where well over 180,000 ha are exclusively used for crop production. In this region, the combination of temperate weather, soil richness and proper rainfall is ideal for potato production, which is reflected in more than 25,000 ha devoted yearly to this crop. Here, soil insects have been mainly controlled in the past by using heptachlor. This compound has been banned for these purposes since 1990 and it has been replaced since by another organochlorine pesticide, lindane, which despite its ban in most of the industrialized world, is still in use in several countries, including Argentina.

Though heptachlor is no longer in use, it has been described as highly carcinogenic (Epstein, 1990) and one of the most persistent pollutants in soils (Brooks, 1974). That could represent a serious problem if its use has been cumulative throughout the years, as it might be the present situation in Balcarce's region.

Lindane, on the other hand, causes several biochemical changes in fish (Ferrando and Andreu-Moliner, 1991) and deleterious effects on the central nervous system of rats (Gonzàlez *et al.* 1987), and it has been considered a probable carcinogen to man (IARC, 1979). This could be hazardous if the pesticide is translocated from soil to underground crops, as it was shown recently in intensively cultivated regions of Greece, where lindane residues

were detected in 40% and 56% of the potato and carrot samples harvested, respectively (Aplada-Sarlis *et al.*, 1994).

In spite of this, little is known about the persistence of these chemicals in soil in Balcarce's region. The objectives of this work were to study the chemical persistence of both pesticides in the top layer of Balcarce's soil in experiments conducted in pots placed at the field, and to see if they can percolate to a deeper soil layer under natural rainfall and climatic conditions.

## Materials and Methods

**Soil collection and treatment :** A representative soil composed of a pool of samples collected from 0-15 cm depth at Balcarce, Argentina, was obtained. All sample sites had no previous history of any organochlorine pesticide application. Each soil sample was previously homogenized, air dried, and passed through a 2-mm sieve before pooling. The average properties of this composite soil are given in Table 1.

**Table :** Physicochemical properties of a composite soil representative of Balcarce's region, Argentina.

| Texture | Sand % | Silt % | Clay % | OM % | pH | CEC |
|---|---|---|---|---|---|---|
| Loam | 37.2 | 37.6 | 25.2 | 7.5 | 6.1 | 33.4 |

OM : organic matter; CEC : cation exchange capacity (meq/100g).

Soil treatments were performed using technical heptachlor containing 92.5% active ingredient (a.i.) or a formulation of lindane at 22.5% a.i., commercially distributed as Lindafor 20 (Rhone-Poulenc), both chemicals dissolved in n-hexane. Aliquots of 30 kg of dry soil weight (DSW) were sprayed with lindane, using a hand sprayer fitted with a 11002-nozzle tip, to achieve a.i. concentrations of 1.70 or 3.40 µg/g DSW. These correspond to 2.0 and 4.0 kg a.i./ha doses at the field, respectively. Heptachlor was applied in a similar way, to obtain an a.i. concentration of 1.70 µg/g DSW. Each aliquot was thoroughly mixed to allow a homogeneous distribution. Non-sprayed soil aliquots were used as controls. Each treated soil was distributed in subsamples of 800 g DSW into drilled pots partially included into slightly larger ones destined to collect water percolating through the soil after rainfall. These pots were then placed randomly at the field at the same location where samples were taken, thus being subjected to the same climatic conditions as the land. Both pesticides were applied to the soil at the usual time of the year farmers do at Balcarce.

**Chemical extraction and GC analysis :** Soil samples were collected every five weeks, starting from pesticide application. At each date of sampling, two pots were frozen at – 20°C until they could be processed simultaneously to avoid variations in the extraction conditions. Water percolating from each pot was collected immediately after each rainfall and also frozen at – 20°C.



Soil frozen samples were thawed at room temperature, dried in an oven at 65°C upto constant weight, and screened through a 20-mesh sieve. Organochlorine pesticide extractions with hexane-acetone (1/1, by vol.) and Florisil cleanups were performed according to AOAC methods 970.52M and 970.520 (Sawyer *et al.*, 1990).

The content of lindane and heptachlor in the extracts was measured quantitatively on a Shimadzu GC-14B chromatograph equipped with an electron capture ($^{63}$Ni) detector. Separations were performed on a 30 m × 0.53 mm i.d. DB-608 megabore column (J&W Scientific, Folsom, CA, USA) using nitrogen as carrier gas. Operating temperatures: injection port 200°C, column 195°C, detector 210°C. The organochlorine pesticides were quantified by comparing the sample chromatograms with standards obtained from Alltech-Sigma.

Spiked soils extracted immediately thereafter with hexane, showed 98.0 ± 1.7% and 90.0 ± 5.1% recovery efficiency for lindane and heptachlor, respectively. Residues were not corrected for percent recovery.

Water samples were thawed at room temperature, extracted and analysed according to Driscoll *et al.* (1991). Recoveries for lindane and heptachlor were 94.5 ± 2.1% and 92.3 ± 2.7%, respectively.

## Results and Discussion

Weather conditions during the field experiment are presented in Fig. 1.

Fig. 2 shows the evolution of lindane concentration in a representative soil of Balcarce, after a single application of the pesticide, at two different initial concentrations.

According to the regression equations obtained from data presented in Fig. 2, lindane concentration (µg/g DSW) was equal to : $-0.14 + 9.33$ weeks$^{-1}$ ($r^2 = 0.98$, $p < 0.025$), and to: $-0.30 + 13.80$ weeks$^{-1}$ ($r^2 = 0.96$, $p < 0.025$) when lindane was applied to the soil at 2.0 and 4.0 kg a.i./ha doses, respectively. Half-lives calculated from these equations were 9.4 and 8.6 weeks for single and double pesticide doses, respectively. Similar results were reported for HCH in an Indian sandy loam soil (Samuel and Pillai, 1991). However, these values are slightly lower than the ones reported here, which among other reasons, could be related to a faster rate of dissipation in the tropics than in temperate regions (Tanabe *et al.*, 1994).

Both the highest average temperature and amount of rainfall were registered during the first twenty-five weeks of the present study (Fig. 1). During this period, 92.4% of the initial lindane applied at 2.0 kg a.i./ha disappeared from the soil (Fig. 2). These data agree with those provided by Waliszewski (1993), who stressed that the loss of lindane is closely related to these climatic conditions. Subsequent analyses of the soil after fifty-five weeks showed a total loss of 96.5% of the initial dose (Fig. 2). Since in the present work only extractable residues were evaluated, we cannot exclude from these data that parts of lindane remained bound to soil particles.

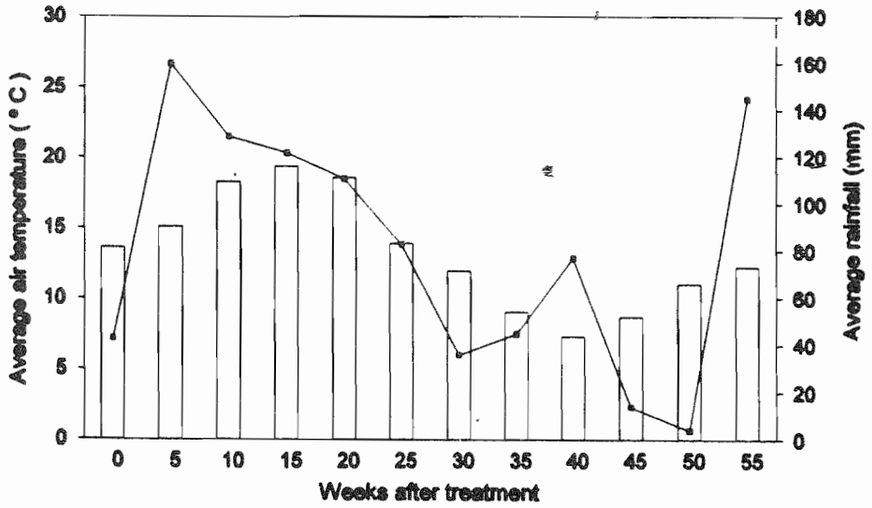


**Fig. 1.** Weather conditions during the field experiment. (□) : Average air temperature, (–) : Average rainfall.

The evolution of heptachlor concentration in a representative soil of Balcarce was followed during fifty-five weeks and results are shown in Fig. 3.

The percentage of heptachlor recovery in soil samples spiked with the pesticide and analysed immediately after that, was 90.0 ± 5.1%. However, only five weeks later and upto forty weeks after treatment, heptachlor

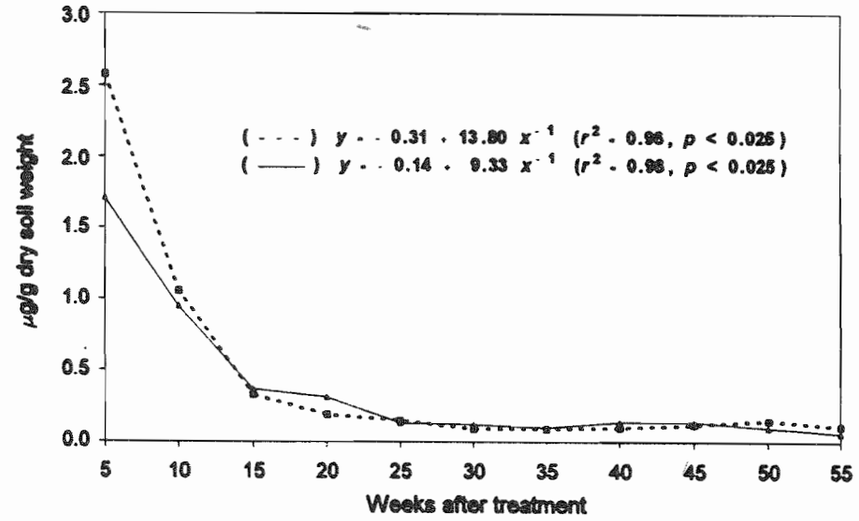


**Fig. 2.** Lindane persistence in a representative soil from Balcarce, Argentina. (▲—▲) : After a single application dose (2 kg/ha); (■ --- ■) : After a double application dose (4 kg/ha).



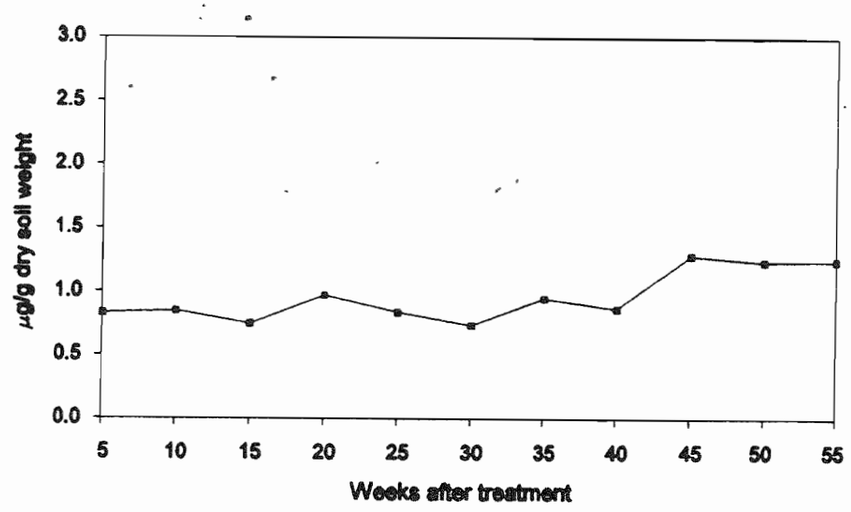


**Fig. 3.** Heptachlor persistence in a representative soil from Balcarce, Argentina. (■—■) : After a single application dose (2 kg/ha).

extracted from samples represented on average 50.0% of the dose initially applied to the soil. This value rose to 73.9%, from week 45 and upto the end of the experiment.

Considering that heptachlor epoxide is the main degradation product of heptachlor, the differences in recovery could be partially due to this product. However, the GLC analyses revealed less than 10% of its presence in the samples at all sampling times (data not shown).

As for lindane, we cannot exclude from these data that at the end of the trial, part of heptachlor remained bound to soil particles. Still, more than 70% of the pesticide could be extracted without chemical modification after one year exposure (Fig. 3). These data agree with a reported half-life in the environment of at least seven and possibly twelve years (Brooks, 1974), meaning that people could be exposed to this pesticide and its persistent epoxi degradation product for another generation. This clearly suggests the need of a much longer term period of study to determine heptachlor half-life in a Balcarce's soil. Given the long history of this pesticide application in this region, it should also be recommended its determination before sowing. These considerations have special relevance if we consider that this compound is carcinogenic (Epstein, 1990), it appears in the milk of cows fed with alfalfa sown in contaminated fields (Waldron *et al.*, 1968) and that at least in laboratory animals, heptachlor ingestion can cause reproductive effects (Crum *et al.*, 1993) and embryotoxicity (Amita Rani *et al.*, 1992).

Considering that the high levels of contamination of the environment and food by hexachlorocyclohexanes (HCH) are mainly due to its technical form and not to purified lindane (Waliszewski, 1993) and that over 90% of the pesticide disappears at Balcarce's soil after six months, its use in this region

was justified by being an inexpensive and safer alternative to the very persistent heptachlor. However, β-HCH is the most hazardous isomer of HCH to man. Its incidence in the adipose tissue was specially high in the agrarian population of Catalonia (Spain), reflecting the past and present use of lindane containing pesticides (Gómez Catalán *et al.*, 1993).

Finally, neither lindane nor heptachlor residues were found in water percolating from soil-containing pots. In this regard, Harris (1969) pointed early the little probability that these pesticides will be moved below the plow layer of soils by percolating water. Moreover, a high adsorption of these pesticides to soils has been related to high organic matter contents (Weber *et al.*, 1993), which is the situation at Balcarce (Table 1). However, our data were obtained with a soil previously dried and sieved. That avoids pesticide lateral movement by erosion, and downward movement in the soil profile because of tillage operation and soil cracking. Thus, the presence of lindane and heptachlor in underground water at several places in this region (data not shown) could be reflecting percolatin due to natural cracks and channels, or to improper agricultural practices.

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## References

Amita Rani, B.E., N.G.K. Karanth and M.K. Krishnakumari : Accumulation and embryotoxicity of the insecticide heptachlor in the albino rat (*Rattus norvegicus*). *J. Environ. Biol.*, **13**, 95-100 (1992).

Aplada-Sarlis, P., K.S. Liapis and G.E. Miliadis : Contamination of potato tubers in Greece with lindane residues. *Bull. Environ. Contam. Toxicol.*, **54**, 135-140 (1994).

Brooks, G.T. : Ch. 3 : Action of chlorinated insecticides. *In* : Chlorinated insecticides. Vol II : Biological and environmental aspects (*Ed* : G. Zweig). CRC Press. Cleveland. 63-144 (1974).

Conchello, M.P., A. Herrera, A. Ariño. R. Lázaro and S. Bayarri : Effect of several kitchen treatments on hexachlorocyclohexane residues in ovine meat. *Bull. Environ. Contam. Toxicol.*, **51**, 612-618 (1993).

Crum, J.A., S.J. Bursian, R.J. Aulerich, D. Polin and W.E. Braselton : The reproductive effects of dietary heptachlor in mink (*Mustela vison*). *Arch. Environ. Contam. Toxicol.*, **24**, 156-164 (1993).

Driscoll, M.S., J.P. Hassett and C.L. Fish : Extraction efficiencies of organochlorine compounds from Niagara River water. *Environ. Sci. Tchnol.*, **25**, 1432-1439 (1991).

Epstein, S.S. : Losing the war against cancer : who's to blame and what to do about it. *Int. J. Health Serv.*, **20**, 53-71 (1990).

Falandysz, J., K.. Kannan, S. Tanabe and R. Tatsukawa : Persistent organochlorine residues in canned cod-livers of the southern Baltic origin. *Bull. Environ. Contam. Toxicol.*, **50**, 929-934 (1993).

Fernández, N., M. Sierra, J.J. Garcia, M.J. Diez, and M.T. Teràn : Organochlorine pesticide residues in black tea, camomile, and linden. *Bull. Environ. Contam. Toxicol.*, **50**, 479-485.

Ferrando, M.D. and E. Andreu-Moliner : Effect of lindane on the blood of a freshwater fish. *Bull. Environ. Contam. Toxicol.*, **47**, 465-470 (1991).



Gómez Catalán, J., J. Planàs, J, To-Figueras, M. Camps and J. Corbella : Organochlorine pesticide residues in the population of Catalonia (Spain). *Bull. Environ. Contam. Toxicol.*, **51**, 160-164 (1993).

González, J.M., J.M. Cabanas, M. Martiinez and J. Muñoz : Alterations in acetylcholinesterase activity in plasma and synaptosomal fractions from C.N.S. of rats acutely intoxicated with lindane. Effect on succinylcholine. *Bull. Environ. Contam. Toxicol.*, **39**, 647-655 (1987).

Harris, C.I. : Movement of pesticides in soil. *J. Agr. Food Chem.*, **17**, 80-82 (1969).

IARC/International Agency for Research on Cancer : Hexachlorocyclohexane (Tecnical HCH and lindane). IARC Monogr. Eval. Carcinog. Risk Chem. Hum. **20**, 195 (1979).

Samuel, T. and M.K.K. Pillai : Impact of repeacted application on the binding and persistence of [$^{14}$C]–HCH in a tropical soil. *Environ. Pollut.*, **74**, 205-216 (1991).

Sawyer, L.D., B.M. McMahon, W.H. Newsome, and G.A. Parker : Ch. 10 : Pesticide and industrial chemical residues. *In* : Official methods of analysis of the Association of Official Analytical Chemists. Vol. 1. (*Ed* : K. Helrich). Association of Official Analytical Chemists Publ. Arlington. 274-311 (1990).

Tanabe, S., H. Iwata and R. Tatsukawa : Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Total Environ.*, **154**, 163-177 (1994).

Waldron, A.C., H.E. Kaeser, D.L. Goleman, J.R. Staubus and H.D. Niemczyk : Heptachlor and heptachlor epoxide residues on fall-treated alfalfa in milk and cow tissues. *J. Agr. Food Chem.*, **16**, 627-631 (1968).

Waliszewski, S.H. : Residues of lindane, HCH isomers and HCB in the soil after lindane application. *Environ. Poll.*, **82**, 289-293 (1993).

Weber, J.B., J.A. Best and J.U. Gonese : Ch. 10 : Bioavailability and bioactivity of sorbed organic chemicals. *In* : Sorption and degradation of pesticides and organic chemicals in soil (*Eds* : D.M. Linn, *et al.*). Soil Science Society of America Publication Number **32**. Madison. 153-196 (1993).