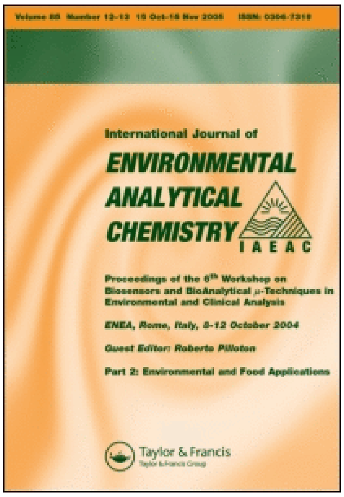

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Chlordane Adsorption Onto Soils and Pig Slurry

E. Loffredo[a]; N. Senesi[a]; V. D'orazio[a]
[a] Istituto di Chimica Agraria, Università di Bari, Bari, Italy

To cite this Article Loffredo, E. , Senesi, N. and D'orazio, V.(1997) 'Chlordane Adsorption Onto Soils and Pig Slurry', International Journal of Environmental Analytical Chemistry, 66: 3, 163 — 174

To link to this Article: DOI: 10.1080/03067319708028360

URL: http://dx.doi.org/10.1080/03067319708028360

Intern. J. Environ. Anal. Chem., Vol. 66, pp. 163–174
Reprints available directly from the publisher
Photocopying permitted by license only

CHLORDANE ADSORPTION ONTO SOILS AND PIG SLURRY

E. LOFFREDO*, N. SENESI and V. D'ORAZIO

Istituto di Chimica Agraria, Università di Bari, Via G. Amendola 165/A, 70126 Bari, Italy

(Received 18 June 1996; In final form 30 September 1996)

The extent of chlordane adsorption onto two horizons of two different soils, and a pig slurry used as soil amendment was investigated. Adsorption isotherms and coefficients were obtained using a slurry-type procedure, followed by solid phase extraction of chlordane, and gas chromatographic analysis with electron capture detector. Adsorption of *cis*- and *trans*-chlordane was better described by a linear model for soils and by a Langmuir-type isotherm for pig slurry. The surface horizon of both soil samples adsorbed chlordane in amounts higher than the corresponding entire soil profile. The highest adsorption capacity was shown by soil samples richer in organic matter. The extent of chlordane adsorption onto pig slurry was between two and more than three orders of magnitude higher than that on soils. In any case, the adsorption capacity was related to the organic matter content of the substrate. *Trans*-chlordane showed a greater affinity than *cis*-chlordane to both soils and pig slurry.

Keywords: Adsorption isotherms; chlordane; gas chromatography; pig slurry; soil; solid phase extraction

INTRODUCTION

Chlordane is a broad-spectrum, non-systemic insecticide (also showing fumigant action) used for both residential and agricultural applications.[1,2] Similar to most other organochlorine insecticides, chlordane is highly toxic and persistent in the environment. These properties have contributed to both its effectiveness and its widespread presence as an environmental and biological contaminant.[2] Chlordane and its metabolites have been found at all trophic levels in specimens from the Northern and Southern hemisphere, as present in the food chain of both

---

*Corresponding author. Fax: +39-80-5442813.

aquatic and terrestrial organisms.[1] The marked toxicity, persistence and preferential bioaccumulation of chlordane has induced several countries, including United States, Japan and most European countries, to ban the use of this product in recent years.[1]

Chlordane is synthesized by the Diels-Alder fusion of hexachlorocyclopentadiene and cyclopentadiene to form the intermediate chlordene which is then chlorinated to obtain chlordane. Technical chlordane is a complex mixture of about twenty chemically similar components containing seven, eight, or nine chlorine atoms. The main constituents of chlordane are the alpha, or *cis*-isomer, and the gamma, or *trans*-isomer, which are present in the mixture in the proportion of 19% and 24%, respectively.[2]

Although a large number of investigations have been conducted on the toxicology and metabolism of chlordane in humans and, in general, in mammals,[2,3] very little information is available on the environmental fate of this compound. Similar to other chlorinated hydrocarbon insecticides, such as aldrin, dieldrin or DDT, chlordane is characterized by an elevated persistence,[3,4] limited horizontal and vertical movement, and accumulation of its residues in the upper soil layers.[4]

Some chlordane characteristics, such as the low water solubility (about 0.1 mg L^{-1} at 25°C), the high lipophilicity (log K_{ow} = 5.16), and the consequent negligible movement through the soil, suggest that adsorption represents the main process that chlordane undergoes in soil. This important phenomenon is expected to greatly affect the overall environmental and biological fate and behaviour of chlordane.

Adsorption of chlordane has been studied on organic substrates[5] and some sediments,[6] but no information is available for soils and soil organic amendments. In very recent work,[6] sorption-desorption of *cis*- and *trans*-chlordane onto different size-fractions of various sediments were shown to be largely independent of the particle size, and directly related to the organic matter content of the whole sediment samples. These results indicated the important role of organic matter in these processes. Further, the values of the partition coefficient for *trans*-chlordane were always higher than those for the *cis*-isomer, indicating a greater affinity of *trans*-chlordane for sediments.[6]

The increasing use of animal manure, such as pig slurry, as soil amendment deserves investigation of the extent of adsorption of chlordane onto this material, which is rich in organic matter and is expected to modify markedly the adsorption processes of chlordane in the amended soil.

The objective of this work was to evaluate the adsorption isotherms of the two main components of chlordane, the *cis*- and the *trans*- isomers, onto soil samples collected from two horizons of two different soils, and onto a pig slurry used as soil amendment.

MATERIALS AND METHODS

Samples

Soil samples were provided by Rothamsted Experimental Station, Harpenden, UK, and Universidade Nova de Lisboa, Lisbon, Portugal, in the framework of a joint EC Research Project. They originate from the surface (0–23 cm, UK-1) and whole (0–130 cm, UK-2) horizons of a sandy soil of the Woburn Cottenham series, and the surface (0–30 cm, PO-1) and whole (0–90 cm, PO-2) horizons of a sandy soil from Portugal. The pig slurry (PS) sample was provided by the Research Institute for Agrobiology and Soil Fertility, Haren, The Netherlands, also involved in the EC Research Project. Some chemical and physical properties of the four soil samples and pig slurry are referred in Table I.

The *cis-* and *trans-* isomers of chlordane [1,2,4,5,6,7,8,8-octachlor-2,3,3a,4,7,7a-hexahydro-4,7-methano-indene], both 99% purity, were obtained from Chem Service, Inc., West Chester, PA, USA.

Chlordane Adsorption

Adsorption of chlordane onto the samples examined was obtained using the slurry-type method. Aliquots of 30 mL of aqueous solutions (7.5% ethanol in

TABLE I Some properties of the four soil samples (UK-1, UK-2, PO-1, PO-2) and pig slurry (PS) examined.

Sample→ *Parameter↓*	*UK-1*	*UK-2*	*PO-1*	*PO-2*	*PS*
Sand (%)	85.50	87.31	93.52	93.00	–
Silt (%)	5.92	5.36	2.10	2.17	–
Clay (%)	8.58	7.34	4.38	4.83	–
pH (in KCl)	5.90	5.94	4.35	4.49	8.6[a]
C org. (%)	1.10	0.38	0.31	0.16	32.09
Organic matter (%)[b]	1.90	0.66	0.53	0.27	55.19
C.E.C. (mmol Kg^{-1})	83	69	22	16	–
Conductivity (dS m^{-1}, 25°C)	0.050	0.046	0.162	0.136	–

[a] pH in H_2O.
[b] calculated by multiplying C org % by 1.72.

H_2O) of a mixture of *trans*- and *cis*-chlordane, at concentrations of 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 and 1 mg L^{-1} for each isomer, were added to 1 g of soil or 30 mg of pig slurry, in glass flasks. Equilibration was achieved by shaking the mixtures mechanically for 20 h at 20°C. Preliminary experiments showed equilibration to be complete within 20 h. All experiments were conducted in triplicate. Soil or pig slurry suspensions were then centrifuged at 11,000 rpm for 15 min, and the supernatant solutions were removed and stored in stoppered glass vials in the dark until further use.

Chlordane Extraction

Chlordane (*trans*- and *cis*-chlordane mixture) was extracted from adequate aliquots of the supernatant solution of each sample using solid phase extraction (SPE) with Supelclean™ Envi™-18, 3 mL (0.5 g) cartridges, and the Merck LiChrolut® Extraction Unit. The extraction procedure adopted consisted of a) conditioning the cartridge by using 3 mL of methanol and then 2 mL of 5% methanol in H_2O; b) addition to the sample of 2 mL aqueous solution of chlordane using a vacuum system adjusted at a constant flow rate <5 mL min^{-1}; c) drying the cartridge in vacuum for some min; d) dropwise elution of the adsorbed product with 2 × 1 mL of *n*-hexane/ acetone (9:1) solution; and (e) appropriate correction of the eluted solution to a known volume. During the extraction, *cis*- and *trans*-chlordane were also concentrated adequately in the solution, depending on their initial concentration, in order to obtain a better gas chromatographic detectability. Four aqueous solutions (7.5% ethanol in H_2O) of a mixture of *cis*- and *trans*-chlordane at concentrations of 0.01, 0.05, 0.1 and 0.2 mg L^{-1} were extracted using the procedure described above, and used as standard solutions for the quantification of *cis*- and *trans*-chlordane.

Chlordane Analysis

Chlordane analyses were performed with a Fisons HRGC Mega 2 series Gas Chromatograph equipped with an electron capture detector (ECD) containing a Ni^{63} beta-emitting radioactive source, and operated in the constant current mode to increase the linearity of ECD response. A GC Mega SE-52 column, 30 m length × 0.53 mm inside diameter, was used. The operating conditions were the following: oven temperature program, from 200°C (1 min) to 230°C (held for 3 min), at 5°C min^{-1}; injector and detector temperatures, 260°C and 310°C, respectively; flow rate for carrier gas, helium, about 8 mL min^{-1}, and for make-up gas, nitrogen, about 42 mL min^{-1}. Split injection technique was adopted by injecting a sample volume of 1 μL using *n*-hexane:acetone =9:1 as solvent.

A series of calibration solutions of *cis*- and *trans*-chlordane at concentrations of 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2, 5 and 10 mg L^{-1} in *n*-hexane:acetone = 9:1 was used to test detector response. Only the linear range between 0.01 and 0.2 mg L^{-1} was used for *cis*- and *trans*-chlordane quantification. In this concentration range, the correlation coefficient of the calibration curves was close to 1 for both analytes. The external standard method was used, and sample concentration was calculated by the linear calibration equation. The extraction procedure adopted yielded the recovery data reported in Table II. Calibration curves of *cis*- and *trans*-chlordane, and gas chromatograms of each isomer and of a mixture of both of them are shown in Figures 1 and 2, respectively. Retention times for *trans*- and *cis*-chlordane were different enough to allow an adequate distinction between the two products.

Adsorption Isotherms

Experimental adsorption data for *cis*- and *trans*-chlordane onto the substrates examined were fitted to both a linear model and nonlinear Freundlich equation, $x/m = KC^{1/n}$, and Langmuir equation, $x/m = (KCb)/(1 + KC)$, where x/m is the amount of *cis*- or *trans*-chlordane adsorbed in μg g^{-1}, and C is the equilibrium solution concentration of *cis*- or *trans*-chlordane in μg mL^{-1}. The constant K is a measure of the magnitude of adsorption, or adsorption capacity of the substrate, the constant 1/n indicates the degree of nonlinearity between solution concentration and amount adsorbed, and b represents the Langmuir adsorption maximum.[7,8] The distribution coefficient, K_d, defined as the mean value of the amount of chlordane adsorbed at the various equilibrium concentrations, calculated by the following equation:

TABLE II Recovery data for chlordane from aqueous solutions with the solid phase extraction method

Chlordane concentration	*trans-chlordane*	*cis-chlordane*
0.02 mg L^{-1}	90.7% ± 3.0%[a]	91.8% ± 2.8%[a]
0.05 mg L^{-1}	103.5% ± 3.1%	104.9% ± 2.4%
0.10 mg L^{-1}	107.4% ± 6.8%	108.4 ± 5.9%
0.20 mg L^{-1}	96.0% ± 6.6%	98.0% ± 6.3%

[a] Standard error calculated for 3 replicates.

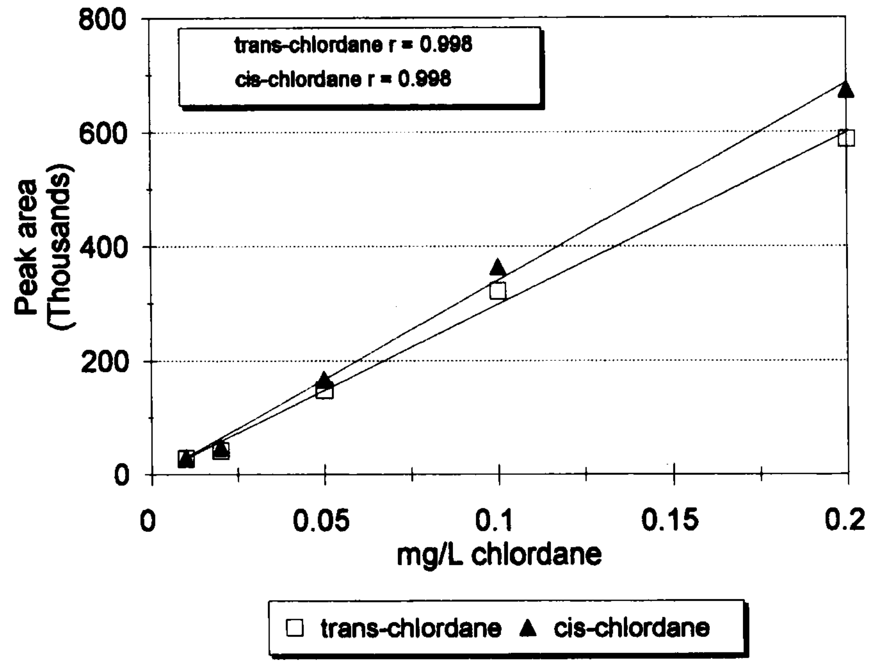

FIGURE 1 Calibration curves for *trans*- and *cis*-chlordane obtained by extracting the standard solutions using the solid phase extraction method. Correlation coefficients of the regression lines are also reported.

$$K_d(mL^{-1}\,g^{-1}) = \left|\frac{x/m(\mu g\,g^{-1})}{C(\mu g mL^{-1})}\right|_{mean}$$

was also considered as an additional index of the adsorption capacity of the various substrates.

RESULTS AND DISCUSSION

Experimental adsorption data of *cis*- and *trans*-chlordane onto the four soil samples examined fit better a linear adsorption model than a non-linear Freundlich or Langmuir model, over the entire concentration range tested. Differently, the best fit of adsorption data for both chlordane isomers onto pig slurry is obtained with a Langmuir-type isotherm. The correlation coefficients, r, for the linear isotherm, in the case of soils, and for the Langmuir isotherm, in the case of pig slurry, are referred in Table III, together with the adsorption coefficients,

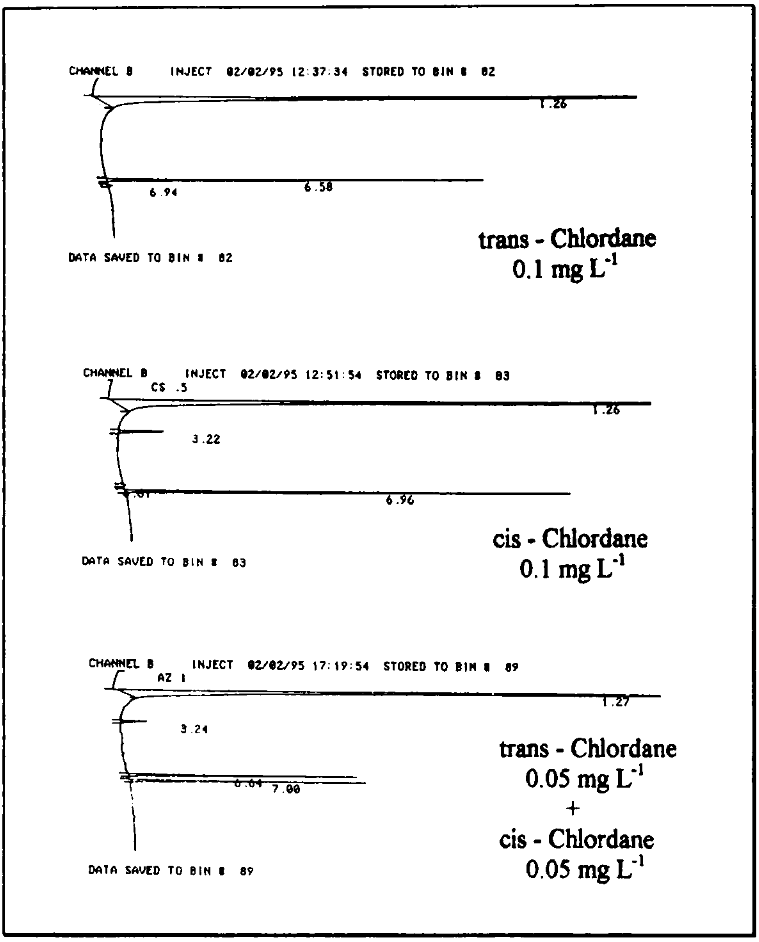

FIGURE 2 Gas chromatograms of *trans*-chlordane, *cis*-chlordane and a mixture of both at equivalent concentrations.

K, and the distribution coefficients, K_d, for both *trans*- and *cis*-chlordane. The adsorption isotherms of *cis*- and *trans*-chlordane onto soils and pig slurry are shown in Figures 3 and 4, respectively.

Linear and non linear relationships are largely observed in the adsorption of nonionic and nonpolar compounds onto a wide variety of soils and soil components, including clay minerals and organic matter.[9] A linear isotherm indicates that a constant partition of chlordane occurs between the solution and the soil substrates, that is, adsorption is directly proportional to the solution concentration and no limiting adsorption (saturation) occurs over the whole concentration

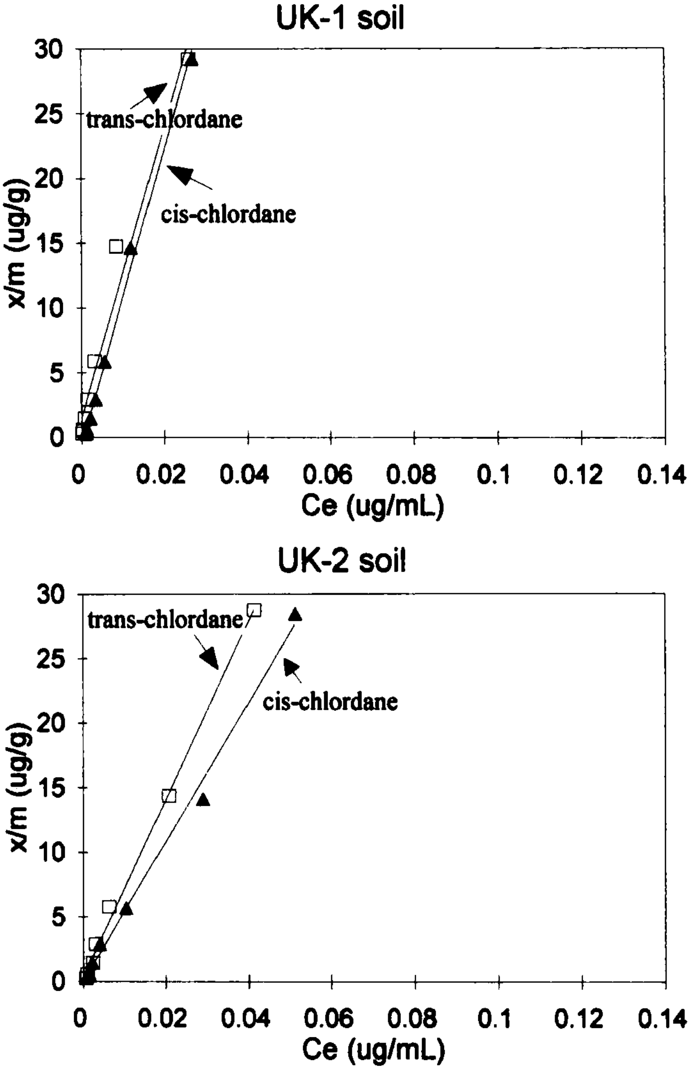

FIGURE 3 Linear adsorption isotherms for *trans*- and *cis*-chlordane onto UK-1, UK-2, PO-1 and PO-2 soils. (*trans*-chlordane, □; *cis*-chlordane, ▲). The calculated standard error is omitted because too low to be visible.

range tested. A Langmuir isotherm suggests that chlordane has a moderately high affinity for the pig slurry in the initial stages of adsorption, whereas it has increasing difficulty in finding vacant sites as they are filled, finally reaching a maximum of adsorption, or saturation.

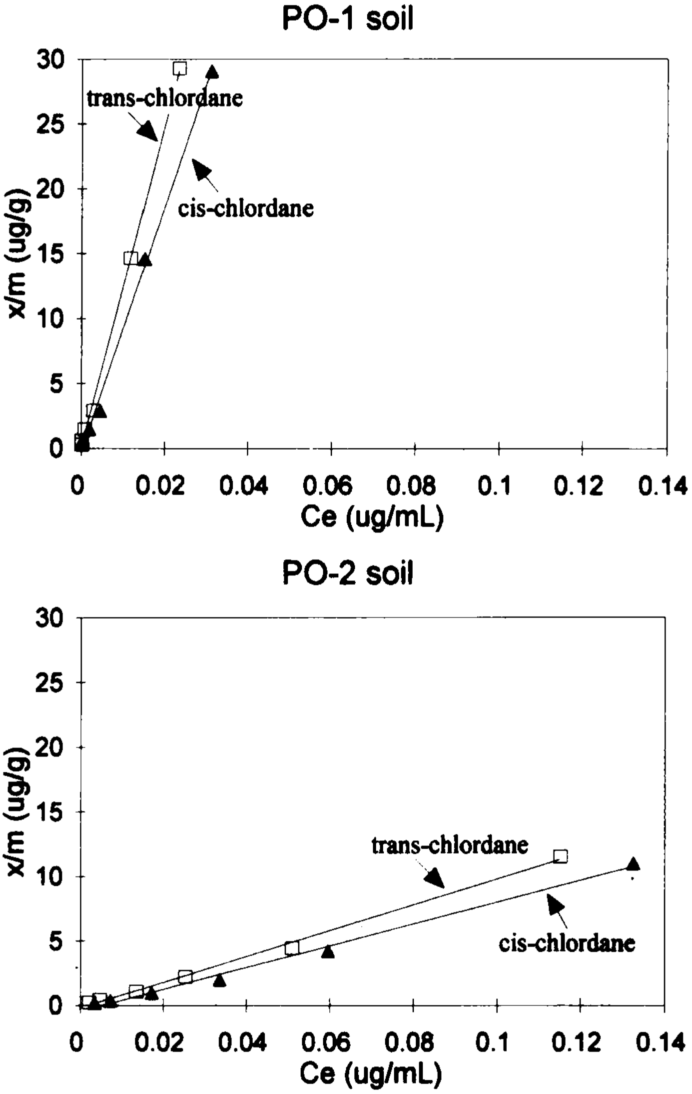

FIGURE 3. Continued

As the model of adsorption of chlordane is profoundly different between soil and pig slurry, it is expected that soil amendment with pig slurry will modify markedly the adsorption mechanism of the amended soil, with respect to that of the non-amended soil.

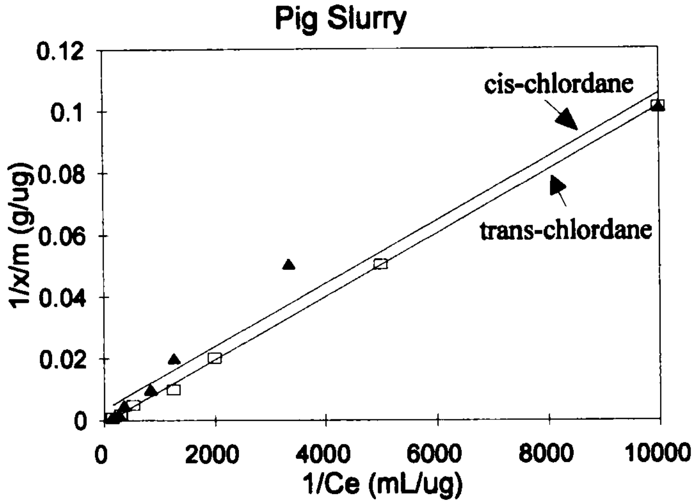

FIGURE 4 Langmuir adsorption isotherms for *trans*- and *cis*-chlordane onto pig slurry. (*trans*-chlordane, □; *cis*-chlordane, ▲). The calculated standard error is omitted because too low to be visible.

The calculated adsorption coefficients, K, and distribution coefficients, K_d, followed a similar trend for chlordane adsorption onto soils (Table III). The two surface horizon soils, UK-1 and, especially, PO-1, show an adsorption capacity for *cis*- and *trans*-chlordane which was much higher, more than twice and more than one order of magnitude, respectively, than that of the corresponding entire soil horizons, UK-2 and PO-2. The large difference in adsorption capacity for

TABLE III Correlation coefficients (r) for linear (soils) and Langmuir (pig slurry) isotherms, adsorption coefficients, K, and distribution coefficients, K_d, for *trans*- and *cis*-chlordane adsorption

		TRANS-CHLORDANE	
Substrate	r[a]	K	K_d (L Kg^{-1})
UK1-soil	0.991	1420	1923
UK2-soil	0.998	699	691
PO1-soil	0.999	1240	1837
PO2-soil	0.998	98	93
Pig Slurry	0.9997	–	118042
		CIS-CHLORDANE	
Substrate	r[a]	K	K_d (L Kg^{-1})
UK1-soil	0.997	1159	1288
UK2-soil	0.997	540	536
PO1-soil	0.998	928	945
PO2-soil	0.993	80	63
Pig Slurry	0.984	–	91691

[a] significant at the 0.001 level.

chlordane between surface and whole soil horizons, and between the two soil types, may be reasonably ascribed to the different amount and composition of organic and mineral adsorbing components in the samples examined. In particular, the much lower adsorption capacity of the whole PO soil (PO-2) with respect to the UK soil, may be due to the much higher organic matter content of the latter with respect to the former.

The extent of chlordane adsorption onto pig slurry resulted between two and more than three orders of magnitude higher than that on soils (Table III). This result confirms the high affinity of chlordane for materials very rich in organic matter, such as pig slurry, and suggests that amendment with pig slurry will affect not only the mechanism but also the adsorption capacity of the amended soil for chlordane.

In all cases examined, both the adsorption coefficient and the distribution coefficient for *trans*-chlordane resulted higher than those for *cis*-chlordane, thus indicating that the *trans*-isomer is more adsorbed than the *cis*- isomer. These results are in good agreement with the higher partition coefficients measured for *trans*-chlordane, with respect to those for *cis*-chlordane, in adsorption experiments recently conducted on various sediments.[6] Thus, the geometrical structure of chlordane appears to play a significant role in its adsorption onto both soil and pig slurry.

CONCLUSIONS

The two main isomers of the insecticide chlordane are adsorbed to various extent by the soils examined, as a function of both the horizon depth and soil type, mainly on dependence on the organic matter content of the sample. The organic-rich pig slurry is able to adsorb chlordane in much higher amounts than mineral soils. Soil amendment with pig slurry is thus expected to cause a marked increase of chlordane adsorption onto the amended soil. As a consequence, a lower bioaccumulation of the chemical in the trophic chain, a smaller movement through the soil, and a lower potential of groundwater contamination can be expected in pig-slurry amended soils, with respect to nonamended soils. The general behaviour of chlordane in soil will also be affected by the different geometrical structure of its isomers present in the technical preparate.

Acknowledgement

This research was supported by the EC Project Grant no EV5V-CT92/0203.

References

[1] H.-R. Buser and M. D. Müller, *Environ. Sci. Technol.*, **26**, 1533–1540 (1992).

[2] A. A. Nomeir and N. P. Hajjar, *Rev. Environ. Contam. Toxic.*, **100**, 1–22 (1987).

[3] W. Ware (Ed.), *Rev. Environ. Contam. Toxic.*, **104**, 47–62 (1988).

[4] W. Bennett, D. L. Ballee, R. C. Hall, J. E. Fahey, W. L. Butts and J. V. Osmun, *Bull. Environ. Contam. Toxic.*, **11**, 64–69 (1974).

[5] R. A. Dobbs and J. M. Cohen, Report no. 600/8-80-023. USEPA Environmental Monitoring and Support Laboratory, Cincinnati, OH (1980).

[6] K. M. Erstfeld, M. S. Simmons and Y. H. Atallah, *J. Environ. Sci. Health*, **B31**, 43–58 (1996).

[7] C. H. Giles, T. H. MacEwan, S. N. Nakhwa and D. Smith, *J. Chem. Soc.*, 3973–3993 (1960).

[8] C. H. Giles, D. Smith and A. Huitson, *J. Colloid Interface Sci.*, **47**, 755–765 (1974).

[9] N. Senesi and Y. Chen, In: *Toxic Organic Chemicals in Porous Media. Ecological Studies* (Z. Gerstl, Y. Chen, U. Mingelgrin and B. Yaron, eds. Springer-Verlag, Berlin, 1989) vol. 73, pp. 37–90.