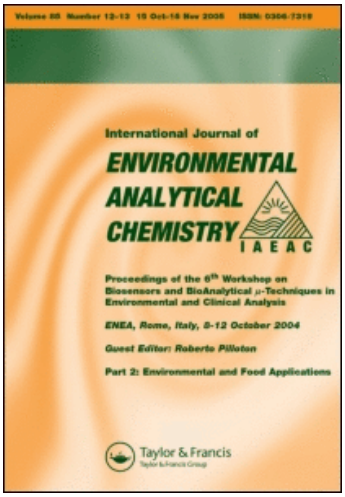

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Solution Phase Interaction of Lindane with Fulvic Acid: Effect of Solution pH and Ionic Strength

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As part of an investigation of the factors influencing the interaction of different classes of pesiticides with humic substances, a study was made of the role of the following physicochemical variables on the adsorption of a typical non-polar pesticide (lindane) by a calibrated fulvic acid fraction which can exist in both colloidal solution and in precipitated form: degree of protonation; ionic atmosphere; and extent of humic matter aggregation. Using the fulvic acid as a typical humic material, and the experimental parameters of pH and ionic strength, along with ultrafiltration techniques, we were able to demonstrate the importance of these physicochemical variables on binding of lindane. From these results predictions could be made about binding mechanisms and environmental implications. The findings are likely to be applicable to all non-polar pesticides having aqueous solubility similar to that of lindane.

KEY WORDS: Lindane, fulvic acid, pesticide retention, pH, ionic strength.

INTRODUCTION

The registration of pesticides is based partly on sorption/desorption testing for modeling of pesticide mobility. These tests include

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measuring the mobility of the pesticide by isotherm and leaching experiments. It is generally assumed that such leaching of pesticides from soils is adequately described by a simple partition between hydrophobic and hydrophilic environments followed by a Hansch correlation.[1] Alternatively, a single chemical interaction site is employed to account for distributions.[2,3] These simple assumptions are adequate for studies where distilled water is the leaching agent. However, soil solutions are more complex and it is possible that at least four factors can affect the partition of pesticides between water and humic components of soil: (a) the degree of protonation of the humic acid; (b) the electrostatic (ionic atmosphere) environment of the organic acids; (c) the state of aggregation of the organic matter; and (d) the distribution of organic matter between precipitated (particulate) and mobile (colloidal) phases. In order to analyze these internal variables we can utilize the experimental parameters, pH, ionic strength, and concentration of metal ions (which induce aggregation) . A study of these parameters will require a lengthy and multidimensional experimental program which has, in fact, been initiated. Specifically, the plan is to investigate interactions between well characterized humic material, i.e. the Armadale Bh horizon fulvic acid,[4,5] and four typical pesticides: atrazine (polar); lindane (non-polar); 2,4-D (carboxylic group); and paraquat (ionic). The first phase of this work involving atrazine[6] gave quantitative evidence of the importance of all four variables. We report now the results obtained with lindane under a variety of conditions of pH and ionic strength.

EXPERIMENTAL

The calibrated fulvic acid used as the test organic soil component had been prepared at Concordia University from an Armadale Bh horizon soil. The method used involved extraction of the soil with sodium hydroxide under inert conditions. The fulvic acid containing extract was introduced onto a Dowex 50 cation exchange resin column. The fulvic acid was recovered from the column by elution and the column regenerated with hydrochloric acid solution. The eluate was freeze dried to obtain the purified fulvic acid solid product. The latter was calibrated by standard methods. Details of

the method of preparation and characterization of the product are given in the literature.[4,7-10] Fulvic acid stock solution was prepared by dissolving 2 g of fulvic acid in 100 ml of distilled water.

Lindane was purchased from Supelco Canada Ltd. (Oakville, Ontario, Canada) in 99% plus purity. A 20.8 μM lindane stock solution (6.1 ppm) was prepared by dissolving 0.02424 g of lindane in the minimum amount of methanol (Accusolv Grade, Anachemia, Montreal, Quebec, Canada) required to obtain solution. This methanol solution was quantitatively transferred to an Erlenmeyer flask and diluted with about 4 liters of distilled water. It was heated gently overnight with stirring, and then stored at room temperature. This stock solution was used for the binding of lindane to fulvic acid tests.

Standard lindane solutions for gas chromatographic (GC) calibration purposes were prepared as follows: lindane, 0.01 g, was dissolved in benzene (Anachemia Accusolv Grade) in a 100 ml volumetric flask and diluted to volume to give a 100 ng/μl standard stock solution. This solution was refrigerated until required. Working GC standards were prepared when necessary in the desired concentrations by dilution of this stock solution with benzene.

Aqueous solutions of 2.5 M potassium chloride, 1 M hydrochloric acid, and 1 M sodium hydroxide were prepared quantitatively using certified reagents and deionized water.

An Amicon Ultrafiltration Stirred Cell, Model 8050 (Amicon Canada Ltd., Oakville, Ontario, Canada) was used with Amicon Diaflo Ultrafiltration Membranes, Grade YM 2 (1000 M.W. cut-off),[11] for separation of free lindane in solution from fulvic acid having bound lindane. Preliminary to use these membranes were soaked for 3 to 4 hours in 70% ethanol solution followed by soaking overnight in distilled water.

Lindane was determined using a Perkin-Elmer Sigma 4B Gas Chromatograph equipped with a 6 ft × 4 mm i.d. glass column packed with 2% OV-1 plus 3% QF-1 on 100–120 mesh Chromosorb W HP maintained at 210°C (electron capture detector, 60 ml/min of 95% argon/5% methane carrier gas) or a Shimadzu GC-6AM gas chromatograph having a 50 cm × 3 mm i.d. stainless steel column packed with 5% OV-101 on 80–100 mesh Chromosorb W AW which was kept at 155°C (electron capture detector, 60 ml/min prepurified nitrogen carrier gas). Injector/detector temperatures were 240°C.

Symmetrical peaks for lindane and linear calibration curves (0 to 3.5 ppm) were obtained with both instruments.

A preliminary study was conducted to establish the stability of lindane in aqueous solution at different pH levels. Seven solutions, each containing 2.4 ng/μl of lindane were prepared, and each was adjusted to a specific pH value in the range of 1.4 to 11.3. Duplicate portions of lindane solution at each pH were shaken at $20 \pm 1°C$ for 1 and 3 days respectively, following which lindane remaining was extracted into benzene and determined by GC. Quantitative results were obtained using calibration curves.

In the first set of experiments, to determine the amount of lindane bound to fulvic acid under various conditions, lindane and fulvic acid stock solutions in required amount were mixed together and diluted to 50 ml volumes with deionized water. The final fulvic acid concentration was 1 g/l in every case. The lindane concentration was varied from 0.6×10^{-3} to 2.76×10^{-3} g/l depending on the particular test. Before dilution, each test mixture was adjusted to the required pH (1.2, 3, 5 or 7) by addition of sufficient 1 M hydrochloric acid or 1 M sodium hydroxide.

In a second set of experiments solutions were prepared to contain 1 g/l fulvic acid and 2.4×10^{-3} g/l lindane, and the final pH was varied from 1.65 to 8.3.

A third series of experiments was carried out preparing solutions as described above, differing only in that they also contained poassium chloride at 0.1 M concentration. The intent was to determine the effect of increasing ionic strength on binding of lindane to fulvic acid.

Blank solutions of exactly the same composition except for the absence of fulvic acid were prepared for each experiment.

Test and blank solutions were shaken overnight at room temperature ($20 \pm 1°C$), subjected to ultrafiltration, and 10 ml of ultrafiltrate collected. The free lindane present in each filtrate was extracted into a 20 ml volume of benzene. The benzene extracts were analyzed for lindane content by GC. The differences between the lindane found in test and blank solution ultrafiltrates were taken as a measure of lindane bound to fulvic acid. This analytical approach had been proven to yield meaningful data in our earlier study of atrazine/fulvic acid binding.[12]

RESULTS AND DISCUSSION

Effect of pH on stability of aqueous lindane solutions

The results of preliminary tests on stability of lindane in aqueous solution are shown in Figure 1. Degradation of lindane was rapid above pH 8 which is in agreement with that reported by Brook.[13] Degradation was also apparent at low pH. Even in the pH 3 to 8 range, about 25% of the original lindane was lost within one day. This factor made the use of the blank solutions obligatory in subsequent binding of lindane to fulvic acid experiments. The implicit assumption was made that loss of lindane by means other than binding to fulvic acid was the same in test solutions and in blanks, and was therefore compensated for experimentally. Since this may not be entirely correct, subsequent experiments were limited to pH values and time spans within which stability of lindane in aqueous solution was a maximum.

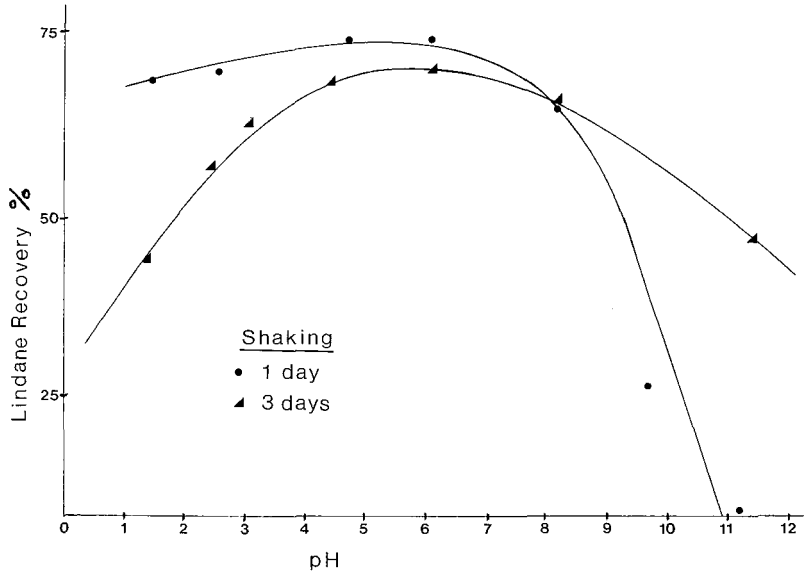

FIGURE 1 Stability of lindane in aqueous solution.

Effect of pH on the binding of lindane to fulvic acid

The results of experiments at both constant pH and constant fulvic acid concentration but variable lindane concentration were used to prepare plots which represented the titration of fulvic acid with lindane. A typical example of the shape of plots obtained at pH 1.2, 3, 5 and 7 is given in Figure 2 for the case of pH 3. At each pH there was an increase in lindane complexed with amount of lindane added up to some maximum. The values of these maxima, which provided a measure of the capacity of lindane to complex with fulvic acid, varied with pH. These maximum binding values are plotted in Figure 3.

Results of tests at constant lindane and fulvic acid concentrations but varying pH are also plotted on Figure 3. Lindane complexing capacities determined in these tests agreed with those obtained above.

From Figure 3 it was observed that lindane binding by fulvic acid, while very small at all pH values (always less than 1 μmole/g of fulvic acid) was inversely related to pH. With increase in pH the degree of protonation of fulvic acid carboxylic acid groups decreases and apparently its surface becomes less attractive to lindane molecules.

A possible mechanism for the binding of lindane to fulvic acid is hydrophobic interaction. This is the conventional interpretation of hydrophobic pesticide adsorption and is supported by correlations with such parameters as water–octanol partition coefficients. However, it is less than completely satisfying as a model to account for the low stoichiometric binding capacity observed, the fairly specific response to parameters such as pH and ionic strength, and the parallel behaviours of lindane and a less hydrophobic pesticide, atrazine.

We can speculate that a more specific mechanism is possible. This is the formation of electron donor-acceptor complexes between donor sites on the fulvic acid with the pesticide as acceptor. This second mechanism is attractive for two reasons. First, it would appear as an interaction with a small number of specific sites and would, therefore, show stoichiometric saturation at low coverage which is precisely what was observed. Second, it would provide an explanation for the otherwise puzzling parallels between binding of

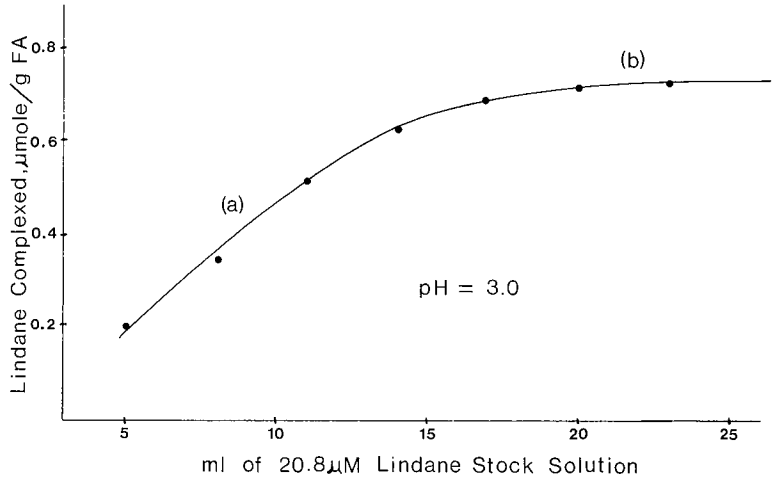

FIGURE 2 Typical complexing curve: (a) equilibrium region; (b) asymptotic approach to the plateau in the capacity region.

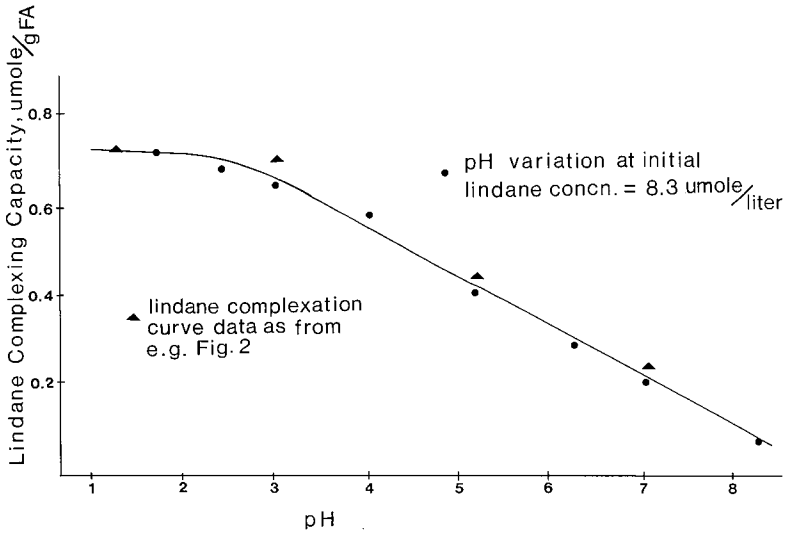

FIGURE 3 Variation with pH of complexing capacity of lindane with fulvic acid.

lindane and atrazine. For both, complexation with fulvic acid increases in the same fashion with decrease in pH. For atrazine, we could explain this on the basis of protonation of atrazine at low pH leading to it undergoing hydrogen bonding with fulvic acid. But this explanation will not hold for lindane because of its inability to undergo protonation.

Complexing capacities such as those illustrated in Figure 3 have been used to define the stoichiometry for law of mass action calculations applied to our solution phase complexing equilibria. This is a more chemically conventional type of data presentation than Freundlich or Langmuir isotherms, especially for single solution phase systems. Conversely, the isotherms are more appropriate to interpretation of sorption at the interfaces between two physical phases. Law of mass action calculation gave $\bar{K}$ values of 2.6×10^{-6} and 2.09×10^{-6} liters/mole at pH 3 and 5, respectively. Because the complexing is not very strong, the experimental errors in the $\bar{K}$ values are moderately large. They are, nevertheless, useful in defining the complexing equilibria which exist. Calculations of $\bar{K}$ at pH below 3 and above 5 gave values within a factor of 2 of the above, but were considered to be less reliable because of the instability of aqueous lindane solutions at low and high pH.

Effect of high ionic strength on the binding of lindane to fulvic acid at various pH

Figure 4 shows the extent of binding observed when the tests described above were repeated but with 0.1 M potassium chloride added to each test solution and blank to increase ionic strength. Binding was diminished at all pH becoming less than 0.1 μmoles/g of fulvic acid at pH 3 and greater. At first glance, the decreased binding at high ionic strength appears to support the contention that interaction between lindane and fulvic acid is hydrophobic. However, there was visual evidence of precipitation of fulvic acid from solution at all pH in the presence of KCl. Such salting out of the fulvic acid colloid results in a precipitate with a much lower surface area than is possessed by dispersed fulvic acid.[5] The feasibility of interaction with lindane via surface adsorption is correspondingly decreased. There is nothing here, therefore, to contradict the possibility of an electron donor-acceptor mechanism.

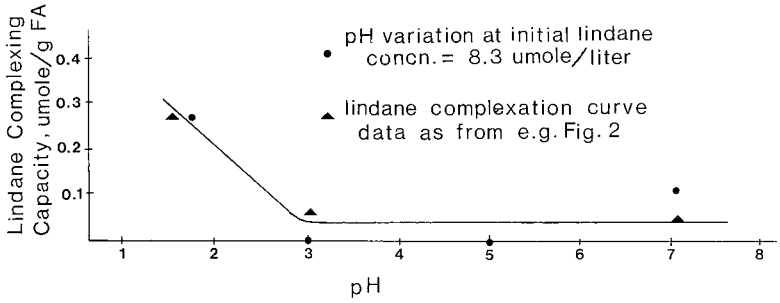

FIGURE 4 Variation with pH of complexing capacity of lindane with fulvic acid in the presence of 0.1 M KCl.

CONCLUSION

The complexation of lindane and fulvic acid has been demonstrated to be very small, less than 1 μmole lindane per gram of fulvic acid under all pH and ionic strength conditions investigated. In addition, increase in pH, ionic strength, and/or degree of aggregation of fulvic acid all serve to decrease the extent of adsorption observed. These findings confirmed the importance of the four variables, degree of protonation of the humic substance, ionic environment of the organic material, state of aggregation of the humic material, and distribution of organic matter between precipitated and colloidal phases, in determining the extent of binding of lindane to a fulvic acid.

Our results are in agreement with those reported by Baluga *et al.*[14] who found that 0.12 μmole lindane was bound per gram of soil having an organic content of 7.9%. They are lower by a factor of about 3, however, than that reported by Carter and Suffet[15] in their study of DDT/humic material interaction. Likely explanations for this difference in behaviour are the differences in hydrophobicity of fulvic acid and humic acid, and the more hydrophobic nature of DDT compared to lindane as exemplified by their solubilities in water, less than 1 to 2×10^{-3} ppm for DDT compared to 7.9 ppm for lindane at 20°C.

The environmental consequence of the very limited interaction observed between lindane and fulvic acid is that the fulvic acid will play only a small role in determining the mobility of non-polar

pesticides like lindane through soils, or, if dissolved organic matter (fulvic acid) is in fact the sole mechanism for mobilization, then mobility of the pesticide will be low and retention high.

While definitive conclusions about the mechanism of the complexation of lindane to fulvic acid are not possible based on this work, some speculation is in order. The generally accepted notion that hydrophobic type binding is the rule for hydrophobic organic compounds has not been excluded. However, the results do hint at an electron donor-acceptor complex formation which could explain the similarity of behaviour of lindane and atrazine, two pesticides of considerably differing polarities, in interaction with fulvic acid.

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