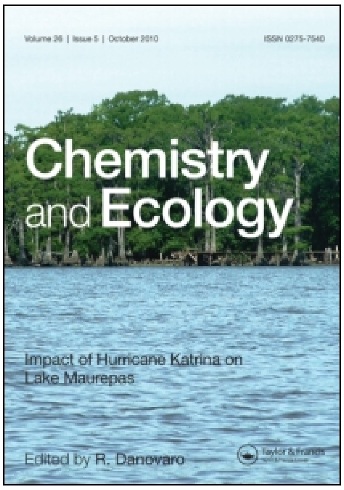

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Chemical Approach to Study the Environmental Implications of Humic Acid and Gamma-Hch Interaction

Virendra Misra[a]; Shri Dhar Pandey[a]; P. N. Viswanathan[a]
[a] Ecotoxicology Section, Industrial Toxicology Research Centre, Lucknow, India

To cite this Article Misra, Virendra , Pandey, Shri Dhar and Viswanathan, P. N.(1998) 'Chemical Approach to Study the Environmental Implications of Humic Acid and Gamma-Hch Interaction', Chemistry and Ecology, 14: 2, 97 — 106
To link to this Article: DOI: 10.1080/02757549808035545
URL: http://dx.doi.org/10.1080/02757549808035545

Chemistry and Ecology, 1998, Vol. 14, pp. 97 – 106
Reprints available directly from the publisher
Photocopying permitted by license only

CHEMICAL APPROACH TO STUDY THE ENVIRONMENTAL IMPLICATIONS OF HUMIC ACID AND GAMMA-HCH INTERACTION

VIRENDRA MISRA*, SHRI DHAR PANDEY
and P. N. VISWANATHAN

Ecotoxicology Section, Industrial Toxicology Research Centre,
Post Box No. 80, M. G. Marg, Lucknow-226 001, India

(Received 25 March 1997; Revised on 20 August 1997)

Pesticide-humic interactions are known to have environmental significance in modifying the toxicity and mobility of agricultural chemicals. To test this, interaction between gamma-hexachlorocyclohexane (gamma-HCH) released from the sand coated with gamma-HCH and humic acid was investigated using thin layer chromatography and spectral studies such as UV (ultraviolet), IR (infrared), mass and FAB (fast atom bombardment) mass spectrometry. These studies revealed the evidence of loose interchelation between gamma-HCH and humic acid. The significance of the results in relation to detoxification of gamma-HCH in aquatic ecosystems are discussed.

Keywords: Gamma-hexachlorocyclohexane (gamma-HCH); humic acid (HA); fast atom bombardment (FAB)

INTRODUCTION

Significant quantities of the pesticide hexachlorocyclohexane gamma-isomer can eventually be transported to the aquatic environment through agricultural runoff. From an environmental context, humic substances present in natural waters, can increase the apparent solubility of non-polar compounds, such as gamma-HCH, through

---

*Corresponding author.

surface activity, binding inorganic and organic compounds either by covalent bonds, as charge transfer complexes, by hydrogen bonding or by Van der Waals interaction (Landrum *et al.*, 1984; Hassett and Anderson, 1979; Carter and Suffet, 1982; Piccolo and Celano, 1994). Humic substances can also serve as reducing agents and chemically alter a pesticide through non-biological transformations. The alteration is enhanced by the presence of reactive groups such as phenolic carboxyl, enolic, heterocyclic, aliphatic OH, semiquinone and stable free radicals contained in humic acid (Parris, 1980; Stevenson, 1982).

Binding of pollutants with humic substances has additional environmental implications including effect on biodegradability, bioactivity, persistence, leachability, volatility, hydrolysis, photolysis and bioaccumulation (Bruggeman, 1982; Wershaw, 1989; Lawrence, 1989; MacCarthy, 1989; Lumsdon and Evans, 1995). Therefore, in view of the environmental significance of humic acid binding with hydrophobic chemicals, the interaction between gamma-HCH released from the sand coated with gamma-HCH and humic acid was proposed in this present paper.

MATERIALS AND METHODS

Gamma-HCH, commercial grade of 99% purity, was purchased from Sigma Chemical Company, USA. Humic acid (sodium salt) from Aldrich Chemical Company (USA) was used also in all the studies, and element composition in natural humic acid was found similar to Aldrich humic acids.

Preparation of the Samples

For hydrophobic interaction between humic acid and gamma-HCH, 10.0 g of pure acid-washed calcinated sea sand (E. Merck) with particle size of 0.1 – 0.3 mm was used as a simulated sediment. For environmental dynamics studies, the sea sand was taken in a conical flask and coated homogenously with gamma-HCH (500 $\mu g\ g^{-1}$) by continuous shaking with the desired amount in *n*-hexane. The solvent was evaporated to dryness under controlled conditions (temperature and pressure) to avoid vaporization of gamma-HCH. A 50.0 ml of 20 µg solution of humic acid was prepared in water and added in the conical flask containing gamma-HCH coated sand. The mixture was equilibrated overnight. The product obtained as a result of binding was in the liquid phase. It was then lyophilized to find the product in solid form. Gamma-HCH, humic acid and the product was then subjected to spectroscopic (UV, IR, Mass, FAB mass and thin layer chromatographic) studies.

Chromatographic Studies

TLC (thin layer chromatography) was carried out on silica gel G plates which were developed with hexane, acetone and acetic acid (35 : 15 : 2) solvent system and spots were seen with iodine vapour.

Spectroscopic Studies

UV studies of all three samples (gamma-HCH, humic acid and the product) were performed at Shimadzu UV-260, UV-visible spectrophotometer. Beckman IR-model acculab – 10 (4000 – 2500 cm^{-1}) was used for infrared studies. Mass spectra of the above samples were recorded at JEOL JMS – D – 300 with JMA – 2000 data system. Due to the polymeric nature of the product, FAB mass spectra of the product was recorded on a JEOL SX 102/DA-6000 mass spectrometer/data systems using xenon (6 KV, 10 mA) on the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. The *m*-nitrobenzyl alcohol (NBA) was used as the matrix unless specified otherwise.

RESULTS AND DISCUSSION

Gamma-HCH and humic acid showed peaks at 266.2 nm and 250 nm, when tested separately, while the product had a peak at 250 nm (Fig. 1). The UV maxima at 266.2 nm was not found in the product. Gamma-HCH and humic acid showed a spot with Rf 0.76 and 0.64 at TLC, whereas Rf of the product on TLC was 0.64 indicating possible binding between the two. Gamma-HCH showed IR peaks at 1330 cm^{-1} and 2970 cm^{-1} (Fig. 2). Humic acid showed peaks at 1550 cm^{-1}, 2900 cm^{-1} and 3400 cm^{-1} (Fig. 3), while the product of

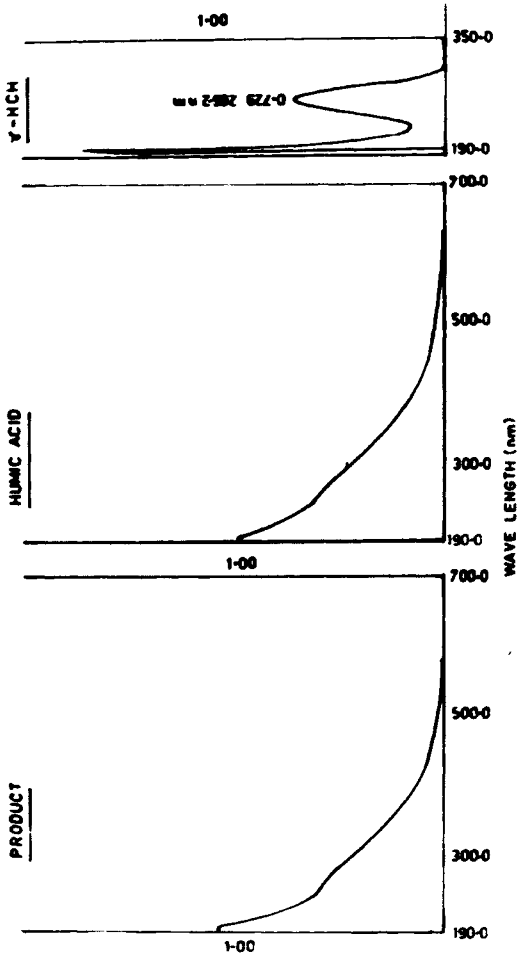

FIGURE 1 Ultraviolet spectra of gamma-HCH, humic acid and product.

gamma-HCH and humic acid showed peaks at 1600 cm^{-1}, 2000 cm^{-1}, 2300 cm^{-1}, 2950 $cm^{-1}$and 3400 cm^{-1} (Fig. 4). The additional peaks at 2000 cm^{-1} and 2300 cm^{-1} showed the formation of a new product. Apart from this, suppression of fingerprint region of the gamma-HCH in the product was noticed; this could be due to the polymeric nature of the humic acid. The mass spectra of the gamma-HCH, humic acid and the product are shown in Figures 5, 6 and 7, respectively. The mass spectrum of the product also showed some indication of a weak

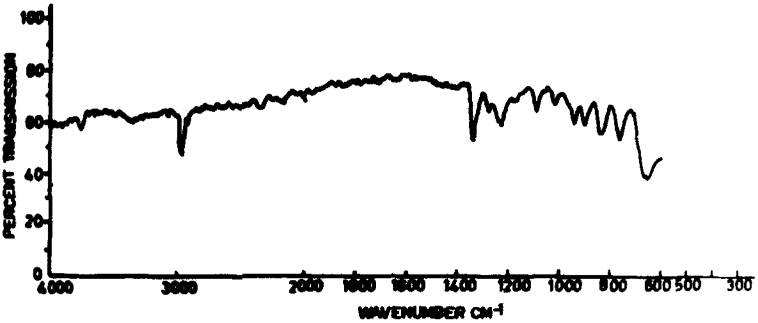

FIGURE 2 Infrared spectra of gamma-HCH.

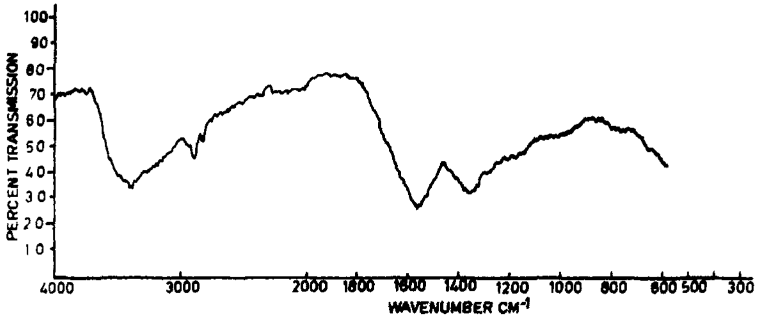

FIGURE 3 Infrared spectra of humic acid.

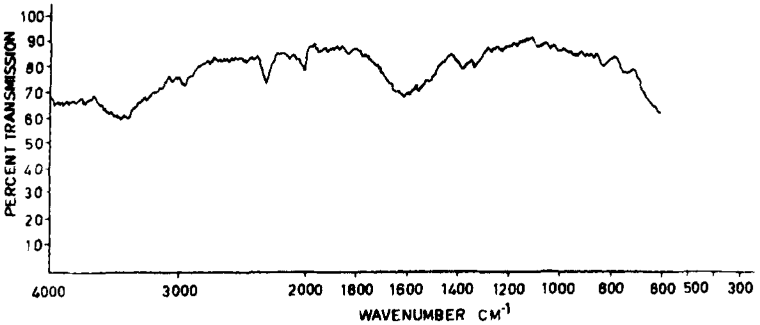

FIGURE 4 Infrared spectra of the product.

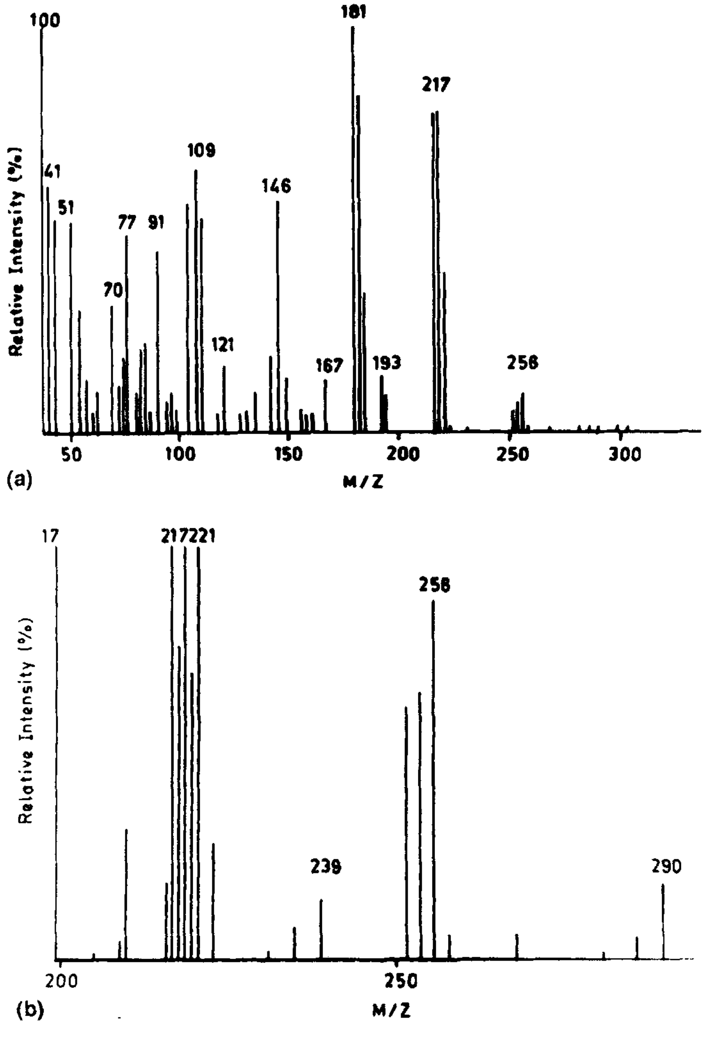

FIGURE 5 Mass fragmentation pattern of gamma-HCH 5(a) and 5(b).

hydrophobic interaction between humic acid and gamma-HCH as evident from the change in mass. Since the molecular weight of the one molecule of humic acid and one molecule of gamma-HCH did not tally with the *m*/*z* ratio of the product detected by the FAB (fast atom bombardment) mass (Fig. 8) suggesting the possibility of a loose interchelation between humic acid and gamma-HCH. Similar ob-

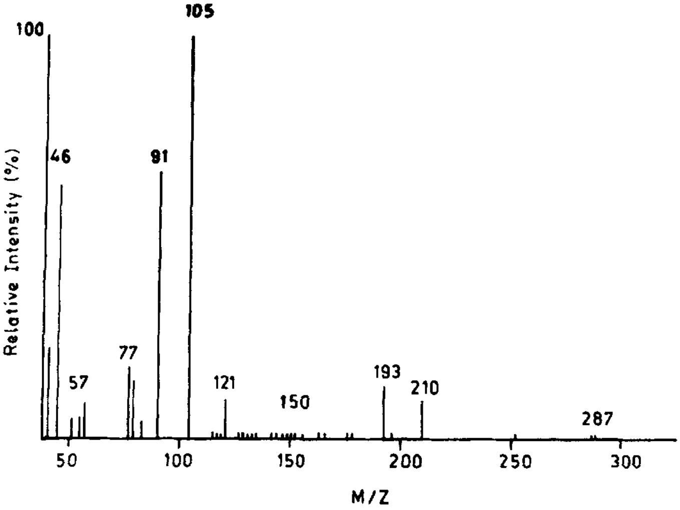

FIGURE 6 Mass fragmentation of humic acid.

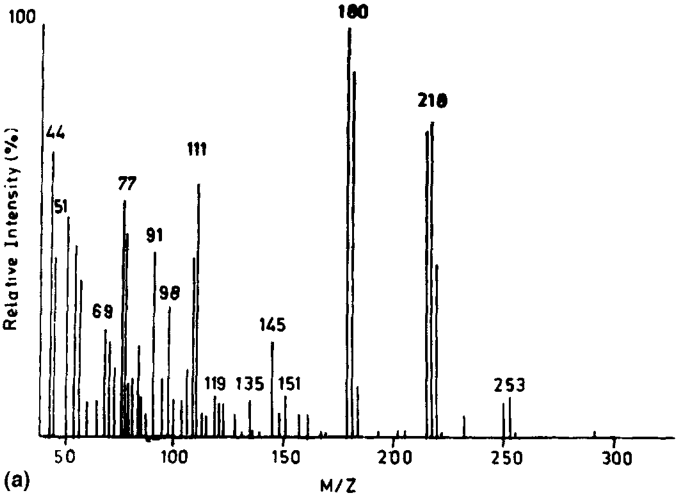

FIGURE 7 Mass fragmentation pattern of the product 7(a) and 7(b).

servations were noticed by Chiou *et al.* (1986) and Sparks (1995), in binding of humic substances to organic contaminants, and Misra *et al.* (1996) who studied the binding of gamma-HCH with humic acid in the aquatic environment. Further study in this direction is in progress.

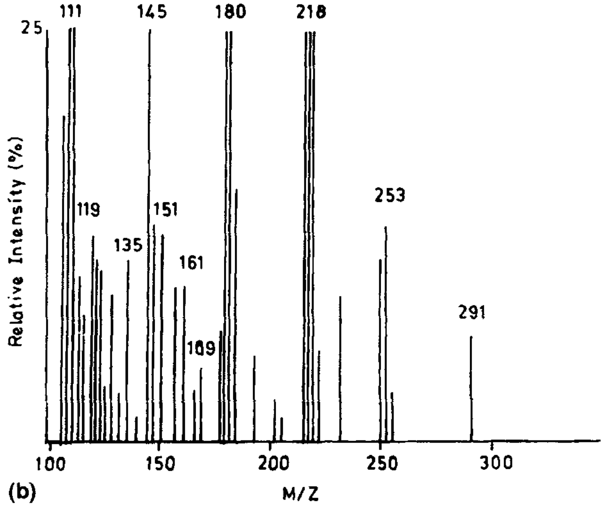

FIGURE 7 (Continued).

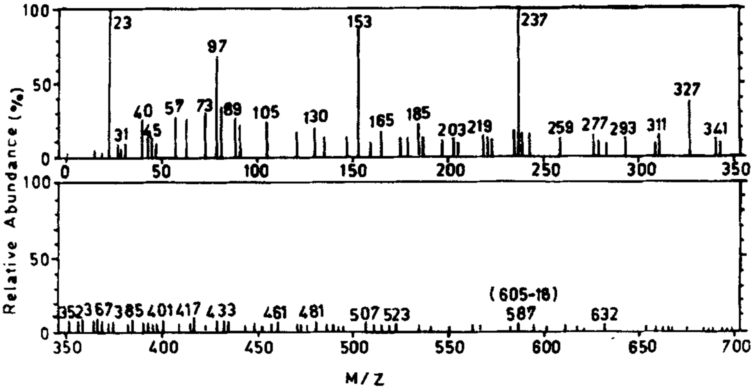

FIGURE 8 Fast atom bombardment (FAB) mass fragmentation pattern of the product.

CONCLUSIONS

On the basis of loose interchelation between humic acid and gamma-HCH, it can be concluded that humic acid may act as an important carrier of gamma-HCH in the aquatic environment and may play a significant role in detoxification of gamma-HCH in the environment.

The studies show that binding with humic acid is a factor regulating the bioavailability of pollutants. However, it is felt that data with humic acid isolated from the natural habitat will be provided site-specific information since Aldrich humic acid may not represent all situations (Ghillebaert *et al.*, 1996).

Acknowledgements

Thanks are due to Dr. R. C. Srimal, Director, Industrial Toxicology Research Centre, Lucknow for his keen interest in this work and Dr. G. K. Jain, Scientist, Division of Pharmaceutics, CDRI, Lucknow for many types of help required. The excellent word processing by Mr. Pramod Kumar Srivastava is also acknowledged. This is ITRC Publication No. 1884B.

References

Bruggeman, W. A. (1982) Hydrophobic interactions in aquatic environment In: *Handbook of Environmental Chemistry*, Ed. O. Hutzinger, **B2**, Springer-Verlag Berlin, Heidelberg, New York, pp. 83–102.

Carter, C. W. and Suffet, I. H. (1982) Binding of DDT to dissolved humic materials. *Environ. Sci. Technol.*, **16**, 735–740.

Chiou, C. T., Kile, D. E., Binton, T. I., Malcom, R. L. and Leenheer, J. A. (1986) A comparison of water solubility enhancement of organic solutes of aquatic humic materials and commercial humic acids. *Environ. Sci. Technol.*, **20**, 502–508.

Ghillebaert *et al.* (1996) Deltamethrin lethal multifactorial activity toward carp Larva related to pH, calcium and humic acid concentrations. *Ecotoxicology, Environmental Safety*, **35**, 24–37.

Hassett, J. P. and Anderson, M. A. (1979) Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. *Environ. Sci. Technol.*, **13**, 1526–1529.

Landrum, P. F., Nihart, S. R., Eadle, B. J. and Gardner, W. S. (1984) Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon to natural waters. *Environ. Sci. Technol.*, **18**, 187–192.

Lawrence, J. (1989) Humic acid and related substances in the environment. In: *Analysis of Trace Organics* in *Aquatic Environment*, Eds. B. K. Afghan and S. Y. Chan Alfred, CRC Press Inc., Boca Raton, Florida USA, pp. 313–337.

Lumsdon, D. G. and Evans, L. J. (1995) Predicting chemical speciation and computer simulation. In: *Chemical Speciation in the Environment*. Ed. Ure, A. M. and Davidson C. M., Blackie Academic and Professional, London, pp. 86–134.

MacCarthy, P. (1989) Aquatic humic substances and their influence in the fate and treatment of pollutants. In: *Amer. Chem. Society*, Eds. I. H. Suffet and P. MacCarthy, Washington, D. C., USA, pp. 17–30.

Misra, V., Pandey, S. D. and Viswanathan, P. N. (1996) Interaction of gamma-hexachlorocyclohexane with chlorophyll in relation to its environmental persistence. *Int. J. Environ. Anal. Chem.*, **64**, 257–1105.

Parris, G. E. (1980) Covalent binding of aromatic amines to humates. 1. Reaction with carbonyls and quinones. *Environ. Sci. Technol.*, **14**, 1099–1105.

Piccolo, A. and Celano, G. (1994) Hydrogen bonding interactions between the herbicide glyphosate and water soluble humic substances. *Environ. Toxicol. Chem.*, **13**, 1737–1741.

Sparks, D. J. (1995) Chemistry of soil organic matter. In: *Environmental Soil Chemistry*, Academic Press, New York, pp. 53–80.

Stevenson, F. J. (1982) *Humic Chemistry, Genesis, Composition and Reactions*, John Wiley and Sons, Inc., New York, pp. 2–53.

Wershaw, R. L. (1989) Application of a membrane model to the sorptive interactions of humic substances. *Environ. Health. Persp.*, **83**, 191–203.