ADSORPTION OF SOME PESTICIDES
ON CLAYS AND SOILS

By

EZZ EL-DEEN ABD-EL HAMEED ZAHER

B. Sc. (Agric.) University of Cairo

THESIS

Submitted in Partial Fulfilment For The Degree of

M. Sc.

in Agriculture Chemistry

Faculty of Agriculture

University of Ain Shams, Cairo

This thesis for the degree of M. Sc.

APPROVED BY.

Dr. ....

Dr. ...A. Fatta..........

Dr. ...S. Y. Metwally.....

Committee in charge

Date / /1972

بسم الله الرحمن الرحيم

ACKNOWLEDGMENT

The author is deeply indebted to Dr. Fathy A. Abd-El Hafez Professor of organic chemistry, Faculty of Agriculture, Ain Shams University for his continuous encouragement, guidance and criticism.

The writer wishes to acknowledge Dr. A. Metually. Leacturer of Chemistry for suggesting the problem, supervising the work and for his valuable help and advice throughout the work.

Acknowledgment is also due to Dr. A. Abdel-Hafez, Lecturer of insecticides, for his kind help, encouragement during the course of the present investigation.

CONTENTS

11. REVIEW OF LITERATURE

111. MATERIALS AND METHODS

A. Materials

B. Experimental

1V. RESULTS AND DISCUSSION

INTRODUCTION

The last decade is characterised by the increased usage of synthetic organic pesticides in various segments of our environment. With the advent of chemical pest control, there has been increasing a wareness of the importance of soil colloids in adsorption, movement, persistance, degradation, and bioactivity of pesticides. The problem of plant toxicity of residues, in food products, and detoxification of pesticides as a result of pesticide-soil colloid interactions are of major importance to the agriculturist, the consumer, water pollution control, research and regulatory agencies, food and agriculture organization, and to the World health organization.

There is a considerable information on the basic nature of these interactions between pesticides and soil colloids which refers to the fate and behavior of pesticides in soil systems and its dependent on at least seven factors:
(i) chemical decomposition, (ii) photochemical decomposition; (iii) microbial decomposition; (iv) volatilisation; (v) movement; (vi) plant uptake, and (vii) adsorption.

The phenomenon of adsorption-desorption appears to directly or indirectly related to the magnitude of the effect of the other six factors. Adsorption therefore appears to be one of the major factors affecting pesticide-soil colloid interactions.

The presence of recent review articles on the adsorption of pesticides by soil colloids (Bailey and White, 1964), adsorption of organic matter by soil constituents (grean land, 1965) and the nature of clay-organic complexes (MaC Ewan, 1962) obviates the necessity of any detailed literature survey. These reviews clearly point out the importance of pH and the chemical character of the adsorbate on the nature and extent of adsorption.

The present investigation is mainly concerned with the determination of the role of the chemical character of the adsorbate and pH on adsorption by a well characterized representative clay mineral with special reference to the nature of the functional groups. Attempts were also made to correlate the extent of retention with various physico-chemical properties of the molecule.

The mechanism of adsorption of organic pesticides by soil colloids was also investigated. In addition, the interpretation of the adsorption isotherm data allows certain mechanistic hypotheses to be formulated.

Review of literature

1. Retention of pesticides by soils:

Swanson et al. (1954), found that the retention of lindane was related to soil porosity which could explain why fine textured soil requires heavier application of BHC. (1, 2, 3, 4, 5, 6 - hexachloro cyclohexane) for effective results in comparison with coarse textured soils.

Upchurch and pierce (1957), and Hartly (1960), postulated two steps for the leaching of Monuron (3, Cp-chlorophenyl) -1,1- dimethylurea) into the soil, the entrance of the herbicide into solution and the adsorption by soil which was affected by soil temperature, organic matter, and concentration of the herbicide in the percolating solution.

Getzen and Chapman (1959), reported that the amount of Phosdrin (2-carbomethoxy-1-methyl vinyl dimethyl phosphate). bound by various soils was correlated, in a positive manner, with the base exchange capacity, organic matter content and nitrogen content, but it was concluded that organic matter content was primarily responsible for insecticide binding.

Fleming (1962), showed in general, that the bioactivity of insecticides is lowest in soils high in organic matter and in heavy textured soils high in clay content, and highest in the light textured soils (sand and loams).

Hsu, and Bates (1965), indicated that amorphous aluminium hydroxide precipitates have a positive charge with a high surface area and sizable anion exchange capacity, these constituents may contribute significantly to the adsorption capacity of the colloidal fraction of certain soils.

Baily and White (1964), noted that the bioactivity of both tested herbicides and insecticides (amibon, amitrole, atrazine, BHC, CDAA, CDEC, CIPC, Chloropicrin, dalapan, DDT; 2, 4- D, dildrin, diphenamide, fenuron, diphenatril, methyl bromide, dipropaline, diuron, DNBP, EPTC, ethylene dibromide, monuron, neburon, NPA, parathion, phosdrin, simazine and trifluralin), were lowest in soils higher in organic matter or clay content while the bioactivity was highest in the light textured soils. The organic matter has the highest cation exchange capacity of all the soil constituents, and accordingly, a high potential adsorption capacity is expected for both those pesticides which may act as cations as well as those that can be adsorbed by physical adsorption.

The presence and amount of such functional groups as the carboxyl, amino, hydroxyl and alcholic hydroxyl would have a great effect on the cation and anion adsorption of pesticides.

2. Retention of pesticides by clays:

Jurinak (1957), indicated that adsorption of EDB (ethylene dibromide) by natural soils is a function of the predominant clay minerals present in soil. Kaolinite and illite had higher adsorption per unit surface than Montmorillonite soils.

Frissel (1961), reported that Montmorillonite adsorbed considerably more of various herbicides (of widely different chemical character) than did Illite or Kaolinite which is quite understandable since the magnitude of the exchange capacity of these minerals are in this order; the suggested mechanism of adsorption is dependent upon the number of cation exchange sites.

Baily and White (1964), reported that clay minerals, Montimorillonite and vermiculite, have a high cation exchange capacity and high surface area. These two minerals have a great capacity for adsorption of both herbicides and insecticides due to Coulombic forces, and, because of such a large surface area and Van der Waal's forces. The clay minerals Illite, Kaolinite, and Chlorite, because of their cation exchange capacity and surface area, would not have as large an adsorption capacity as Montmorillonite and vermiculite. They also indicate that the surface area of crystalline and amorphous oxides and hydroxide of silica, iron, aluminium appears to be similar in magnitude to that of Montmorillonite and Vermiculite.

Pommar (1963), reported that potentiometric titration studies of H-saturated ontmorillonite indicate that Montmorillonite behaved as a mixture of two acids resulting from the presence of two types of exchange sites, interlayer and edge, both occupied by hydrogen ions. The interlayer sites, which hold the hydrogen ions less tightly have the stronger bonds with proton and are responsible for the weaper acid function. He also indicated that in the case of beidellites, the pattern is reversed and the interlayer position represented the weaker acid function.

3. Nature of adsorbate:

Studies on clay-organic complexes, Bradly, and MaC Ewan (1945), both concluded that a CH ... O bond was formed with the hydrogen of the methylene group (CH_2) directed to clay surface.

Leopold (1956), reported that increasing chloro-substitution reduced solubility of the phenoxy acids and that a strong inverse correlation between solubility and extent of adsorption existed. The relationship between solubility and extent of adsorption appears to be valid only within the same family of compounds.

In addition to the influence of the functional group on adsorption, Sheet and Crafts (1957), indicated that the number of chlorine atoms in substituted ureas (Feniron, Monuron, Duiron, and Neburon) affect the electron distribution in the molecule and adsorption onto the colloid. They also considered N-alkyl substitution to alter adsorption onto soil colloids.

Abel (1957), and Wolf et al. (1958), found the degree of adsorption of four substituted-ureas (Feniron, Monuron, Duiron, and Neburon) to be inversely related to the order of their solubilities.

Work Coggins and Crafts (1959), were able to show that substituted-ureas become positively charged upon dissociation in water.

The degree of acidity or basicity of the compound exhibited in aqueous solution should be very important in determining the extent of adsorption and ease of desorption by colloidal systems.

Tensmeyer, and Hoffmann (1960) examined the nature of the complexes formed between calcium-montmorillonite, 2,5 hexadione, and 2, 5, 8 - nonanetrione, significant changes in the carboxyl - stretching frequencies were observed due to adsorption of these compounds on clay surface.

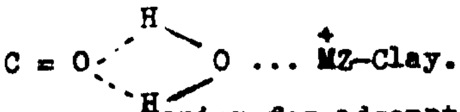
Frissel (1961), indicated that the adsorption of certain substituted ureas and S-trizines in an acid enviroment was due to ion exchange.

Weidhaas et al (1961), reported that the degree of loss of parathion (O,O-diethyl O-nitro-phenyl thionophosphate) and DDT. (dichloro diphenyl trichloro =ethane) from aqueous solution to soil was not a function of water solubility of these two insecticides. The nature of the functional group appears to play a very important role in adsorption.

Kohl and Taylar (1961), studied the reaction of clay minerals with organic acids, ketones, carboxylate polymers with infrared spectroscopy, they observed changes in the infrared frequency of the carboxyl group, which they attributed to hydrogen bonding between the carboxyl and the mineral surface.

Ahlrichs, (1961), found that carboxyl compounds reacted strongly with the aluminium associated with clay surfaces.

Infrared studies of the bonding mechanism of carbamates on clay minerals by Maitland and Megitt (1966), Baily and White (1967), revealed a decrease in the carbonyl stretching and an increase in the CN stretching frequencies. This was interpreted in terms of the coordination of the carbamates, EptC., (ethyl N, N- di-n-propylthiol carbamate) to the exchange metal ion through the oxygen of the carbonyl group with a bridging effect of co-ordinated water.



$$\mathrm{C=O}\overset{H}{\underset{H}{\cdots}}\mathrm{O}\cdots\overset{+}{\mathrm{M}}\mathrm{Z\text{-}Clay}$$

This appeared to be the primary mechanism for adsorption except when aluminium was the exchangeable cation.

Farmer and Ahlrichs (1966), studied the adsorption mechanism for urea and its herbicidal derivatives by Montmorillonite and noted that the predominant adsorption mechanism is the formation of coordination compounds between the adsorbate and the exchangeable cation on the clay, except for acid clay systems.

Harter and Ahlrichs (1967), infrared studies on the reaction of urea and its pesticide derivatives with Montmorillonite system (H-fe-AL) gave evidence of the protonation of amino group and subsequent reaction with the silicate surface.

Baily and White (1967), suggested that adsorption of the organic compound (pesticide) possessing a basic chemical