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ON THE POSSIBILITY TO PREDICT THE MOVEMENT OF PESTICIDES IN THE SOILS

The heats of adsorption of methyl parathion and lindane were measured chromatographically on different types of soil or simple inorganic materials. The general picture emerging was that lindane is adsorbed about twice as strongly as methyl parathion. For the same pesticides, experiments were carried out in lysimeters containing different types of soil. It was found that the total amount of methyl parathion passing through the lysimeters with the rainfall, taken as percent of the initially applied quantity, was larger, or at least equal to the corresponding amount measured for lindane. This result might be related to the larger heats of adsorption measured for the latter. An explanation is proposed using the term of hopping time of molecules which is related to their enthalpy of adsorption on solid substrates.

NOTATIONS

$(-\Delta H_{ads})$ – enthalpy of adsorption,
τ – hopping time,
V_g – retention volume,
MP – methyl parathion,
P_i -- probability of movement,
GC – gas chromatograph,
ECD – electron capture detector,
(ΔS_{ads}) – entropy of adsorption,
τ_0 – constant,
A – surface area,
L – lindane,
B – N-butylamine,
j_i – number of adsorbing sites,
TCD – thermal conductivity detector.

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1. INTRODUCTION

An important problem dealing with the fate of pesticides in the environment is the distance they can cover in the soil with flowing waters. This is important since pesticides are capable of travelling long distances which might be the cause of pollution of clear and sometimes potable waters [1]. The movement of pesticides through the soil mass towards a final target depends, of course, on the soil composition as well as on the kind of organic molecules. The strength of interaction between a certain molecule and a solid substrate is usually expressed by the enthalpy of adsorption ($-\Delta H_{ads}$). Now, it is known that this quantity might be related to the time τ during which a molecule remains adsorbed on the surface [2] by the relationship $\tau = \tau_0 \exp (\Delta H_{ads}/RT)$. It is supposed that after time τ, the molecule is desorbed to the flowing stream. If there are no new adsorbing sites in its way, then it might moved unperturbed to its destination. Otherwise, it might be adsorbed again on a new site, stay there for a time τ, and be desorbed again, and so on. It is clear from the above that the distance, which two different molecules can cover in the same stream during the same time, should be inversely proportional to τ, which in turn is exponentially dependent on ($-\Delta H_{ads}$) via the above equation. The purpose of this work is to examine the consequences of the above ideas in relation to the movement of two widely used pesticides, methyl parathion and lindane, in the soils. The heats of adsorption of these molecules were measured by gas chromatography in the laboratory, while the distance they covered was set equal in lysimeter experiments and the amount of them washed through the lysimeters, calculated as the percent of the initially applied quantity, was measured as a function of time and rainfall.

2. EXPERIMENTAL AND RESULTS

The heats of adsorption ($-\Delta H_{ads}$) of such pesticides as methyl parathion (MP) and lindane (L) as well as of n-butylamine (B) on different substrates (soils or simple inorganic materials) were determined by gas chromatography [3]. N-butylamine was used since it is a common base used often for estimation of the surface acidities in non-aqueous experiments [4]. The solid substrate was used as a stationary phase in G.C. column into which small amounts of pesticides were injected. Then the retention volume (V_g) was measured at the different temperatures. From these data it is possible to calculate ($-\Delta H_{ads}$) via the well-known relationship [3]:

$$\ln V_g = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} + \ln A \tag{1}$$

where ΔS_{ads} is the entropy of adsorption and A is the surface area of the sample used to fill the column. A Varian 3700 G.C. equipped with a T.C. Detector and a Varian 3300 G.C. Detector were used in the experiments. The surface area of the dried samples were determined by conventional BET method. The characteristics of the solid samples used as well as the ($-\Delta H_{ads}$) of methyl parathion, lindane and n-butylamine measured on them are shown in the table. The relationships between ($-\Delta H_{ads\ B}$), on one hand, and ($-\Delta H_{ads\ MP}$)
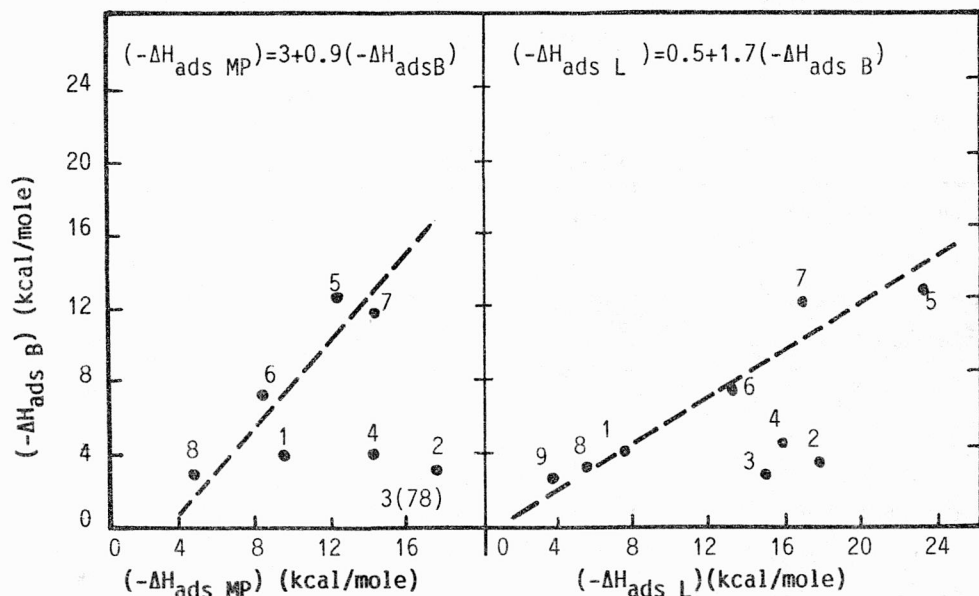
Fig. 1. Relationships between the enthalpies of adsorption $(-\Delta H_{ads})$ of *n*-butylamine, methyl parathion and lindane on different substrates. The numbers correspond to those in table

and/or $(-\Delta H_{ads\ L})$, on the other, are shown in figure 1. The straight lines drawn in this figure are described by the equations:

$$(-\Delta H_{ads\ MP}) = 3 + 0.9(-\Delta H_{ads\ B}), \tag{2}$$

$$(-\Delta H_{ads\ L}) = 0.5 + 1.7(-\Delta H_{ads\ B}). \tag{3}$$

The above G.C. experiments were coupled, as was mentioned in the introduction, with experiments in lysimeters (soil cubes of 1 m acme) as follows: a certain amount of the above mentioned pesticides (45 mg of methyl parathion and 30 mg of lindane) were dissolved in water and applied uniformly on the top of lysimeter on October 15th, 1985. From that date up to June 20th, 1986 we measured the amount of pesticides passing through the soil column to the exit at its bottom, with the rainfall. Each sample was analyzed when the water filtrate reached a volume of 10 dm^3. The analyses were carried out using a G.C. Varian 3700 with T.C. Detector and G.C. Varian 3300, E.C. Detector. The total amount of each pesticide passing through the lisymeters is shown in figure 2 as a function of rainfall, as well as the type of soil in it.

These results show that, depending of the soil type, a greater or equal fraction of methyl parathion is washed through it, as compared to lindane, in spite of the much larger rate (approximately 5-fold) of the hydrolytic decomposition of the first [5]. These results

Solid substrates and $(-\Delta H_{ads})$ of n-butylamine, methyl parathion and lindane, measured
by gas chromatography

Substrate (type and origin)	Surface area		$(-\Delta H_{ads})$ (kcal/mol)		
	BET (m^2/g)	n-butylamine	methyl parathion	lindane
1. Silt loam (SiL) soil (Ioannina GR)	3.4	4.23	9.43	7.34
2. Sandy clay loam (SCL) soil (Ioannina GR)	3.4	3.17	16.65	17.59
3. Clay (C) soil (Thessaloniki GR)	18.6	2.49	78.61	14.99
4. Sandy loam (SL) soil (Thessaloniki GR)	8.2	4.20	14.10	15.47
5. Kaoline (commercial)	25.0	12.63	12.12	23.02
6. Phosphorite ore (Ioannina GR)	18.0	7.15	8.26	13.40
7. γ-Al_2O_3 (commercial)	105.0	11.61	14.23	16.60
8. Red mud (Viotia GR)	11.8	3.10	4.63	5.20
9. Fly ash (Ptolemaida GR)	7.8	2.59	3.21	3.54

indicate that it is the weaker adsorption of methyl parathion on soils which permits this, as it will be explained clearly in the following discussion.

3. DISCUSSION

A molecule i, once adsorbed on a surface, remains on it for a period of time τ given by the equation:

$$\tau = \tau_0 \exp(-\Delta H_{ads\ i}/RT) \qquad (4)$$

where τ_0 is a constant for each particular system. Then application of equation (4) to the cases of methyl parathion and lindane, in combination with equation (2) and (3) and setting $RT = 0.6$ cal/mol, results in

$$\tau_L = \tau_{MP} \exp[1.2(-\Delta H_{ads\ B}) - 4] \qquad (5)$$

assuming that $\tau_{0\ MP} = \tau_{0\ L}$. Now, according to the data in the table, $(\Delta H_{ads\ B})$ acquires values between 3 and 12 kcal/mol. Substituting these values in equation (5), we obtain:

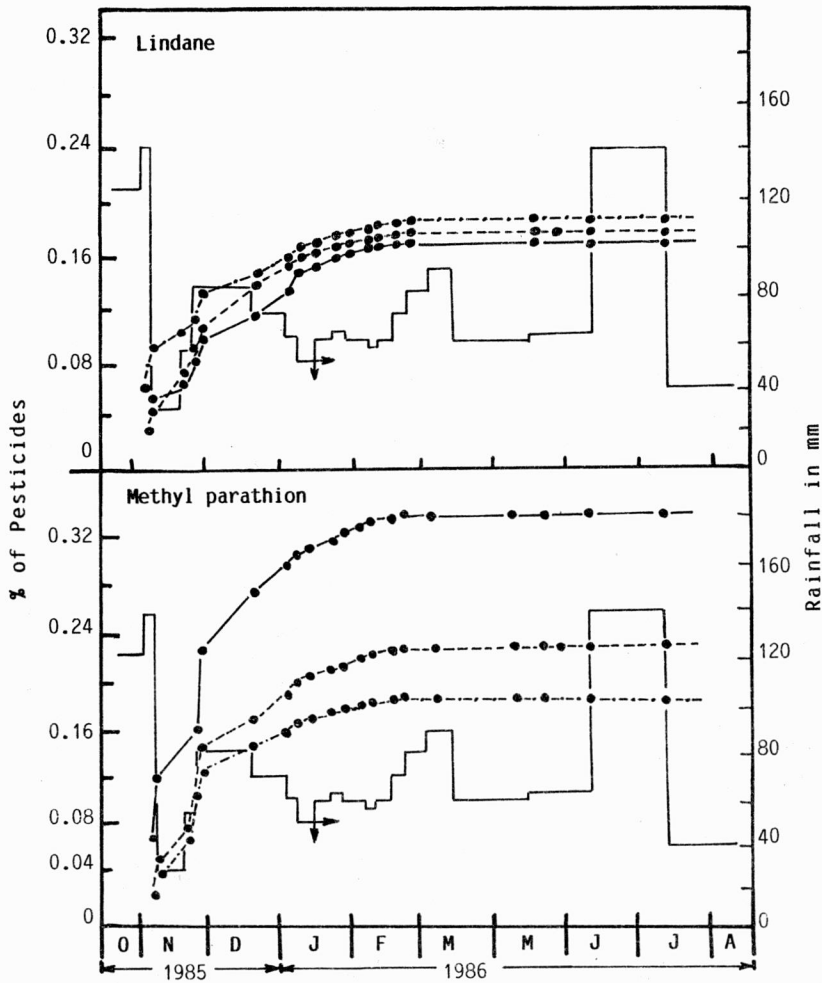$$\tau_L = A \tau_{MP} \qquad (6)$$

Fig. 2. Cumulative amount of methyl parathion and lindane, as a percent function of the applied quantity, passed through the lysimeter as a function of rainfall between two measurements. The type of soil in each lysimeter was (—) SiL, (- - - -) C and (.-.-.-) L

where the values of A range from 1 to 30,000. The result reveals that lindane molecules might remain adsorbed on the surface at least equal, up to some thousand times, as compared to methyl parathion. This is in line with the results obtained in the case of lysimeter measurements which show that, depending on the soil, pH, organic matter, etc., methyl parathion molecules were washed in larger, or at least equal fractions, in spite of their larger hydrolytic decomposition [6].

To be more precise, let us consider the probability P_i of molecule i passing through the lysimeter. It will be proportional to molecule solubility S_i (molecules/cm^3), volume of water flowing through it Q (cm^3/cm^2), but because P_i is inversely proportional to time τ_i

and the number of adsorbing sites j_i met on their way, molecules remain adsorbed per site, in other words,

$$P_i = \frac{S_i \text{ (molecules/cm}^3)\, Q \text{ (cm}^3/\text{cm}^2)}{\tau_i \text{ (s/sites)}\, j_i(\text{sites})} = \frac{S_i Q}{\tau_i j_i} \left(\frac{\text{molecules}}{\text{s cm}^2}\right). \tag{7}$$

The values of S_i are 55 and 7.3 ppm in water for methyl parathion and lindane, respectively, at 20°C [7]. Substitution of those values in equation (7) yields

$$\frac{P_{MP}}{P_L} = \frac{55}{7.3} \frac{j_L}{j_{MP}} \frac{\tau_L}{\tau_{MP}}. \tag{8}$$

Substituting τ_L in eq. (8) by relation (5) provides

$$\frac{P_{MP}}{P_L} = 7.5 \frac{j_L}{j_{MP}} \exp(1.2(-\Delta H_B) - 4) = 0.14 \frac{j_L}{j_{MP}} \exp(1.2(-\Delta H_B)). \tag{9}$$

It is difficult to estimate the number of adsorbing sites j_i, but obtaining the higher values for the weakly adsorbed species is expected. This a common feature of solid surfaces characterized by a distribution of adsorption sites, where the strongly bounding ones usually are not so numerous as the weakly bounding [4]. Experiments of anhydrous titration carried out in our laboratory and concerning the soils similar to those in table showed that the surface concentration of the acidic sites increases by about one order of magnitude if pK value of the base used as indicator increases by one unit [8]. So, if we accept that methyl parathion and lindane differ in their pK values by about one unit, then $j_L/j_{MP} = 1/10$, and the equation (9) becomes

$$\frac{P_{MP}}{P_L} = 0.014 \exp(1.2(-\Delta H_{ads\,B})). \tag{10}$$

As noticed previously, the values of $(-\Delta H_{ads\,B})$ range between 3 and 12 kcal/mol. Therefore, according to equation (10), the P_{MP}/P_L ratio should range from 0.5 to ca. 25,000. This result shows that the probability of methyl parathion molecule passage through the soil is much higher, or at least equal, as that of lindane ones. This is apparent in figure 2, which proves that larger, or at least equal, fractions of the former pesticide were washed through the lysimeters due to their looser adsorption on the soil components. In favour of this explanation is the fact that soil of the SiL type (see figure 2), which contains much less organic matter (0.72%) as compared to C and L type soils (2.8% and 2.3%, respectively) [8], seems to adsorb much less methyl parathion molecules, allowing a larger fraction of them to pass through.

Thus, although the movement of pesticides in soils is of very complex nature, we believe that the above explanation has some merit in describing some features of it, related to their adsorption on different soil types.

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MOŻLIWOŚĆ PRZEWIDYWANIA PRZEMIESZCZANIA SIĘ PESTYCYDÓW W GLEBIE

Zbadano proces adsorpcji wybranych pestycydów (parationu metylu i lindanu) na różnych rodzajach gleby lub materiałach nieorganicznych. Ciepło adsorpcji parationu metylu i lindanu zmierzono metodą chromatograficzną. Wykazano, że lindan jest adsorbowany dwukrotnie silniej niż paration metylu. Te same pestycydy badano korzystając z lizymetrów zawierających różne rodzaje gleby. Stwierdzono, że całkowita ilość parationu metylu przenikająca przez lizymetry pod wpływem opadu deszczowego (liczona jako procent w stosunku do ilości początkowej) była większa lub co najmniej równa ilości przenikającego lindanu. Zaproponowano wyjaśnienie zachodzących zjawisk biorąc pod uwagę parametr czasowy, który jest związany z entalpią adsorpcji molekuł na substratach stałych.

ВОЗМОЖНОСТЬ ПРОГНОЗИРОВАНИЯ ПЕРЕМЕЩЕНИЯ ПЕСТИЦИДОВ В ПОЧВЕ

Исследован процесс сорбции избранных пестицидов (паратиона метила и линдана) на разных видах пощвы или неорганических материалах. Тепло адсорбции паратиона метила и линдана измерено хроматографищеским методом. Было обнаружено, щто линдан абсорбируется двоекратно сильнее, щем паратион метила. Те же пестициды были исследованы с использованием лизиметров, содержачих разные виды пощвы. Было установлено, щто полное колищество паратиона метила, протекаючее щерез лизиметры под влиянием осадков (сщитаемое как процент по отнохению к нащальному колиществу) было больхе или по крайней мере равно колиществу протекаючего линдана. Предложено выяснение происходячих явлений с ущетом временного параметра, который связан с энтальпией адсорбции молекул на твердых субстратах.