Adsorption characteristics of endosulfan pesticide in three soils in Palestine

Shehdeh Jodeh, Karbalaa Jaradat and Nidal Zatar

Abstract
In this paper, adsorption features were studied in detail in three soil samples from Palestine. The samples were red soil, chalk soil and sandy soil, according to the American Society for Testing and Materials (ASTM) scale for the classification of soil. Adsorption rates on soil samples were calculated from kinetic studies. The values varied based on the type of soil.

Maximum specific adsorption capacities \( (q_{\text{max}}) \) for soil samples using the Langmuir model, were as follows: 0.387 (red soil), 0.281 (chalk soil), and 0.075 (sandy soil) in mg/g of endosulfan.

Maximum adsorption was measured in the red soil followed by the chalk soil, but it was lowest in the sandy soil. Also, the proportion of organic matter plays a major role in adsorption on soil samples.

There was a significant reduction in the process of adsorption in the soil samples, in parallel with the decline in pH, and increasing adsorption with increase in concentration of pesticides.

Finally, the results showed that endosulfan mobility is more possible in the sandy soil followed by red, followed by chalk soil. This may be attributed to the crystal lattices of the clay minerals in the red soil, which plays an important role in both processes of adsorption, as it could be a major role for the chemical and biological processes that play a role in the clay and sandy soil samples.

Key words: adsorption, endosulfan, kinetics, soil, surfactant

1 INTRODUCTION

Persistent organic pollutants (POPs) are a set of chemicals that are toxic, persist in the environment for long periods of time, and biomagnify as they move up through the food chain. POPs have been linked to adverse effects on human health and animals, such as cancer, damage to the nervous system, reproductive disorders, and disruption of the immune system. POPs circulate globally via the atmosphere, oceans and other pathways. So, therefore, if released in one part of the world, they can travel to regions far from their source of origin (Rissato et al. 2006).

With mounting evidence indicating the long-range transport potential of these substances to regions where they have never been used or produced, and the consequent threats they pose to the environment, the international community has called for urgent global action to reduce and eliminate their release into the environment (Burger et al. 2001). Organochlorines (OCs) represent an important group of POPs which, as toxic environmental contaminants, have caused worldwide concern (Law et al. 2003; Covaci et al. 2005; Wurl and Obbard 2005).

The lipophilic nature, hydrophobicity and low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and the subsequent magnification of concentrations in organisms, progressing into the food
chain (Tanabe 2002). Specifically, one of the key environmental concerns with regard to some POPs is their occurrence in polar regions, at surprisingly high levels.

Organochlorine pesticides (OCPs) are still widely distributed in the environment due to their persistence and semi-volatile nature, resulting in long-distance transportation (Li et al. 2002). Also, accumulation of OCPs in the lipid content of animals is a common phenomenon due to their hydrophobic properties (Sijm and van der Linde 1995). Investigation of the sorption phenomena of pesticides in soils is of great importance from the environmental point of view. Pesticide sorption affects other processes like transport; degradation; volatilization; and bioaccumulation, which influence the final fate of these compounds in the soil environment (Gao et al. 1998). All these processes influence the extent of surface-water and groundwater contamination. Moreover, soils are a heterogeneous mixture of several components, many of which are organic and inorganic compounds of varying composition and surface activity. They can bind pesticides and reduce bioavailability (Torrents and Jayasundera 1997). Thus, knowledge of the pesticide adsorption–desorption characteristics of soils is necessary for predicting pesticide mobility and fate in soil environments and also to understand whether bioremediation is a feasible option for the clean-up of contaminated soil.

Numerous studies have reported the strong relationship between total organic carbon in the soil and the mobility of pesticides.

In this study, we focused on studying the adsorption characteristics of endosulfan on various soils, as they are of fundamental importance for quantifying the transport of pesticides and the selection of a proper remediation technique. The importance of organic matter; particle size; and temperatures, as well as the pH of the soil, for sorption, has been emphasized by many workers (Gao et al. 1998). These factors, however, have not been studied in detail for endosulfan, which is used widely in agriculture in Palestine. Therefore, investigation of these processes will provide a better understanding of endosulfan’s sorption and transport in soil environments.

2 MATERIALS AND METHODS

2.1 Soil

Samples of the most common soils in Palestine (red, sandy and chalk) were selected for this study. The soils were identified and classified based on sieve analysis and hydrometer tests (ASTM H-152) The organic matter of the soil was determined using the chromic acid method (Walkley and Black 1934). The electrical conductivity was measured using a conductivity meter (IS 2720 (part 21), 1977). Total soluble solids were estimated by electrical conductivity. The soil pH was measured by using a direct-reading-type pH meter with a glass electrode and a calomel reference electrode. The specific gravity was determined using the pycnometer method (IS 2720 (part 3/sec 1), 1987). The moisture percentage of each soil was determined, and taken into account when an exact weight was required for analysis. The properties of the collected soils are given in Table 1. The soils were sieved through IS (International Standard) sieve no. 10 (2-mm aperture as per IS 2720 (part 4), 1987) The fraction passing through the sieve was collected and preserved in air-tight plastic containers for further study.

2.2 Endosulfan standard solutions

A stock 100-ppm solution of endosulfan was prepared by transferring exactly 0.2875 mL (0.350 g/mL) of solution of endosulfan (Thionex®) into a one-litre volumetric flask. The volume was made up to the mark with methanol:water solution (70:30% v/v). The instruments used for analysis were the UV-visible spectrophotometer (Shimadzu 1601PC); pH meter (3520 pH meter, Jenway); conductometer (4510 conductivity meter, Jenway); and an orbital shaker (Remi Instruments Ltd.).

2.3 The pretreatment of the soil samples

Soil samples chosen for the experiment were already contaminated with endosulfan. Therefore, it was necessary to treat the soil samples by removing their existing endosulfan content before they were used. This was done by treating the samples with 0.1 M perchloric acid (HClO₄) (this acid was chosen because of its ability to remove organic compounds and other metals from soil samples) many times, until no traces were found in the extract. Soils were then washed thoroughly with distilled water and stored under distilled water. Portions of
these treated samples were taken for the adsorption and desorption experiments.

2.4 Kinetic study
The adsorption–kinetic study was carried out in batch mode, using a 250-mL conical flask with 5 g of appropriate soil (shown in Table 1) with a solid:solution mass ratio of 1:20) and 100 mL of 10 ppm technical endosulfan solution. Sorbent masses were accurate to ± 0.001 g and solution volumes to ± 0.5 mL. The studies were conducted in triplicate for all soils in an orbital shaker (REMI Instruments Ltd.) at 150 rpm for a period of 24 h at room temperature (25 ± 2°C). From the triplicate flasks, 5 mL of sample were collected at time intervals of 0.25, 0.5, 1, 1.5, 2, 3, 4, 6, 8 and 24 h. The collected samples were filtrated and analysed by UV-visible spectrophotometer, and the results are presented in Table 2.

2.5 Equilibrium study
Adsorption equilibrium studies were conducted for all soils with an adsorbent quantity of 5 g, with technical endosulfan concentrations of 0.1, 0.2, 0.6, 0.8, 1, 2, 4, 6, 8 and 10 ppm, in identical conical flasks containing 100 mL of distilled water. A blank was used when the endosulfan adsorption was measured in all of the samples. After the addition of soil samples, the reaction mixtures were agitated in an orbital shaker at 150 rpm for 3 h (estimated equilibrium time) at 25 ± 2°C. After 3 h, 5 mL of sample were collected from each conical flask, the collected samples were filtrated and analysed using a UV-visible spectrophotometer.

2.6 Effect of pH on adsorption of endosulfan in soil samples
Known amounts of red, chalk, and sandy soils were used in this study. The initial pH of the soil was adjusted to 1.5, 2, 3, 5, 6 and 7 with concentrated hydrochloric acid (HCl). Five grams of acid-treated soil were taken from each pH value, and the kinetic study was conducted as stated earlier. Also one of the acid-treated soils (pH = 2) was brought up to neutral pH, and the kinetic study was conducted. An adsorption kinetic study was conducted with an initial endosulfan concentration of 10 ppm, as before. The supernatant was decanted and replaced with distilled water at pH 2, 4, 6, 7, 8 and 10, using an HCl/NaOH solution, and a desorption kinetic study was conducted.

2.7 Effect of temperature on adsorption of endosulfan in soil samples
Adsorption equilibrium studies for estimating the effect of temperature on adsorption of endosulfan on soil samples were conducted for all soils with an adsorbent quantity of 5 g, at an endosulfan concentration of 10 ppm (100 mL) in identical conical flasks, at different temperatures (25, 30, 35, 40 and 45°C). After the addition of the endosulfan solution to the soil samples, the reaction mixtures were agitated in a Heto shaker (SBDO50-1 BIO) for three hours at 100 rpm. After three hours, 5-mL samples were collected from each flask, and analysed using a UV-visible spectrophotometer. The supernatant was then treated with ethanol, tap water, and distilled water, and a desorption kinetic study was conducted at temperatures of 25, 30, 35, 40 and 45°C.

![Table 1. Properties of the different soils used in the present study](image1)

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>Red soil</th>
<th>Chalk soil</th>
<th>Sandy soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.469</td>
<td>2.168</td>
<td>2.688</td>
</tr>
<tr>
<td>pH value</td>
<td>8.46</td>
<td>7.101</td>
<td>8.5</td>
</tr>
<tr>
<td>Electrical conductivity (E&lt;sub&gt;c&lt;/sub&gt;, µS)</td>
<td>230</td>
<td>184.1</td>
<td>84.5</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>39</td>
<td>46</td>
<td>2</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>61</td>
<td>54</td>
<td>3</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>9.6</td>
<td>8.4</td>
<td>0.32</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>8</td>
<td>2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

![Table 2. Kinetics of endosulfan adsorption on soil samples](image2)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Endosulfan remaining (ppm)</th>
<th>Endosulfan remaining (ppm)</th>
<th>Endosulfan remaining (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>red soil solution</td>
<td>chalk soil solution</td>
<td>sandy soil solution</td>
</tr>
<tr>
<td>0.00</td>
<td>10.0 ± 0.20</td>
<td>10.0 ± 0.13</td>
<td>10.0 ± 0.27</td>
</tr>
<tr>
<td>0.25</td>
<td>7.11 ± 0.17</td>
<td>7.11 ± 0.17</td>
<td>7.0 ± 0.31</td>
</tr>
<tr>
<td>0.50</td>
<td>6.72 ± 0.16</td>
<td>6.85 ± 0.12</td>
<td>6.9 ± 0.18</td>
</tr>
<tr>
<td>1.00</td>
<td>6.67 ± 0.16</td>
<td>6.71 ± 0.18</td>
<td>6.8 ± 0.23</td>
</tr>
<tr>
<td>1.50</td>
<td>6.53 ± 0.15</td>
<td>6.67 ± 0.13</td>
<td>6.7 ± 0.14</td>
</tr>
<tr>
<td>2.00</td>
<td>6.44 ± 0.16</td>
<td>6.53 ± 0.17</td>
<td>6.7 ± 0.15</td>
</tr>
<tr>
<td>3.00</td>
<td>6.41 ± 0.16</td>
<td>6.45 ± 0.18</td>
<td>6.7 ± 0.24</td>
</tr>
<tr>
<td>4.00</td>
<td>6.43 ± 0.18</td>
<td>6.46 ± 0.19</td>
<td>6.7 ± 0.24</td>
</tr>
<tr>
<td>6.00</td>
<td>6.44 ± 0.14</td>
<td>6.45 ± 0.21</td>
<td>6.7 ± 0.35</td>
</tr>
<tr>
<td>8.00</td>
<td>6.35 ± 0.16</td>
<td>6.45 ± 0.23</td>
<td>6.67 ± 0.32</td>
</tr>
<tr>
<td>24.0</td>
<td>6.29 ± 0.14</td>
<td>6.39 ± 0.25</td>
<td>6.57 ± 0.22</td>
</tr>
</tbody>
</table>
3 RESULTS AND DISCUSSION

Standard solutions of endosulfan were prepared. The absorbances were measured at 214 nm (from previous studies such as those by Wink (1985) and Balkom (1995)) against a blank solution. A linear relationship was obtained between the absorbance and the concentration of endosulfan within the range (0.1–10 ppm). From the calibration curve, the detection limit was found to be 0.01 ppm, with an absorptivity of 0.1291 cm$^{-1}$ mg$^{-1}$. The relative standard deviation is 0.524% for five measurements.

3.1 Adsorption

3.1.1 Adsorbent soil samples

The soil samples collected showed a wide variation in clay content (Cambodian Agronomic Soil Classification System (CASC)), ranging from 2% to 46%. Organic-matter (OM) content varied from 0.32% to 9.6%, whereas insignificant variations of pH and specific gravity were observed (Table 1).

3.1.2 Kinetic study

The adsorption kinetics exhibited an immediate rapid adsorption and reached pseudo-adsorption equilibrium within a short period of 1.5 h in sandy soil; 2.0 h in chalk soil; and 3.0 h in red soil.

After pseudo-equilibrium, less than 2% variation of endosulfan concentration in the adsorbate was observed, even after 24 hours, as shown in Figure 1 and Figure 2.
Adsorption characteristics of endosulfan pesticide in three soils in Palestine

Table 2. Beck and Jones (1996) studied the sorption of atrazine and isoproturon, and they found that the herbicides were removed from the solution within the first hour of the 24-h sorption experiments. The rapid initial adsorption of endosulfan is a surface phenomenon. Due to the hydrophobic nature of endosulfan, the vacant sites in the soil particles were filled up rapidly in the initial stages and followed a linear variation. This is followed by a slow migration and diffusion of the compound (the rate of adsorption decreased drastically and reached a steady state) into the organic-matter matrix and mineral structure (Gao et al. 1998). The same trend was observed by Parkpian et al. (1998) while studying the adsorption of endosulfan on Rangsit lowland soils and Phrabat upland soils, and also by Kumar and Philip (2006) while studying the adsorption and desorption characteristics of endosulfan in Indian soils.

From the results, it is clear that the sorption of endosulfan in soils is rapid in the initial period, and the portion of pesticide participating in long-term behaviour is insignificant as compared to that participating in the preliminary phase of rapid sorption.

The kinetic rates were estimated by Lagergren’s pseudo-first-order model (1898), and by Ho’s pseudo-second-order model (1995), given in equations below, respectively:

\[
\log(q_e - q_t) = \log q_e - k't
\]  
\[
(1/q_t) = (1/h) + (1/q_e)t
\]

where \(q_e\) is the amount of adsorbate sorbed at equilibrium; \(q_t\) is the amount of adsorbate sorbed on the surface of the sorbent at any time; \(k\) is the rate constant of sorption; \(t\) is the time; and \(h = k.q_e^2\).

But none of the above models gave a good fit for any of the specimens. This may be attributed to the non-homogeneity of the soil. Hence, the data were plotted between the square root of time (\(t^{1/2}\)) and the equilibrium concentration (\(q_e\)).

A tangent starting from the origin was drawn as shown in (Figure 2), and the rate of kinetic equilibrium was calculated as the slope of the tangent. The calculated rate constants or endosulfan were: 1.56 mg g\(^{-1}\) h\(^{-1/2}\) for red soil; 1.07 mg g\(^{-1}\) h\(^{-1/2}\) for chalk soil; and 0.0390 mg g\(^{-1}\) h\(^{-1/2}\) for sandy soil. The kinetic rate constants for different soils are given in Table 3.

Table 3. Rate of adsorption of endosulfan

<table>
<thead>
<tr>
<th>Type of soil</th>
<th>Rate of adsorption (mg g(^{-1}) h(^{-1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red soil</td>
<td>1.561 ± 0.150</td>
</tr>
<tr>
<td>Chalk soil</td>
<td>1.072 ± 0.110</td>
</tr>
<tr>
<td>Sandy soil</td>
<td>0.039 ± 0.001</td>
</tr>
</tbody>
</table>

3.1.3 Equilibrium study

In order to find the short-term behaviour of endosulfan in different types of soils, adsorption isotherm studies were conducted at 25 ± 2°C with an equilibrium time of 3 h. Using Langmuir ((x/m) = (q\(_{\text{max}}\) b\(q_e/(1 + bq_e)\)) and Freundlich ((x/m) = K\(q_e^{1/n}\)) equilibrium models (Freundlich 1926), where \((x/m)\) (mg/g) is the amount of pesticide adsorbed per gram of adsorbent; \(q_e\) (mg/L) is the equilibrium concentration in solution; \(q_{\text{max}}\) is the

![Figure 3. Linearized Langmuir isotherm of endosulfan on: (a) red soil; (b) chalk soil; and (c) sandy soil](image-url)
maximum adsorption capacity of the adsorbent; \( b \) is Langmuir’s constant; and \( K \) and \( 1/n \) are Freundlich’s adsorption coefficient and adsorption constant. The isotherm constants and the maximum adsorption capacity of the soils were calculated for 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8 and 10 ppm endosulfan concentrations in order to understand the behaviour clearly. The relation between \( 1/q_e \) vs. \( 1/(x/m) \) is shown in Figure 3, the adsorption of endosulfan followed the Langmuir isotherm better than the Freundlich isotherm.

Although the soil is a heterogeneous material, the adsorption data followed the Langmuir isotherm, which is a representation of a monolayered, homogeneous/uniform adsorption. This may be due to the lower concentration of adsorbate in the solution, which was not sufficient to compete for the abundantly available adsorption sites in the soil.

The maximum adsorption \( (q_{\text{max}}) \) of endosulfan concentrations occurred in red soil, followed by chalk soil, and then sandy soil (Table 4).

The same trend was reported by Torrents and Jayasundera (1997), who conducted the sorption study of nonionic pesticides and found that the intensity of sorption was a function of herbicide and clay content. The \( q_{\text{max}} \) value of red soil for endosulfan was 0.387 mg/g of soil. Red soil has more vacant sites per surface area compared to sand particles (Gao et al. 1998). The organic matter in red soil was 9.6%, which increased the endosulfan adsorption. On the other hand, sandy soil has fewer porosity and adsorption sites (the organic-matter content is 0.32%) which resulted in minimum endosulfan adsorption (0.075 mg/g of soil).

### Table 4. Adsorption isotherm values for endosulfan using Langmuir and Freundlich isotherms

<table>
<thead>
<tr>
<th>Type of soil</th>
<th>Langmuir isotherms</th>
<th>Freundlich isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( b )</td>
</tr>
<tr>
<td>Red</td>
<td>0.387</td>
<td>1.429</td>
</tr>
<tr>
<td>Chalk</td>
<td>0.218</td>
<td>1.099</td>
</tr>
<tr>
<td>Sand</td>
<td>0.075</td>
<td>0.089</td>
</tr>
</tbody>
</table>

3.2 Effect of organic-matter content (OM) on endosulfan adsorption

The properties of chalk soil and red soil were similar, but there is a difference in OM content (Table 1). Although the CASC in the red soil was only 61%, the adsorption of endosulfan was higher (0.387 mg/g).

It was noticed that the OM content in the red soil was 9.6%, which probably influenced the migration of endosulfan molecules to it (Berglof et al. 2002; Yu and
Zhou 2005). The increase in organic content increased the sorption of the nitroaromatic herbicide dinoseb by either non-specific partitioning or specific charge-related mechanisms (Martins and Mermod 1998). In addition, the results are in accordance with Iraqi and Iraqi (2000), who demonstrated that, beyond 2% organic matter in soils, the adsorption of parathion takes place almost entirely on the organic surfaces. The decrease in OM content, which is 8.4% in chalk soil (as compared to red soil), reduced the adsorption rate of endosulfan from 0.387 to 0.213 mg g\(^{-1}\) h\(^{1/2}\) (Table 3). It is important to note that the extent of a mineral’s contribution to sorption depends on both the ratio of clay minerals and the soil organic-carbon contents (Hsieh and Kao 1998; Spark and Swift 2002). Soil rich in OM may retain the pesticides and reduce the possibility of contaminating the surface and groundwater sources.

3.3 Effect of the pH of the soil samples on adsorption
Adsorption kinetic studies were carried out using the treated soil samples with an endosulfan concentration of 10 ppm for a pseudo-equilibration time of 3 h. The total amount of endosulfan adsorbed at each pH value is shown in Figure 4. No adsorption of endosulfan was observed at pH 1.5. Above this level (between 2 and 3) it increased very slowly. Above pH 3.0, the trend in adsorption differed, according to soil type, as shown in the figure below.

Acid treatment destroyed the crystal lattices of the soil particles, a lattice structure which might have reduced the adsorption (Kumar et al. 2006). To verify the above assumption, acid-treated soil with a pH of 2 was neutralized (pH 7.0) and a kinetic study was conducted. The adsorption of endosulfan in the treated soil was only about 0.12 in red soil; 0.09 ppm in chalk soil; and 0.03 ppm in sandy soil. From the results, the possibility that the crystal lattice of the soil particles might have been rebuilt if the pH had been adjusted was eliminated. The adsorption of endosulfan on glassware was insignificant compared to the adsorption of endosulfan on soil.

![Figure 5. Effect of concentration of endosulfan solution on adsorption of endosulfan on soil samples (temperature = 25 ± 2°C)](image-url)
3.4 Effect of concentration of endosulfan on adsorption

From the equilibrium study, which was carried out for different concentrations of endosulfan, it was clear that as the concentration of the endosulfan solution increased, the amount adsorbed increased, as is shown in Figure 5.

3.5 Effect of temperature on adsorption of endosulfan on soil samples

An adsorption–equilibrium study was conducted in order to determine the effect of temperature on the adsorption of endosulfan on different soil samples. From the results, it was clear that the amount adsorbed was affected by temperature, and the adsorbed amount increased with the increase in temperature (Figure 6).

4 CONCLUSIONS

From the results, it is clear that the sorption of endosulfan in soils is rapid in the initial period, and that the portion of pesticide participating in long-term behaviour is insignificant as compared to that participating in the preliminary phase of rapid sorption.

The equilibrium rate constant for endosulfan adsorption on soils cannot be calculated by the existing pseudo-first-order and pseudo-second-order rate equations because of the non-homogeneity of the soil. The adsorption of endosulfan in all soils followed the Langmuir isotherm, and it is inferred that the adsorption was monolayer.

Both physical and chemical forces affected adsorption. The effect of chemical forces was predominant in red soil and chalk soil. The adsorption of endosulfan towards soil particles was highly influenced by CASC and OM content. Narrow variations in the pH of the soil medium did not have any influence on endosulfan adsorption or desorption. The decrease in the pH of the soil reduced the adsorption, and the increase in concentration increased the adsorption. The presence of clay, silt and OM immobilizes endosulfan in the soil. Hence, increasing the CASC and OM content in the contaminated soil/zone can be an alternative solution to prevent the mobility of endosulfan.

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