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Adsorption-desorption study of bromophos methyl and quinalphos in Greek soils

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The adsorption and desorption of bromophos methyl [O, O-dimethyl - O-(2, 5dichloro-4 bromophenyl) phosphorothioate] and quinalphos <math>[O, O-diethyl O-2quinoxalinyl phosphorothioate] on five soils from different Greek locations with varying physical and chemical properties was studied by batch equilibration method. Adsorption isotherms fitted well to the Freundlich equation. The adsorption capacity of the soils for bromophos methyl was higher than quinalphos. Freundlich adsorption coefficient (K_{fads}) , showed significant correlation with soil organic matter, indicating that soil organic matter content was the main controlling factor for the adsorption of these pesticides on the soils. Desorption isotherms also conformed well to the Freundlich equation and there was a hysteresis effect in all the soils. The Freundlich K_{fdes} values were also higher for the soils with the highest organic matter per cent.

Keywords: bromophos methyl; quinalphos; per cent balance; organic matter; adsorption

1. Introduction

Organophosphorus pesticides are extensively used all over the world as chemicals for a variety of crops owing to their low persistence in the environment. But organophosphorus pesticides are the most acutely toxic pesticides among other chemicals used at present. The acute toxicity of these compounds is produced by inhibition of the enzyme acetylcholinesterase in the central and peripheral nervous systems [1]. The exposure and toxicity effects of organophosphorus pesticides have been well documented by several researchers [1–3].

Bromophos methyl [O, O-dimethyl - O-(2, 5-dichloro-4 bromophenyl) phosphorothioate]is a broad spectrum, non-cumulative, non-systemic halogen-containing organophosphorus insecticide. It is a cholinesterase inhibitor with contact and stomach action, having slight mammalian toxicity [4]. Bromophos methyl is listed in the WHO (World Health Organization) pesticides classification as an obsolete pesticide [5]. Bromophos methyl is used on various crops, mainly fruit and vegetables, for control of a large number of important sucking and chewing insect pests, such as vegetable root maggots, aphids, sawflies, fruit flies, codling moths, mangold flies and beetles. It is also used for stored products, as a seed protection agent for grain [4]. The metabolite of bromophos methyl mostly found in plants and soil is 2, 5-dichloro-4-bromophenol, while small amounts

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of bromoxon and monodesmethyl-bromophos are also found in tomato plants [6]. Hydrolysis and photo-degradation are the main abiotic degradation processes for pesticides in aquatic and terrestrial environment. Photo-degradation of bromophos methyl in water and soil is described by many researchers [7,8]. Reports on the biodegradation and hydrolysis have also been published [9,10].

Quinalphos (O, O-diethyl O-2-quinoxalinyl phosphorothioate) is an ester of phosphorothioic acid belonging to organophosphorus pesticides. It is moderately hazardous according to WHO hazardous classification and dangerous for the environment according to the EC (European Commission) risk classification [5]. It is frequently used for control of pests over certain crops such as cotton, groundnuts, rice, tea, coffee, soybeans, etc. [4]. In soils under aerobic conditions the quinalphos persists with a half-life of 2 weeks and it is hydrolysed to 2-hydroxyquinoxaline and further broken down to polar metabolites and carbon-di-oxides [11]. Photolytic degradation of quinalphos in water and soils has been reported [12,13]. Many studies have also been published about the toxicity of quinalphos and its metabolites on plants and soil microorganisms [14], mammals [15,16] and aquatic organisms [17].

An understanding of adsorption-desorption in the soil environment is very important for predicting the fate and behaviour of pesticides after their application. Adsorption is a key aspect which controls the pesticides activity, mobility, persistence and environmental fate [18]. On the other hand, desorption process determines the release rate, transformation and bio-availability of the pesticides in soil [19,20]. These above processes affect the quality of natural water resources. Soil is a complex mixture of various components with varying physicochemical properties. Therefore, soil organic matter, particle size, pH and other soil parameters may affect the adsorption and desorption of organophosphorus pesticides [21–23].

Although bromophos methyl and quinalphos were with drawn from EC member-states since 2003, residues of these pesticides are still detected in food commodities and water resources [24–27]. This was attributed to unauthorised use of available stocks or illegal imports from non-EC member-states where these compounds are available at reduced cost [28]. The literature review reveals that no detailed studies are available on the sorption-desorption of bromophos methyl and quinalphos. The aim of this work was to study the adsorption-desorption behaviour of quinalphos and bromophos methyl in a variety of soils originated from Greece with different physical and chemical characteristics.

2. Experimental

2.1 Chemicals and soils

The pesticides bromophos methyl (99.1% purity) and quinalphos (98.9% purity) were of residue analysis grade and purchased from Riedel-de Haen (Germany). The physicochemical properties of the two pesticides are shown in Table 1. All other chemicals, solvents and salts were of the highest purity level supplied by Merck proanalysis or Lab Scan, Pestiscan.

Five soil samples were collected from different agricultural areas of Greece (Tirfi Ioannina, N. Malgara, Preveza, Orestiada and Kozani) with no previous history of pesticides use. The soils were sampled from the surface layers (0–20 cm), then air dried and sieved to pass through a 2-mm mesh for further use. Soil pH values were measured in slurries made at a soil: water ratio of 1:1 [29]. Organic carbon content (% OC) of the soils

| Properties | Bromophos methyl | Quinalphos | | |
|---|------------------------------|--------------------------------|--|--|
| Chemical structure | MeO P-O MeO S Cl | MeO MeO S CI Br | | |
| Molecular weight Water solubility (mg L^{-1}) | 366.1 40 | 298.3 22 | | |
| Vapour pressure (mPa at 20° C) Henry's constant (m ³ atm mol ⁻¹) | $1/1.54 \times 10^{-6}$ | 0.346 4.64×10^{-8} | | |
| Log K _{ow} | 4.88 | 4.44 | | |

Table 1. Physicochemical properties of selected pesticides [3,4].

Table 2. Characteristics and composition of the soil samples.

| Soil | Location | Soil Texture | % OM | Sand | Silt | Clay | pН |
|------|----------------|--------------|------|------|------|------|-----|
| 1 | Tirfi Ioannina | Sandy Loam | 5.49 | 67 | 29 | 4 | 6.6 |
| 2 | N. Malgara | Sandy Loam | 2.18 | 55 | 31 | 14 | 7.4 |
| 3 | Preveza | Sandy Loam | 1.98 | 75 | 11 | 14 | 5.5 |
| 4 | Orestiada | Loam | 1.91 | 45 | 31 | 24 | 7.8 |
| 5 | Kozani | Clay | 0.70 | 24 | 28 | 48 | 7.7 |

was determined by Walkley-Black method and the total organic mater content (% OM) was calculated by using Equation (1):

$$(\% \text{ OM}) = 1.72 \times (\% \text{ OC})$$
 (1)

Precautions were taken to avoid contamination during sampling, drying, grinding and storage. Selected properties of the test soils are listed in Table 2.

2.2 Adsorption-desorption experiment

The batch adsorption experiments were carried out in three replicates using 15 ml polypropylene centrifuge tubes containing 1.0 g of soil and 10 ml 0.01M CaCl₂ solution of quinalphos or bromophos methyl at different concentrations levels (0.5, 1.0, 2.5, 5.0 and $10.0 \,\mu g \,m L^{-1}$). The CaCl₂ (0.01 M) was used as the background electrolyte in order to maintain the ionic strength [30]. To evaluate interference due to soil, an adsorption test with CaCl₂ (0.01M) solution but without pesticide was carried out, as described below. Besides, blank samples (no soil added) indicated that losses due to adsorption onto polypropylene centrifuge tubes were negligible. According to preliminary experiments, adsorption equilibrium was reached within 24 h equilibration period (results not shown). The centrifuge tubes, prepared as above, were subsequently capped and shaken in a wrist

action shaker for 24 h at room temperature. At the end of the apparent equilibration period the samples were centrifuged at 4500 rpm for 5 min, and the concentration of pesticides was determined in the supernatant.

Desorption in water was studied in the same soils used for adsorption. After adsorption, the supernatant was carefully decanted and was replaced with 10 ml of fresh 0.01 M CaCl_2 solution. The centrifuge tube was capped and shaken for a further 6 h (preliminary kinetic experiments demonstrated that desorption apparent equilibrium was reached within 6 h) and centrifuged as described above, then the supernatant was analysed for pesticides.

A second desorption step was carried out in the same soils after desorption with water, using 10 ml of acetone and shaking for 30 min.

2.3 Extraction and analysis of pesticide

For residue analysis, 5 ml of supernatant, each after adsorption and desorption, was extracted twice with 2.5 ml *n*-hexane using a vortex for 1 min. In the combined extracts a small amount of anhydrous Na₂SO₄ was added to remove residual water. The acetone desorption phase was filtered through glass wool fibre, containing anhydrous Na₂SO₄ as a part of clean-up procedure for the samples. An aliquot of $1.0 \,\mu$ L of the *n*-hexane and acetone extract was injected into a Shimadzu 14B gas chromatograph equipped with ⁶³Ni electron capture detector (ECD) at 300°C. A DB 1 column (J & W Scientific, Folsom, CA, USA), 30 m of length, 0.32 mm i.d., coated with dimethylpolysiloxane of a film thickness of 0.25 μ m, was used. The temperature programme was: from 80°C (2 min) to 290°C (10 min) at 21°C min⁻¹. Injector temperature was set to 250°C and the injector mode was splitless. Helium and nitrogen was used as the carrier (1.5 mL min⁻¹) and the make-up (35 mL min⁻¹) gases, respectively. Under these conditions, retention times of bromophos methyl and quinalphos were 11.10 and 11.40 minutes respectively. The recovery obtained with the extraction method used was greater than 90% for both the pesticides investigated.

2.4 Data analysis

The experimental adsorption data have been analysed by the linearised Freundlich and Langmuir equations (Equations (2) and (3)):

$$\ln X_{ads} = \ln(K_{f_{ads}}) + \frac{1}{n} \ln(C_e^{ads})$$
⁽²⁾

$$\frac{1}{X_{ads}} = \frac{1}{C_e^{ads} K_a Q_{\max}} + \frac{1}{Q_{\max}}$$
(3)

 X_{ads} is calculated using Equation (4):

$$X_{ads} = \left(C_0 - C_e^{ads}\right) V/m \tag{4}$$

where X_{ads} is the adsorbed amount ($\mu g g^{-1}$), K_{fads} and 1/n are empirical Freundlich adsorption constants. C_e^{ads} and C_0 are equilibrium concentration and initial concentration ($\mu g m L^{-1}$) of the pesticides, K_a is the Langmuir constant and Q_{max} is the maximum

adsorption capacity ($\mu g g^{-1}$), V is the volume of water used (L) and m is the weight of the sample used (g).

Desorption isotherms were also fitted to the linearised Freundlich equation (Equation (5)):

$$\ln X_{des} = \ln(K_{f_{des}}) + \frac{1}{n} \ln(C_e^{des})$$
⁽⁵⁾

 X_{des} is calculated as

$$X_{des} = \left(m_{ads} - m_e^{des}\right)/m \tag{6}$$

where X_{des} is the pesticide remaining adsorbed on the soil at desorption equilibrium $(\mu g g^{-1})$, K_{fdes} is the Freundlich desorption constant. C_e^{des} is the desorption equilibrium concentration $(\mu g m L^{-1})$, m_{ads} is the amount of pesticide adsorbed on soil at adsorption equilibrium (μg) and m_e^{des} is the amount of pesticide in the aqueous phase at desorption equilibrium (μg) . The value of 1/n also indicates the degree of linearity (1/n < 1) of the isotherms.

The variation of standard free energy (ΔG^0) of adsorption and desorption was calculated for each soil from the value of K_{om} using the equation:

$$\Delta G^0 = -RT \ln K_{om} \tag{7}$$

where ΔG^0 is the free energy change (Kcal/mol), *R* is the gas constant (1.986 cal K mol⁻¹) and T is the absolute temperature (273 + 25°C = 298 K).

The calculation of per cent balances of quinalphos and bromophos methyl for five different concentrations were determined according to Konstantinou and Albanis [31].

Finally, regression analysis with analysis of variance (ANOVA) was done for every case of K_{fads} value with different soil parameters to find the significant interactions by Minitab[®] 11.2, 32 bit statistical software.

3. Results and discussion

3.1 Adsorption isotherms

Adsorption isotherms for bromophos methyl and quinalphos in soils are presented in Figures 1 and 2. The adsorption data for the two compounds showed good linearity and were successfully described by the linear forms of the Freundlich and Langmuir equations. However, R^2 value by itself cannot express the good fit of the data to the above equations. Thus, the error function [32] was calculated in order to assess which model best describes our adsorption data. Error function can be expressed as (Equation (8)):

$$F_{\text{error}} = \sqrt{\frac{\sum_{i}^{p} \left((q_{i}cal - q_{i}\exp)/q_{i}\exp)^{2} \right)}{p}}$$
(8)

where q_i cal is each value of $(x/m)_{ads}$ predicted by the fitted model and q_i exp is each value of $(x/m)_{ads}$ measured experimentally, p is the number of experiments conducted.

By comparing the results of the values of error function presented in Table 3, it can be concluded that the Freundlich isotherm model fitted better to the adsorption data for both pesticides. Moreover, Langmuir parameters K_a and Q_{max} for all the soils (except Soil 1 for quinalphos) were negative and this could not explain the adsorption process [33].



Figure 1. Adsorption-desorption isotherms of bromophos methyl on different soils. Open circles (\circ) indicate adsorption whereas solid circles (\bullet) indicate desorption points.



Figure 2. Adsorption-desorption isotherms of quinalphos on different soils. Open circles (\circ) indicate adsorption whereas solid circles (\bullet) indicate desorption points.

According to the Freundlich isotherms, the K_{fads} value is a relative measurement of the affinity of the adsorbent (soil) for the adsorbate. K_{fads} values ranged from 12.2 to 254.7 for bromophos methyl, and from 3.7 to 50.2 for quinalphos. The highest K_{fads} value for both pesticides corresponds to soil with the highest OM content (Soil 1) and this trend is also decreased with decreasing OM content.

| | | Freundlich constants | | | | Langmuir constants | | | |
|---------------------|-----------------------|---|---|---|---|---|--|---|---|
| Compound | Soil | K _{fads} | 1/n | R^2 | Ferror | Q_{\max} | K_a | R^2 | Ferror |
| Bromophos methyl | 1 2 3 4 5 | $254.7(\pm 0.01) 79.4(\pm 0.06) 65.4(\pm 0.04) 49.4(\pm 0.03) 12.2(\pm 0.02)$ | $\begin{array}{c} 1.23(\pm 0.02)\\ 1.07(\pm 0.10)\\ 1.35(\pm 0.07)\\ 1.20(\pm 0.16)\\ 1.33(\pm 0.04) \end{array}$ | 0.980 0.979 0.967 0.990 0.991 | 0.020 0.056 0.035 0.009 0.007 | $\begin{array}{c} -149.2(\pm 1.2) \\ -41.6(\pm 0.09) \\ -92.6(\pm 0.31) \\ -55.1(\pm 0.25) \\ -20.8(\pm 0.08) \end{array}$ | -0.84 -1.29 -0.36 -0.53 -0.34 | 0.994 0.917 0.987 0.983 0.990 | 0.059 0.527 0.115 0.159 0.857 |
| Quinalphos | 1 2 3 4 5 | $50.2(\pm 0.08) \\ 17.1(\pm 0.02) \\ 13.5(\pm 0.04) \\ 11.0(\pm 0.02) \\ 3.7(\pm 0.06)$ | $\begin{array}{c} 0.90(\pm 0.03)\\ 1.04(\pm 0.07)\\ 1.31(\pm 0.09)\\ 1.03(\pm 0.02)\\ 1.16(\pm 0.08) \end{array}$ | 0.956 0.995 0.941 0.985 0.979 | 0.063 0.011 0.002 0.012 0.014 | $\begin{array}{c} 37.7(\pm 0.02) \\ -55.8(\pm 0.22) \\ -15.7(\pm 0.13) \\ -147.1(\pm 0.21) \\ -23.31(\pm 0.07) \end{array}$ | $2.53 \\ -0.25 \\ -0.43 \\ -0.06 \\ -0.12$ | 0.942 0.992 0.789 0.996 0.990 | 0.186 1.034 0.366 0.076 0.158 |

Table 3. Freundlich and Langmuir constants values and function error (F_{error}) for bromophos methyl and quinalphos adsorption in soils.

Figure in parentheses is the respective standard error.

The $1/n_{ads}$ parameter describes the degree of curvature of the isotherms. The $1/n_{ads}$ values for bromophos methyl (Table 3) were greater than 1, indicating the S-type of adsorption isotherms [34,35]. This type of isotherm indicates a low affinity between bromophos methyl and soil at low concentration, and the adsorption becomes easier as the pesticide concentration increases. In most cases, this behaviour is attributed to the strong competition between the water molecules and the pesticide for the adsorption sites of soil [36]. But in our case, the S-type isotherm may be due to cooperative interactions among adsorbed organic compound that stabilise the sorbate and enhance its affinity for the surface [37]. The S-shaped isotherms of organophosphorus pesticides on different adsorbents have also been described by many researchers [38,39]. The $1/n_{ads}$ values for quinalphos (Table 3) were also S-type except Soil 1 which was near 1 or less than 1, indicating the C-or L-type of adsorption isotherms [34,35]. L-shaped isotherms indicated a relatively high quinalphos and soil affinity at low concentration, and adsorption decreases as the aqueous concentration of pesticides increases.

Freundlich organic matter distribution coefficient (K_{f-om}) has been presented in Table 4 and the experimental data expressed that K_{f-om} of Soil 1 was higher than that for other four soils studied for both pesticides. A significant positive correlation was observed between Freundlich adsorption capacity and K_{f-om} values. Pesticides with K_{f-om} values below 500 are considered mobile with respect to leaching [40]. According to this, both pesticides can be classified as not mobile.

The variation of standard free energy (ΔG^0) values showed that the adsorptivity of the soils was in the order of Soil 1 > Soil 2 > Soil 3 > Soil 4 > Soil 5, and this was also the trend of organic matter content of the soil, indicating adsorption was mostly governed by the organic matter content, greater the ΔG^0 value, higher the extent of adsorption is. ΔG^0 values ranged from -4.42 to -5.0 for bromophos methyl and from -3.71 to -4.04 for quinalphos. From Table 4, we can see that all ΔG^0 values were negative showing that adsorption is an exothermic process and an increase in temperature would be expected to reduce adsorption and favour desorption.

The correlation of adsorption constant K_{fads} with soil properties can be used to predict the adsorption of pesticide in different soils or to help in determining the factors

| Compound | Soil | $*K_{f-om}$ | ΔG^0 | Hysteresis Index (HI) |
|------------------|------|-------------|--------------|-----------------------|
| Bromophos methyl | 1 | 4639.34 | -5.00 | 0.85 |
| 1 5 | 2 | 3642.20 | -4.86 | 0.89 |
| | 3 | 3303.03 | -4.80 | 0.96 |
| | 4 | 2586.39 | -4.65 | 1.21 |
| | 5 | 1742.86 | -4.42 | 1.25 |
| Quinalphos | 1 | 914.39 | -4.04 | 1.06 |
| | 2 | 784.40 | -3.95 | 1.15 |
| | 3 | 681.82 | -3.86 | 1.21 |
| | 4 | 575.92 | -3.76 | 1.29 |
| | 5 | 528.57 | -3.71 | 1.34 |

Table 4. K_{f-om} , ΔG^0 and hysteresis index (HI) values of bromophos methyl and quinalphos.

 $K_{f-om} = 100 \times K_{fads}/OM$, where OM is the soil organic matter content in%.

Table 5. Correlation coefficient of K_{fads} with soil parameters for pesticides.

| Compound | ОМ | pН | Clay |
|------------------|--------|--------|--------------------|
| Bromophos methyl | 0.995* | -0.331 | $-0.755 \\ -0.756$ |
| Quinalphos | 0.994* | -0.318 | |

*Significant at 0.05 level (2-tailed).

responsible for adsorption. Table 5 presents the statistical correlations between the K_{fads} values and various soil properties (OM, soil pH and clay). For both pesticides, K_{fads} values were strongly and significantly correlated to the OM content. Data from previous studies also indicate a good correlation between K_{fads} and OM for the organophosphorus pesticides; the higher the OM, the larger K_{fads} value is [21–23].

On the other hand, clay content was not significantly correlated with Freundlich adsorption values. In addition, adsorption of both pesticides showed very poor correlation with soil pH. This may be attributed to the non-ionisable nature of these pesticides. Mandal and Adhikari [23] also concluded that pH showed very little effect on the adsorption of methyl parathion and fenitrothion in soils. Generally, organic matter in soil is closely associated with the inorganic soil components and thus provides a large surface area for adsorption. As a result, adsorption of both pesticides increased with the increase of organic matter content in the soil while no other properties appeared to influence their adsorption behaviour. The role of organic matter content for adsorption of nonionic pesticides showed the same behaviour [41,42].

3.2 Desorption isotherms

Desorption isotherms were constructed using the points resulting from single desorption step measured from all equilibrium points of the adsorption isotherms. Freundlich constants for desorption of bromophos methyl and quinalphos are presented in Table 6. The K_{fdes} was the highest in the Soil 1 and the lowest in the Soil 5 for both pesticides,

| Compound | Soil | K_{fdes} | 1/n | R^2 | |
|------------------|------|-------------------|------------------|-------|--|
| Bromophos methyl | 1 | 376.2(±0.04) | 1.04(±0.02)* | 0.984 | |
| 1 5 | 2 | $93.7(\pm 0.02)$ | $0.95(\pm 0.02)$ | 0.999 | |
| | 3 | $73.0(\pm 0.04)$ | $1.29(\pm 0.06)$ | 0.945 | |
| | 4 | $51.4(\pm 0.02)$ | $1.45(\pm 0.04)$ | 0.993 | |
| | 5 | 36.6(±0.05) | $1.66(\pm 0.07)$ | 0.905 | |
| Quinalphos | 1 | $111.1(\pm 0.03)$ | $0.95(\pm 0.12)$ | 0.987 | |
| | 2 | $37.7(\pm 0.09)$ | $1.20(\pm 0.02)$ | 0.985 | |
| | 3 | $39.6(\pm 0.02)$ | $1.58(\pm 0.01)$ | 0.972 | |
| | 4 | $22.0(\pm 0.01)$ | $1.33(\pm 0.08)$ | 0.979 | |
| | 5 | 16.6(±0.02) | 1.55(0.07) | 0.989 | |

Table 6. Freundlich desorption constants for bromophos methyl and quinalphos in different soils.

*Figure in parentheses is the respective standard error.

indicating that soils with high organic matter content have greater affinity for bromophos methyl and quinalphos than those with lower organic matter content. As shown in Tables 3 and 6, for bromophos methyl, the Soil 1, Soil 2 and Soil 3 have the values $1/n_{ads}$ greater than $1/n_{des}$ This indicates that a significant amount of pesticides adsorbed is not easily desorbed. The opposite behaviour was found for Soil 4 and Soil 5 and this may occur owing to a low amount of organic matter. For quinalphos $1/n_{des}$ greater than $1/n_{ads}$, was observed for all soils, indicating that the rate of desorption is higher than the rate of adsorption. According to O'Connor et al. [43], the ratio of Freundlich exponents, $(1/n_{des})/(1/n_{ads})$ was assumed to express the hysteresis index (HI). Hysteresis is either not observed when values of HI > 1 and it is evident when HI < 1. In this study, for bromophos methyl, Soil 1, Soil 2 and Soil 3 showed hysteresis. This fact suggests that a fraction of the sorbed bromophos is tightly bound to the soil particles and does not readily desorb. On the other hand, Soil 4 and Soil 5 did not show hysteresis, indicating soil particles desorbed pesticide molecules easily. For quinalphos, hysteresis was not observed for all soils. For both pesticides, the highest hysteresis effect (the lowest HI) was observed in Soil 1 which also had the highest organic matter content, whereas the lowest hysteresis effect (the highest HI) was observed in the soil containing the lowest organic matter.

3.3 Adsorption-desorption per cent balances

The mean per cent balances for the adsorbed and desorbed amounts of bromophos methyl and quinalphos for five different concentrations from different soils are summarised in Table 7. It had been observed that adsorption is decreasing with decreasing organic matter content. The highest adsorbed mean percentage was found in Soil 1 for both pesticides which also possessed the highest organic matter content and the lowest for Soil 5 that contained the lowest organic matter. A similar result was also reported by Patakioutas and Albanis [44] for pirimiphos-methyl adsorption on different soils.

The amount desorbed by the single desorption with 10 ml water ranged from 3.16% to 33.34% for bromophos methyl and from 7.55% to 51.56% for quinalphos. Soils containing less organic matter showed greater desorption [45] and the pesticides residue

| Compound | Soil | %OM | Adsorbed% | *Desorbed in water% | *Desorbed in acetone% | *Non-desorbable amount% |
|------------------|------|------|-----------|------------------------|-----------------------|----------------------------|
| Bromophos methyl | 1 | 5.49 | 93.9 | 3.16 | 32.37 | 64.47 |
| 1 2 | 2 | 2.18 | 87.7 | 8.79 | 37.33 | 53.88 |
| | 3 | 1.98 | 81.4 | 17.3 | 53.25 | 29.45 |
| | 4 | 1.91 | 80.2 | 23.1 | 58.31 | 18.59 |
| | 5 | 0.70 | 54.8 | 33.34 | 62.43 | 4.23 |
| Quinalphos | 1 | 5.49 | 84.68 | 7.55 | 17.02 | 75.44 |
| | 2 | 2.18 | 62.6 | 25.59 | 22.05 | 52.36 |
| | 3 | 1.98 | 56.6 | 30.54 | 38.36 | 31.1 |
| | 4 | 1.91 | 52.5 | 37.8 | 32.02 | 30.18 |
| | 5 | 0.70 | 28.0 | 51.56 | 36.57 | 11.87 |

Table 7. Adsorbed, desorbed with water or acetone and non-desorbable amounts (%) of bromophos methyl and quinalphos from aqueous solutions by soils.

*According to the adsorbed amount.

moved downward freely through the soil column. This observation might cause concern regarding the possibility of ground water contamination, especially from the soil with lower organic matter content. The percentage amounts desorbed in 10 ml acetone ranged from 32.37% to 62.43% for bromophos methyl and from 17.02% to 36.57% for quinalphos. High organic matter plays a vital role for binding the pesticide molecules with soil. For this reason binding molecules were not desorbed with water vigorously from high organic matter content soil but they did well in organic solvent. The use of organic solvents such as acetone, methanol and acetonitrile, which are very good solvents for many pesticides, causes considerable desorption and they may break bonds that water may not be able to break. Finally, the pesticides amounts defined as non-desorbable amount that were relatively high for all analytes, ranged from 4.23% to 64.47% for bromophos methyl and from 11.87% to 75.44% for guinalphos. In general, the percentages of non-desorbed pesticide were low in case of bromophos methyl than quinalphos and increased with the organic matter content of the soils. The non-desorbable amounts of selected pesticides which dominate in the high organic matter content soil are a promising source of contamination in the course of time by different weathering processes. Similar observation was also found by Konda et al. [46]. The increase in the amounts desorbed by the acetone with increasing soil organic matter indicates that adsorption of pesticides onto organic matter is likely to occur principally via weak induction (London) forces or dispersion forces which are characteristics of the physical adsorption process.

4. Conclusion

Adsorption and desorption studies of bromophos methyl and quinalphos indicate that selected soils adsorb high amount of these organophosphorus pesticides. The isotherms fitted to the Freundlich equation well. Soil organic matter content is a major parameter that affects mainly the adsorption behaviour of these studied organophosphorus pesticides. Bromophos methyl showed maximum adsorption and minimum desorption. This suggests that bromophos methyl is a relatively safer pesticide than quinalphos. According to the above results, in the natural environment, soils with significant organic matter content are expected to immobilise these pesticides, preventing their movement to the water table.

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