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AN ANALYSIS OF REDICIDE SORPTION BEHAVIOUR IN AGRICULTURAL SOIL

ABSTRACT

An agricultural field soil was studied to evaluate the sorption behavior of a new pesticide called Redicide. Through the use of Linear isotherm and Freundlich isotherm models, K_d and K_{oc} were determined. The results included high sorption coefficients for both models with the Linear isotherm model producing a K_d value of 505.63 L/kg and K_{oc} a value of 9468.72, suggesting that Redicide in agricultural soil was highly absorbed.

The results determined were analysed against other soil types, which had also been tested for sorption behavior of Redicide. Redicide sorption in agricultural soil was far higher than any other soil, however there has been no suggestions for why this occurred, particularly when all soils had similar parameters.

No explanation was found for the Redicide behavior in the agricultural field, so it has been suggested that further research and studies are conducted to analyse the behavior of Redicide in different forms of soil.

1. INTRODUCTION

As the worlds population expands with an estimated global population of 9 billion by 2050, it is important that crop yields are maintained and increased (Bilsborrow *et al*., 2013). Over the last three decades, there has been an observed increase in crop yields as a result of the development of high yield crop varieties and the increasing use of fertilisers and pesticides (Bindrabon et al., 2000). However, this widespread use of chemicals is a growing concern due to its effect on the natural environment and its ability to damage soil structure (Wagenet & Hutson, 1990).

 Pesticides and fertilisers which are being added to the soil propose several problems as it can behave in different ways once released into the soil. Its different behaviour includes being sorbed by different soil compartments, transforming to other compounds or being leached from the soil into surface or ground waters (Smith, 1995; Sablijic, 1989).

The process of sorption, which occurs to pesticides when entering the soil is described as the attraction of chemicals to soils and vegetation, so pesticides often bind to soil particles. This process means that pesticides remain in the soil for longer and are therefore available for plant uptake, however strongly sorbed pesticides are less available to plants (Kerle et al., 2007). The pesticides potential sorption is influenced by several factors including whether the pesticide has a strong or weak ionic attraction and hydrogen bonding, or the nature of the soil such as moisture, texture and organic matter content (Durovic et al., 2009). Soils which are sandy are usually found to have lower levels of sorption due to less surface area, compare to clay soils which tend to have high sorption levels due to high surface area (Kerle et al., 2007).

Laboratory experiments are best used to express the sorption of a pesticide to soil, with the experimental data collected been expressed as equilibrium isotherm curves. Isotherm models are widely used to determine the sorption performance. For the purpose of this study the focus will be on Linear and Freundlich models. The Linear isotherm model assumes that all surfaces are homogenous and that they infinite, suggesting that if there was an increase in the initial concentration then there will also be an in increase in the amount of sorbate absorbed, whilst the Freundlich Isotherm model considers that the surfaces may be heterogonous and that not all soil has the

same sorption ability (Ayawei et al., 2015). From these isotherm models the sorption coefficient (K_d) can be determined which is essential for explaining the soils capacity to remove sorbate from the solution (Schwarzenbach *et al.,* 2005).

Based on the effect that pesticides can have on soils due to sorption it is important to test all new pesticides before entering the market. A new pesticide called Redicide has recently been developed but the sorption behavior of the compound in soil is yet unknown. Therefore, the purpose of this study is to determine the sorption behavior of Redicide, by determining how much Redicide has been sorbed to the soil at different concentrations, and then

2. METHOD

Using soil already collected from an Agricultural field, 0.5g of soil was weighed into tubes 14 times. Solutions of 1, 2, 4, 6, 8 and 10 mg/L Redicide were prepared in water from an original Redicide concentration of 1 g/L. The correct concentrations were achieved through the following process of 1 in 10 dilutions.

The concentrations diluted from the original Redicide concentration of 1g/L were put in a Jenway 6700 Vis. Spectrophotometer at a wavelength of 553nm so the absorbance of each standard could be determined. A calibration curve could be created by plotting the absorbance of Redicide in water against the concentrations.

Redicide-soil solutions were developed by adding 10ml of diluted Redicide to the tubes containing 0.5g of soil with this being repeated twice for each concentration level. Redicide-water solutions were developed as controls with 10ml of Redicide and water. This was also repeated twice for each concentration. Another control that was included in this study was two tubes each containing 0.5g of soil and 10ml of water.

The samples made up were then centrifuged for 5 minutes at 3000rpm using the Hettich Zentifugen Rotanta 460, before being shaken at 150rpm using the Stuart Orbital Shaker SSL1 from 15:00hours on the Friday to 10:00hours on the following Thursday.

Following the agitation of samples for 7 days, the samples were analysed. Samples containing Redicide-water were placed in the Jenway 6700 Vis. Spectrophotometer so the absorbance of each Redicide-water concentration could be established.

Samples containing soil, first had to be filtered by removing 10ml of solution from the tube and filtered using a clean 0.2um syringe filter. The Jenway 6700 Vis. Spectrophotometer was then used to determine absorbance of Redicide-soils solutions.

Once absorbance was determined the concentrations of Redicide at different stages needed to be calculated along with the sorption coefficient. This was achieved by a variety of different equations explained in **Appendix A**.

3. RESULTS

All results were calculated from the raw data presented in **Appendix B**. From the experimental test results, the C_s value was calculated. Using the C_s value results, a graph showing the initial concentration (C_e) and the mass sorbed per unit mass of sorbent (C_s) was plotted (**Figure 1**). Full results regarding Redicide absorption can be found in Appendix B. There are 8 values in total which have a Ce value of 0, suggesting that the initial concentrations of Redicide in soil were very low. As seen from the plot, all Ce values were relatively low with the highest initial concentration being 0.27mg/L. The trend line on **Figure 1** suggests that the linear model is inappropriate, as it does not fit all values in the concentration range. The Kd value determined using the slope of the regression equation in **Figure 1** is 505.63L/kg, whilst the K_{oc} value was 9486.72.
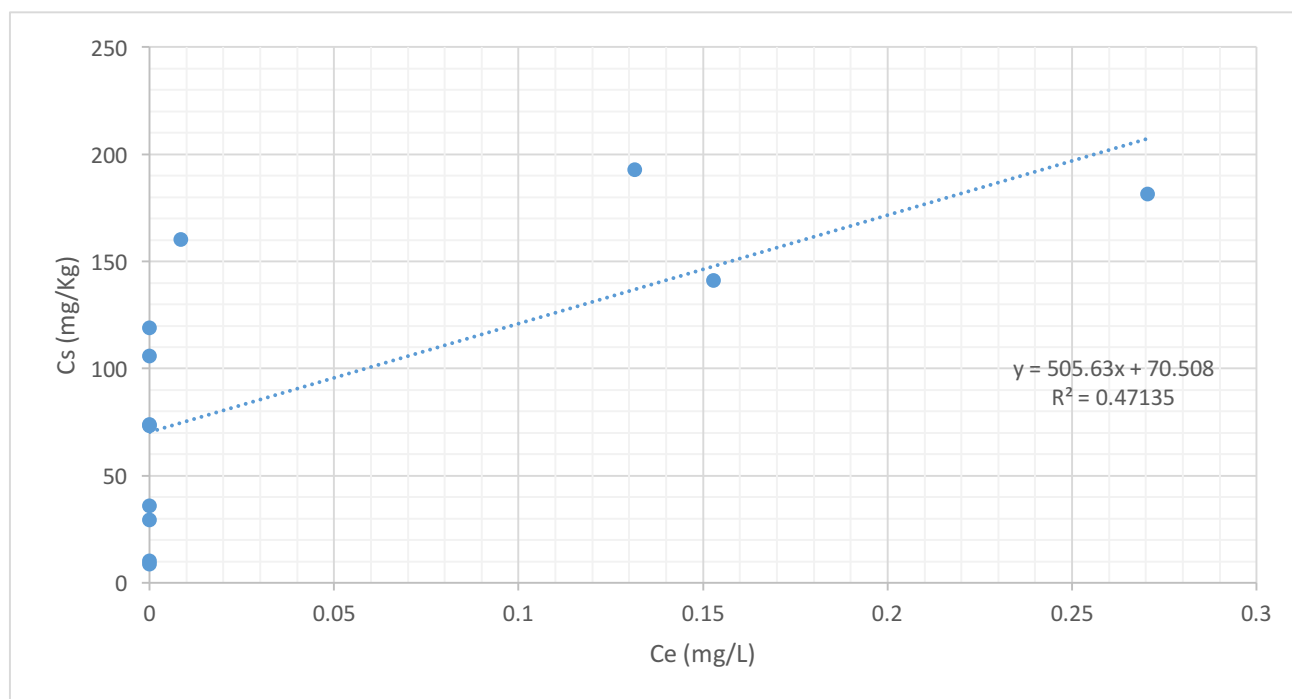

Figure 1. Linear isotherm model for test results with Ce plotted against Cs. Ce refers to the initial Redicide concentration. Cs is the mass of Redicide sorbed per unit mass of sorbent (mg/g). A trend line, with regression equation and R^2 value is included.

Figure 2 has been produced by plotting the log 10 of Cs and Ce showed in **Figure 1** so that a Freundlich Isotherm can be produced. Only readings for concentrations 8 and 10 mg/L were plotted, as the other values plotted in **Figure 1** had concentrations of 0, and therefore could not be transformed using log10. Through the use of equations in **Appendix A**, a Kd value of 603.567 was produced which is significantly higher than the Kd value produced using Linear Isotherm model.

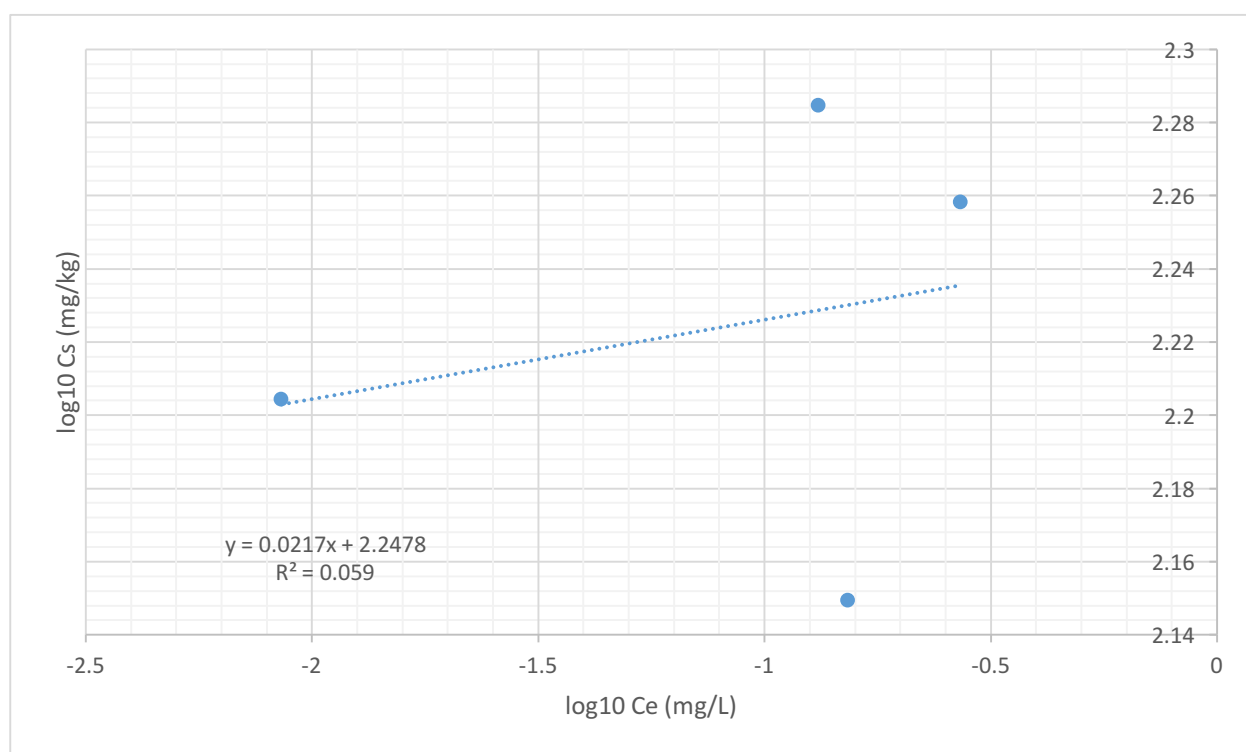**Figure 2. Freundlich isotherm model for test results with log Ce plotted against log Cs. Ce refers to the initial Redicide concentration. Cs is the mass of Redicide sorbed per unit mass of sorbent (mg/g). A trend line, with regression equation and R2 value is included. Only 4 data points were considered for this graph as other concentrations had Ce values of 0.**

4. DISCUSSION

Its important to understand the different sorption behaviours of pesticides such as Redicide in soil as this could be beneficial to understanding the maximum concentration of pesticide that can be applied to soil before it becomes a threat to the environment. The current understanding of pesticides and the effect that their compounds have on soil is inadequate (Rojas et al., 2013), and is still leading to environmental problems including water contamination (De Wilde et al., 2009).

Analysis of agricultural soil reveals that high amounts of Redicide were absorbed in the soil as it had a distribution coefficient (K_d) of 505.63 L/k. A higher K_d value indicates that the pesticide is able to be sorbed more strongly to the soil. This can also be backed by the K_{oc} value which read 9468.72, suggesting that the mobility of pesticides in the soil is weak so sorption is stronger. These values can be compared to other types of soil which have previously been tested for sorption (**Table 2**).

Table 1. Four soil types used to test the behaviour of redicide in soil. Kd and Koc values vary between the soils with agriculture having a significantly higher sorption coefficient compared to other soils tested.

Soil Name	Kd (L/kg)	Koc
Campus Field	215.29	2694.49
Walled Garden	126.35	1817.99
Common Land	48.795	392.55
Agriculture	505.63	9468.72

When comparing agricultural soil to other soils tested it had the highest sorption coefficient and thus Redicide was more readily absorbed by the soil, with common land having the least amount of Redicide absorbed, which is shown by a K_d of 48.79 L/kg and a K_{oc} of 392.55. The soil collected from campus field and walled garden had relatively lower K_d and K_{oc} readings compared to agriculture. This suggests that there was a specific factor of the agricultural soil causing it to have a high sorption coefficient. When comparing the different soil types and their sorption coefficients it is important to take into consideration the different parameters of the soil which explain the soil type, pH and the organic matter content (**Table 3**) as previous studies have found that these factors are the main influences in sorption coefficient values.

Table 2. Parameters of different soil sites. These parameters have the potential to explain why redicide behaved differently in agricultural soil compared to other soil types.

Parameter	I	II	III	IV
Name	Campus field	Common land	Agricultural field	Walled garden
Clay (%)	0.8	0.8	1.2	1.2
Silt (%)	39	39.3	49	48.4
Sand (%)	60.1	60	49.8	50.4
pH	6.7	7.1	6.7	7.3
Organic matter (%) loss on ignition	7.99	12.43	5.34	6.95

Studies have found that soil amendments play a role in changing the physiochemical properties, and therefore the sorption ability of soils (Singh, 2008). Agricultural soils are normally subject to amendments such as manure or compost as they are usually low in organic carbon content (Nicolas et al., 2012). These amendments to soil have also been found to cause immobility in pesticides, thus causing high levels of sorption by soils (Rojas et al., 2013). However, this is not the case as the organic matter content of agriculture was the lowest of the 4 soil types. There is the potential that the soil samples collected were topsoil, which may influence the organic matter content, as the agricultural field may have only a small amount of organic matter incorporated, whilst the other 3 soil types have larger amounts of turf grass incorporated. It may also be dependent on the type of organic matter content that is present in the soil, as agricultural fields may have crop residues which is the cause of high sorption coefficients (Kerle et al., 2007)

pH has found to be one of the biggest factors that effects sorption coefficients in soils with pH dependent distributions being observed for many studies on pesticides (Sheng et al., 2005). Studies have reported that K_d decreases the more the soil becomes acidic

or basic (Delle Site, 2001), suggesting that K_d may be highest for soils within the neutral pH range. All soils had similar pH suggesting that this was not the main influence of the high sorption coefficient.

All soil being compared was made up of clay, silt and sand all of which have different abilities for sorption. Clay is found to have the most sorption due to its large particles size, whilst sand has the least sorption as it particles are smaller, therefore having a smaller surface area (Baskaran et al., 1996; Kerle et al.,2007). Agricultural field had the largest proportion of silt and clay, with only 49.8% of the soil being made up of the sand, which could be the influence of the sorption coefficient. However, this could be contradicted by walled garden data which had a similar soil structure, but had a far lower sorption coefficient.

5. CONCLUSION

Although similar studies have been conducted, they found that organic matter content and pH were the main influences of sorption coefficients (Delle Site, 2001). For this study there has been inconclusive results as to why the sorption coefficient was so high. It could potentially be down to a number of factors including inaccuracy within the data set, but it may also be a result of different parameters. It would be beneficial for future research to determine what causes these anomalies, so that the sorption coefficient of pesticides can be accurately measured, particularly as pesticide use is becoming growing concern to the environment.

Word count: 1994

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APPENDIX A- EQUATIONS USED TO ESTABLISH SORPTION

On the calibration curve created using the absorbance to Redicide concentrations, a linear trend line was added, as the equation of the line would later be used to convert absorbance obtained. Before the concentrations of different phases could be calculated the correct absorbance for each soil-Redicide sample was determined by the following equation:

$$Abs_{corrected} = Abs_{soil\text{-}redicide} - Abs_{soil\ water(Mean)}$$

From these corrected absorbances and the calibration curve equation the $Abs_{corrected}$ can be converted in a concentration known as the Ce value.

$$Ce = \frac{y - c}{m}$$

Where y is the $Abs_{corrected}$, C is the slope and m is the intersect.

The concentration of Redicide-water control samples is achieved using the same process as Ce, to give the Co value.

The concentration of Redicide in the soil is calculated by the following equation:

$$Cs = \frac{(C0 - Ce).V}{m}$$

Where V = volume of solution and m = mass of soil.

From the above equation the Linear Isotherm model can be created by plotting C_S against C_e. The gradient of the line created by plotting these concentrations if the sorption coefficient (K_d). The organic carbon normalised coefficient was determined from the K_d reading by the following equation:

$$Koc = Kd \times (100 \div OC(\%)$$

As well as the Linear Isotherm model the Freundlich Isotherm model was also used. This process included transforming the C_e and C_s data by log 10, before being

plotted against one another. The K_d value for the Freundlich Isotherm model was determined through the following equation:

$$Kd = Kf \times CIW^{n-1}$$

Where K_f is the 10 to the power of the intersect, CIW is the highest C_e value plotted and n is the slope value.

APPENDIX B- RAW DATA

Samples: Redicide & soil			Samples: Redicide & water			Control: Soil & water	
Sample	Absorbance value		Controls	Absorbance value		1	0.026
A1	0.028		A1	0.158		2	0.01
A2	0.013		A2	0.172		Mean:	0.018
B1	0.022		B1	0.413			
B2	0.018		B2	0.352			
C1	0.053		C1	0.762			
C2	0.044		C2	0.769			
D1	0.071		D1	1.19			
D2	0.088		D2	1.067			
E1	0.097		E1	1.577			
E2	0.124		E2	1.426			
F1	0.146		F1	1.824			
F2	0.12		F2	1.904			

			Step 2: Correcting absorbance using the soil & water controls				
Corrected absorbance							
Sample							
A1	0.01						
A2	-0.005						
B1	0.004						
B2	0						
C1	0.035						
C2	0.026						
D1	0.053						
D2	0.07						
E1	0.079						
E2	0.106						
F1	0.128						
F2	0.102						

			Using the corrected absorbance and the calibration curve to convert absorbance to concentration				
	Ce values						
Sample	Concentration						
A1	-0.360235168						
A2	-0.4404062						
B1	-0.392303581						
B2	-0.413682523						
C1	-0.226616782						
C2	-0.274719401						
D1	-0.130411545						
D2	-0.039551042						
E1	0.008551577						
E2	0.152859433						
F1	0.270443613						
F2	0.131480492						

		Step 3: Determining Co					
Co values							
Sample	Concentration						
A1	0.430785676						
A2	0.505611972						
B1	1.793693212						
B2	1.467664351						
C1	3.659005879						
C2	3.696419027						
D1	5.946552646						
D2	5.289150187						
E1	8.014965259						
E2	7.207910208						
F1	9.335114912						
F2	9.762693747						
		Step 4: Finding Cs using the equation.					
	Cs values						
Sample	Concentration						
A1	0.007910208	8.6156			V=volume=10ml=0.01L		
A2	0.009460182	10.1222			m=soil mass= 0.05g=0.0005mg		
B1	0.021859968	35.8738					
B2	0.018813469	29.3532					
C1	0.038856227	73.181					
C2	0.039711384	73.9282					
D1	0.060769642	118.931					
D2	0.053287012	105.783					
E1	0.080064137	160.1282737					
E2	0.070550508	141.1010155					
F1	0.090646713	181.293426					
F2	0.096312133	192.6242651					