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Modeling Relationship between Organic Carbon Partition Coefficient and Pesticides Solubility of Pesticides used along the Shore of Lake Naivasha, Kenya

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Abstract Pesticides have many different properties that affect their behaviour in the environment. Pesticide's solubility in water has a great impact on leaching potential and environmental fate. The objective of this study was to determine the relationship between organic carbon based partition coefficient (k_{oc}) and pesticides solubility (S) of pesticides used along the shore of Lake Naivasha using regression analysis. The properties (S, and soil/water equilibrium partition coefficient (k_d)) of pesticides selected from an inventory of pesticides used in farms around Lake Naivasha, were determined from the manufacturers' materials safety data sheets. The organic carbon (f_{oc}) of the soil from the study area was then determined using the loss-on-ignition (LOI) method and used to calculate k_{oc}. The results showed that the soils around Lake Naivasha had a mean organic carbon (f_{oc}) content of 1.770% and a regression equation for k_{oc} and S for the area to be $\log k_{oc} = -0.368\log S + 3.256$. It was concluded that this relationship can be used to estimate the organic carbon based partition coefficient (k_{oc}) of a pesticide where S is available, and the results compared with values determined experimentally and from other models.

Keywords Pesticides, Groundwater contamination, Partition coefficient, Solubility, Organic carbon, Lake Naivasha

1. Introduction

Pesticides have many different properties that affect their behaviour in the environment. Pesticide properties include physical and chemical characteristics such as solubility, adsorption, volatility, and the potential for degradation. Some of these properties play a significant role in the contamination processes of groundwater. For a water contaminant to be available for the downward movement of the water flow, it should be water soluble, not strongly adsorbed to soil particles, resistant to biotic and abiotic degradation reactions, and not very volatile [1-3]. Other factors influencing the processes of pesticide transport are climate, soil pedology, physical and chemical conditions and soil biota and management ([4] and [5]).

Pesticide's solubility in water has a great impact on leaching potential and environmental fate. In the study of the environmental fate of organic chemicals, the octanol/ water partition coefficient (k_{ow}) has become a key parameter. It has been shown to be correlated to water solubility, soil/sediment sorption coefficient (k_d), and bioconcentration [6, 7]. Of the three properties that can be estimated from k_{ow}, water solubility is the most important because it affects both the fate and transport of chemicals [8, 9]. For example, highly soluble chemicals become quickly distributed by the hydrologic cycle, have low sorption coefficients for soils and sediments, and tend to be more easily degraded by microorganisms [10, 11].

Pesticide chemicals that dissolve readily in water are highly soluble and, thus, are generally carried with the water flow. Such pesticides have a tendency to leach from the soil to groundwater. As the water solubility of a pesticide increases, there is a greater likelihood it will be leached through the soil to groundwater or runoff into surface water. In general, pesticides with solubility of greater than 30 part per million have an increased tendency to leach [12].

Once a pesticide enters a soil, a portion adheres to soil particles and some remains in solution in the soil water [13]. The soil/water equilibrium partition coefficient, also known as the adsorption coefficient (k_d) is defined as the ratio between the concentration in soil and the concentration in water. It can therefore be used to estimate the dissolved or the adsorbed fraction in a soil-water system for any chemical. In a study of six pesticides (bentazone, dimethoate, MCPA, pirimicarb, propiconazole and fenpropimorph), [14] it was found that the ratio of lost to

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applied pesticide decreased with increasing adsorption coefficient.

Each pesticide behaves differently in different soil. In order to evaluate the behaviour of a pesticide at a specific site, the organic carbon normalized soil/water equilibrium partition coefficient (k_{oc}) is used. K_{oc} provides a measure of mobility in which the effects of soil type and management history are specifically accounted for. Organic carbon content (f_{oc}) of a site (estimated to be 58 percent of the organic matter content, is used in the calculation [15, 16]. The US EPA k_d/k_{oc} conversion is based on an organic matter content of 2 percent and an organic carbon content of 1.16 percent [15].

$$k_d = C_s/C_w \quad [17, 18] \tag{1}$$

Where k_d = soil/water equilibrium partition coefficient,

C_s = Pesticide concentration in soil

C_w = pesticide concentration in water

$$k_{oc} = k_d/f_{oc} \quad [19\text{-}21] \tag{2}$$

Where f_{oc} = fraction of organic carbon in the soil.

The larger the k_{oc}, the more strongly the pesticide attaches to soil particles and organic matter. The smaller the k_{oc} value the greater the pesticide concentration in water. Therefore, pesticides with smaller k_{oc} values are more likely to leach.

The objective of this study was to determine the relationship between organic carbon based partition coefficient (k_{oc}) and pesticides solubility (S) of pesticides used along the shore of Lake Naivasha. Lake Naivasha is located in Nakuru County in the Eastern Rift Valley, about 100km Northwest of Nairobi, Kenya's capital. Bordering the lake are some of the biggest flower farms in the world, where 80% of the cut flowers production is found around the Lake basin, making it the most important area for cut flowers in Kenya [26].

2. Material and Methods

2.1. Pesticide Properties

An inventory of pesticides used in farms around Lake Naivasha was first prepared from which 39 pesticides were selected based on their WHO toxicity classification and annual rates of application (Table 1). The properties of selected pesticides (solubility (S), and soil/water equilibrium partition coefficient (k_d)) were determined from the manufacturers' materials safety data sheets and other literature. The organic carbon (f_{oc}) of the soil from the study area was then determined and used to calculate the organic carbon partition coefficient (k_{oc}).

2.2. Soil Organic Carbon Determination

Nineteen (19) soil samples for soil organic carbon analysis were conveniently sampled from farms along the shore of Lake Naivasha (Fig. 1). The soils were sampled at a depth of 15-30 cm to eliminate plant roots which could have given higher than correct values of organic matter and organic carbon. The samples were collected on different days of the week and stored at 4°C to minimize organic compounds loss. The organic matter in the samples was determined at Moi University School of Environmental Studies Analytical Laboratory using the loss-on-ignition (LOI) method [27, 28].

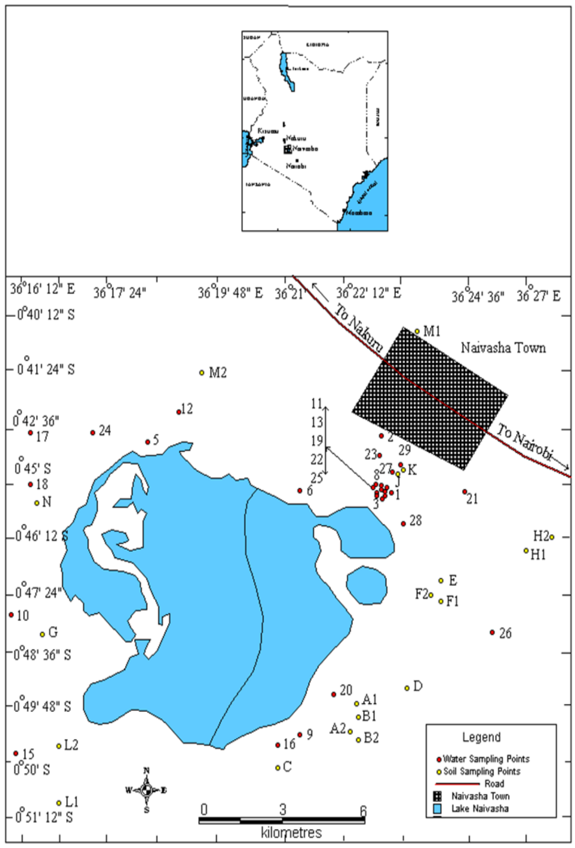

Figure 1. Soil sampling sites

The loss-on-ignition method was used to destroy the organic matter in the sample by heat destruction. The samples were first oven dried at 105°C to remove moisture (water content) and then weighed to determine their initial weights (w_i). A known weight (w_i) of sample was placed in a ceramic crucible which was then heated to 400 ±5°C overnight [27-30]. The sample was then cooled in a desiccator and weighed (w_f).

The organic matter (OM) was determined gravimetrically and calculated as the difference between the initial(*wi*) and final (*wf*) sample weights divided by the initial sample weight (*wi*) times 100% [28] :

$$\text{i.e. OM} = (w_i - w_f)*100/w_f \tag{3}$$

A conversion factor of 1.724 was used to convert organic matter (OM) to organic carbon (f_{oc}) (based on the assumption that organic matter contains 58% organic carbon, i.e.,

$$f_{oc} = OM/1.724 \; [27].$$

The organic carbon partition coefficient (k_{oc}) was calculated using pesticide partition coefficient (k_d) and the mean organic carbon (f_{oc}) according to equation 2.

Table 1. Selected properties of pesticides used along the shore of Lake Naivasha

S. No.	Common name	WHO Class	Application Rate/ha/yr	Solubility (mg/L)	Partition Coefficient (Kd)	Organic carbon partition (Koc)
1	Alpha cypermethrin	II	1600 mls	0.01	216002.4	122035.3
2	Beta cyfluthrin	II	2000 mls	0.0012	74588.0	42140.1
3	Bifenthrin	II	1600 mls	0.01	7324.2	4138.0
4	Deltamethrin	II	1000 mls	0.0341	84035.0	47477.4
5	Lambda cyhalothrin	II	1000mls	0.005	221033.4	124877.6
6	Taufluvalinate	II	360mls	0.002	17400.0	9830.5
7	Oxamyl	I	26800gms	280000	6.4	3.6
8	methomyl	Ib	4000mls	58000	17.4	9.8
9	Paraquat	I	9200mls	62000	11.6	6.6
10	Kresoxim-methyl	I	2000gms	2	506.9	286.4
11	myclobutanil	1	800gms	142	334.1	188.7
12	Chlorfenapyr	II	800gms	0.148	14500.0	8192.1
13	Chlorpyrifos	II	1920gms	2	12146.4	6862.4
14	Abamectin	II	2000mls	0.78	5800.0	3276.8
15	Diafenthiuron	II	2400mls	0.06	2379.2	1344.2
16	Fenarimol	II	1200mls	13.7	1186.7	670.4
17	Imidacloprid	II	2000mls	510	164.7	93.1
18	Pyrimethanil	II	1600gms	121	921.0	520.4
19	Spiroxamine	II	4000mls	405	839.8	474.5
20	Dodemorph acetate	II	10000mls	520	234.6	132.5
21	Fenazaquin	II	2000mls	11	1528.9	863.8
22	Fenhexamid	II	4000gms	4.39	2262.0	1278.0
23	Milbemectin	II	2000mls	4	3271.2	1848.1
24	Dimethoate	II	4000mls	25000	23.2	13.1
25	Fenamiphos	Ia	30000mls	700	402.5	227.4
26	Chlorothalonll	II	8000mls	0.6	1600.8	904.4
27	Amitraz	III	6000mls	0.09	32.13	18.15
28	Copper hydroxide	III	8000gms	2.9	2818.80	1592.54
29	Dimethomorph	III	8000gms	50	466.32	263.46
30	Dimethylamonium chloride	III	8000mgs	3000000	1.39	0.79
31	Fosetyl Al	III	8000gms	136,000	377.00	212.99
32	Iprovalicarb	III	9000gms	17.8	122.96	69.47
33	Indoxacarb	III	10000mls	9.49	3828.00	2162.71
34	Oxycarboxin	III	8000gms	1400	75.40	42.60
35	Propamocarb Hydrochloride	III	6360gms	1005000	75.40	42.60
36	Propargite	III	6000mls	1.25	7354.40	4155.03
37	Sulphur	III	8000gms	0	5063.40	2860.68
38	Tetradifon	III	8000mls	0.0008	8799.76	4971.62
39	phosphanoglycine	III	6800gms	11600	27840.00	15728.81

The logarithm of the organic carbon partition coefficient ($logk_{oc}$) was plotted against that of solubility (logS) to determine the relationship between the two properties influencing the mobility of a pesticide into groundwater (Fig. 2).

3. Results and Discussion

Table 1 shows the solubility and soil/water equilibrium partition coefficient (k_d) of selected pesticides. Table 2 shows the values of organic matter and organic carbon of soils around Lake Naivasha. The mean organic carbon (f_{oc}) of 1.770% (table 2 was used to calculate the organic carbon based partition coefficient (k_{oc}) of 39 pesticides shown in Table 1. Figure 2 shows a plot of the logarithm of organic carbon based partition coefficient (log k_{oc}) versus the logarithm of solubility (log S).

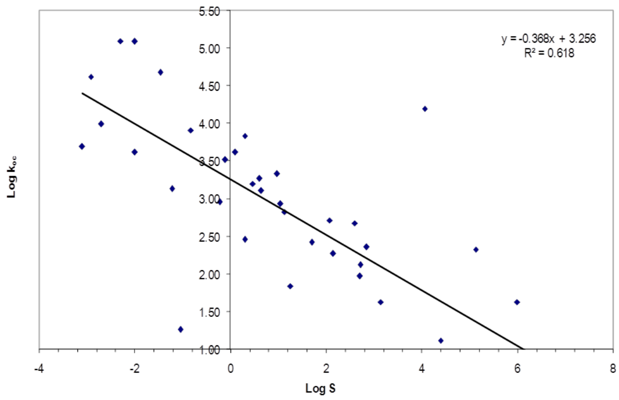

Figure 2. Plot of Log Koc versus Log S of pesticides used on the shore of Lake Naivasha

Table 2. Soils organic matter and organic carbon

S. NO.	Sample	% organic matter (OM)	% organic carbon (f_{oc})
1	A1	1.823	1.057
2	A2	2.036	1.181
3	B1	1.948	1.130
4	B2	2.477	1.437
5	C	1.990	1.154
6	D	2.815	1.633
7	E	2.471	1.433
8	F1	2.608	1.513
9	F2	2.535	1.471
10	G	4.875	2.828
11	H1	4.262	2.472
12	H2	4.478	2.598
13	J	3.388	1.965
14	K	3.663	2.125
15	L1	2.191	1.271
16	L2	1.757	1.019
17	M1	3.307	1.918
18	M2	4.011	2.326
19	N	5.356	3.107
Mean f_{oc}			1.770

Figure 2 provides a relationship between pesticide solubility (S) and the organic carbon based partition coefficient (K_{oc}) of the pesticides. Both properties describe the mobility of the pesticide in the soil. A linear best fit was found to describe the relationship with an equation:

$$y = -0.368x+3.256 \quad (r^2=0.618) \tag{4}$$

From equation 4 and Figure 2 the relationship between K_{oc} and S is:

$$\log k_{oc} = \log(bS^n) \tag{5}$$

Where *b* is a constant

Eqn. 5 may be written as:

$$\log k_{oc} = n \log S + \log b \tag{6}$$

Eqn. 6 gives us the relationship between K_{oc} and S for the study area as:

log k_{oc} = -0.368logS+3.256; (S in mg/l, n=39, r^2 = 0.618) (7)

The relationship shown in regression equation 7 implies that an increase in solubility, S of the pesticide will result in a decrease in organic carbon based soil water partition coefficient (K_{oc}) (i.e. negative correlation). This means the concentration of a highly soluble pesticide in soil particles will reduce, and a large fraction of the pesticide will be concentrated in water (solution); thereby increasing its leaching potential.

Equation *7* is similar to the one obtained by Kanazawa (Log k_{oc} = -0.356*logS + 3.01; S in ppm, n = 15, r^2 = 0.79, [24]. Equation *7* is also comparable to the ones obtained by Kenaga and Goring (Log k_{oc} = -0.55*logS + 3.64; S in mg/l, n = 106, r^2 = 0.71, [22] and Mingelgrin and Gerstl (Log k_{oc} = -0.58*logS + 4.24 for polar hydrocarbons; S in µmoles/l, n = 15, r^2 = 0.410, [25].

Legislation in many countries requires extensive testing of all manufactured chemicals for environmental evaluation and registration [31]. Since the solubility (S) of a pesticide is usually provided in the manufacturer's material safety data sheet, the above relationship can be used to estimate the organic carbon based partition coefficient (k_{oc}), and the results compared with values determined experimentally and from other models.

4. Conclusions

The soils around Lake Naivasha had a mean organic carbon (f_{oc}) content of 1.770%. The relationship between the organic carbon based partition coefficient (k_{oc}) and solubility (S) for the area along the shores of Lake Naivasha was determined to be:

log k_{oc} = -0.368logS + 3.256.

This relationship can therefore be used to estimate the organic carbon based partition coefficient (k_{oc}) of a pesticide where S is available, and the results compared with values determined experimentally and from other models.

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