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APPLICATION NOTE

Adsorption coefficient relationships versus typical soil characteristics for different agrochemical classes

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INTRODUCTION

EAG-Hercules is a CRO specializing in Environmental Fate, Metabolism, and Analytical Chemistry. The Environmental Fate group has completed numerous GLP projects conducted under OPPTS/OCSPP guideline 835.1230 and OECD guideline 106 (Adsorption/Desorption by the Batch Equilibrium Method). The purpose of this poster is to evaluate the correlation between the soil sorption properties of various test substances and the characteristics of the test systems used in the studies.

The data set included 48 test substances of various types (herbicides, insecticides, fungicides, antibiotics) from different chemical families (pyrethroids, nitrogen-containing compounds, sulfur-containing compounds, amides, pyrazoles), and 109 discrete soil and sediment samples of various types (sand, sandy loam, silt loam, loam, clay, etc.) from 79 sites.

The distribution coefficients for adsorption (K_d) for the test substances were plotted against five commonly relevant soil characteristics (percent organic matter, pH in water, pH in 0.01M $CaCl_2$, cation exchange capacity, and percent clay). The coefficient of determination (r^2) was then calculated. Please note that if a test substance was tested on one or two soils (e.g. “data gap” studies) then coefficients of determination were not determined considering that test substance alone.

All calculations were performed using Microsoft Excel.

EVALUATION OF FULL DATA SET

Unsurprisingly, when the data from all 48 test substances was evaluated on a single plot, little correlation was found between the soil adsorption coefficients and the five relevant soil characteristics [the highest r^2 (0.02) was observed for percent organic carbon]. This is due to the wide range of test substances and soils tested, as K_d values ranged from less than 1 (hydrophilic compounds) to greater than 400,000 (extremely hydrophobic compounds).

Similarly, when the data from within each of the six groups was considered together, generally little correlation was found with the exception of a small group of amines (n=3). Even among families with similar chemistries and functional groups, K_d can vary greatly between test substances.

However, some general trends could be observed by comparing which soil characteristics were most frequently observed to have the highest correlation with K_d within each test substance.

PYRETHROIDS

Pyrethroids are a class of synthetic organic insecticides adapted from natural insecticides (pyrethrins) found in chrysanthemum flowers. These compounds are hydrophobic and have large K_d values as they preferentially adsorb onto the soil. Of the six chemical groups examined in this project, pyrethroids had by far the largest K_d values, with a median value of 502.

The percent organic carbon was the most relevant characteristic for four of the seven test substances in this class. Cation exchange capacity was the most relevant characteristic for two of the test substances. Percent clay was the most relevant characteristic for the final test substance in this class.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	3	0.850	0.543	0.596	0.903	0.036
Compound 2	6	0.002	0.231	0.158	0.006	0.483
Compound 3	5	0.996	0.628	0.081	0.135	0.166
Compound 4	5	0.729	N/A	0.002	0.010	0.003
Compound 5	4	0.332	N/A	0.125	0.997	0.817
Compound 6	5	0.944	0.137	0.261	0.908	0.604
Compound 7	4	0.961	N/A	0.491	0.204	0.356
Average		0.688	0.385	0.245	0.452	0.352

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PYRAZOLES

This class of compounds containing a pyrazole moiety are used as fungicides, insecticides and/or herbicides. These compounds tend to have much lower K_d values than pyrethroids. Ten pyrazoles were included in the dataset, with a median K_d value of 12. For the nine compounds considered separately, percent clay was the most relevant soil characterestic for four of the compounds, with organic carbon content the most relevant for two compounds, and cation exchange capacity, pH in water, and pH in 0.01M $CaCl_2$ the most relevant for one compound each.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	5	0.337	0.409	0.326	0.575	0.637
Compound 2	4	0.880	0.496	N/A	0.731	0.417
Compound 3	4	0.002	0.313	N/A	0.044	0.091
Compound 4	5	0.585	N/A	0.075	0.028	0.795
Compound 5	4	0.945	N/A	0.004	0.997	0.860
Compound 6	4	0.337	N/A	0.111	0.110	0.419
Compound 7	4	0.651	N/A	0.024	0.553	0.805
Compound 8	4	0.019	0.801	0.941	0.462	0.025
Compound 9	5	0.872	0.712	0.068	0.291	0.500
Average		0.514	0.546	0.221	0.421	0.506

AMIDES

Three amide insecticides were included in the data set. Amide insecticides are structurally similar to carbamates but are generally less reactive. These compounds tend to have low K_d values, with a median value of 1.9 for the group.

Unlike the other groups, amides did show some correlation among the entire group. Soil percent organic matter and cation exchange capacity showed the highest correlation to K_d, with r^2 values of 0.67 and 0.43, respectively.

When considered separately, cation exchange capacity was the soil characteristic parameter most correlated to Kd, with r2 values exceeding 0.9 for all three compounds.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	4	0.586	0.065	0.000	0.907	0.751
Compound 2	3	0.277		0.322	0.940	0.806
Compound 3	4	0.991	0.354	0.960	0.997	0.746
Average		0.559	0.496	0.362	0.653	0.591

SULFUR-CONTAINING COMPOUNDS

This group included organothiophosphate insecticides and other related compounds. A total of 14 compounds in this family were studied. Similar to amides, sulfur-containing compounds also tend to have low K_d values, with a median value of 2.4 for the group.

The pH of soil in 0.01M $CaCl_2$ was the soil characteristic most frequently exhibiting the highest correlation to K_d for sulfur-containing compounds, with three test substances yielding r-squared values in excess of 0.7. Percent clay and organic carbon content were the most correlated parameters for two compounds each, and cation exchange capacity was the most correlated for one compound.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	4	0.683	N/A	0.150	0.053	0.784
Compound 2	4	0.004	N/A	0.767	0.197	0.008
Compound 3	4	0.801	N/A	0.001	0.529	0.688
Compound 4	4	0.681	N/A	0.168	0.225	0.736
Compound 5	4	0.146	N/A	0.716	0.007	0.172
Compound 6	4	0.054	N/A	0.828	0.053	0.065
Compound 7	5	0.558	0.089	0.004	0.693	0.246
Compound 8	4	0.971	0.897	0.661	0.625	0.801
Average		0.487	0.493	0.412	0.298	0.438

NITROGENOUS COMPOUNDS (TRIAZOLES, UREAS)

This group included compounds such as triazoles and ureas. A total of 7 compounds in this group were studied. These compounds had moderate K_d values, with a median value of 16 for the group.

The percent organic matter was the soil characteristic most frequently exhibiting the highest correlation to K_d for nitrogenous compounds, with three test substances yielding r-squared values in excess of 0.73. Percent clay and pH in $CaCl_2$ were the most highly correlated parameters for one compound each.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	5	0.017	N/A	0.513	0.003	0.104
Compound 2	4	0.407	0.144	N/A	0.122	0.760
Compound 3	4	0.978	0.100	0.077	0.051	0.011
Compound 4	4	0.773	0.761	0.754	0.087	0.043
Compound 5	5	0.733	0.153	0.083	0.123	0.006
Average		0.582	0.290	0.357	0.077	0.185

OTHER TEST SUBSTANCES

The final group included compounds not linked by specific chemistries, and included antibiotics, organophosphates, and biologics. A total of 7 compounds in this group were studied. These compounds had moderate K_d values, with a median value of 13 for the group.

Unsurprisingly, for such a varied group of chemicals various soil properties were relevant depending on the compound. Organic carbon content, pH in $CaCl_2$, and clay content were the soil characteristics most frequently exhibiting the highest correlation to K_d, with two test substances each. Soil pH in water was the most highly correlated parameter for one compound.

Test Substance	#of Soils	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Compound 1	4	0.619	0.010	N/A	0.452	0.854
Compound 2	3	0.991	0.582	0.979	0.990	0.538
Compound 3	3	0.137	0.175	0.121	0.031	0.265
Compound 4	4	0.762	0.077	N/A	0.001	0.434
Compound 5	4	0.067	0.968	0.992	0.751	0.231
Compound 6	5	0.007	0.399	0.248	0.134	0.170
Compound 7	5	0.701	0.690	0.814	0.274	0.054
Average		0.335	0.462	0.544	0.238	0.231

CONCLUSIONS

Due to the wide range of chemical and soil properties, no definitive correlation was observed between soil characteristics and adsorption coefficients for the data set at large. However, some characteristics were more likely to show correlation to K_d. The results are summarized in the table below.

Based on this set of 39 compounds, organic carbon content was the soil characteristic most frequently correlated with the adsorption properties of the test substance. Percent clay (n=10) was also found to have frequent correlation with K_d. The pH of soil in $CaCl_2$ and cation exchange capacity were less frequently found to be the most relevant soil characteristics for 7 test substances each, and the pH of soil in water was found to be the least relevant soil characteristic, with only 2 test substances showing the highest correlation between this Pyrethrin soil characteristic and K_d.

Instances of highest correlation

Group	# in set	RSQ OC	RSQ pH H20	RSQ pH CaCL2	RSQ CEC	RSQ Clay
Pyrethroids	7	4	-	-	2	1
Pyrazoles	9	2	1	1	1	4
Amides	3	-	-	-	3	-
Sulfur-containing	8	2	-	3	1	2
Nitrogenous	5	3	-	1	-	1
Miscella-neous	7	2	1	2	-	2
Total Instances		13	2	7	7	10