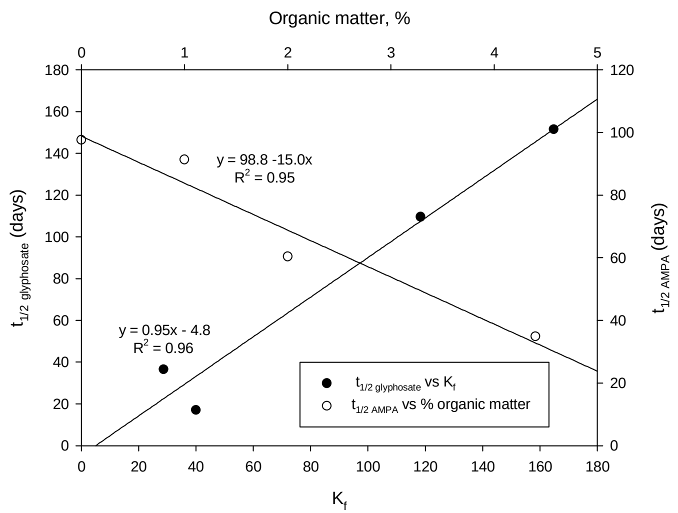
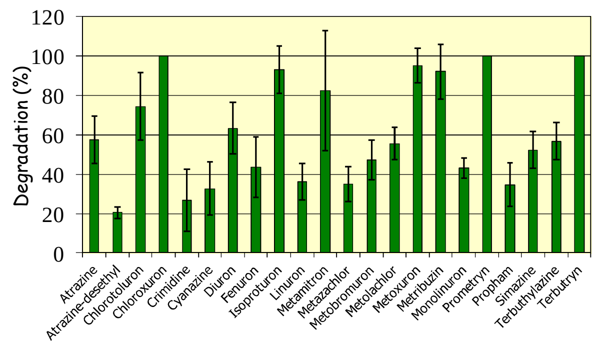
Modelling Variation Of Pesticide Degradation And Sorption In Soil

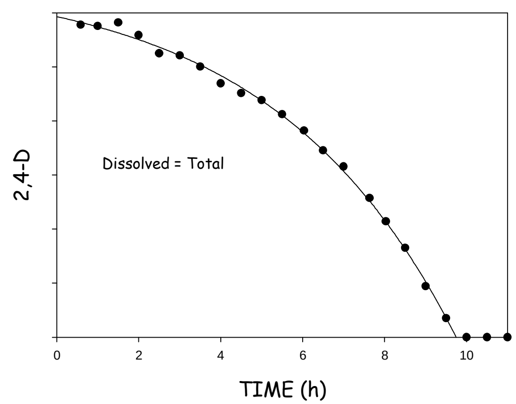
Degradation of glyphosate determned by adsorption



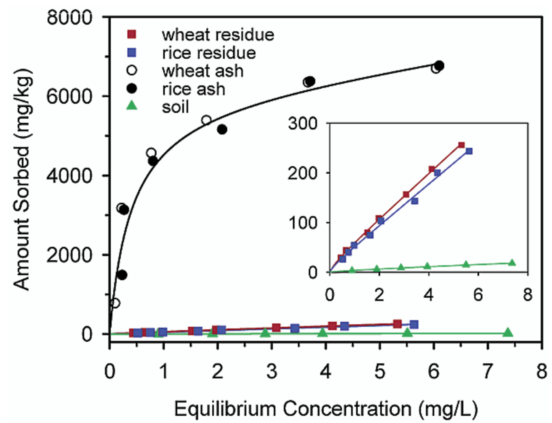
Degradation of AMPA proportional to amount of organic matter. Determined by microbial amount and/or activity?

Microorganisms and enzymes important for degradation of pesticides





Black carbon inportant for adsorption of pesticides.
Clay? Al/Fe-oxides?



$$-\frac{dc}{dt} = kc_a Nq$$

How To Explain Variation In Degradation And Adsorption Of Pesticides In Soil?

- Large variation in degradation and adsorption of pesticides in different soils (e.g. for glyphosate the Pesticide Properties DataBase gives 50% degradation in 4-180 days in agricultural soil)

- No recommendation on how this variation shall be addressed in modelling

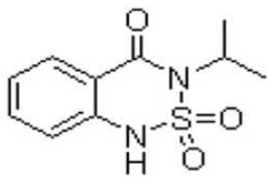
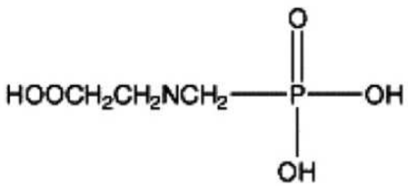
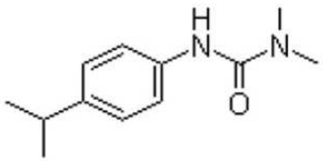
- Degradation and adsorption are among the most influential factors for pesticide losses to surface- and ground waters

- Degradation and adsorption are expensive to measure for large-scale (e.g. catchment, regional) modelling

- In order to explain variation in degradation and adsorption we performed:
  1. An experimental study of the influence of physical, chemical and biological factors on degradation and adsorption of three herbicides (glyphosate, bentazone, isoproturon) in agricultural soils from a small catchment (13 km^2) with large variation in soil properties
  2. A meta analysis of literature data on variation in degradation

Model Substances

Table 2
Selected pesticides and their properties (data from the e-Pesticide Manual (3.0), British Crop Protection Council, 2003).

Herbicides	Structural formulae	pKa	mol wt	Solubility in water (mg L^{-1})
Bentazone		3.3	240.3	570
Glyphosate		2.3, 5.7,10.2	169.1	10,500
Isoproturon		n.a	206.3	65

How To Explain Variation In Degradation And Adsorption Of Pesticides In Soil?

Experimental Study

Table 1
Physico-chemical properties of soils.

Soils	pH	Texture			Textural class	SOC	$CaCO_3$	Total N	Water content at pF_2 (−100 cm)	Geometric mean particle diameter (d_g)	Available P	Available K
		Sand	Silt	Clay								
		%	%	%	International	%	%	%	g/g	mm	mg kg^{-1}	mg kg^{-1}
1	7.6	49	32	18	Loam	1.6	9.2	0.16	0.253	0.095	58	68
2	6.2	87	8	4	Sand	1.2	0.1	0.08	0.115	0.588	63	69
3	7.0	43	27	30	Clay Loam	2.3	0.1	0.22	0.363	0.049	99	116
4	7.1	58	25	17	Sandy Loam	2.1	0.4	0.21	0.3	0.131	89	84
5	6.9	68	17	15	Sandy Loam	2.1	0.2	0.21	0.285	0.199	111	114
6	6.5	70	21	9	Sandy Loam	1.1	0.1	0.09	0.175	0.263	90	120
7	6.5	85	9	6	Loamy Sand	1.6	0.1	0.15	0.169	0.494	159	70
8	7.6	55	28	17	Sandy Loam	2.6	0.2	0.25	0.265	0.118	56	68
9	6.4	12	45	44	Silty Clay	6.7	0.3	0.54	0.643	0.010	57	205
10	6.9	17	54	29	Silty Clay Loam	10.2	0.5	0.87	0.540	0.020	73	170
11	6.9	22	33	45	Clay	2.5	0.9	0.25	0.383	0.014	134	162
12	7.3	56	24	20	Sandy Loam	5.4	0.4	0.53	0.477	0.110	142	209
13	6.0	63	27	10	Sandy Loam	0.9	0.1	0.08	0.240	0.198	132	126
14	6.1	83	11	6	Loamy Sand	1.3	0.1	0.13	0.227	0.460	148	54
15	7.5	35	39	25	Clay Loam	3	0.1	0.28	0.410	0.046	101	97
16	7.1	31	40	29	Clay Loam	1.9	0.2	0.19	0.347	0.033	89	164

Soil samples from 16 places in a catchment were used

Texture from sand to clay,

clay content 4-45 %, organic carbon 0.9-10.2 %

Active Microorganisms (r), Basal respiraion, Microbial Biomass (SIR), Amount OF Ligninolytic Enzymes (MnP, Laccase) And Mineralisation Of ^{14}C-labelled Lignin (k DHP) Were Measured

Table 5
Microbiological characteristics of the soils.

Soils	r	Basal Respiration	SIR	MnP	Laccase	k DHP
	$\mu g\ CO_2$–C $g^{-1}\ h^{-1}$	$\mu g\ CO_2$–C $g^{-1}\ h^{-1}$	$\mu g\ CO_2$–C $g^{-1}\ h^{-1}$	mU $min^{-1}\ g^{-1}$ dw soil	mU $min^{-1}\ g^{-1}$ dw soil	day^{-1}
1	0.172 ± 0.01[a]	0.337 ± 0.023	6.49 ± 1.4	39.93 ± 2.75	614.5 ± 14.84	0.034 ± 0.01
2	0.408 ± 0.15	0.268 ± 0.117	1.75 ± 0.3	55.02 ± 2.76	428.7 ± 0.87	0.033 ± 0.003
3	0.341 ± 0.13	0.39 ± 0.199	3.94 ± 0.5	35.55 ± 2.07	374.4 ± 4.36	0.053 ± 0.004
4	0.356 ± 0.096	0.249 ± 0.12	4.69 ± 1.5	38.96 ±.69	936.6 ± 15.61	0.042 ± 0.002
5	0.088 ± 0.04	0.374 ± 0.098	1.58 ± 1.2	53.08 ± 4.82	248.8 ± 2.62	0.055 ± 0.001
6	0.302 ± 0.12	0.176 ± 0.054	1.54 ± 0.01	53.08 ± 4.82	395.2 ± 13.03	0.036 ± 0.005
7	0.133 ± 0.03	0.148 ± 0.040	1.51 ± 0.6	56.24 ± 4.48	242.4 ± 14.18	0.052 ± 0.002
8	0.581 ± 0.11	0.407 ± 0.017	5.60 ± 0.3	42.12 ± 0.35	980.6 ± 14.84	0.054 ± 0.001
9	2.18 ± 0.72	0.618 ± 0.236	11.02 ± 0.1	149.73 ± 0.34	208.6 ± 4.36	0.054 ± 0.01
10	2.84 ± 0.55	0.799 ± 0.137	6.33 ± 1.2	124.57 ± 1.71	244.3 ± 2.40	0.058 ± 0.04
11	0.532 ± 0.20	0.415 ± 0.154	5.34 ± 0.7	49.10 ± 1.03	712.2 ± 1.96	0.026 ± 0.006
12	0.226 ± 0.08	0.371 ± 0.058	4.79 ± 1.5	156.02 ± 7.87	140.4 ± 11.12	0.074 ± 0.008
13	0.446 ± 0.15	0.460 ± 0.01	1.25 ± 0.5	58.54 ± 0.0	222.8 ± 13.1	0.039 ± 0.0
14	0.161 ± 0.018	0.402 ± 0.001	2.35 ± 0.1	78.86 ± 0.68	145.9 ± 18.33	0.057 ± 0.004
15	0.521 ± 0.091	0.572 ± 0.377	6.52 ± 0.3	53.22 ± 0.68	477.0 ± 3.7	0.043 ± 0.003
16	1.35 ± 0.024	0.737 ± 0.192	10.4 ± 0.8	45.48 ± 0.68	793.5 ± 19.20	0.035 ± 0.01
Mean	0.644	0.421	4.69	68.01	447.9	0.047
CV %	122	44	65	58	62	27

Results

• Large variation in half-lives: Bentazone 20-139 days, Isoproturon 7–63 days, Glyphosate 14–116 days

• Bentazone with pH and active microorganisms (69 %)
• Isoproturon with pH, organic carbon and active microorganisms (42 %)
• Glyphosate with adsorption and laccase activity (88 %)

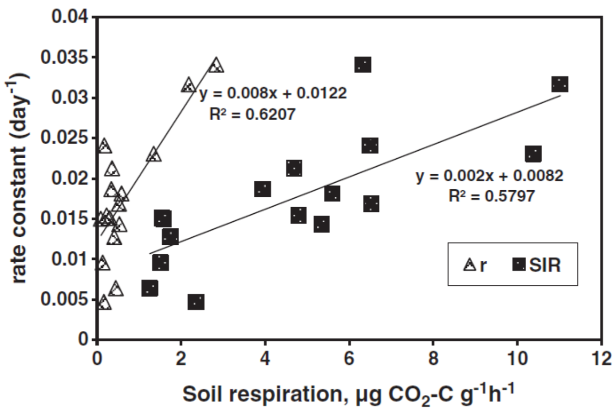


Fig. 1. Relationship between the degradation rate constant k (day^{-1}) for bentazone and microbial respiration rate (r and SIR).

Bentazone: Rate constant vs active microorganisms (r) and biomass (SIR)

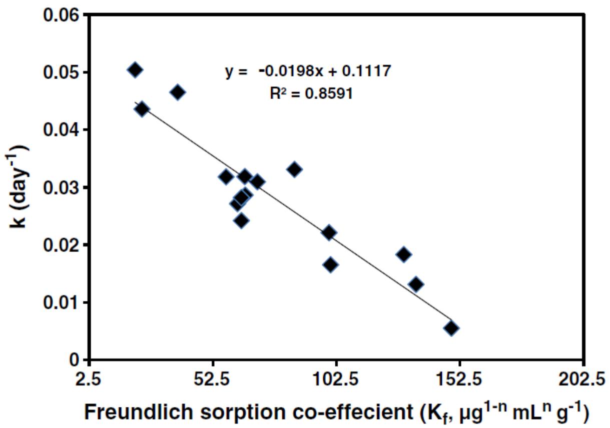
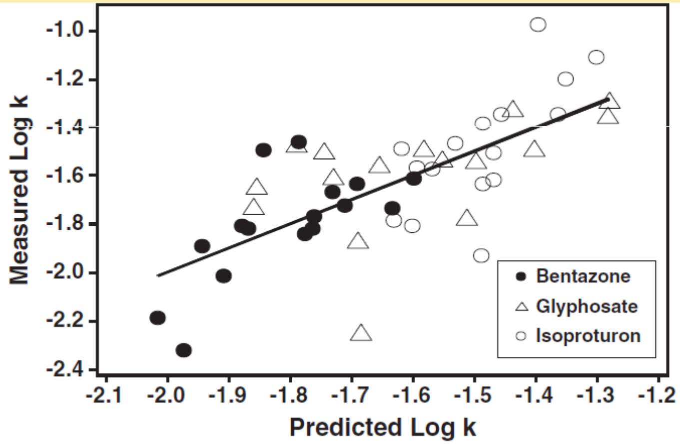


Fig. 2. Relationship between the degradation rate constant k (day^{-1}) for glyphosate and the Freundlich sorption coefficient (K_f, µg^{1-n} mL^n g^{-1}).

Glyphosate: Rate constant vs adsorption (K_f)



Bentazone, Isoproturon, Glyphosate:

$$k = k_{ref} \times K_f^m \times SIR^n \qquad R^2 = 0.50$$

Contents lists available at ScienceDirect
Science of the Total Environment
journal homepage: www.elsevier.com/locate/scitotenv

Measurements and modeling of pesticide persistence in soil at the catchment scale

A. Ghafoor[a,*], N.J. Jarvis[a], T. Thierfelder[b], J. Stenström[c]

[a] Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), P.O. Box 7014, SE-75007 Uppsala, Sweden
[b] Department of Energy and Technology, Swedish University of Agricultural Sciences (SLU), Box 7032, SE-75007, Uppsala, Sweden
[c] Department of Microbiology, Swedish University of Agricultural Sciences (SLU), P.O. Box 7025, SE-75007 Uppsala, Sweden

How To Explain Variation In Degradation Of Pesticides In Soil? Meta-Analysis Of Literature Data

- The experimental study showed that a multiplicative model with variables for microbial biomass and bioavailability (adsorption) explained up to 50 % of the variation in the persistence of bentazone, isoproturon and glyphosate

- How does this model work for other pesticides?

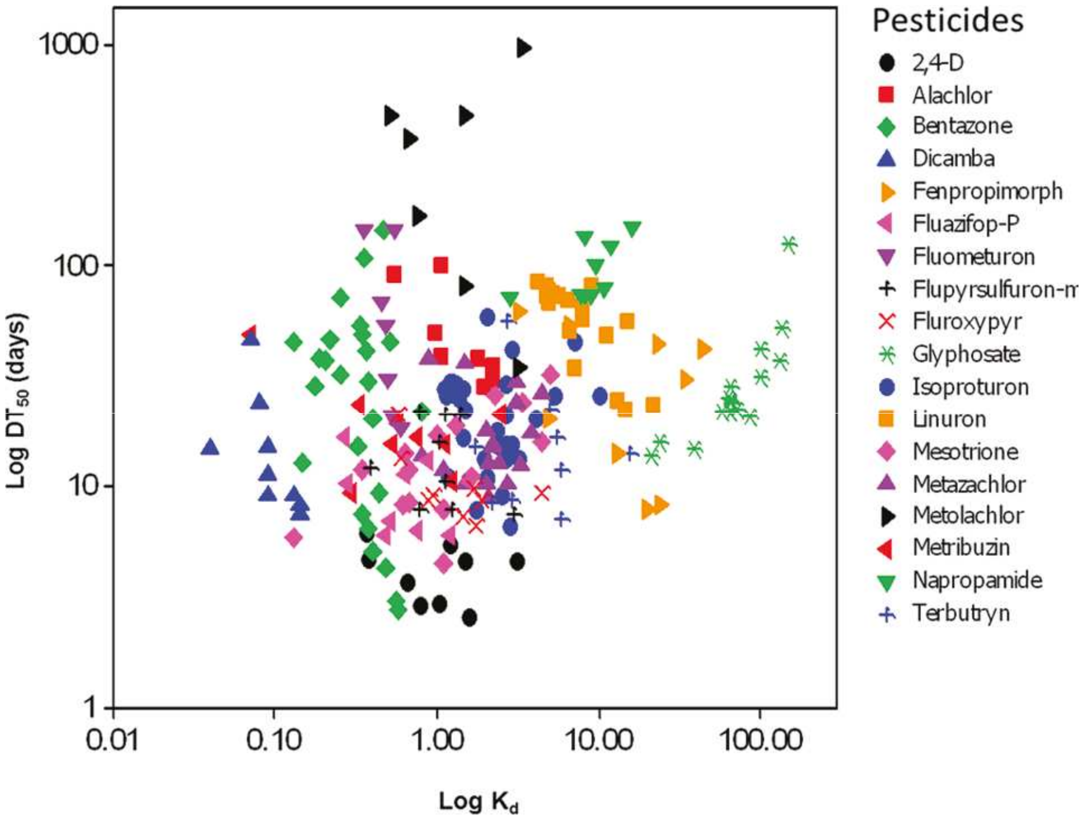
- A meta-analysis of literature data was done

Table 1. Summary of the Studies Included in the Database

study	compound	microbial parameter	number of soils (per substance)	experimental moisture conditions
Walker and Thompson [45]	linuron	basal respiration	18	"field capacity" (initially air-dried for 48 h)
Walker et al. [46]	napropamide		9	−33 kPa
Allen and Walker [14]	metazachlor	basal respiration	18	−33 kPa (initially air-dried for 24 h)
Mueller et al. [38]	fluometuron	biomass, basal respiration[a]	7	−50 kPa
Walker et al. [13,f]	alachlor	biomass, basal respiration[a]	8	−33 kPa
Walker et al. [5,f]	isoproturon	biomass[a,b,c]	10[d]	0.098 g g^{-1} (−33 kPa)
Dyson et al. [19]	mesotrione		15	−30 kPa[e]
Kah et al.[40] Kah and Brown [47]	2,4-D, dicamba, fluoroxypyr, fluazifop-P, flupyrsulfuron-methyl, metribuzin, fenpropimorph, terbutyn	dehydrogenase activity	9	−33 kPa
Larsbo et al. [33]	isoproturon, bentazone		9	60% of WHC[g]
Si et al. [39]	metolachlor	biomass[a,b,c]	7	60% of WHC[g]
Ghafoor et al. [8]	bentazone, isoproturon, glyphosate	biomass, basal respiration[c]	16	−10 kPa

[a] By fumigation−incubation. [b] By fumigation−extraction. [c] By substrate-induced respiration. [d] Locations showing metabolic degradation were excluded. [e] Water contents estimated using the pedotransfer function derived by Oosterveld and Chang.[48] [f] Clay content not available. [g] Water holding capacity (WHC).

A Literature Search Gave 11 Studies With 230 DT_{50}/K_d-Values For 18 Different Pesticides



Useable data gave large variation in DT_{50} och K_d-values

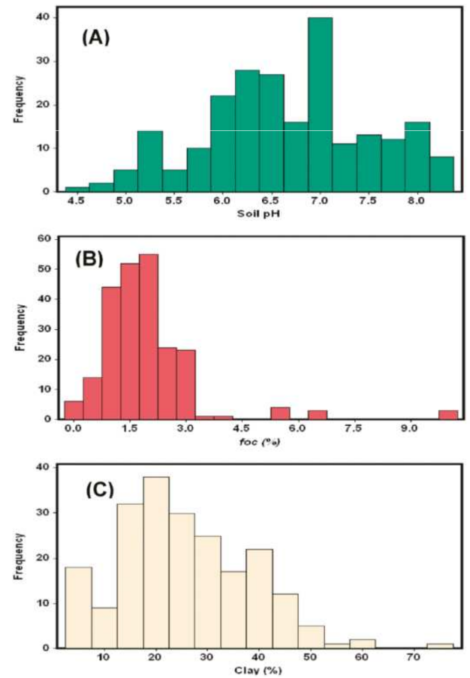


Figure 3. Histograms of the (A) soil pH, (B) soil organic carbon content (f_{oc}), and (C) soil clay content for the soils in the database.

Useable data gave large variation in pH, organic carbon and clay content

Model

$$k = k_{ref} F_L M_b$$

k = rate constant
k_{ref} = pesticide-specific parameter
F_L = bioavialability
M_b = microbial biomass

M_b often not available, especially not in large-scale modelling

$$k = k_{ref} F_L f_{oc}^n$$

f_{oc}=fraction organic carbon, proxy variable for M_b

An Interesting Result

• Some studies show increased degradation rates with increasing amounts of organic material in soil, other studies show the opposite

Is due to competing effects of the soil organic material on persistence:

- Increasing amounts increase microbial biomass and activity but decreases degradation due to increasing sorption

$$k = k_{ref} F_L f_{oc}^n$$

$$F_L = \left(\frac{1}{m_g + f_{oc} K_{oc}} \right)$$

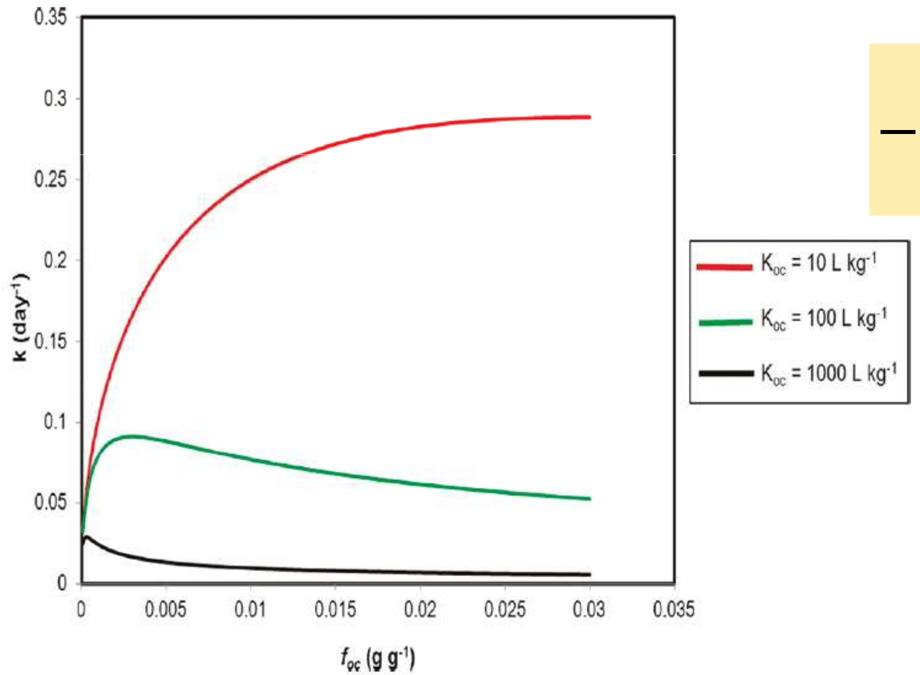
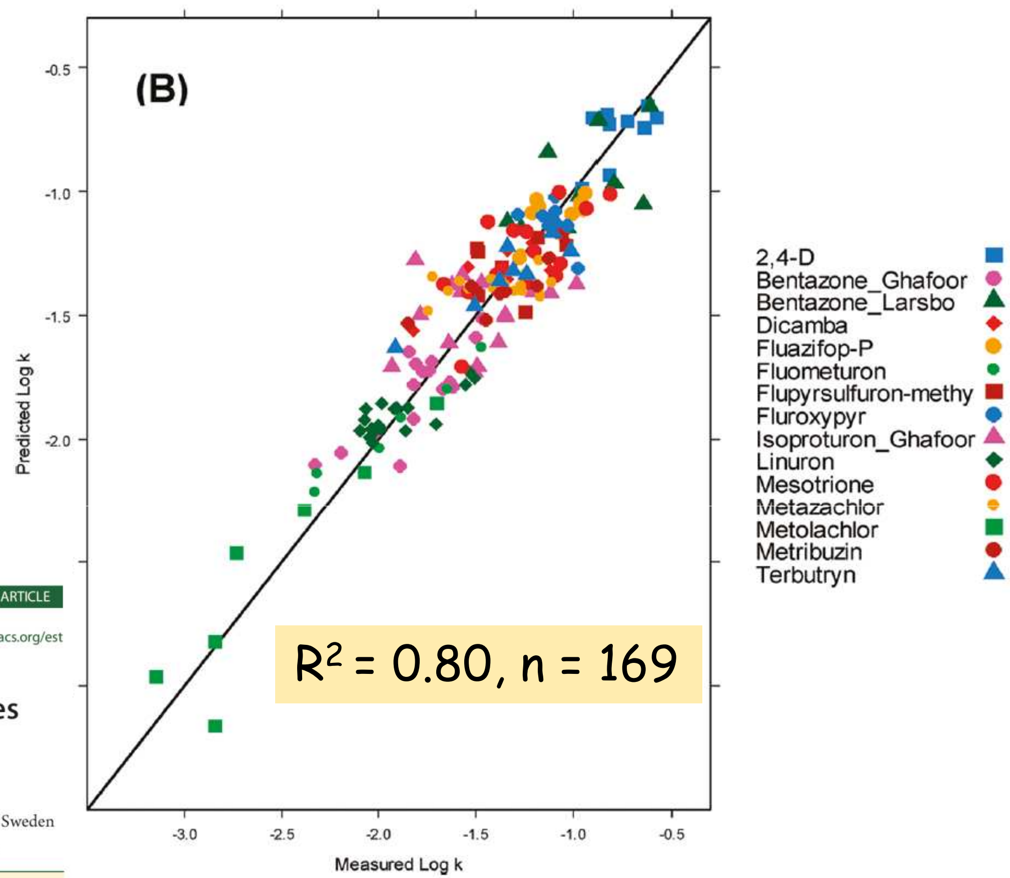


Figure 1. Degradation rate constant predicted as a function of the soil organic carbon content for pesticides of contrasting K_{oc} values, calculated with eq 6 assuming that $K_d = f_{oc} K_{oc}$ (with $m_g = 0.3$ g g^{-1}, $n = 0.5$, and $k_{ref} = 1$ L kg^{-1} day^{-1}).

$$-\frac{dc}{dt} = k c_a N q$$

Results

$$k = k_{ref} F_L^m f_{oc}^n f_{clay}^p \left(\frac{z_r}{z} \right)^q$$



$R^2 = 0.80$, n = 169

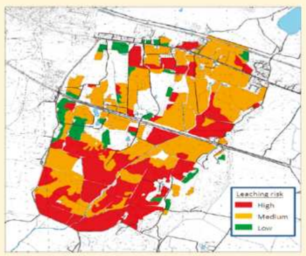
Environmental Science & Technology ARTICLE
pubs.acs.org/est

Modeling Spatial Variation in Microbial Degradation of Pesticides in Soil

Abdul Ghafoor,*,† Julien Moeys,† John Stenström,‡ Grant Tranter,† and Nicholas J. Jarvis†

†Department of Soil and Environment, Swedish University of Agricultural Sciences (SLU), P.O. Box 7014, 750 07 Uppsala, Sweden
‡Department of Microbiology, Swedish University of Agricultural Sciences (SLU), P.O. Box 7025, 750 07 Uppsala, Sweden

ABSTRACT: Currently, no general guidance is available on suitable approaches for dealing with spatial variation in the first-order pesticide degradation rate constant *k* even though it is a very sensitive parameter and often highly variable at the field, catchment, and regional scales. Supported by some mechanistic reasoning, we propose a simple general modeling approach to predict *k* from the sorption constant, which reflects bioavailability, and easily measurable surrogate variables for microbial biomass/activity (organic carbon and clay contents). The soil depth was also explicitly included as an additional predictor variable. This approach was tested in a meta-analysis of available literature data using bootstrapped partial least-squares regression. It explained 73% of the variation in *k* for the 19 pesticide−study combinations (*n* = 212) in the database. When 4 of the 19 pesticide−study combinations were excluded (*n* = 169), the approach explained 80% of the variation in the degradation rate constant. We conclude that the approach shows promise as an effective way to account for the effects of bioavailability and microbial activity on microbial pesticide degradation in large-scale model applications.



Environ. Sci. Technol. 2011, 45, 6411–6419

How To Explain Variation In Adsorption Of Pesticides In Soil?

Experimental Study

- Sorption important for binding, leaching, transport

- Models very sensitive to magnitude of sorption coefficient

- K_{oc} often used in models, *i.e.* that it is constant for a certain compound. However, bad prediction of adsorption using K_{oc} for compounds that preferentially adsorb on inorganic soil constituents and in soils with low concentrations of organic material, *e.g.* subsoil

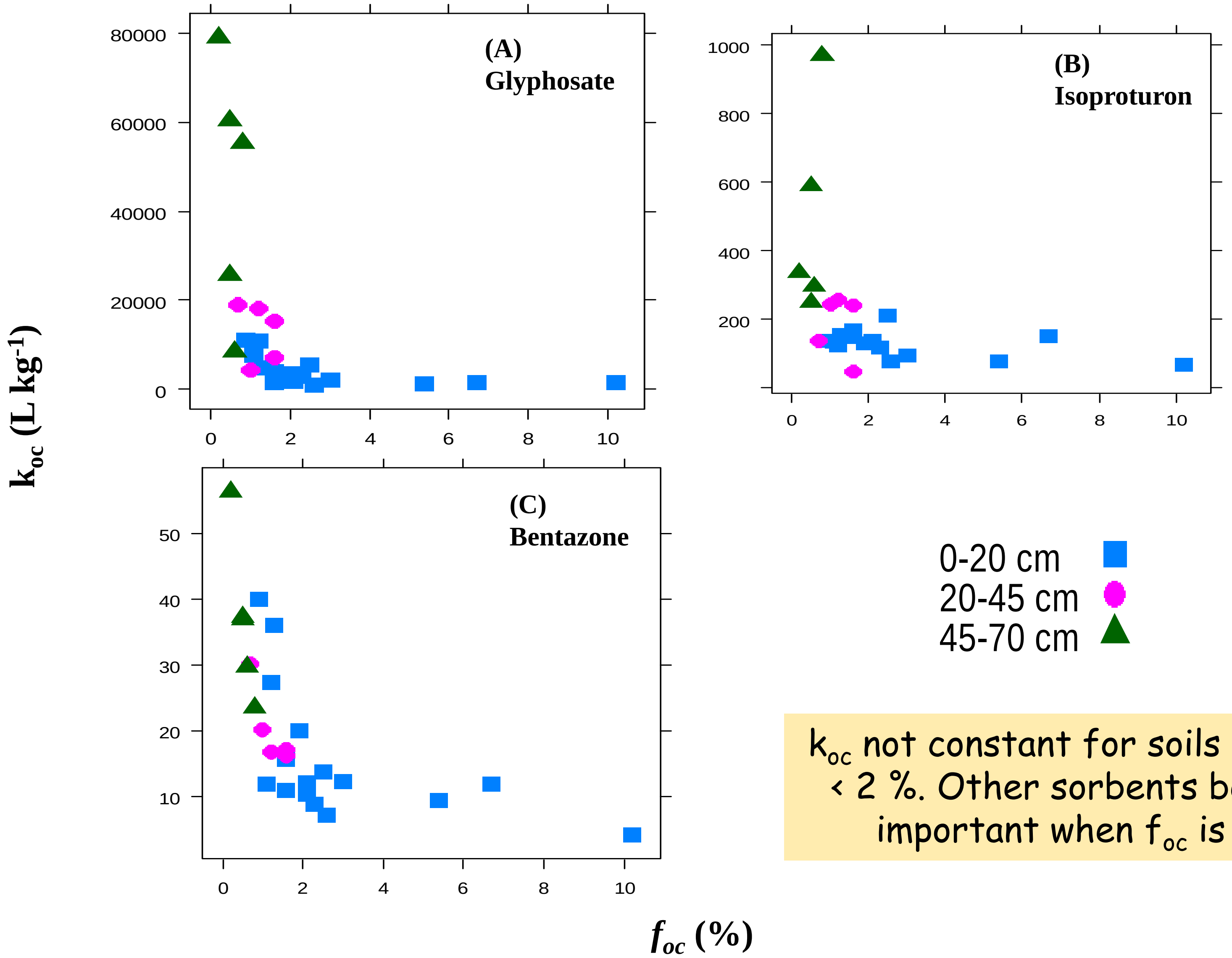
- Sorption of the test substances glyphosate, bentazone and isoproturon was measured in the same topsoils as were used in the degradation study

- In addition, sorption was measured in subsoils from some of these topsoils

Properties Of The Subsoils

Soil depth	Soils	pH (H2O)	Texture			Textural class	f_{oc}	f_{clay}/f_{oc}	$CaCO_3$	Available P	$f_{(Al_{ox}+Fe_{ox})}$	CEC
			Sand	Silt	Clay							
cm			%	%	%	International	%	%	%	mg kg^{-1}	%	cmol kg^{-1}
20-45	Soil 2	5.62	89	7	3	Sand	0.70	4.46	0.20	45.55	0.296	3.23
	Soil 5	7.10	62	19	19	Sandy Loam	1.20	15.24	0.10	107.24	0.314	11.49
	Soil 11	6.94	19	32	49	Clay	1.60	29.68	0.10	45.05	0.499	24.23
	Soil 14	7.28	80	13	7	Sandy Loam	1.00	6.58	0.90	95.65	0.151	12.65
	Soil 15	7.22	34	32	35	Clay Loam	1.60	21.66	0.10	74.31	0.405	19.14
45-70	Soil 2	6.55	88	9	3	Sand	0.20	16.79	0.50	25.87	0.204	2.69
	Soil 5	7.56	57	20	23	Sandy Clay Loam	0.50	44.78	0.10	138.52	0.277	10.71
	Soil 11	7.36	14	34	53	Clay	0.80	70.22	0.10	53.75	0.397	24.08
	Soil 14	7.96	60	27	13	Sandy Loam	0.60	22.07	3.50	34.81	0.158	15.91
	Soil 15	7.60	30	27	44	Clay	0.50	91.27	0.10	152.45	0.362	19.13

Relation Between k_{oc} And Amount Of Organic Carbon, f_{oc}, For Glyphosate (A), Isoproturon (B), And Bentazone (C) In Top- and SubSoil



k_{oc} not constant for soils with f_{oc} < 2 %. Other sorbents become important when f_{oc} is low

Estimated Parameter Values And Their Significance For Different Models That Explain Adsoption Of Bentazone And Isoproturon According To Eq (2), And Glyphosate According To Eq (3)

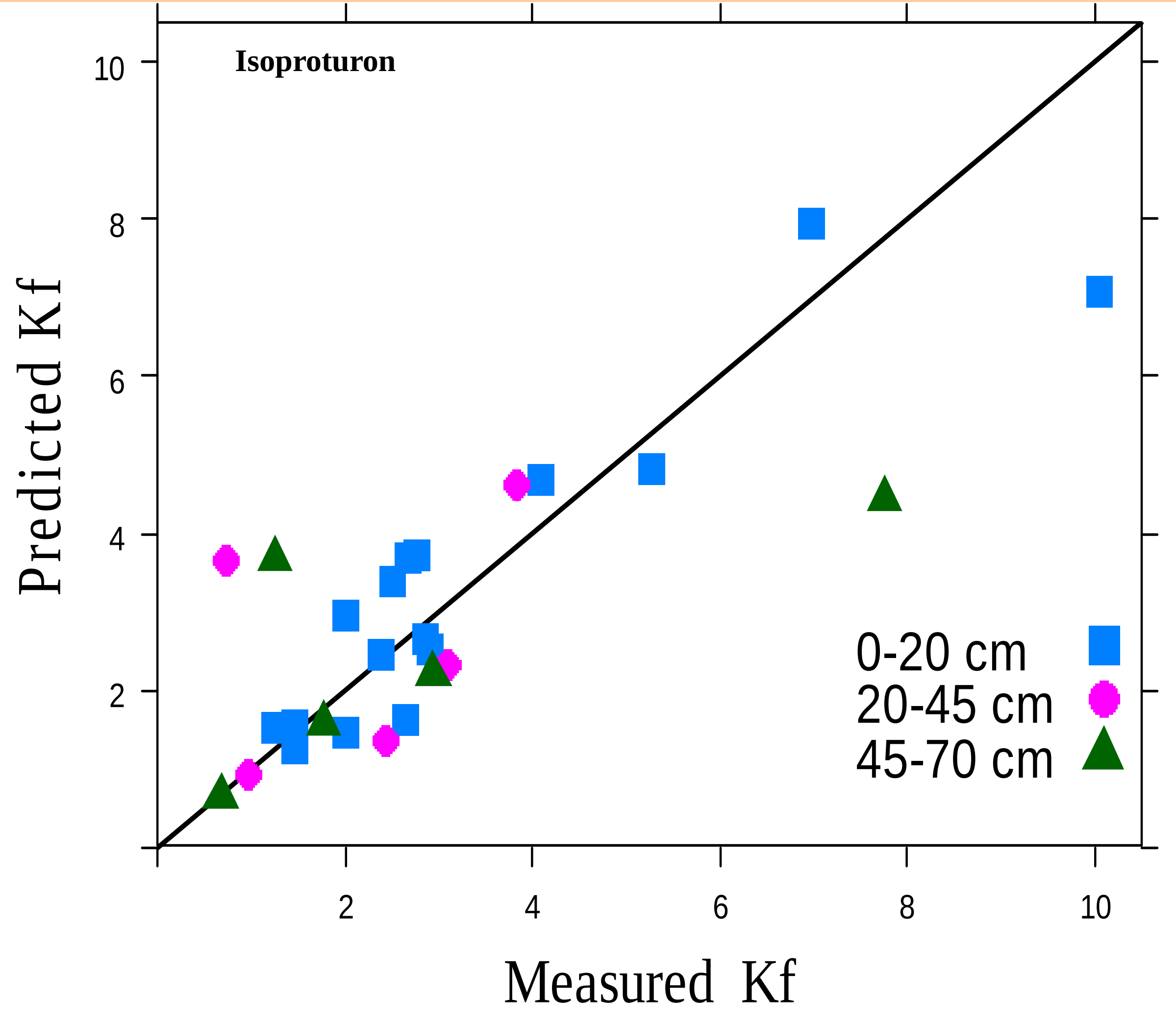
$$K_f = \left(\frac{pH_{ref}}{pH}\right)^n \cdot \left(\sum_{i=1}^{m} f_i \, . \, k_i\right) \quad (2)$$

$$K_f = \left(\frac{pH_{ref}}{pH}\right)^n \cdot \left\{k_{oc} f_{oc} + \left(\frac{f_{oc(ref)}}{f_{oc}}\right) . \sum_{i=1}^{m} f_i \, . \, k_i\right\} \quad (3)$$

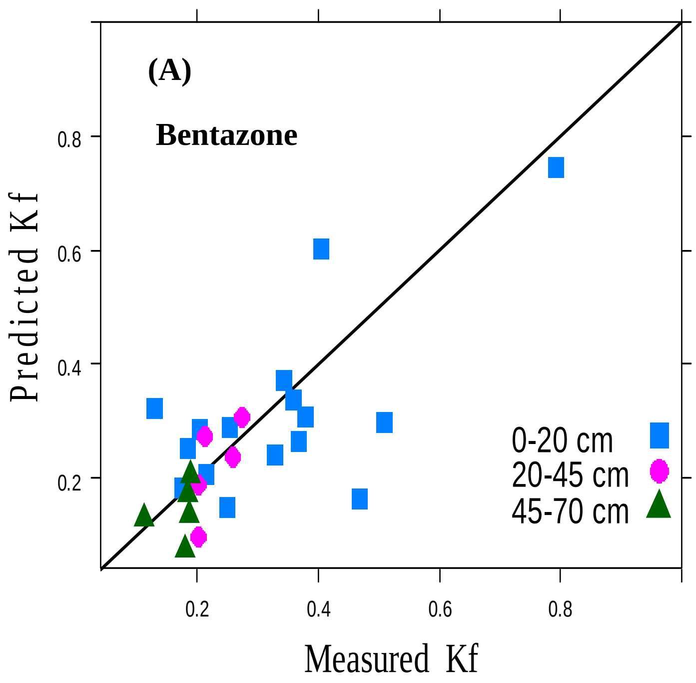
Organic material can cover and thereby mask the effect of other adsorbents

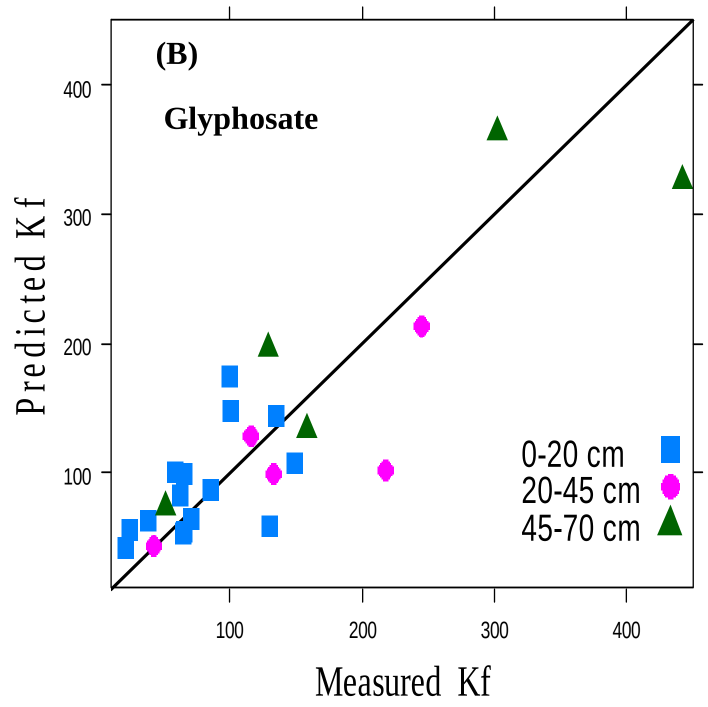
Models	Compound	Equation	Parameter estimates				Performance
			k_{oc}	k_{clay}	k_{ox}	n	RMSE
	Isoproturon						
1		2	67.7***	-	-	-	1.64
2		2	55***	6.94**	-	-	1.30
3		2	49***	8.55***	-	3.11*	1.18
	Bentazone						
4		2	4.35***	-	-	-	0.12
5		2	7.50***	-	-	6.40**	0.14
6		2	2.41*	-	53***	2.05*	0.11
	Glyphosate						
7		3	-	496***	-	-	76
8		3	-	683***	-	5.85***	54
9		3	824*	624***	-	5.1***	48

Relation Between Measured And Predicted K_f For Isoproturon With The Parameters OC And Clay



Relation Between Measured And Predicted K_f For (A) Bentazone With The Parameters OC, OX And pH And (B) Glyphosate With The Parameters OC, Clay And pH





Conclusions

- Inorganic sorbents dominated sorption in sub-surface soils

- The sorption by inorganic sorbents were only masked by organic matter in surface soils with organic carbon contents larger than about 2 %

- Interactions between organic and inorganic sorbents affected glyphosate sorption