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ARTICLE

Sorption Characteristics of Atrazine and Imazethapyr in Soils of New Zealand: Importance of Independently Determined Sorption Data

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We investigated sorption characteristics of two commonly used herbicides, atrazine and imazethapyr, in 101 soils with allophanic and non-allophanic clays of New Zealand using the batch equilibration technique. Soil properties, such as organic carbon (OC) content, texture, pH, amount and type of clay, and cation-exchange capacity (CEC), were tested against the sorption coefficients (K_d) of these herbicides. There was a wide variation in the sorption affinities of the soils, as the K_d values of atrazine and imazethapyr ranged from 0.7 to 52.1 and from 0.1 to 11.3 L kg^{-1}, respectively. For atrazine, the sorption affinities for the allophanic set of soils (mean K_d of 8.5 L kg^{-1}) were greater than for the non-allophanic set of soils (mean K_d of 7.5 L kg^{-1}). However, no effect of allophanic status was found for imazethapyr sorption (mean K_d of 0.82 and 0.76 L kg^{-1} for allophanic and non-allophanic, respectively). None of the measured soil properties could alone explain adequately the sorption behavior of the herbicides. The variation of OC soil sorption coefficients, K_{oc}, was also larger for atrazine (mean K_{oc} of 126.9 L kg^{-1}) than for imazethapyr (mean K_{oc} of 13.2 L kg^{-1}). The prediction equations for atrazine and imazethapyr developed overseas failed to provide the acceptable values of sorption coefficients for the soils of New Zealand. The study highlights the danger of using sorption coefficient data from the literature for practical assessments of the herbicide leaching in New Zealand soils.

KEYWORDS: Allophanic; non-allophanic; sorption coefficient; K_d; K_{oc}; risk assessment

INTRODUCTION

Sorption is one of the major processes affecting the fate of herbicides in the soil. Although there is a great body of information in the literature on sorption of herbicides in soils of various countries (*1*−*5*), there are only a few reports available on the sorption of these chemicals in New Zealand soils that are physicochemically distinct from many soils elsewhere (*6*). The soil pattern associated with this country's landscape is complex, partly because of the different kinds of parent materials and partly because of the varied conditions under which they have been transformed into soils (*7*). Therefore, information on the sorption behavior of commonly used herbicides is essential for better understanding and predicting their mobility in New Zealand soils.

Various simulation models have been developed and widely used for predicting pesticide behavior in soil and their transport through the soil profile. The sorption coefficient (K_d) is a measure of the extent of interaction of the chemical with soil and its components and is a salient characteristic that plays an important role in these models (*8*). Soil characteristics, such as pH, particle size distribution or texture, amount and type of clay, and amount and quality of organic carbon (OC), vary widely between agroclimatic regions (*9*). Despite soil composition heterogeneity, most theoretical descriptions of herbicide sorption have been based on the predictive models that use average K_d values (*10*). Moreover, studies to predict herbicide fate and leaching potential often lack direct measurements of K_d, and therefore, it is common practice to use data from the literature, usually mean values calculated from a database or best estimates selected by experienced personnel, such as those provided by Wauchope et al. (*11*). These and other values of soil properties contained in such databases are used in computer models (*12*, *13*) and decision-aid models (*14*). The K_d values are also often predicted from soil properties, such as soil OC content (*6*). The mean values of such variables obtained from diverse soil environments are usually associated with a large standard deviation or error, as illustrated by the tabulated data by Weber et al. (*15*).

The sorption coefficient is not always a constant. It depends in a complex, poorly understood way upon experimental conditions and other factors, such as the nature of soil organic matter (SOM), that can produce a wide range of values for this variable even for non-ionic, hydrophobic compounds (*16*). For ionizable compounds, the contribution and subtle interplay of several additional factors, such as the amount and type of clay, pH, and cation-exchange capacity (CEC), may also exacerbate the difficulties in extrapolating sorption coefficient values. Therefore, predictions based on the published sorption coefficient data that

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do not necessarily represent local soils may lead to erroneous estimates of sorption coefficients and, consequently, the risk assessment based on these values. Thus, knowledge on various soil properties that influence herbicide sorption in soil is critical to identify soil−herbicide behavior with varying degrees of risk for groundwater contamination. Furthermore, use of independently determined data may result in a better prediction of the fate and transport of these herbicides in the soil.

The objectives of the present study were (1) to investigate the sorption affinities of two commonly used herbicides, atrazine and imazethapyr, in an extensive range of soils from the North and South Islands of New Zealand, (2) to evaluate the soil characteristics that influence the sorption of these herbicides, and (3) to assess if extrapolation of sorption data from other regions is acceptable for local soils.

MATERIALS AND METHODS

Description of Sites and Soils. A total of 101 surface soils (0−7.5 cm) from North (soils 1−55) and South (soils 56−101) Islands of New Zealand with no recent history of application of atrazine and imazethapyr were sampled and characterized. The soils represented a wide range of characteristics, with OC ranging from 19.9 to 418.8 g kg^{-1}, pH ranging from 4.4 to 6.9, clay ranging from 0 to 660 g kg^{-1}, and CEC ranging from 3.5 to 41.2 milliequiv 100 g^{-1} (**Table 1**). Among these soils, 50 soils contained allophane clay, whereas 51 soils were non-allophanic.

Herbicides. Atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine), and imazethapyr [(*R*,*S*)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid] were obtained from Dr. Ehrenstorfer, GmbH, Germany, and were of $>99\%$ purity. For the soil pH range used in this study (pH 4.4−6.9), atrazine can be considered as a weak base/neutral molecule. Imazethapyr is a weak acid with a pK_a value of 3.9. Their chemical structures are shown in **Figure 1**.

Herbicide Sorption Studies. Sorption of atrazine and imazethapyr from aqueous solution was determined at 22 ± 2 °C employing the batch equilibration method, using 0.01 M $CaCl_2$ as a background electrolyte. Two sets of measurements were made, both in duplicate. The first set, for determination of sorption isotherms for the herbicides, used solution concentrations of 1.0, 2.5, and 5.0 mg L^{-1} for atrazine and 0.1, 0.2, 0.4, and 0.6 mg L^{-1} for imazethapyr. The second set employed a single solution concentration (2.5 mg L^{-1} for atrazine and 0.4 mg L^{-1} for imazethapyr). Isotherm measurements from the first set allowed for an evaluation of the assumption of sorption linearity (*17*). Duplicate soil samples were equilibrated with herbicide solutions at the soil solution ratios of 1:5 by being shaken for 16 h in glass tubes sealed with Teflon-lined caps. An equilibration time of 16 h was found to be sufficient to attain solution equilibrium (*3*). At the end of the equilibrium period, the suspension was centrifuged for 20 min at 590 g and the supernatant solution was filtered through RC25 (diameter of 25 mm and pore size of 0.45 μm) microfilters (Sartorius Australia, Victoria, Australia).

The herbicide concentrations in solution were determined by a Schimadzu SCL-10A high-performance liquid chromatograph (HPLC) equipped with a UV/vis detector and a Maxima chromatography workstation. For both herbicides, the analytical column used was Prodigy (150 × 4.6 mm) packed with 5 μm octadecylsilane (ODS) (*3*) held at 35 °C (Phenomenex, Torrence, CA). For atrazine, the mobile phase was 60:40 methanol/water; for imazethapyr, it was 44:56 methanol/water containing 0.5% (v/v) acetic acid and 1-hexanesulfonic acid (0.3%, w/v) as an ion-pairing agent. HPLC analyses were run isocratically, with a sample injection volume of 50 μL and flow rate of 1 mL min^{-1}. Detection was at 230 and 254 nm for atrazine and imazethapyr, respectively. Under these conditions, the retention time for atrazine was 7.0 min and the retention time for imazethapyr was 8.4 min. To maximize instrumental sensitivity, the wavelengths for absorption of each herbicide were previously established (spectra not shown) using a polychrom diode array UV detector (Varian 9065).

Herbicide sorption at equilibrium was calculated as the difference in herbicide concentrations between the initial solution and the solution at equilibrium with soil. Blanks that included each of the soils with only 0.01 M $CaCl_2$ solution (no test chemical) and a single control of the test chemical solution with no soil were also performed to check for analytical interference because of soil extracts and compound loss resulting from the interaction with experimental materials.

Determination of Sorption Coefficients. The sorption coefficients (K_d, L kg^{-1}) were determined from either the slope of the linear plots of sorbed *v* aqueous herbicide concentrations or the single solution concentration of each herbicide. The sorption coefficients were also normalized to OC (K_{oc}).

RESULTS AND DISCUSSION

Soil Characteristics. The soils used in this study varied widely in their physical and chemical properties (**Table 1**). The presence of allophane or humus aluminum complexes, as determined by a positive reaction to the NaF kit developed by Fieldes and Parrott (*18*), showed that many of the North Island soils (42 samples) contained allophane clay. Allophane was also found to be present in 8 soils from the South Island. Allophane occurs commonly in volcanic terrains, such as in the North Island of New Zealand, and is typically associated with the weathering of volcanic ash (tephra) deposits in humid, temperate environments (*19*). However, it can also occur in other climates (*20*) and on non-volcanic materials under certain soil-forming conditions, such as podzolization (*21*). Therefore, finding allophane in South Island soils (remote from volcanic areas) was not surprising, because it can form from silicon and aluminum in acid solution with a pH of about 5 (*22*). Parfitt and Webb (*23*) also found allophane in some soils from the South Island that contained Al/Si mole ratios between 1.8 and 2.8, indicating that the allophane in these soils largely has an imogolite-like structure. Two soils (18 and 90) were exceptionally rich in OC (276 and 419 g kg^{-1}, respectively) and were organic soils. These soils were treated as outliers in the regression analyses.

Sorption of Atrazine and Imazethapyr. Atrazine and imazethapyr sorption isotherms constructed for 7 selected soils (soils 1, 2, 3, 4, 5, 6, and 101) were linear over the concentration range used and showed good fit to the measured data with a r^2 value >0.97 (isotherms not shown). Therefore, to determine the sorption coefficients for the other soils, we used single solution concentrations of each herbicide. The sorption coefficients, K_d (expressed as the ratio of the concentration of sorbed herbicide to the aqueous-phase herbicide concentration), for atrazine and imazethapyr are given in **Table 1**. The K_d values of both herbicides were highly variable over the set of soils. Those of atrazine ranged from 0.7 to 52.1 L kg^{-1} (mean of 8.0 L kg^{-1}), and those for imazethapyr ranged from 0.05 to 11.3 L kg^{-1} (mean of 0.89 L kg^{-1}). The magnitude of the K_d values is indicative of moderate to strong sorption for atrazine and very weak to moderate sorption for imazethapyr. These are in concordance with the hydrophobicity of the herbicides, as represented by their respective octanol−water partition coefficient (K_{ow}) values ($\log P = 2.5$ for atrazine and 1.04 for imazethayr at 25 °C).

Values of the sorption coefficient can vary considerably among different soils, because both the properties of the soil and the test substance affect sorption. The ranges of K_d for atrazine reported in the literature include 3.2−8.4 (*24*), 1.7−4.7 (*14*), 3.02−4.09 (*25*), and 1.0−5.5 L kg^{-1} (*2*). For imazethapyr, Ahmad et al. (*3*) reported K_d ranging from 0.02 to 6.94 in 25 soils from Australia and Pakistan. The alkaline soils of Pakistan showed much smaller K_d values for imazethapyr than the soils of Australia. This large range in K_d resulted from different properties of soils with geographical variations.

In the present study, the sorption affinities of atrazine for the allophanic set of soils (mean K_d of 8.5 L kg^{-1}) were greater than for the non-allophanic set of soils (mean K_d of 7.5 L kg^{-1}) ($p < 0.001$). This may be in part due to the strong reactivity of the

Table 1. Soil Characteristics[a] and Sorption Coefficients (K_d and K_{oc}) for Atrazine and Imazethapyr

										atrazine			imazethapyr		
soil	site	soil series	clay type[b]	pH (H_2O)	OC (%)	sand (%)	silt (%)	clay (%)	CEC (milliequiv 100 g^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[d] (L kg^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[e] (L kg^{-1})
1	Dunmore		A	5.1	10.6	11	59	30	24.5	10.6	101	10.6	1.70	16	1.06
2	Gordonton		NA	6.4	2.8	16	39	45	17.6	2.6	92	2.8	0.27	10	0.28
3	Hastings		A	6.3	2.4	2	66	32	21.0	2.8	114	2.4	0.21	9	0.24
4	Rukuhia	Horotiu	A	6.9	5.5	19	58	23	16.8	4.0	74	5.5	0.57	10	0.35
5	Metawhero		NA	6.1	2.0	11	62	27	18.6	2.9	146	2.0	0.43	22	0.20
6	Patumahoe		A	6.5	2.4	5	31	64	16.1	3.4	141	2.4	0.38	16	0.24
7	Ohaeawai	Papakauri	A	5.7	15.6	10	38	52	24.7	11.7	75	15.6	1.58	10	1.56
8	Kaikohe	Awarua	A	5.0	9.2	5	30	65	16.4	13.0	142	9.2	1.52	17	0.92
9	Whangarie heads	Ruakaka	A	5.1	11.5	11	39	50	28.7	12.4	108	11.5	0.87	8	1.15
10	Whangarie	Whakapai	A	5.4	6.5	7	27	66	13.7	11.6	178	6.5	0.63	10	0.65
11	Whangarie	Wharekohe	A	5.6	5.2	32	46	23	13.3	3.3	62	5.2	0.64	12	0.52
12	Wellsford	Whangaripo	NA	5.2	4.8	23	37	40	13.1	1.8	36	4.8	0.64	13	0.48
13	Warkworth	Warkworth	NA	5.5	5.0	14	73	12	12.5	3.9	78	5.0	0.67	13	0.50
14	Kaiwaka	Aponga	NA	5.3	7.8	1	55	43	24.1	10.9	140	7.8	0.83	11	0.78
15	Parakai	Kaipara	A	5.9	7.2	7	36	57	28.4	7.1	98	7.2	0.62	9	0.72
16	Helensville	Red Hill	NA	5.5	7.8	19	42	39	15.2	10.3	132	7.8	0.52	7	0.78
17	Waitao	Waitoa	NA	5.5	7.8	23	38	40	12.7	4.0	52	7.8	0.71	9	0.78
18	Hamilton		NA	5.1	27.6	18	54	29	29.8	52.1	189	27.6	0.64	2	2.76
19	Bruntwood	Horotiu	A	5.6	7.2	45	38	18	10.3	11.5	160	7.2	0.43	6	0.72
20	Hamilton	Te Kowhai	A	5.7	6.7	32	31	36	15.7	3.7	56	6.7	0.50	8	0.67
21	Te Kuiti	Te Kuiti	A	5.5	12.5	14	55	31	12.5	9.3	74	12.5	0.76	6	1.25
22	Whatawhata		A	4.9	8.6	5	36	60	12.9	5.8	68	8.6	1.13	13	0.86
23	Whatawhata		A	4.9	7.0	7	35	58	10.2	6.1	86	7.0	1.17	17	0.70
24	Kuratau	Taupo	A	5.3	9.0	52	41	8	11.2	8.9	99	9.0	1.04	12	0.90
25	Oruanui	Oruanui	A	5.3	7.2	48	43	9	6.2	6.0	83	7.2	0.61	8	0.72
26	Tahorakuri	Taupo	A	5.2	8.9	31	58	11	7.5	7.2	81	8.9	1.28	14	0.89
27	Galatea	Galatea	A	5.3	4.3	68	26	6	7.1	4.3	99	4.3	0.33	8	0.43
28	Kinloch	Oruanu	A	5.2	7.9	40	46	14	7.7	6.6	83	7.9	1.18	15	0.79
29	Kinloch	Oropi	A	5.4	5.2	70	25	6	7.1	3.4	64	5.2	0.63	12	0.52
30	Fielding		A	5.1	10.2	9	55	36	6.1	4.7	46	10.2	1.55	15	1.02
31	Kohinui		NA	5.0	5.1	7	68	25	10.0	4.8	95	5.1	1.55	30	0.51
32	Mangateretere		A	5.6	10.5	29	42	29	15.0	7.6	72	10.5	1.36	13	1.05
33	Awatoto		A	5.4	4.7	18	58	24	11.3	14.0	298	4.7	0.31	7	0.47
34	Porangahau		A	5.3	4.7	7	47	46	13.2	15.0	317	4.7	0.36	8	0.47
35	Mangamutu		A	5.5	7.8	20	46	34	11.4	17.0	217	7.8	0.60	8	0.78
36	Waiouru		A	5.8	3.7	45	31	25	12.9	14.1	375	3.7	0.55	15	0.37
37	Ohukune		A	5.4	5.7	25	50	25	15.1	13.0	227	5.7	0.31	5	0.57
38	Willowford		NA	5.4	6.4	28	45	26	16.2	10.4	162	6.4	0.65	10	0.64
39	Sherenden		A	5.2	4.9	33	43	24	10.2	4.8	98	4.9	0.81	17	0.49
40	Makirikiri South		NA	5.9	4.6	80	9	10	16.0	4.5	98	4.6	0.19	4	0.46
41	Waipowa		A	5.8	3.6	84	10	6	7.4	4.2	118	3.6	0.36	10	0.36
42	Clifton		A	5.5	3.6	35	48	18	12.3	10.3	284	3.6	0.69	19	0.36
43	Takapau		A	5.6	3.7	30	43	27	13.0	12.1	326	3.7	0.88	24	0.37
44	Manutuke	Ponawa	A	5.6	3.8	34	45	21	12.8	7.1	186	3.8	0.22	6	0.38

Table 1. Continued

										atrazine			imazethapyr		
soil	site	soil series	clay type[b]	pH (H_2O)	OC (%)	sand (%)	silt (%)	clay (%)	CEC (milliequiv 100 g^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[d] (L kg^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[e] (L kg^{-1})
45	Manutuke	Ponawa	NA	5.5	5.5	36	48	17	12.0	5.7	105	5.5	0.33	6	0.55
46	Rauweka	Waitaha	A	6.7	2.0	13	54	33	22.5	16.4	821	2.0	0.06	3	0.20
47	Whitiwhiti	Pakarae	A	5.4	4.6	36	47	17	10.2	5.2	115	4.6	0.27	6	0.46
48	Motu	Matawai	A	5.1	8.5	54	40	7	7.9	11.5	136	8.5	0.93	11	0.85
49	Motu	Motawai	A	5.0	7.0	50	46	3	5.7	7.6	109	7.0	1.41	20	0.70
50	Stratford	Stratford	A	5.3	11.0	52	36	11	9.2	8.0	73	11.0	1.50	14	1.10
51	Auroa	Egmont	A	5.8	9.7	32	41	27	17.5	13.0	134	9.7	0.50	5	0.97
52	Pihama	Glenn	NA	5.6	10.0	37	36	28	25.1	14.0	140	10.0	1.31	13	1.00
53	Newall	Opua	A	5.4	14.4	26	45	29	14.7	6.6	46	14.4	1.35	9	1.44
54	Okato	Oanui	A	5.1	19.2	21	50	29	13.1	14.6	76	19.2	1.74	9	1.92
55	Hurford	Punehu	A	5.4	13.4	34	41	25	17.6	10.5	78	13.4	1.31	10	1.34
56	Little River	Barry	NA	5.2	8.2	2	66	31	19.3	5.8	71	8.2	1.77	22	0.82
57	Little River	Pawson	NA	5.1	4.9	7	66	27	10.2	4.2	88	4.9	1.60	33	0.49
58	Brookside	Waterton	NA	5.8	5.2	9	54	38	22.2	8.0	154	5.2	0.66	13	0.52
59	Springston	Temuka	NA	5.9	19.1	6	63	32	41.2	27.8	146	19.1	1.86	10	1.91
60	Springston	Lismore	A	5.7	4.2	28	54	18	11.4	5.5	131	4.2	0.74	18	0.42
61	Dorie	Lismore	NA	5.6	6.5	7	48	45	7.9	4.6	70	6.5	0.96	15	0.65
62	Dromore	Templeton	NA	6.0	3.9	17	58	25	13.7	1.2	31	3.9	0.51	13	0.39
63	Winchmore	Lismore	NA	5.7	3.1	17	62	22	9.8	7.0	228	3.1	0.52	17	0.31
64	Burnham	Lismore	NA	5.4	2.9	11	64	24	9.2	1.0	34	2.9	0.67	23	0.29
65	Rolleston	Wakanui	NA	5.5	4.2	14	58	28	10.9	2.0	48	4.2	0.38	9	0.42
66	Hawarden	Culverden	NA	5.5	4.1	15	58	26	12.5	7.0	169	4.1	0.65	16	0.41
67	Hawarden	Hui Hui	NA	5.4	3.8	31	38	31	16.4	3.9	104	3.8	0.71	19	0.38
68	Hawarden	Lismore	A	5.1	2.9	23	55	22	6.8	9.0	306	2.9	1.61	55	0.29
69	Ikamatua	Hokitika	NA	5.8	2.6	69	30	2	6.5	0.7	26	2.6	0.58	22	0.26
70	Rotomanu	Hokitika	A	4.9	3.6	1	95	4	4.9	10.0	279	3.6	0.76	21	0.36
71	Greymouth	Mohinapua	A	4.7	11.5	18	34	48	19.9	7.8	68	11.5	1.08	9	1.15
72	Ikamatua	Ahaura	NA	4.7	6.4	10	79	12	9.4	16.0	250	6.4	1.65	26	0.64
73	Kokatahi	Waiuta	NA	5.2	4.9	51	42	7	4.5	3.0	61	4.9	0.52	11	0.49
74	Upper Kowhitirangi	Har Hari	NA	4.5	4.0	20	80	0	3.5	8.0	200	4.0	0.82	21	0.40
75	Outram	Wehenga	NA	5.3	5.3	12	63	26	11.9	7.4	140	5.3	0.57	11	0.53
76	Invermay	Warepa	NA	5.4	5.0	5	71	24	15.4	6.2	123	5.0	0.49	10	0.50
77	Invermay	Warepa	NA	5.7	5.3	5	71	23	18.8	4.7	88	5.3	0.65	12	0.53
78	Alexandria	Lowburn	NA	6.6	2.8	54	38	8	9.9	0.8	29	2.8	0.05	2	0.28
79	Alexandria	Lowburn	NA	5.9	2.0	61	32	7	4.5	2.3	117	2.0	0.12	6	0.20
80	Lumsden	Oreti	NA	5.6	4.5	64	19	17	11.6	9.0	199	4.5	0.42	9	0.45
81	Lumsden	Oreti	NA	5.4	7.3	13	43	44	9.2	9.1	125	7.3	0.91	13	0.73
82	Winton	Pukemutu	NA	5.4	5.8	3	76	21	10.8	5.5	95	5.8	0.83	14	0.58
83	Winton	Oporo	NA	5.4	5.1	10	57	33	14.7	4.0	79	5.1	0.95	19	0.51
84	Winton	Drummond	NA	5.5	4.2	5	67	28	13.6	5.3	124	4.2	0.74	17	0.42
85	Winton	Mataura	NA	5.5	6.4	17	38	45	12.5	5.8	91	6.4	0.99	16	0.64
86	Woodlands	Waikiwi	NA	5.2	8.0	8	67	25	10.3	6.3	78	8.0	1.51	19	0.80
87	Woodlands	Waikiwi	NA	5.9	5.8	5	66	29	14.9	5.7	98	5.8	0.63	11	0.58
88	Woodlands	Waikiwi	NA	5.6	4.8	4	67	29	10.4	1.4	29	4.8	0.29	6	0.48

Table 1. Continued

										atrazine			imazethapyr		
soil	site	soil series	clay type[b]	pH (H_2O)	OC (%)	sand (%)	silt (%)	clay (%)	CEC (milliequiv 100 g^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[d] (L kg^{-1})	measured K_d (L kg^{-1})	calculated K_{oc}[c] (L kg^{-1})	calculated $K_{d\ database}$[e] (L kg^{-1})
89	Woodlands	Waikiwi	NA	5.8	5.9	2	66	32	14.9	5.2	89	5.9	0.86	15	0.59
90	Woodlands	Otanomomo	NA	4.4	41.9	6	68	26	40.4	43.8	105	41.9	11.26	27	4.19
91	Invercargill	Riverton	A	5.6	2.4	98	1	1	7.7	2.4	100	2.4	0.36	15	0.24
92	Gore	Waikoikoi	NA	5.4	4.6	22	50	28	12.8	12.5	274	4.6	0.39	9	0.46
93	Gore	Waikoikoi	NA	5.5	4.0	7	72	21	11.3	1.0	25	4.0	0.52	13	0.40
94	Gore	Kaihiku	NA	5.3	4.6	27	43	30	17.9	3.5	76	4.6	1.24	27	0.46
95	Gore	Kaiwera	NA	5.1	5.0	49	34	17	16.1	3.7	73	5.0	1.43	28	0.50
96	Gore	Kaweku	NA	5.7	4.2	13	52	35	17.1	4.3	102	4.2	0.30	7	0.42
97	Lumsden	Tengawai	A	5.2	6.2	26	47	27	15.4	5.2	85	6.2	0.85	14	0.62
98	Otautau	Monowai	NA	5.4	8.8	58	29	12	9.0	3.0	34	8.8	0.49	6	0.88
99	Te Anau	Monowai	A	5.6	9.1	24	67	9	10.2	7.1	78	9.1	0.55	6	0.91
100	Te Anau	Monowai	A	5.7	7.3	46	37	17	10.0	7.1	97	7.3	0.22	3	0.73
101	Templeton	Templeton	NA	5.1	2.8	8	65	27	16.2	3.8	135	2.8	0.39	14	0.28

[a] Determined by the method described by Fieldes and Perrot (*18*), Rayment and Higginson (*59*), Merry and Spouncer (*60*), and Standard Association of New Zealand (*61*). [b] A, allophanic; NA, non-allophanic. [c] Calculated from $K_{oc} = K_d \times 100/C$. [d] Calculated using the K_{oc} value of 100 L kg^{-1} from the Pesticide Properties Database (*62*). [e] Calculated using the K_{oc} value of 10 L kg^{-1} from the Pesticide Properties Database (*62*).

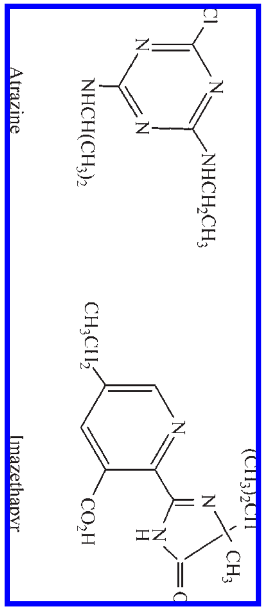

Figure 1. Chemical structures of atrazine and imazethapyr.

allophanic nature of clay and/or the different nature of soil OC within allophanic soils. The large humus accumulation in allophanic soils containing large amounts of amorphous or crypto-crystallized minerals is well-known (*26*) and attributed to very stable humus−Al and Fe complexes (*27*). However, other reports (*28*, *29*) indicate that SOM in allophanic soils may be highly decomposed, which may be, at least in part, responsible for the greater sorption in allophanic soils. Baskaran et al. (*30*) reported that sorption of atrazine in allophanic soils increased after removal of OC, indicating that the allophanic clays may also contribute to the sorption of ionizable herbicides, such as atrazine and imazethapyr.

Effect of Soil Properties on the Sorption of Atrazine and Imazethapyr. *Soil OC.* In general, both herbicides were more strongly sorbed by soils containing more OC than containing less (**Figures 2** and **3**). The OC contents in certain soils (e.g., soils 1, 7, 9, 54, and 59) were most likely responsible for the sorption of atrazine and imazethapyr (K_d range from 10.6 to 27.8 and from 0.87 to 1.86 L kg^{-1} for atrazine and imazethapyr, respectively) in these soils (**Table 1**). Soils 18 and 90 with OC contents of 27.6 and 41.9%, respectively, showed exceptional K_d values for atrazine (K_d = 52.1 and 43.8 L kg^{-1}, respectively) and therefore, being outliers, were excluded from the regression analyses. However for imazethapyr, soil 18 did not show such affinity (K_d = 0.64 L kg^{-1}). The soils 5, 6, 64, 78, and 79 containing OC contents from 2.0 to 2.9% showed smaller sorption capacities, with the K_d values ranging from 0.8 to 3.36 and from 0.05 to 0.62 L kg^{-1} for atrazine and imazethapyr, respectively (with soil 78 being the most weakly reactive for the herbicides). However, this was not consistent for the whole set of soils, and also, neither herbicide demonstrated a similar trend for their affinities. For example, soil 46, containing 2% OC, showed a K_d value of 16.4 L kg^{-1} for atrazine, whereas for imazethapyr, it was just 0.06 L kg^{-1}. It is interesting that soils 92 and 93 originating from the Gore region and apparently having similar properties (**Table 1**) exhibited quite contrasting sorption affinities (K_d values of 12.5 and 1.0 L kg^{-1}, respectively) for atrazine.

Generally, the sorption of weakly basic/neutral (triazine) and weakly acidic (imidazolinone) herbicides in soils has been reported to be related to soil OC (*31*). For example, atrazine sorption was correlated positively to OC in 109 Italian soil horizons (*32*), 5 Wisconsin surface soils (*33*), and 3 surface and subsurface Argentinean soils (*4*). Brouwer et al. (*34*) found a positive linear relationship by plotting K_d values for atrazine from four studies against soil OC. In another study (*35*), no correlation was found between atrazine sorption and OC levels; however, many of the soils had relatively lower soil OC contents compared to the soils in our studies.

In our studies, the variation of K_{oc} values for both herbicides also remains considerable (**Table 1**). The K_{oc} values of atrazine varied greatly with different soils (mean K_{oc} of 127 ± 100 L kg^{-1}) compared to that of imazethapyr (mean K_{oc} of 13.2 ± 7.6 L kg^{-1}). It was also greater for North Island soils (mean K_{oc} of 147 L kg^{-1}) compared to South Island soils (mean K_{oc} of 112 L kg^{-1}) (p < 0.001). However, for imazethapyr, the mean K_{oc} for the South

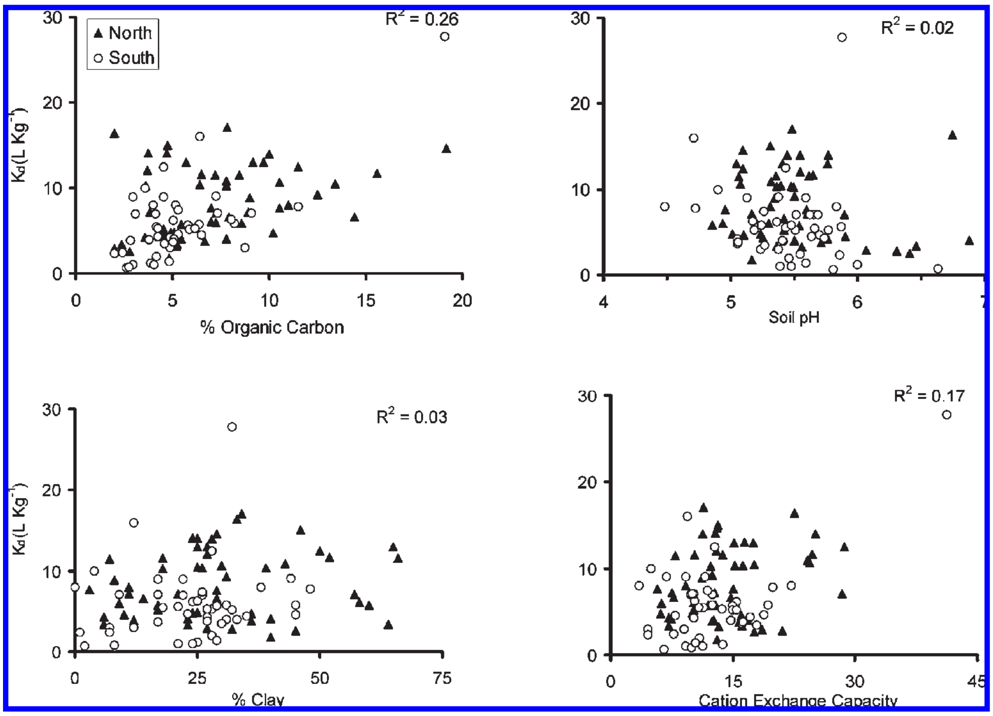

Figure 2. Correlations of different soil properties to K_d values of atrazine in New Zealand soils (excluding soils 18 and 90).

Island set of soils (15.6 L kg^{-1}) exceeded the mean K_{oc} value (11.2 L kg^{-1}) for the North Island set of soils ($p < 0.001$). This shows that the OC content alone does not describe the observed variation in the sorption of this herbicide. If organic matter were the only constituent of soils contributing to sorption, then K_{oc} values would be consistent among the soils and unique to the compound and could be used to compare the relative sorption of various soils. This re-enforces that differences in chemical (structural and molecular) composition of the organic matter in these soils may provide additional information relevant to herbicide partitioning to the SOM. Previously large variations in the SOM composition have been reported in allophanic and non-allophanic soils (*36−38*).

Soil pH. Sorption of both atrazine and imazethapyr in various soils was generally influenced by the soil pH. The pH ranged from 4.4 to 6.9. For acidic compounds, sorption may increase with a decrease in pH as a result of a corresponding increase in the percentage of the undissociated form (*39*). The sorption of imazethapyr was more related to soil pH ($R^2 = 0.28$) than that of atrazine ($R^2 = 0.02$). Soils of low pH (**Table 1**; e.g., soils 1, 5, 9, 18, 70, 71, 72, and 74) showed greater K_d values for atrazine and imazethapyr than the soils having high pH (e.g., soils 2, 3, 4, and 6). Soil 46 having pH 6.7 gave an exceptionally small K_d (0.06 L kg^{-1}) for imazethapyr.

Imazethapyr is a weak acidic herbicide with a pK_a of 2.1 (*40*); thus, it exists predominantly in anionic form under pH conditions near neutral. Generally, at pH above 5.5, sorption of imazethapyr decreased to below 1 L kg^{-1}. Ahmad et al. (*3*) found that imazethapyr sorption decreased as the pH increased in some Australian and Pakistani soils. Renner et al. (*41*) reported decreased sorption of imazethapyr in a Hillsdale sandy loam soil as the pH increased from 3.0 to 8.0. Imazethapyr has an octanol−water partition coefficient (K_{ow}) value of 31 at pH 7. The water solubility of free acid of imazethapyr is 1400 mg L^{-1} (*40*). The water solubility of acidic molecules generally decreases with a decreasing pH and is escorted by an increase in K_{ow}. Therefore, the combined decrease in water solubility and increase in K_{ow} at low pH can result in greater sorption. Atrazine is a weak-base herbicide with a pK_a of 1.7 (*40*), and in acidic conditions, protonization favors sorption onto the negatively charged clay surfaces. For such weakly basic molecules, sorption is sensitive to pH near the pK_a value. Strong sorption is often observed at pH values near pK_a (*1*) because the higher degree of protonation results in increased interactions with the soil matrix because of cation exchange. Therefore, the increased sorption observed in low pH soils may be explained by this protonation. However, many other factors are pH-dependent in the sorption process. For example, the sorption affinities of clays are altered as the pH changes. Cumulatively, such factors yielded a higher sorption of atrazine and imazethapyr below soil pH 5.5. These results are similar to those of a study of the pH effect on imazethapyr sorption by Che et al. (*42*). However, in the present study, there was a poor relationship between soil pH and the K_d values for atrazine ($R^2 = 0.02$) and the influence of pH on imazethapyr sorption was relatively higher ($R^2 = 0.28$). The variations may result from dissimilarities in the chemical properties of the herbicides and interplay of other factors. The lower water solubility of atrazine signifies polarity differences between this chemical and imazethapyr, which might account for the increased sorption affinity of atrazine compared to imazethapyr.

From the practical perspective, the soil reaction or pH of well-managed arable soils in New Zealand is maintained by adding amendments, such as limestone and calcium phosphate, to enhance soil fertility. Consequently, changes in soil pH to beyond 5.5 would have a large effect on the retention of imazethapyr and would attenuate the leaching potential of this weakly acidic herbicide into groundwater. Moreover, soil pH management may be of considerable importance as a remedial or risk management action. When the soil is acidified, an increased retention of imazethapyr can be expected, permitting time for soil elimination processes and preventing groundwater contamination. This may have application in situations where imazethapyr has been accidentally spilled on the soil surface at high concentrations.

Clay. The sorption of atrazine and imazethapyr was independent of the clay content of the soils investigated (**Figures 2** and **3**). Indeed one soil (soil 74), despite having no clay content, showed

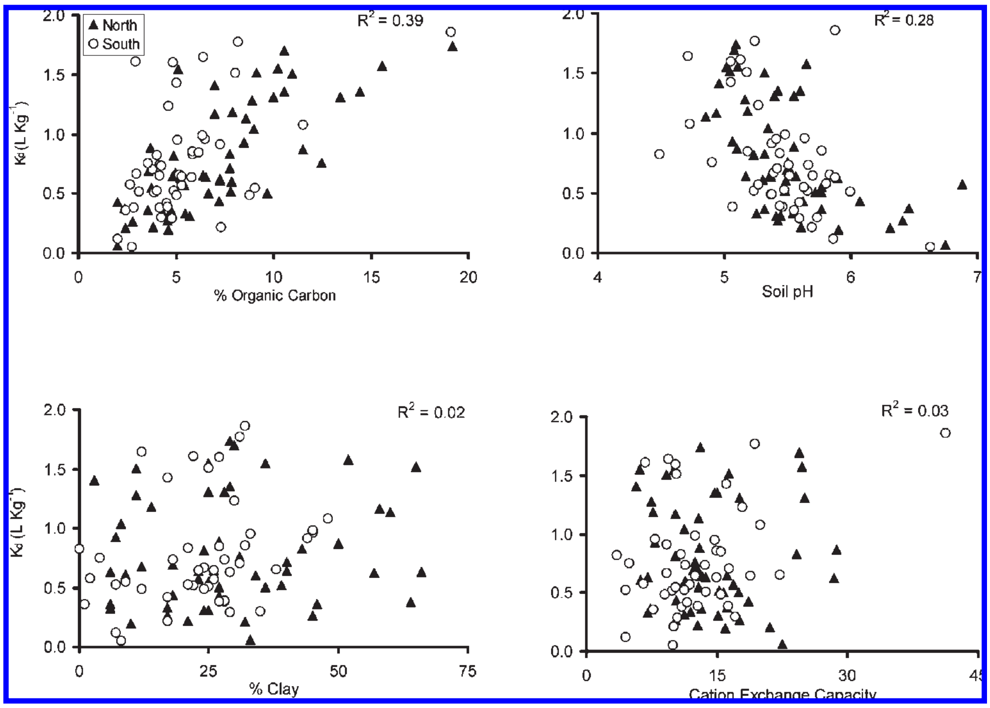

Figure 3. Correlations of different soil properties to K_d values of imazethapyr in New Zealand soils (excluding soils 18 and 90).

K_d values of 8.0 and 0.82 L kg^{-1}, whereas soil 10 containing the most clay (66%) gave K_d values of 11.6 and 0.63 for atrazine and imazethapyr, respectively. Soils 18 and 90 with nearly similar clay contents (29 and 26%, respectively) gave exceptionally great K_d values (52.1 and 43.8 L kg^{-1}, respectively) for atrazine. For imazethapyr, the corresponding values were 0.64 and 11.3 L kg^{-1}. These soils also contained exceptionally great OC (**Table 1**), which in part may be responsible for the increased sorption in these soils. However, in the case of soil 18, imazethapyr sorption was smaller than expected, which could be due to the influence of other factors, such as pH and CEC. Other soils smaller in clay content included soils 24, 27, 29, 41, 48, 49, 69, 70, and 91 (clay content of 1−8%), but the variation in their sorption potentials for the herbicides was large, indicating the interplay of other contributors.

Seybold et al. (*33*) also found no significant correlation between any of the various clay minerals with the sorption of atrazine. In contrast, imazethapyr sorption was reported to be positively correlated with soil clay content (*39*). We generally found that soils containing allophane clays were more reactive to both herbicides (mean K_d of 8.5 and 0.82 L kg^{-1} for atrazine and imazethapyr, respectively) than the non-allophanic set of soils (mean K_d of 7.5 and 0.76 L kg^{-1} for atrazine and imazethapyr, respectively). However, a detailed investigation of the clay mineralogy was not completed in this study.

CEC. The K_d values for atrazine were poorly correlated (R^2 = 0.17) to the CEC in all soils (excluding soils 18 and 90), and the relationship was non-existent in the case of imazethapyr (R^2 = 0.03) (**Figures 2** and **3**). The effect of CEC on the sorption of herbicides has been investigated less frequently. Loux et al. (*39*) found imazethapyr sorption positively correlated with CEC. However, Kan et al. (*43*) reported that, as ionic strength increased, K_d increases. A “salting out” effect occurs as the ionic strength increases, causing the aqueous solubility of the molecular species to decrease. Consequently, the sorption of these molecular species on soils is likely to increase. However, Laird et al. (*44*) reported that smectite clay with lower CEC was a more effective sorbent of atrazine; these characteristics may increase the size of the sorptive domains between exchangeable cations. Higher ionic strengths are often encountered in surface soils when agrochemicals, such as fertilizers, are applied. The addition of salts in amendments used to increase the soil fertility may also decrease sorption from the competition of inorganic anion-exchange sites, which may enhance the potential of off-site migration and leaching of recently applied herbicides.

Correlation of Sorption with Soil Properties and K_d Prediction Equations for Atrazine and Imazethapyr. Regression of sorption with soil properties is often used to predict the herbicide sorption on various soils and to help determine the soil factors that dominate in the sorption process. Regression of K_d against selected soil properties showed that atrazine sorption was influenced by soil OC content (R^2 = 0.26) and CEC (R^2 = 0.17) (**Figure 2**). In the case of imazethapyr, soil OC (R^2 = 0.39) and pH (R^2 = 0.28) were the main predictors of sorption (**Figure 3**). Clay content did not show any correlation with the K_d of either of the herbicides.

Multiple regression analyses (excluding soils 18 and 90) revealed that soil OC content, pH, and to a lesser extent sand were the primary soil properties in the best-fit (p < 0.001) K_d equation obtained for imazethapyr, as shown by the following equation:

$$\log K_d \text{ (imazethapyr)} = 3.39 + 1.60 \log \% \text{ OC} - 0.70 \text{ pH} - 0.006 \% \text{ sand} \quad (R = 0.74, p < 0.001) \qquad (1)$$

The effect of sand is unexpected, but it could represent the combined effect of the other soil components (clay and silt).

For atrazine, the best-fit K_d equation was obtained using soil OC content, pH, and CEC. The K_d values of atrazine increased as the soil OC and CEC increased and pH decreased. The best-fit equation for calculating soil K_d values of atrazine based on soil properties in non-allophanic soils is

$$\log K_d \text{ (atrazine)} = 1.37 + 0.75 \log \% \text{ OC} - 0.27 \text{ pH} + 0.02 \text{ CEC} \quad (R = 0.68, p < 0.001) \qquad (2)$$

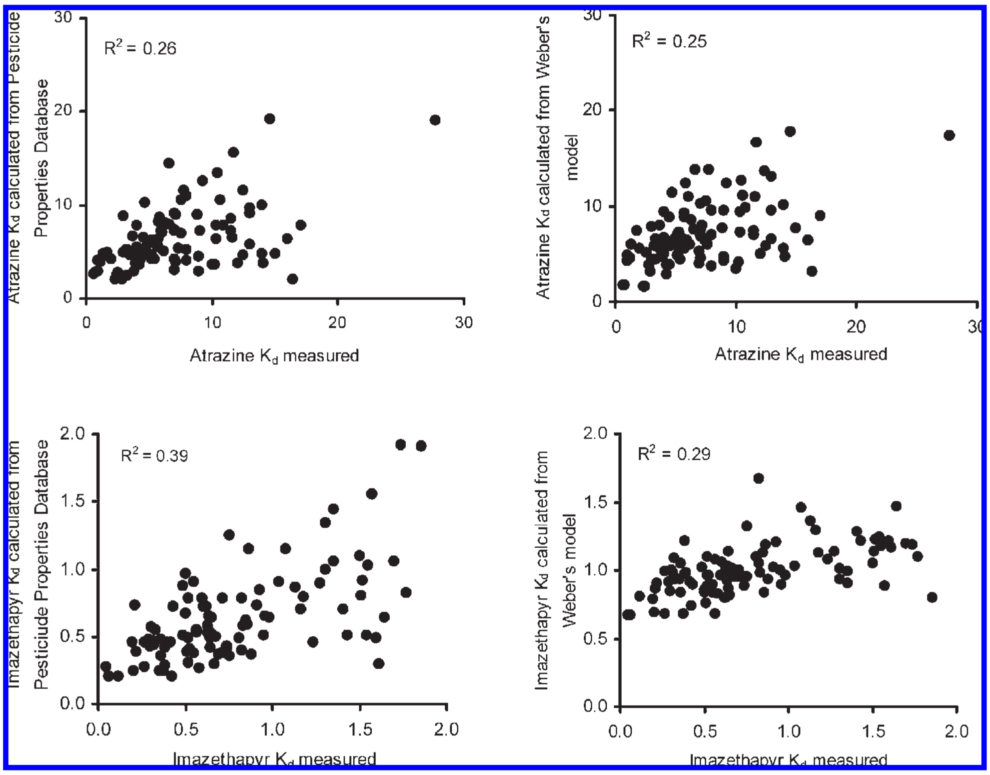

Figure 4. Relationships between measured K_d values of atrazine and imazethapyr and corresponding K_d values calculated from Pesticides Properties Database (*62*) and Weber's models (*45*).

Equation 1 corresponds to the sorption of imazethapyr in allophanic and non-allophanic soils of New Zealand. Eq 2 corresponds to the sorption of atrazine, in non-allophanic soils. However, we could not propose an equation for prediction of sorption in allophanic soils because the R^2 value of 12.7% was not significant at $p < 0.05$.

Weber et al. (*45*) correlated the literature-reported pesticide K_d values with the significantly related soil properties and developed equations for the estimation of K_d values for improved soil mobility predictions using models. The best-fit equations for calculating soil K_d values of atrazine and imazethapyr based on the soil properties presented by them are

$$K_d(\text{atrazine}) = 4.1 + 0.43(\text{organic matter}) + 0.09(\text{clay}) - 0.81(\text{pH}) \quad (R = 0.77, p < 0.01) \qquad (3)$$

$$K_d(\text{imazethapyr}) = 10.0 - 2.8(\text{pH}) + 0.21(\text{pH})^2 \quad (R = 0.58, p < 0.01) \qquad (4)$$

It is obvious that these eqs 3 and 4 by Weber et al. (*45*) do not match those that we have developed for New Zealand soils (eqs 1 and 2) and, therefore, are not applicable for the New Zealand soils. As an example, let us try to estimate the K_d value of atrazine using the prediction equation proposed by Weber et al. (eq 3) and compare it to that obtained from the model that we developed for the non-allophanic soils of New Zealand (eq 2) based on real data on the local soils. Considering a New Zealand non-allophanic soil containing 10% organic matter content (OC/OM index of 0.54), clay content 20%, pH 6.5, and CEC 10 milliequiv 100 g^{-1}, one obtains a K_d value of 4.94 from eq 3 proposed by Weber et al. (*45*). In contrast, using eq 2 above that we developed for the New Zealand non-allophanic soils, one can obtain a K_d value of 2.31. This clearly demonstrates that equations developed using the literature data on overseas soils are poor for predicting the sorption behavior of the herbicides in New Zealand soils.

To determine risk assessment of herbicides, much of the modeling work carried out in New Zealand (and elsewhere) has used leaching models, such as GLEAMS (*46*), LEACHM (*47*), HYDRUS-2D (*48*), and PESTRISK (*49*). These models have used the sorption coefficient (K_d and K_{oc}) values either sourced from pesticide databases on North American and European soils (*11*), inverse modeling techniques, or estimations made by the nonlinear parameter optimization package called PEST (parameter estimation) (*50*). Perhaps the major source of error in the pesticide modeling is the inaccurate use of the sorption coefficients, particularly for ionizable compounds, such as atrazine and imazethapyr. The majority of the leachability indices developed by various researchers (*51*−*53*) employ K_{oc} as the most important single value in ranking pesticides. Some modelers consider that K_{oc} is normally distributed and obtain K_d by multiplying K_{oc} by fixed values of soil OC (*54*), whereas many others derive K_d values on the basis of fixed values of K_{oc} and distribution of soil OC values, mostly from published databases (*55*, *56*). In fact, the K_{oc} approach was introduced to demonstrate the linear relationship between the K_d and OC content and was initially established for hydrophobic non-ionic compounds (*57*) for the reason that this variable has been considered independent of any particular soil (*58*). Even so, the K_{oc} concept tends to be used by several modelers for all chemicals (including herbicides) regardless of their ionization status. However, as evident from the results presented here, the K_{oc} approach is often invalid for compounds such as atrazine and imazethapyr. For comparison, we calculated K_d values (referred to as calculated K_d database) of both herbicides for the soils used in our present studies using their OC content and the K_{oc} value from the Pesticides Properties Database (*62*). It can be seen from the data given in **Table 1** that there is a great divergence between the measured (actual) and calculated K_d values, and overall, there was poor correlation between the measured and calculated values of these pesticides (**Figure 4**). Using a K_{oc} value from the mentioned database, lower K_d values were obtained as compared to the measured K_d values for a total of 46 and 61 soils for atrazine and imazethapyr, respectively, which may result in overestimates of leaching potentials of these herbicides if predicted using various models currently in use. Very small K_d values for atrazine were obtained for several samples, e.g., sample 46 (calculated K_d database of 2.0 L kg^{-1} versus measured K_d of 16.4 L kg^{-1}), whereas larger values were obtained for imazethapyr (calculated K_d database of 0.2 L kg^{-1} versus measured K_d of 0.06 L kg^{-1}. For sample 90, which contained abundant OC content, the calculated K_d value for atrazine was in fairly good agreement with the measured value, which is likely due to the dominant role in sorption of atrazine of the organic matter component in this organic soil. However, in the case of imazethapyr, the calculated value for this sample was unrealistically lower (calculated K_d database of 4.2 versus measured K_d of 11.3 L kg^{-1}), which can be due to the major role of low soil pH (4.4). Overall, there was fairly good agreement between the measured K_d and calculated K_d values for only 12 soils for atrazine and just 4 soils in the case of imazethapyr. The differences between measured and calculated K_d are likely due to (1) the fact that sorption was calculated only as a function of the carbon content, (2) the influence of clay type and contents and the soil pH, and (3) the chemical composition of SOM.

In conclusion, our results demonstrate that the transfer of herbicide sorption data from one country or even region to another requires knowledge of various soil properties and highlight the need for extreme caution before ranking imazethapyr and atrazine for leaching risks. For these chemicals, the predictions made with the literature databases or theoretically calculated sorption coefficients are not acceptable for New Zealand soils. Therefore, we propose prediction models for imazethapyr and atrazine (eqs 1 and 2), which are based on the fresh data generated on the soils of New Zealand. For allophanic soils, with different types of parent materials and varied conditions under which the SOM has been decomposed, it needs further investigation into the chemistry of the SOM and the role of its various components in sorption affinity of these herbicides.

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LITERATURE CITED

(1) Barriuso, E.; Feller, Ch.; Calvet, R.; Cerri, C. Sorption of atrazine, terbutryn and 2,4-D herbicides in two Brazilian oxisols. *Geoderma* **1992**, *53*, 155–167.

(2) Socias-Viciana, M. M.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E.; Flores-Cespedes, F. Sorption and leaching of atrazine and MCPA in natural and peat-amended calcareous soils from Spain. *J. Agric. Food Chem.* **1999**, *47*, 1236–1241.

(3) Ahmad, R.; Kookana, R. S.; Alston, A. M. Sorption of ametryn and imazethapyr in twenty-five soils from Pakistan and Australia. *J. Environ. Sci. Health, Part B* **2001**, *36*, 143–160.

(4) Daniel, P. E.; Bedmar, F.; Costa, J. L.; Aparicio, V. C. Atrazine and metribuzin sorption in soils of the Argentinean humid pampas. *Environ. Toxicol. Chem.* **2002**, *21*, 2567–2572.

(5) Nemeth-Konda, L.; Fuleky, G.; Morovjan, G.; Csokan, P. Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere* **2002**, *48*, 545–552.

(6) Sarmah, A. K.; Müller, K; Ahmad, R. Fate and behaviour of pesticides in agroecosystem—A review with a New Zealand perspective. *Aust. J. Soil Res.* **2004**, *42*, 125–154.

(7) Molloy, L. *Soils in the New Zealand Landscape*; New Zealand Society of Soil Science and Mallinson Rendel: Wellington, New Zealand, 1988; p 239.

(8) Boesten, J. J. T. I.; van der Linden, A. M. A. Modelling the influence of sorption and transformation on pesticide leaching and persistence. *J. Environ. Qual.* **1991**, *20*, 425–435.

(9) Ahmad, R.; Kookana, R. S. Extrapolation of pesticide sorption data between agroclimatic regions. In *Environmental Protection and Risk Assessment of Organic Contaminants*; Kookana, R. S., Sadler, R., Sethunathan, N., Naidu, R., Eds.; Science Publishers, Inc.: Enfield, NH, 2002; pp 97−123.

(10) Alexander, M.; Scow, K. M. Kinetics of biodegradation in soil. In *Reactions and Movement of Organic Chemicals in Soil*; Sawhney, B. I., Brown, K., Eds.; Soil Science Society of America and American Society of Agronomy: Madison, WI, 1989; pp 243−269.

(11) Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W. M.; Burt, J. P. The SCS/ARS/CES pesticide database for environmental decision-making. *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1–164.

(12) Carsel, R. F.; Smith, C. N.; Milch, L. A.; Dean, J. D.; Galius, P. *User Manual for Pesticide Root Zone Model* (*PRZM*); U.S. Environmental Protection Agency: Athens, GA, 1984.

(13) Davis, F. M.; Leonard, R. F.; Knisel, W. G. *Gleams User Manual*; U.S. Deparment of Agriculture, Agricultural Research Service Southeast Watershed Research Laboratory: Tifton, GA, 1990.

(14) Weber, J. B. Relative pesticide leaching potential (PLP) indices and ratings for commonly used pesticides, relative soil leaching potential (SLP) indices and ratings, and groundwater contamination potential (GWCP) risk of potential-soil combinations. *North Carolina Agricultural Chemicals Manual*; North Carolina State University: Raleigh, NC, 2003; pp 21−26.

(15) Weber, J. B.; Wilkerson, G. W.; Linker, H. M.; Wilcut, J. W.; Leidy, R. B.; Senseman, S.; Witt, W. W.; Barrett, M.; Vencill, W. K.; Shaw, D. R.; Mueller, T. C.; Miller, D. K.; Brecke, B. J.; Talbett, R. E.; Peeper, T. F. A proposal to standardize soil/solution herbicide distribution coefficients. *Weed Sci.* **2000**, *48*, 75–88.

(16) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Bromilow, R. H. Differences in the sorption behaviour of carbaryl and phosalone in soils from Australia, Pakistan, and the United Kingdom. *Aust. J. Soil Res.* **2001**, *39*, 893–908.

(17) Green, R. E.; Karickhoff, S. W. Sorption estimates for modelling. In *Pesticides in the Soil Environment: Processes, Impacts and Modelling*; Hung, H. H., Ed.; Soil Science Society of America (SSSA): Madison, WI, 1990; SSSA Ser. 2, pp 79−101.

(18) Fieldes, M.; Perrott, K. W. The nature of allophane in soils. Part 3—Rapid field and laboratory test for allophane. *N. Z. J. Sci.* **1966**, *9*, 623–629.

(19) Parfitt, R. L.; Kimble, J. M. Conditions for formation of allophane in soils. *Soil Sci. Soc. Am. J.* **1989**, *53*, 971–977.

(20) Parfitt, R. L. Soils formed in tephra in different climatic regions. Transactions XIV Congress of the International Society of Soil Science, Kyoto, Japan, **1990**; Vol. *7*, pp 134−139.

(21) Lowe, D. J. Teaching clays: From ashes to allophane. In *Clays: Controlling the Environment*; Churchman, G. J., Fitzpatrick, R. W., Eggleton, R. A., Eds.; Proceedings of the 10th International Clay Conference, Adelaide, Australia, CSIRO Publishing: Melbourne, Australia, 1993; pp 19−23.

(22) Anderson, H. A.; Berrow, M. L.; Farmer, V. C.; Hepburn, A.; Russell, J. D.; Walker, A. D. A re-assessment of podzol formation processes. *J. Soil Sci.* **1982**, *33*, 125–136.

(23) Parfitt, R. L.; Webb, T. H. Allophane in some South Island yellow−brown shallow and stony soils and high country and upland yellow−brown earths. *N. Z. J. Sci.* **1984**, *27*, 37–40.

(24) Novak, J. M.; Moorman, T. B.; Cambardella, C. A. Atrazine sorption at the field scale in relation to soils and landscape position. *J. Environ. Qual.* **1997**, *26*, 1271–1277.

(25) Novak, J. M.; Moorman, T. B.; Karlen, D. L. Influence of soil aggregate size on atrazine sorption kinetics. *J. Agric. Food Chem.* **1994**, *42*, 1809–1812.

(26) Wada, K. J. *The Distinctive Properties of Andosols*; Springer: New York, 1985; p 233.

(27) Boudot, J. P.; Hadi, B. A. B.; Chone, T. Carbon mineralization in Andisols and aluminium-rich highland soils. *Soil Biol. Biochem.* **1986**, *18*, 457–461.

(28) Calderoni, G.; Schnitzer, M. Effects of age on the chemical structure of paleosol humic acids and fulvic acids. *Geochim. Cosmochim. Acta* **1984**, *48*, 2045–2051.

(29) Hatcher, P. G. The chemical structure of highly aromatic humic acids in three volcanic ash soils as determined by dipolar dephasing NMR studies. *Geochim. Cosmochim. Acta* **1989**, *53*, 125–130.

(30) Baskaran, S.; Bolan, N. S.; Rahman, A.; Tillman, R. W. Pesticide sorption by allophanic and non-allophanic soils of New Zealand. *N. Z. J. Agric. Res.* **1996**, *39*, 297–310.

(31) Liu, S. L.; Weber, J. B. Retention and mobility of AC 252214 (imazaquin), chlorsulfuron, prometryn and SD 95481 (cinmethylin) in soils. *Proc. Weed Sci. Soc.* **1985**, *38*, 465–474.

(32) Payá-Pérez, A. B.; Cortés, A.; Sala, M. N.; Larsen, B. Organic matter fractions controlling the sorption of atrazine in sandy soils. *Chemosphere* **1992**, *25*, 887–898.

(33) Seybold, C. A.; McSweeney, K.; Lowery, B. Atrazine adsorption in sandy soils of Wisconsin. *J. Environ. Qual.* **1994**, *23*, 1291–1297.

(34) Brouwer, W. W. M.; Boesten, J. J. T. I.; Siegers, W. G. Adsorption of transformation products of atrazine by soil. *Weed Res.* **1990**, *30*, 123–128.

(35) Roy, W. R.; Krapac, I. G. Adsorption and desorption of atrazine and deethylatrazine by two low organic carbon geologic materials. *J. Environ. Qual.* **1994**, *25*, 549–556.

(36) Ahmad, R.; Kookana, R. S.; Alston, A. M.; Skjemstad, J. O. The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ^{13}C CPMAS NMR spectroscopy. *Environ. Sci. Technol.* **2001**, *35*, 878–884.

(37) Ahmad, R.; Nelson, P. N.; Kookana, R. S. The molecular composition of soil organic matter as determined by ^{13}C NMR and elemental analyses and correlation with pesticide sorption. *Eur. J. Soil Sci.* **2006**, *57*, 883–893.

(38) Buurman, P.; Peterse, F.; Martin, G. A. Soil organic matter chemistry in allophonic soils: A pyrolysis−GC/MS study of a Costa Rican Andosol catena. *Eur. J. Soil Sci.* **2007**, *58*, 1330–1347.

(39) Loux, M. M.; Liebl, R. A.; Slife, F. W. Adsorption of imazaquin and imazethapyr on soils, sediments, and selected adsorbents. *Weed Sci.* **1989**, *37*, 712–718.

(40) Tomlin, C. D. S. *The e-Pesticide Manual*, version 2.2; British Crop Protection Council: Farnham, U.K., 2009.

(41) Renner, K. A.; Meggitt, W. F.; Penner, D. Effect of soil pH on imazaquin and imazethapyr adsorption to soil and phytotoxicity to corn (*Zea mays*). *Weed Sci.* **1988**, *36*, 78–83.

(42) Che, M.; Loux, M. M.; Traina, S. J.; Logan, T. J. Effect of pH on sorption and desorption of imazaquin and imazethapyr on clays and humic acid. *J. Environ. Qual.* **1992**, *21*, 698–703.

(43) Kan, A. T.; Fu, G.; Tomson, M. B. Adsorption/desorption hysteresis in organic pollutant and soil/sediment interaction. *Environ. Sci. Technol.* **1994**, *28*, 859–867.

(44) Laird, D. A.; Barriuso, E.; Dowdy, R. H.; Koskinen, W. C. Adsorption of atrazine on smectites. *Soil Sci. Soc. Am. J.* **1992**, *56*, 62–67.

(45) Weber, J. B.; Wilkerson, G. G.; Reinhardt, C. F. Calculating pesticide sorption coefficients (K_d) using selected soil properties. *Chemosphere* **2004**, *55*, 157–166.

(46) Close, M. E.; Pang, L.; Watt, J. P. C.; Vincent, K. W. Leaching of picloram, atrazine and simazine through two New Zealand soils. *Geoderma* **1998**, *84*, 45–63.

(47) Close, M. E.; Watt, J. P. C.; Vincent, K. W. Simulation of picloram, atrazine and simazine transport through two New Zealand soils using LEACHM. *Aust. J. Soil Res.* **1999**, *37*, 53–74.

(48) Pang, L.; Close, M. E.; Watt, J. P. C.; Vincent, K. W. Simulation of picloram, atrazine and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. *J. Contam. Hydrol.* **2000**, *44*, 19–46.

(49) Green, S. R.; Clothier, B. E.; Mill, T. M.; Holland, P. T.; Cunliffe, J.; Hamill, P. Modelling and transport of pesticides through soil. *Abstracts of the Workshop on Environmental Aspects of Pesticide Use*; Ruakura Research Centre: Hamilton, New Zealand, Nov 1999; p 12.

(50) Doherty, J. PEST: A unique computer program for model-independent parameter optimization. *Water down under 94. Adelaide, Australia*; The Institution of Engineers: Barton, Australian Capital Territory (ACT), Australia, 1994; pp 551−554.

(51) Cohen, S. Z.; Creeger, S. M.; Carsel, R. F.; Enfield, C. G. Potential for pesticide contamination of groundwater resulting from agricultural uses. In *Treatment and Disposal of Pesticide Wastes*; Kruger, R. F., Seiber, J. N., Eds; American Chemical Society: Washington, D.C., 1984; ACS Symp. Ser. 259, pp 297−325.

(52) Gustafson, D. I. Groundwater Ubiquity Score: A simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **1999**, *8*, 339–357.

(53) Jury, W. A.; Focht, D. D.; Farmer, W. F. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *Environ. Qual.* **1987**, *16*, 422–428.

(54) Nofziger, D. L.; Chen, J. S.; Han, C. T. Evaluating the chemical movement in layered soil model as a tool for assessing risk of pesticide leaching to groundwater. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **1994**, *29*, 1133–1155.

(55) Lafrance, P.; Banton, O. Implication of spatial variability of organic carbon on predicting pesticide mobility in soil. *Geoderma* **1995**, *65*, 331–338.

(56) Zacharias, S.; Heatwole, C. D.; Persaud, N.; Bruggeman, A. C.; Kumar, D.; Smith, C. N. Stochastic simulation of field-scale pesticide transport using Opus and GLEAMS. *J. Environ. Qual.* **1999**, *28*, 411–423.

(57) Hamaker, J. W.; Thompson, J. M. Adsorption. In *Organic Chemicals in the Soil Environment*; Goring, C. A. I., Hamaker, J. W., Eds.; Marcel Dekker: New York, 1972; pp 49−143.

(58) Hamaker, J. W. The interpretation of soil leaching experiments. In *Environmental Dynamics of Pesticides*; Haque, R., Freed, V. H., Eds.; Plenum Press: New York, 1975; pp 115−133.

(59) *Australian Laboratory Handbook of Soil and Water Chemical Methods*; Rayment, G. E., Higginson, F. R., Eds.; Inkata Press: Melbourne, Australia, 1992; pp 17−23.

(60) Merry, R. H.; Spouncer, L. R. The measurement of carbon in soils using a microprocessor-controlled resistance furnace. *Commun. Soil Sci. Plant Anal.* **1988**, *19*, 707–720.

(61) Standard Association of New Zealand. Soil classification and chemical tests. Methods of Testing Soils for Civil Engineering Purposes, New Zealand Standard 4402, Part 1, 1980.

(62) Hornsby, A. G.; Wauchope, R. D.; Herner, A. E. *Pesticide Properties in the Environment*; Springer Verlag: New York, 1996.

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