WFL Publisher
Science and Technology
Meri-Rastilantie 3 B, FI-00980
Helsinki, Finland
e-mail: info@world-food.net

Journal of Food, Agriculture & Environment Vol.12 (3&4): 424-433. 2014
www.world-food.net

A proposal to standardize herbicide sorption coefficients in Brazilian tropical soils compared to temperate soils

Kassio Ferreira Mendes [1]*, Marcelo Rodrigues Dos Reis [2], Ana Carolina Ribeiro Dias [3], José Ari Formiga [4], Pedro Jacob Christoffoleti [4] and Valdemar Luiz Tornisielo [1]

*[1] Laboratory of Ecotoxicology, Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba - São Paulo - Brazil, CEP: 13416-000. [2] Institute of Agricultural Sciences, Federal University of Viçosa, Rio Paranaíba - Mina Gerais, Brazil, CEP: 38810-000. [3] Department of Agronomy, State University of Mato Grosso, Alta Floresta - Mato Grosso, Brazil, CEP: 78580-000. [4] Department of Crop Sciences, College of Agriculture "Luiz de Queiroz", University of São Paulo, Piracicaba , São Paulo, Brazil, CEP: 13416-000. *e-mail: kassio_mendes_06@hotmail.com*

Received 17 June 2014, accepted 30 September 2014.

Abstract

Current mathematical models for predicting herbicide behaviour in tropical soils use sorption coefficients (K_d) and organic carbon affinity (K_{oc}) obtained from temperate soils, indicating that the information obtained may be distorted. Moreover, organic matter content in tropical soils varies greatly when methods and laboratories are compared; consequently, those conditions cause K_{oc} values to vary. Thus, the objectives of this paper were to review the scientific literature and discuss problems associated with the determination, calculation and interpretation of K_d and K_{oc} values for Brazilian tropical soils, evaluate K_d and K_{oc} values of tropical soils using the values described in the databases for temperate soils, correlate K_d values with tropical soil properties and suggest a method for calculating standardized K_d values applicable to soils with properties similar to those reported for tropical soils. K_{oc} values were calculated based on an OC/OM (organic carbon/organic matter) index of 0.54 for 22 herbicides. Pearson correlation was used to compare K_d values and soil properties (organic matter, OM; clay mineral, CM; potential hydrogen, pH and cation exchange capacity, CEC) for each herbicide in tropical soils. The results indicate that K_d and K_{oc} values for herbicides in tropical soils presented an OC/OM index ranging from 0.395 to 1.275, with some similarities and differences compared to temperate soil values. The K_d values of the majority of the herbicides correlate with the variation of OM and CEC contents in tropical soils. Standardized values confer more precision and accuracy to the mathematical models when used to represent herbicide behaviour in soils with similar properties to topical soils.

Key words: Databases, environmental behaviour, mathematical models, soil properties.

Introduction

Herbicides play an important role in modern agriculture, but concerns about food safety and environmental impacts of herbicide residues have increased [1,2]. Surface and subterranean waters have become contaminated because of agricultural and non-agricultural applications of herbicides, due to the processes of runoff and soil leaching [3].

Herbicide registration processes focus on requirements such as environmental impacts and animal toxicology. Additionally, after being available on the market, most products go through a revalidation procedure to meet newer country-specific legislation to comply with current guidelines and national security profiles. Recently, global conservation programs have been developed to protect all countries from environmental contaminants. Studies of herbicide applications and production system efficiency are tools to monitor environmental impacts and support food safety [1].

It should be noted that applied pre-emergent herbicides are more problematic compared to post-emergent herbicides, because they are deposited directly into the soil and therefore more subject to leaching and runoff, thus leading to further environmental contamination [4,5].

Soil herbicide behaviour is controlled by a set of complex processes, such as degradation (chemical, microbiological and photodegradation) [6], retention (sorption from soil colloids) [7], leaching, volatilization, runoff and absorption by plants.

There is evidence that herbicides applied to soil tend to be more easily transported by groundwater. The hypotheses proposed to explain this transport include preferential flow and colloidal material transport, as well as a combination of processes. The rate and magnitude of rapid transport are affected by many parameters, such as the physico-chemical properties of the herbicide, hydrology and soil use [8]. Therefore, non-volatile and water-soluble molecules are moved through the soil profile, following the flow of water by the difference in water potential between two points [9].

Leaching refers to the entrainment of the herbicides in the soil matrix or the groundwater. Intensity is dependent on herbicide physico-chemical properties and soil and climate characteristics. Understanding these processes is important for predicting herbicide behaviour in distinct soil types and selecting appropriate dosages, with the goal of avoiding harmful environment effects and residual effects on succeeding crops [10, 11]. The sorption process is comprised of solute movement (an herbicide molecule) from the aqueous phase to a solid surface (soil) connected by means of physico-chemical interactions [8]. Sorption is influenced by soil conditions (texture, organic matter content, nutrients, cations and pH), environment (temperature, humidity and light) and herbicide characteristics (water solubility, sorption coefficient, vapour pressure and chemical composition).

Factors that influence herbicide sorption, such as organic matter (OM), pH and temperature, were evaluated [12-14]. The OM, associated to the soil and sediment, is known to play an important role in herbicide sorption [15-17], which could result in hydrogen bond formation [18].

As a function of its high specific surface area and functional group diversity, OM can interact with organic molecules in different ways. The forces responsible for the sorption reactions of herbicides in soil include physical forces (Van der Waals), hydrogen bonds, hydrophobic bonds, electrostatic bonds, reactions of coordination and exchange bonds, among others [19].

Soil OM consists of partially humidified organic waste at various decomposition stages and is considered a key indicator of soil quality. It acts as a source of nutrients, increases cation retention, acts on metal complexation and is a source of carbon and energy to soil microorganisms, in addition to aiding water infiltration and retention and functioning as an essential component of soil sustainability maintenance [20].

OM is considered heterogeneous, consisting of hard and soft components and may be sequestered by a combination of both mechanisms (Fig. 1) that exhibit different herbicide sorption behaviours. Most accessible components are denominated rubbery OM (soft) and the less accessible components, which exhibit different sorption behaviour, are denominated rigid or glassy (hard) [21].

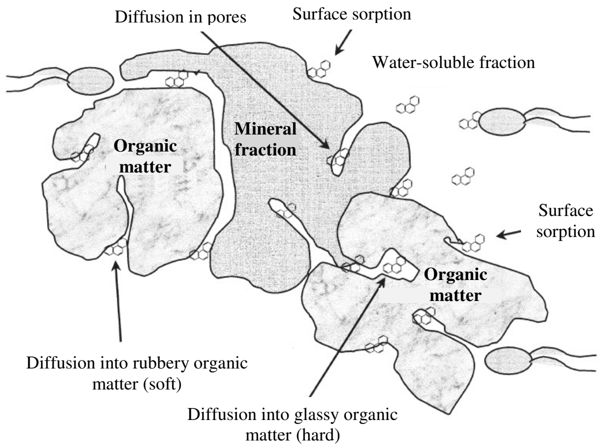

Figure 1. Summary of the physical behaviour (surface sorption) of an herbicide in the soil.

Source: Adapted from Semple *et al.* [48]; D'Agostinho and Flues. [21].

Therefore, herbicide can be superficially sorbed by OM adhered to the mineral fraction or the soluble organic fraction. In a second phase, herbicide can diffuse into micropores and mesopores and interact with soft OM (more accessible micropores) or hard OM (less accessible micropores). Most adsorbents are highly porous bodies with a very large internal surface area and a smaller external surface comprising only a small fraction of total surface adsorbent. Nonlinear sorption is generally the result of the sorption process in hard fraction OM soil. Moreover, temperature and pH have different effects on herbicide sorption [22].

Herbicide bioavailability can decrease depending on the sorption process, but can also increase detoxification problems depending on soil properties and the molecules themselves [23]. Sorption behaviour is fundamental for determining the negative effects of herbicide sorbed in soil, in contact with the succession culture.

The equilibrium sorption is calculated as the difference in concentration between the initial solution and the solution in equilibrium with the soil, in a single solution concentration for each soil. Assuming the sorption to be an instantaneous, reversible and a linear process, the sorption coefficient (K_d) value in L kg^{-1}, which is commonly used to determine herbicide sorption intensity on soil, was estimated.

K_d is calculated for the initial herbicide concentration, as represented by Equation (1):

$$K_d = C_s/C_e \qquad (1)$$

C_s is the concentration of herbicide sorbed to soil (μg g^{-1}) and C_e is the concentration of herbicide in solution at equilibrium (μg mL^{-1}).

This coefficient is normalized to the organic carbon (OC) content of soil evaluated by K_{oc}, calculated with Equation (2):

$$K_{oc} = K_d \times 100/OC(\%) \qquad (2)$$

The value calculated for K_d is a very important parameter for mathematical models used for assessing environmental contamination. Therefore, when starting a risk analysis and defining the K_d value to be applied to the model, the pesticide being used must first be evaluated.

In the second phase, the percentage of OM present in the soil being studied and the soil particle size must be evaluated; especially the percentage of clay, which can contribute to the increase of area-specific OM attached to the clay mineral and allowing greater interaction of the compound to the soil [21]. In the OM composition, OC content prevails (from 50 to 58%), with soil test laboratories traditionally using a conversion factor ranging from 1.724 for OM (equal to 58% OC) to 2.0 for OM (equal to 50% OC) when reporting the OM content of soil. Therefore, the determination of total OC has been used to quantitatively estimate the organic fraction of the soil [24].

Different analytical procedures have been used to determine the carbon content of the soil, from those based on the oxidant agent dichromate method and its variants to those employing automated dry combustion, which may underestimate or overestimate actual soil OC values [25]. The quantitative scaling of carbon stored by the different systems of soil use and management requires the application of methodologies that have been verified and shown to be representative for the region.

Many mathematical models are described in the literature, such as the screening criteria of the U.S. Environmental Protection Agency (EPA) [26], Groundwater Ubiquity Score (GUS) index [27], Attenuation Factor (AF), Retardation Factor (RF) [28], Attenuation Factors for multilayered soils (AFi) [29], LIX index (Screening Leachability) [30] and TLPI (Temperature Leaching Potencial Index) [31], to evaluate the leaching potential of herbicides in soil. The absence of K_d and K_{oc} values in herbicides used on tropical soils, typically Brazilian in these models, is pointed out as a limitation by the fact that the essential values have been derived from databases of temperate soils, meaning that the information may be distorted.

Considering the importance and lack of information on herbicide behaviour in soil under varied environmental conditions, the objectives of this paper were to review the scientific literature and discuss problems associated with the determination, calculation and interpretation of K_d and K_{oc} values for Brazilian tropical soils; evaluate K_d and K_{oc} values of tropical soils with the values described in databases for temperate soils; and to correlate K_d values with the tropical soils properties, suggesting a method for calculating standardized K_d values applicable to soils with properties similar to those reported in tropical soils.

Materials and Methods

The methodology adopted in this paper was in form of research literature reviews in scientific journal articles by nationally recognized Brazilian authors. The respective sources are reported in Table 1, demonstrating the values of sorption coefficients (K_d) and OC affinity (K_{oc}) for tropical soil conditions in Brazil.

After obtaining the data, a database was prepared for soil

Table 1. Values reported in the literature of herbicide sorption coefficients (K_d), OC affinity coefficients (K_{oc}) in Brazilian tropical soils, selected soil property values, calculated OC and OC/OM indices, and calculated OC and K_{oc} values, assuming an OC/OM index of 0.54 as proposed by Weber *et al.* [32].

Herbicide	Reported values[a]						Calculated values		Calculated values assuming OC/OM = 0.54		Source
	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	OM (%)	CM (%)	pH	CEC ($cmol_c$ kg^{-1})	OC[b] (%)	OC/OM index[c]	OC[d] (%)	K_{oc}[e] (L kg^{-1})	
Acetochlor	0.76	86.00	1.63	22.0	5.50	9.00	0.884	0.542	0.880	86.364	Ferri *et al.* [49]
	1.22	116.00	1.94	22.0	5.40	9.00	1.052	0.542	1.048	116.412	
	1.67	126.00	2.46	22.0	4.70	9.00	1.325	0.539	1.328	125.753	Ferri *et al.* [50]
	2.75	166.00	3.07	22.0	4.70	9.00	1.657	0.540	1.658	165.862	
Alachlor	0.53	150.00	0.65	10.0	4.30	3.00	0.353	0.543	0.351	150.997	Oliveira Jr. *et al.* [40]
	0.54	94.00	1.07	6.0	4.50	4.40	0.574	0.536	0.578	93.426	
	1.48	102.00	2.68	42.0	4.80	14.50	1.451	0.541	1.447	102.280	
	2.15	77.00	5.15	75.0	6.30	26.10	2.792	0.542	2.781	77.310	
	2.19	126.00	3.22	34.0	4.50	14.40	1.738	0.540	1.739	125.934	
	5.51	74.00	13.80	14.0	4.60	46.80	7.446	0.539	7.452	73.940	
Ametryn	4.57	n/a	1.70	44.0	5.80	11.87	n/a	n/a	0.918	497.821	Andrade *et al.* [38]
	5.49	n/a	1.70	44.0	4.90	2.37	n/a	n/a	0.918	598.039	
	6.35	n/a	1.70	44.0	4.40	2.29	n/a	n/a	0.918	691.721	
	13.44	n/a	2.55	25.0	5.90	4.47	n/a	n/a	1.377	976.035	
	33.50	318.44	18.89	59.8	4.10	50.00	10.520	0.557	10.201	328.399	Matallo *et al.* [51]
Aminocyclopyrachlor	0.05	10.00	0.92	10.0	5.40	n/a	0.500	0.543	0.497	10.060	Oliveira Jr. *et al.* [45]
	0.06	9.00	1.20	5.0	7.20	n/a	0.667	0.556	0.648	9.529	
	0.09	16.00	1.13	7.0	6.50	n/a	0.562	0.497	0.610	14.754	
	0.14	22.00	1.18	11.0	6.50	n/a	0.636	0.539	0.637	21.978	
	0.23	32.00	1.26	7.0	5.10	n/a	0.719	0.571	0.680	33.823	
	0.29	32.00	1.67	17.0	5.70	n/a	0.906	0.542	0.902	32.151	
	0.34	33.00	1.89	11.0	4.90	n/a	1.030	0.545	1.021	33.301	
	0.48	27.00	3.31	50.0	6.10	n/a	1.778	0.537	1.787	26.861	
	0.50	27.00	3.39	56.0	5.70	n/a	1.852	0.546	1.831	27.307	
	0.50	47.00	1.96	17.0	6.00	n/a	1.064	0.543	1.058	47.259	
	0.62	39.00	2.96	65.0	6.00	n/a	1.590	0.537	1.598	38.798	
	0.85	39.00	4.02	59.0	6.20	n/a	2.179	0.542	2.171	39.152	
	1.07	66.00	3.02	57.0	5.20	n/a	1.621	0.537	1.631	65.604	
	1.17	57.00	3.80	57.0	5.90	n/a	2.053	0.540	2.052	57.018	
Atrazine	1.34	67.00	3.44	23.3	5.80	9.00	2.000	0.581	1.858	72.120	Arantes *et al.* [42]
	2.16	81.86	4.55	58.3	5.10	8.90	2.639	0.580	2.457	87.912	
	2.86	105.15	4.68	32.7	6.00	7.60	2.720	0.581	2.527	113.178	
	3.03	135.27	3.86	33.7	5.40	11.70	2.240	0.580	2.084	145.393	
	4.87	225.46	3.72	34.0	5.20	7.50	2.160	0.581	2.009	242.409	
	5.96	248.33	4.13	53.0	5.10	11.70	2.400	0.581	2.230	267.264	
	0.51	145.00	0.65	10.0	4.30	3.00	0.352	0.541	0.351	145.299	Oliveira Jr. *et al.* [40]
	0.85	146.00	1.07	6.0	4.50	4.40	0.582	0.544	0.578	147.059	
	1.69	61.00	5.15	75.0	6.30	26.10	2.770	0.538	2.781	60.770	
	3.81	219.00	3.22	34.0	4.50	14.40	1.740	0.540	1.739	219.091	
	4.06	280.00	2.68	42.0	4.80	14.50	1.450	0.541	1.447	280.580	
	10.53	140.00	13.80	14.0	4.60	46.80	7.521	0.545	7.452	141.304	
	1.60	233.90	1.67	27.0	6.10	9.03	0.684	0.409	0.902	177.383	Inoue *et al.* [43]
	1.72	247.50	1.67	29.0	6.30	9.03	0.695	0.416	0.902	190.687	
	1.93	143.10	3.00	46.0	5.60	16.19	1.349	0.450	1.620	119.136	
	1.95	170.00	2.72	39.0	6.00	14.68	1.147	0.422	1.469	132.743	
	2.35	148.80	3.28	56.0	6.00	17.69	1.579	0.481	1.771	132.693	
	2.42	194.50	2.58	64.0	6.20	13.93	1.244	0.482	1.393	173.726	
	28.58	271.67	18.89	59.8	4.10	50.00	10.520	0.557	10.201	280.169	Matallo *et al.* [51]
Dicamba	0.07	11.00	1.07	6.0	4.50	4.40	0.636	0.594	0.578	12.111	Oliveira Jr. *et al.* [40]
	0.12	34.00	0.65	10.0	4.30	3.00	0.353	0.543	0.351	34.188	
	0.13	9.00	2.68	42.0	4.80	14.50	1.444	0.539	1.447	8.984	
	0.15	9.00	3.22	34.0	4.50	14.40	1.667	0.518	1.739	8.626	
	0.22	8.00	5.15	75.0	6.30	26.10	2.750	0.534	2.781	7.911	
	0.52	7.00	13.80	14.0	4.60	46.80	7.428	0.538	7.452	6.978	
Diclosulam	1.95	98.00	3.68	35.5	5.0	n/a	1.990	0.541	1.987	98.138	Lavorenti *et al.* [52]
	2.03	159.00	2.37	34.1	4.4	n/a	1.277	0.539	1.280	158.594	

Table 1. Continued.

Herbicide	Reported values[a]						Calculated values		Calculated values assuming OC/OM = 0.54		Source
	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	OM (%)	CM (%)	pH	CEC (cmol$_c$ kg^{-1})	OC[b] (%)	OC/OM index[c]	OC[d] (%)	K_{oc}[e] (L kg^{-1})	
Diuron	1.44	145.00	1.83	35.0	4.90	n/a	0.993	0.543	0.988	145.749	Carbo *et al.* [44]
	2.65	180.00	2.72	27.0	4.60	n/a	1.472	0.541	1.467	180.641	
	4.34	310.00	2.59	32.0	4.30	n/a	1.400	0.540	1.399	310.221	
	4.58	627.00	1.35	40.0	4.50	n/a	0.730	0.541	0.729	628.258	
	8.42	2,631.00	0.59	35.0	5.10	n/a	0.320	0.542	0.319	2,639.498	
	10.99	2,290.00	0.89	37.0	4.20	n/a	0.489	0.550	0.481	2,284.823	
	14.31	917.00	2.89	33.0	4.70	n/a	1.560	0.540	1.561	916.720	
	2.70	145.00	1.46	45.0	5.00	n/a	1.862	1.275	0.788	342.639	Dores *et al.* [53]
	3.10	n/a	0.87	48.4	5.10	n/a	n/a	n/a	0.470	659.574	
	14.70	917.00	2.87	31.6	5.10	n/a	1.603	0.558	1.550	948.387	
	5.07	741.60	1.67	29.0	6.30	9.03	0.684	0.409	0.902	562.084	Inoue *et al.* [43]
	10.14	1,482.50	1.67	27.0	6.10	9.03	0.684	0.409	0.902	1,124.168	
	12.98	1,131.60	2.72	39.0	6.00	14.68	1.147	0.422	1.620	801.234	
	13.40	966.60	3.00	46.0	5.60	16.19	1.184	0.395	1.469	912.185	
	15.77	1,267.70	2.58	64.0	6.20	13.93	1.244	0.482	1.771	890.457	
	17.05	1,079.80	3.28	56.0	6.00	17.69	1.579	0.481	1.393	1,223.977	
Hexazinone	0.13	36.00	0.65	10.0	4.30	3.00	0.361	0.555	0.351	37.037	Oliveira Jr. *et al.* [40]
	0.18	30.00	1.07	6.0	4.50	4.40	0.600	0.561	0.578	31.142	
	0.71	25.00	5.15	75.0	6.30	26.10	2.840	0.551	2.781	25.530	
	0.74	42.00	3.22	34.0	4.50	14.40	1.762	0.547	1.739	42.553	
	0.75	52.00	2.68	42.0	4.80	14.50	1.442	0.538	1.447	51.831	
	1.58	21.00	13.80	14.0	4.60	46.80	7.524	0.545	7.452	21.202	
Imazaquin	0.33	66.31	0.92	8.0	5.90	n/a	0.498	0.541	0.497	66.398	Barizon *et al.* [54]
	0.58	52.77	2.04	20.0	6.10	n/a	1.099	0.539	1.102	52.632	
	1.63	108.82	2.78	70.0	5.50	n/a	1.498	0.539	1.501	108.594	
Imazethapyr	0.08	22.00	0.65	10.0	4.30	3.00	0.364	0.560	0.351	22.792	Oliveira Jr. *et al.* [40]
	0.10	17.00	1.07	6.0	4.50	4.40	0.588	0.550	0.578	17.301	
	0.29	17.00	3.22	34.0	4.50	14.40	1.706	0.530	1.739	16.676	
	0.42	6.00	13.80	14.0	4.60	46.80	7.000	0.507	7.452	5.636	
	0.54	19.00	5.15	75.0	6.30	26.10	2.842	0.552	2.781	19.417	
	0.76	53.00	2.68	42.0	4.80	14.50	1.434	0.535	1.447	52.522	
Indaziflam	4.86	972.00	0.92	10.0	5.40	n/a	0.500	0.543	0.497	977.867	Alonso *et al.* [7]
	5.22	855.00	1.13	7.0	6.50	n/a	0.610	0.540	0.610	855.738	
	9.42	434.00	4.02	59.0	6.20	n/a	2.170	0.540	2.171	433.901	
	12.44	1,173.00	1.96	17.0	6.00	n/a	1.060	0.541	1.058	1,175.803	
	21.14	1,321.00	2.96	65.0	6.00	n/a	1.600	0.540	1.598	1,322.904	
	27.44	1,339.00	3.80	57.0	5.90	n/a	2.049	0.539	2.052	1,337.232	
Metamitron	23.05	219.11	18.89	59.8	4.10	50.00	10.520	0.557	10.201	225.958	Matallo *et al.* [51]
Metolachlor	1.80	179.00	0.87	48.4	5.10	n/a	1.005	1.155	0.470	382.978	Dores *et al.* [53]
	3.10	261.00	2.87	31.6	5.10	n/a	1.188	0.414	1.550	200.00	
	3.90	n/a	1.46	45.0	5.00	n/a	n/a	n/a	0.788	494.924	
Metsulfuron-methyl	0.09	16.00	1.07	6.0	4.50	4.40	0.562	0.525	0.578	15.571	Oliveira Jr. *et al.* [40]
	0.12	33.00	0.65	10.0	4.30	3.00	0.364	0.560	0.351	34.188	
	0.13	5.00	5.15	75.0	6.30	26.10	2.600	0.505	2.781	4.674	
	0.15	10.00	2.68	42.0	4.80	14.50	1.500	0.560	1.447	10.366	
	0.16	9.00	3.22	34.0	4.50	14.40	1.778	0.552	1.739	9.201	
	0.27	4.00	13.80	14.0	4.60	46.80	6.750	0.489	7.452	3.623	
Nicosulfuron	0.14	39.00	0.65	10.0	4.30	3.00	0.359	0.552	0.351	39.886	Oliveira Jr. *et al.* [40]
	0.14	24.00	1.07	6.0	4.50	4.40	0.583	0.545	0.578	24.221	
	0.31	18.00	3.22	34.0	4.50	14.40	1.722	0.535	1.739	17.826	
	0.32	11.00	5.15	75.0	6.30	26.10	2.909	0.565	2.781	11.507	
	0.35	24.00	2.68	42.0	4.80	14.50	1.458	0.544	1.447	24.188	
	0.38	5.00	13.80	14.0	4.60	46.80	7.600	0.551	7.452	5.099	
	0.81	82.7	1.81	22.0	5.60	n/a	0.979	0.541	0.977	82.907	Regitano and Koskinen [55]
Picloram	0.92	n/a	1.70	35.0	6.33	18.75	n/a	n/a	0.918	100.218	Assis *et al.* [56]
	2.40	n/a	3.10	26.0	4.96	4.96	n/a	n/a	1.674	143.370	
Prometryn	86.28	820.15	18.89	59.8	4.10	50.00	10.520	0.557	10.201	845.799	Matallo *et al.* [51]
Simazine	0.34	96.00	0.65	10.0	4.30	3.00	0.354	0.545	0.351	96.866	Oliveira Jr. *et al.* [40]
	0.54	93.00	1.07	6.0	4.50	4.40	0.581	0.543	0.578	93.426	
	0.76	27.00	5.15	75.0	6.30	26.10	2.815	0.547	2.781	27.328	
	1.09	75.00	2.68	42.0	4.80	14.50	1.453	0.542	1.447	75.328	
	2.02	117.00	3.22	34.0	4.50	14.40	1.726	0.536	1.739	116.159	
	6.45	86.00	13.80	14.0	4.60	46.80	7.500	0.543	7.452	86.554	
	3.60	367.00	1.81	22.0	5.60	n/a	0.981	0.542	0.977	368.475	Regitano *et al.* [57]
	4.00	299.00	2.48	40.0	5.50	n/a	1.338	0.539	1.339	298.730	
	36.10	343.16	18.89	59.8	4.10	50.00	10.520	0.557	10.201	353.887	Matallo *et al.* [51]

Table 1. Continued.

Herbicide	Reported values[a]						Calculated values		Calculated values assuming OC/OM = 0.54		Source
	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	OM (%)	CM (%)	pH	CEC ($cmol_c$ kg^{-1})	OC^b (%)	OC/OM $index^c$	OC^d (%)	K_{oc}^e (L kg^{-1})	
Sulfometuron-methyl	0.14	38.00	0.65	10.0	4.30	3.00	0.368	0.566	0.351	39.886	Oliveira Jr. *et al.* [40]
	0.21	37.00	1.07	6.0	4.50	4.40	0.568	0.531	0.578	36.332	
	0.46	17.00	5.15	75.0	6.30	26.10	2.706	0.525	2.781	16.541	
	0.73	50.00	2.68	42.0	4.80	14.50	1.460	0.545	1.447	50.449	
	0.77	44.00	3.22	34.0	4.50	14.40	1.750	0.543	1.739	44.278	
	1.18	16.00	13.80	14.0	4.60	46.80	7.375	0.534	7.452	15.835	
Tebuthiuron	0.72	258.21	0.48	8.0	7.30	n/a	0.279	0.581	0.259	277.992	Souza *et al.* [46]
	0.79	374.30	0.36	8.0	7.30	n/a	0.211	0.586	0.194	407.216	
	1.58	135.40	2.02	62.0	5.70	n/a	1.167	0.578	1.091	144.821	
	1.61	159.40	1.74	62.0	5.90	n/a	1.010	0.580	0.940	171.276	
	2.50	138.20	3.12	36.0	5.40	n/a	1.809	0.580	1.685	148.368	
	2.57	151.40	2.93	36.0	5.90	n/a	1.697	0.579	1.582	162.452	
2,4-D	0.13	27.80	0.92	10.0	5.00	n/a	0.468	0.509	0.497	26.157	Spadotto *et al.* [47]
	0.23	21.30	2.04	16.0	5.60	n/a	1.080	0.529	1.102	20.871	
	0.31	26.70	2.22	28.0	5.60	n/a	1.161	0.523	1.199	25.855	
	0.36	42.90	1.48	13.0	6.30	n/a	0.839	0.567	0.799	45.056	
	0.40	31.10	2.41	41.0	5.50	n/a	1.286	0.534	1.301	30.746	
	0.43	40.90	2.04	27.0	6.60	n/a	1.051	0.515	1.102	39.020	
	0.49	32.20	2.78	54.0	5.80	n/a	1.522	0.547	1.501	32.645	
	0.81	53.70	2.78	41.0	5.70	n/a	1.508	0.542	1.501	53.964	
	0.90	70.70	2.41	24.0	6.50	n/a	1.273	0.528	1.301	69.178	
	0.91	60.30	2.78	51.0	5.80	n/a	1.509	0.543	1.501	60.626	
	0.94	82.00	2.04	50.0	5.00	n/a	1.146	0.562	1.102	85.299	
	0.97	98.80	1.80	5.0	6.40	n/a	0.982	0.546	0.972	99.794	
	1.02	70.00	2.59	39.0	6.00	n/a	1.457	0.562	1.399	72.909	
	1.07	89.10	2.22	19.0	4.60	n/a	1.201	0.541	1.199	89.241	
	1.17	80.60	2.59	61.0	5.70	n/a	1.452	0.561	1.399	83.631	
	1.29	99.40	2.41	42.0	6.10	n/a	1.298	0.538	1.301	99.154	
	1.60	102.30	2.96	52.0	5.30	n/a	1.564	0.528	1.598	100.125	
	2.10	131.30	2.96	64.0	4.90	n/a	1.599	0.540	1.598	131.414	
	4.63	306.50	2.78	2.0	4.80	n/a	1.512	0.544	1.501	308.461	

[a] OM, organic matter; OC, organic carbon; CM, clay mineral; pH, potential hydrogen (H_2O or $CaCl_2$); CEC, cation exchange capacity; n/a, not available. [b] (%OC) = K_d/K_{oc} × 100. [c] (%OC)/(%OM) ratio. [d] (%OC) = (%OM) × 0.54. [e] K_{oc} = K_d/(%OC) × 100.

conditions in tropical climate, with the maximum number of herbicides found in Brazilian scientific literature, where possible reporting the soil chemical properties (organic matter, OM; clay mineral, CM; potential hydrogen, pH and cation exchange capacity, CEC) wherein the sorption experiments were performed for each herbicide.

In addition, the OC percentage and K_{oc} values were calculated based on the OC/OM index equal to 0.54 proposed by Weber *et al.* [32]. This is a mean value used to provide a more accurate comparison of K_{oc} values among herbicides with the limited information on tropical soil properties currently available [32].

A comparative analysis with Student's t-test at the 0.01 and 0.05 levels was done using K_d and K_{oc} values from tropical soils, typically Brazilian, with K_d and K_{oc} values referring to temperate soils described in the FOOTPRINT [33] and EXTOXNET [34] databases, as shown in Table 2.

Herbicide K_d values were calculated for hypothetical tropical soils with OM contents of 1.0, 2.5, and 5.0% (0.54, 1.35, and 2.70% OC, respectively), based on the OC/OM index of 0.54 of Weber *et al.* [32] described in Table 3.

For herbicides used on Brazilian tropical soils reported in the literature, linear equations were described to calculate K_d values from the analysis of significant Pearson correlation at the 0.01 and 0.05 level among each

Table 2. Reported mean values of herbicide sorption coefficients (K_d) and OC affinity coefficients (K_{oc}) in Brazilian literature on tropical soils compared to temperate soils from reference database [33, 34].

Herbicide	Reported mean K_d (L kg^{-1})[a]		Reported mean K_{oc} (L kg^{-1})[a]	
	Trs[b]	Tes	Trs[b]	Tes
Acetochlor	1.600 ± 0.84*	3.210[c]	123.500 ± 33.04**	156.000[c]
Alachlor	2.067 ± 1.83[ns]	2.890[d]	103.833 ± 29.43**	335.000[c]
Ametryn	12.670 ± 12.16	n/a	318.440	316.000[c]
Aminocyclopyrachlor	0.460 ± 0.36**	0.390[c]	32.571 ± 16.45**	24.000[c]
Atrazine	4.327 ± 6.29**	2.340[d]	171.765 ± 68.15**	100.000[c]
Dicamba	0.202 ± 0.16*	-0.530[d]	13.000 ± 10.37*	2.000[d]
Diclosulam	1.990 ± 0.05	n/a	128.500 ± 43.13[ns]	90.000[d]
Diuron	8.852 ± 5.41**	8.300[c]	988.787 ± 731.04**	813.000[c]
Hexazinone	0.682 ± 0.52*	-4.400[d]	34.333 ± 11.46**	54.000[c]
Imazaquin	0.847 ± 0.68	n/a	75.967 ± 29.24	n/a
Imazethapyr	0.365 ± 0.26	n/a	22.333 ± 15.97*	52.000[c]
Indaziflam	13.420 ± 9.09	n/a	1,015.667 ± 343.09**	1,000.000[c]
Metamitron	23.050	0.890[c]	219.110	77.700[c]
Metolachlor	2.933 ± 1.05*	0.670[c]	220.000 ± 57.98[ns]	120.000[c]
Metsulfuron-methyl	0.153 ± 0.06	n/a	12.833 ± 10.75	n/a
Nicosulfuron	0.350 ± 0.22**	0.440[d]	29.100 ± 25.99*	30.000[c]
Picloram	1.660 ± 1.04[ns]	0.140[d]	n/a	13.000[c]
Prometryn	86.280	3.340[d]	820.150	400.000[c]
Simazine	6.100 ± 10.81[ns]	1.960[d]	167.018 ± 130.43**	130.000[c]
Sulfometuron-methyl	0.582 ± 0.39**	-0.500[d]	33.667 ± 14.09*	85.000[c]
Tebuthiuron	1.628 ± 0.79**	1.780[d]	202.818 ± 95.62**	80.000[c]
2,4-D	1.040 ± 1.00**	1.240[c]	77.242 ± 63.66**	88.400[c]

[a] Trs, tropical soils; Tes, temperate soils; n/a, not available. [b] Mean reported from Brazilian literature as described in Table 1. K_d and K_{oc} values associated with standard deviation (±SD) of the mean. Significant at the * 0.05 and ** 0.01 level by Student's t-test; [ns], nonsignificant. [c] Source: FOOTPRINT [33]. [d] Source: EXTOXNET [34].

Table 3. Reported mean of herbicide OC affinity coefficients (K_{oc}) and calculated herbicide sorption coefficient (K_d) values from Brazilian literature on tropical soils, assuming soils with 1.0, 2.5 and 5.0% OM contents and OC/OM index of 0.54 proposed by Weber *et al.* [32].

Herbicide	Reported mean K_{oc} (L kg^{-1})[c]	Calculated K_d values (L kg^{-1})[a,b] Assuming 1.0% OM (0.54% OC)	Assuming 2.5% OM (1.35% OC)	Assuming 5.0% OM (2.70% OC)
Acetochlor	123.500	0.667	1.667	3.334
Alachlor	103.833	0.561	1.402	2.804
Ametryn	318.440	1.720	4.299	8.598
Aminocyclopyrachlor	32.571	0.176	0.440	0.879
Atrazine	171.765	0.928	2.319	4.638
Dicamba	13.000	0.070	0.176	0.351
Diclosulam	128.500	0.694	1.735	3.470
Diuron	988.787	5.339	13.349	26.697
Hexazinone	34.333	0.185	0.464	0.927
Imazaquin	75.967	0.410	1.026	2.051
Imazethapyr	22.333	0.121	0.302	0.603
Indaziflam	1,015.667	5.485	13.712	27.423
Metamitron	219.110	1.183	2.958	5.916
Metolachlor	220.000	1.188	2.970	5.940
Metsulfuron-methyl	12.833	0.069	0.173	0.346
Nicosulfuron	29.100	0.157	0.393	0.786
Prometryn	820.150	4.429	11.072	22.144
Simazine	167.018	0.902	2.255	4.509
Sulfometuron-methyl	33.667	0.182	0.454	0.909
Tebuthiuron	202.818	1.095	2.738	5.476
2,4-D	77.242	0.417	1.043	2.086

[a] OM, organic matter; OC, organic carbon. [b] $K_d = K_{oc} \times (\%OC)/100$. [c] Reported mean from Brazilian literature described in Table 1.

of the tropical soil properties (OM, CM, pH and CEC) of Brazil available in the scientific literature (Table 4).

Results and Discussion

Table 1 contains reported sorption coefficients (K_d), OC affinity (K_{oc}), selected tropical soil property values and calculated OC and OC/OM indices for 22 herbicides. The computed OC/OM indices, with reported values ranging from 0.395 to 1.275, emphasize larger discrepancies for the soils tested with diuron and metolachlor.

Corroborating with the data, Weber *et al.* [32] found OC/OM indices ranging from 0.100 to 1.538 for 20 herbicides, reflecting the inaccuracy of the values reported in the literature (i.e., the K_{oc} and K_d values determined from %OM values are inaccurate).

In general, the OC/OM index of 0.54 used to calculate %OC from the reported %OM values were close to 0.54 for most studied herbicides (Table 1). This fact can be justified by calculations already proposed by Weber *et al.* [32] with herbicide sorption coefficients evaluated in temperate soils listed in the Weed Science Society of America Herbicide Handbook and Supplement.

In many cases, the newly calculated K_{oc} values, which assume the OC/OM index equal to 0.54 using Equation (2), do not vary greatly from the K_{oc} values reported in literature. For example, for acetochlor, where OM = 1.63%, an OC/OM index of 0.54 resulted in OC = 0.880% (1.63 × 0.54 = 0.880), was similar to the values reported in the literature (OC = 0.884%), providing K_{oc} = 86.364 L kg^{-1} (0.76/0.880 × 100), similar to K_{oc} of 86 L kg^{-1} (Table 1). In some cases, however, the values vary greatly, as in the case of atrazine, which shows variation of 24% in K_{oc} (233.90 vs. 177.383 L kg^{-1}), diuron with 36% (145.00 vs. 342.639 L kg^{-1}) and metolachlor with 114% (179.00 vs. 382.978 L kg^{-1}).

In addition, all of the newly calculated K_{oc} values are based on the same OC/OM index described in Table 1. For selected herbicides, linear equations are provided later in this paper to allow more accurate computation of K_d values for tropical soils with the reported properties (Table 4).

The differences of mean K_d values among herbicides reported in the literature on tropical soils and databases on temperate soils [33, 34] are usually evident for acetochlor, aminocyclopyrachlor, atrazine, dicamba, diuron, hexazinone, metolachlor, nicosulfuron, sulfometuron-methyl, tebuthiuron and 2,4-D. For example, metamitron and prometryn showed variation of 96% (23.050 vs. 0.890 L kg^{-1} and 86.280 vs. 3.340 L kg^{-1}) between tropical and temperate soils (Table 2). The similarities of mean K_d values reviewed in the literature are expressive for alachlor, picloram and simazine.

For mean K_{oc} values, alachlor in temperate soils showed a value of 335.000 L kg^{-1}, differing from tropical soils where the mean value was 103.833 L kg^{-1}. These differences were also observed for acetochlor, aminocyclopyrachlor, atrazine, dicamba, diuron, hexazinone, imazethapyr, indaziflam, nicosulfuron, simazine, sulfometuron-methyl, tebuthiuron and 2,4-D.

By comparison, similar mean K_{oc} values were observed for diclosulam and metolachlor across temperate and tropical soils (Table 2). It should be emphasized that the missing information (n/a, not available) in databases with temperate soils corresponded to 27 and 9% for mean K_d and mean K_{oc} values, demonstrating the difficulty in comparing sorption coefficients.

Usually in sorption herbicide studies, K_d is calculated considering the herbicide-soil interactions as not only a surface phenomenon, but one that occurs homogeneously in the entire soil volume with K_d or K_{oc} [35]. Higher and lower values of these coefficients are indicative of greater and lesser retention of herbicides by soil [36].

For hydrophobic herbicides such as aromatics, halogenates, phenols and bisphenols, which have low water solubility, their mobility and the risk of leaching to groundwater are related to low sorption in soil matrices and lower quantified values of K_{oc}. Therefore, herbicides with high K_{oc} values are found in groundwater and drainage, presumably as a result of leaching from a combination of factors with emphasis on rapid and torrential rain after herbicide application and the presence of preferred channels, which occurs more easily in the tropics [8].

Given the above and considering the mean K_d and K_{oc} values reported in databases using temperate soils (Table 2), it is not recommended to estimate herbicide behaviour in tropical soils using mathematical models based on temperate soils as this can distort the compiled information.

Silva *et al.* [19] report that in Brazil, K_{oc} has been widely used to predict the sorption capacity of several herbicides in soil and it is also used, along with the texture, to recommend herbicide dosages. Standardizing K_d in relation to soil OC, however, provides no consensus among researchers in this area, since the sorption of herbicides to soil OM occurs in heterogeneous form, as a function of the mechanisms and organic fraction involved in the sorption process, the indices of which may not represent reality. At the same time, K_d and K_{oc} are not always sufficiently accurate to describe the sorption of an herbicide in the concentration range considered.

Table 3 contains the mean K_{oc} values of 21 herbicides in tropical soils, with the exception of picloram, which was listed and referenced in Table 1. Assuming an OC/OM index of 0.54, Equation

Table 4. Pearson correlation of herbicide sorption coefficient (K_d) and OC affinity coefficients (K_{oc}) values vs. selected soil properties and equations for calculating K_d values when soil property values were available (values taken from Brazilian literature).

Herbicide	Chemical family	Mean K_d (L kg^{-1})[b]	Reported soil property values[a, d]				Equation[c]	R^2	*n*[e]
			OM (%)	CM (%)	pH	CEC ($cmol_c$ kg^{-1})			
Acetochlor	Nonionizable	1.600	0.990*				K_d = - 1.440 + 1.336 (OM)	0.99	4
					-0.844		K_d = ns		
Alachlor	Nonionizable	2.067	0.986**				K_d = 0.416 + 0.373 (OM)	0.99	6
				0.039			K_d = ns		
					0.092		K_d = ns		
						0.969**	K_d = 0.079 + 0.109 (CEC)	0.97	
Ametryn	Base	12.670	0.970**				K_d = 4.432 + 1.552 (OM)	0.97	5
				0.524			K_d = ns		
					-0.508		K_d = ns		
						0.925*	K_d = 4.840 + 0.551 (CEC)	0.92	
Aminocyclopyrachlor	Acid	0.460	0.866**				K_d = - 0.190 + 0.285 (OM)	0.87	14
				0.833**			K_d = 4.432 + 1.552 (CM)	0.83	
					-0.233		K_d = ns		
Atrazine	Base	4.327	0.923**				K_d = - 1.517 + 1.310 (OM)	0.92	19
				0.226			K_d = ns		
					-0.501*		K_d = 27.338 - 4.290 (pH)	0.50	
						0.809**	K_d = - 1.931 + 0.402 (CEC)	0.81	
Dicamba	Acid	0.202	0.990**				K_d = 0.054 + 0.033 (OM)	0.99	6
				-0.025			K_d = ns		
					0.099		K_d = ns		
						0.958**	K_d = 0.027 + 0.010 (CEC)	0.96	
Diuron	Nonionizable	1.600	0.535*				K_d = 1.968 + 3.340 (OM)	0.54	
				0.385			K_d = ns		16
					0.434		K_d = ns		
						0.855*	K_d = - 1.201 + 1.013 (CEC)	0.86	6
Hexazinone	Base	0.682	0.943*				K_d = 0.232 + 0.101 (OM)	0.94	6
				0.161			K_d = ns		
					0.141		K_d = ns		
						0.954**	K_d = 0.124 + 0.031 (CEC)	0.95	
Imazaquin	Acid	0.847	0.897				K_d = ns		3
				0.999**			K_d = 0.161 + 0.021 (CM)	0.99	
					-0.870		K_d = ns		
Imazethapyr	Acid	0.365	0.313				K_d = ns		6
				0.683			K_d = ns		
					0.511		K_d = ns		
						0.455	K_d = ns		
Indaziflam	Acid	13.420	0.677				K_d = ns		6
				0.733			K_d = ns		
					-0.071		K_d = ns		
Metolachlor	Nonionizable	2.933	0.415				K_d = ns		3
				-0.323			K_d = ns		
					-0.790		K_d = ns		
Metsulfuron-methyl	Acid	0.153	0.934**				K_d = 0.100 + 0.012 (OM)	0.93	6
				-0.092			K_d = ns		
					-0.108		K_d = ns		
						0.891*	K_d = 0.092 + 0.003 (CEC)	0.89	
Nicosulfuron	Acid	0.350	0.098				K_d = ns		
				0.110			K_d = ns		7
					0.503		K_d = ns		
						0.793	K_d = ns		6
Simazine	Base	6.100	0.851**				K_d = - 2.311 + 1.522 (OM)	0.85	
				0.384			K_d = ns		9
					-0.403		K_d = ns		
						0.730	K_d = ns		7
Sulfometuron-methyl	Acid	0.582	0.836*				K_d = 0.284 + 0.067 (OM)	0.84	6
				0.103			K_d = ns		
					-0.018		K_d = ns		
						0.839*	K_d = 0.216 + 0.020 (CEC)	0.84	
Tebuthiuron	Nonionizable	1.628	0.986**				K_d = 0.439 + 0.670 (OM)	0.99	6
				0.490			K_d = ns		
					-0.864*		K_d = 6.793 – 0.826 (pH)	0.87	
2,4-D	Acid	1.040	0.486*				K_d = - 1.103 + 0.921 (OM)	0.49	19
				-0.075			K_d = ns		
					-0.414		K_d = ns		

[a] OM, organic matter; OC, organic carbon; CM, clay mineral; pH, potential hydrogen (H_2O or $CaCl_2$); CEC, cation exchange capacity. [b] Reported mean from Brazilian literature as described in Table 1. [c] Most significant linear equation; ns, nonsignificant. [d] Significant at the * 0.05 and ** 0.01 levels. [e] Number of values correlated.

(2) was used to calculate the hypothetical K_d values of herbicides in tropical soils with OM contents of 1.0, 2.5, and 5.0% (0.54, 1.35, and 2.70% OC), as proposed by Weber *et al.* [32].

For example, acetochlor with a mean K_{oc} value of 123.5 L kg^{-1} and 1% OM content (0.54% OC) in tropical soil showed a K_d of 0.667 L kg^{-1} (123.5 × 0.54/100); and with OM content of 2.5 and 5.0%, the K_d values were 1.667 and 3.334 L kg^{-1} (Table 3). For 2,4-D with K_{oc} equal to 77.242 L kg^{-1}, the resultant K_d values were 0.417, 1.043 and 2.086 L kg^{-1}, as a function of increased OM content.

Aminocyclopyrachlor and indaziflam herbicides are two new molecules in the development stage in Brazil, according to Guerra *et al.* [37] with K_{oc} values of 32.571 and 1,015.667 L kg^{-1}, respectively. Aminocyclopyrachlor presents K_d values of 0.176, 0.440 and 0.879 L kg^{-1}, while indaziflam presents K_d values of 5.485, 13.712 and 27.423 L kg^{-1}, as a function of increased OM content (Table 3).

It is important to report that works developed by Weber *et al.* [32] using mean K_{oc} values to calculate K_d values may be quite inaccurate. Nevertheless, the calculation of K_d values at levels close to the OM contents of the soils being modeled are much more accurate than the mean K_d value for all soils.

For herbicides with K_d values between 1 and 10 L kg^{-1}, small changes in sorption may result in large variations in the quantity of product in the solution of the soil and consequently on its leaching [38].

The 2,4-D herbicide presents K_{oc} in the form of acid salt and ester; however, only values for the acid salt form are listed in Table 3. This is because, as proposed by Weber *et al.* [32], only the acid forms remain for significant periods of time in soil. Ester formulations are inactive until they are readily hydrolyzed in soil, changing from the ester to the acid form, with the acid forms being much more mobile [39].

Several additional problems reported by Weber *et al.* [32] are apparent in using mean K_{oc} values for estimating K_d values in soils with different OM contents, as is the case of herbicides with arsenic acid moieties (cacodylic acid and DSMA) and phosphoric acid moieties (fosamine and glufosinate), which bind and react with CM and metallic hydrous oxides but not with OM, rendering K_{oc} values meaningless. The authors also report that strongly basic herbicides (difenzoquat^{2+}, diquat^{2+} and paraquat^{2+}) that ionize to cationic species in solution react primarily with CM in soils, again resulting in K_{oc} values with little significance. It is an important report in this work that herbicides belonging to these groups described above were not listed (Table 3).

K_d values of 18 herbicides reported in literature were correlated with four properties (OM, CM, pH and CEC) of tropical soils and described in Table 4. Diclosulam (n = 2), metamitron (n = 1), picloram (n = 2) and prometryn (n = 1) were not correlated and the differences may be attributed to the small number of values reported for each herbicide from the Brazilian literature. The significant correlation coefficients and linear equations to calculate K_d values using the described soil properties were found for 14 herbicides, with the exceptions being imazethapyr, indaziflam, metolachlor and nicosulfuron.

OM content was correlated with K_d values of five weakly acidic herbicides (aminocyclopyrachlor, dicamba, metsulfuron-methyl, sulfometuron-methyl and 2,4-D), four weakly basic herbicides (ametryn, atrazine, hexazinone and simazine) and four nonionizable herbicides (acetochlor, alachlor, diuron and tebuthiuron) (Table 4). CM content was correlated only with the K_d value for aminocyclopyrachlor and imazaquin, both of which are weakly acidic. Soil solution pH was inversely correlated with K_d values of atrazine (weakly basic) and tebuthiuron (nonionizable). CEC of tropical soils was correlated with K_d values of three weakly acidic herbicides (dicamba, metsulfuron-methyl and sulfometuron-methyl), three weakly basic herbicides (ametryn, atrazine and hexazinone) and two nonionizable herbicides (alachlor and diuron) (Table 4).

In the case of highly weathered tropical soils, where the clay fraction is predominantly composed by oxides and hydroxides of Fe and Al silicate clays 1:1, of low reactivity (kaolinite), most of the CEC part is due to soil OM, which explains the concurrence of significance for the correlations [40, 41]. In general, Brazilian recommendations for herbicide rates applied to the soil are based on the texture rather than the OM content as the main parameter of initial reference, generating doubt about the adequacy of this criterion [40].

These data are in general agreement with Silva *et al.* [19] where OM and CEC are the soil constituents most highly correlated with binding of most organic herbicides registered for use in tropical soils. CM is correlated with cationic herbicide retention and the pH is inversely correlated with the retention of many herbicides, being strictly related to the capacity of electrolytic dissociation - pK_a. The differences in correlation between K_d values and soil properties may be attributed to the small number of values (minimum n = 3) reported for each herbicide in tropical soils (Table 4), corroborating with the data of Weber *et al.* [32].

Oliveira Jr. *et al.* [40] studied the correlation between soil properties and found that sorption coefficients (K_d and K_{oc}) of certain herbicides in Brazilian soils were significantly correlated with the OC and CEC content of the soil for most studied herbicides. Generally, weakly acidic herbicides (imazethapyr, metsulfuron-methyl, nicosulfuron and sulfometuron-methyl) showed less sorption, while weakly basic herbicides (atrazine, hexazinone and simazine) and nonionizable (alachlor) were more sorbed by the OC and CEC content of tropical soils. Since most of the CEC in our soils is related to OM, this characteristic can be considered the most important for these herbicides.

Linear equations for estimating the calculation of K_d values (Table 4), as also reported in the literature for alachlor, atrazine, dicamba, diuron, hexazinone, imazethapyr, metsulfuron-methyl, nicosulfuron, simazine, sulfometuron-methyl [40, 42-44], aminocyclopyrachlor [45], indaziflam, [7] tebuthiuron [46] and 2,4-D [47] using tropical soil properties, may be useful for calculating the optimum rates for herbicide applications and should improve the predictability of herbicide sorption using mathematical models in soils with similar properties.

In addition to the soil properties evaluated and correlated with K_d values by the authors cited in this work, more works are expected to be developed on herbicide sorption in tropical soils correlated with climatic factors, such as temperature and soil humidity; and edaphic factors, such as the humified part of OM (composed of fulvic, humic and humin acids) and the characteristics of clay minerals, iron oxide and aluminum.

Conclusions

The OC/OM index values proposed in this paper were on average close to 0.54 for most herbicides found in literature using tropical soils, but ranged from 0.395 to 1.275.

K_d and K_{oc} values of herbicides in tropical soils do not indicate inferiority or superiority when compared to values found in temperate soils, with similarities and differences among the values reported in the scientific literature. The K_d and K_{oc} values of temperate soils are still used in research on herbicide behaviour in tropical soils, however, being a resource for estimating environmental contamination.

Research in Brazil is already generating information such as sorption coefficients, however, they are not tabulated in a database as has been done for temperate soils. Thus, it was possible to group the information related to K_d and K_{oc} values of herbicides in tropical soil conditions.

The K_d values of most of herbicides were linearly correlated with OM content and CEC variation in tropical soils, generating standardized values to more accurately estimate the behaviour of herbicides in soils with similar properties and to offer better accuracy when using mathematical models.

Acknowledgements

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo/FAPESP for financial support for the completion of this research.

References

[1] Zhang, C. Z., Zhang, Z. Y., Liu, X. J., Jiang, W. and Wu, Y. D. 2010. Dissipation and environmental fate of herbicide H-9201 in carrot plantings under field conditions. Food Chem. **119**(3):874-879.

[2] Kubo, T., Ohno, M., Nagasawa, S., Kose, T. and Kawata, K. 2012. Behavior of herbicide pyrazolynate and its hydrolysate in paddy fields after application. Bull. Environ. Contam. Toxicol. **89**(5):985-989.

[3] Rozemeijer, J. C. and Broers, H. P. 2007. The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands). Environ. Poll. **148**(3):695-706.

[4] Sanches, S. M., Silva, C. H. T. P., Campos, S. X. and Viera, E. M. 2003. Pesticidas e seus respectivos riscos associados à contaminação da água. Pesticidas: R. Ecotoxicol. Meio Ambiente **13**:53-58 (in Portuguese).

[5] Wahanthaswamy, M. V. and Patil, B. V. 2004. Toxicity of pesticides to earthworm, *Eudrillus eugeniae* (Kinberg). Karnataka. J. Agric. Sci. **17**(1):112-114.

[6] Diao, J., Xu, P., Wang, P., Lu, Y., Lu, D. and Zhou, Z. 2010. Environmental behavior of the chiral aryloxyphenoxypropionate herbicide diclofop-methyl and diclofop: Enantiomerization and enantioselective degradation in soil. Environ. Sci. Technol. **44**(6):2042-2047.

[7] Alonso, D. G., Koskinen, W. C., Oliveira Jr., R. S., Constantin, J. and Mislankar, S. 2011. Sorption-desorption of indaziflam in selected agricultural soils. J. Agric. Food Chem. **59**(24):13096-13101.

[8] Estévez, M. A., Periago, E. L., Carballo, E. M., Gándara, J. S., Mejuto, J. C. and Río, L. G. 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric. Ecosyst. Environ. **123**(4):247-260.

[9] Prata, F., Cardinali, V. C. B., Lavorenti, A., Tornisielo, V. L. and Regitano, J. B. 2003. Sorção e dessorção de glifosato em solos com distintos níveis de fósforo. Sci. Agric. **60**(1):175-180 (in Portuguese).

[10] Inoue, M. H., Oliveira Jr., R. S., Regitano, J. B., Tormena, C. A., Tornisielo, V. L. and Constantin, J. 2003. Critérios para avaliação do potencial de lixiviação dos herbicidas comercializados no Estado do Paraná. Planta Daninha **21**(2):313-323 (in Portuguese).

[11] Rossi, C. V. S., Alves, P. L. C. A. and Marques Jr., J. 2005. Mobilidade do sulfentrazone em latossolo vermelho e em chernossolo. Planta Daninha **23**(4):701-710 (in Portuguese).

[12] Martin, S. M., Kookana, R. S., Zwieten, L. V. and Krull, E. 2012. Marked changes in herbicide sorption-desorption upon ageing of biochars in soil. J. Hazard. Mater. **231-232**:70-78.

[13] Sun, K., Gao, B., Ro, K. S., Novak, J. M., Wang, Z., Herbert, S. and Xing, B. 2012. Assessment of herbicide sorption by biochars and organic matter associated with soil and sediment. Environ. Poll. **163**:167-173.

[14] Piwowarczyk, A. A. and Holden, N. M. 2013. Phenoxyalkanoic acid herbicide sorption and the effect of co-application in a haplic cambisol with contrasting management. Chemosphere **90**(2):535 -541.

[15] Kumar, K. and Philip, L. 2006. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. Chemosphere **62**(7):1064-1077.

[16] Tang, Z. W., Zhang, W. and Chen, Y. M. 2009. Adsorption and desorption characteristics of monosulfuron in Chinese soils. J. Hazard. Mater. **166**(2-3):1351-1356.

[17] Liu, Y., Xu, Z., Wu, X., Gui, W. and Zhu, G. 2010. Adsorption and desorption behavior of herbicide diuron on various Chinese cultivated soils. J. Hazard. Mater. **178**(1-3):462-468.

[18] Xu, D., Xu, Z., Zhu, S., Cao, Y., Wang, Y., Du, X., Gu, Q. and Li, F. 2005. Adsorption behavior of herbicide butachlor on typical soils in China and humic acids from the soil samples. J. Colloid Interface Sci. **285**(1):27-32.

[19] Silva, A. A., Vivian, R. and Oliveira Jr., R. S. 2007 Herbicidas: comportamento no solo. In Silva, A. A. and Silva, J. F. (eds). Tópicos em manejo de plantas daninhas. UFV, Viçosa, MG, Brazil, pp. 189-248 (in Portuguese).

[20] Vezzani, F. M. and Mielniczuk, J. 2009. Uma revisão sobre qualidade do solo. Rev. Bras. Ciênc. Solo **33**(4):743-755 (in Portuguese).

[21] D'Agostinho, A. and Flues, M. 2006. Determinação do coeficiente de distribuição (K_d) de benzo(a)pireno em solo por isotermas de sorção. Quím. Nova **29**(4):657-661 (in Portuguese).

[22] Morrica, P., Barbato, F., Giordano, A., Seccia, S. and Ungaro, F. 2000. Adsorption and desorption of imazosulfuron by soil. J. Agric. Food Chem. **48**(12):6132-6137.

[23] Waldner, G., Friesl-Hanl, W., Haberhauer, G. and Gerzabek, M. H. 2012. Differences in sorption behavior of the herbicide 4-chloro-2-methylphenoxyacetic acid on artificial soils as a function of soil pre-aging. J. Soils Sediments **12**(8):1292-1298.

[24] Nelson, D. W. and Sommers, L. E. 1996. Total carbon, organic carbon, and organic matter. In Black, C. A. (ed.). Methods of Soil Analysis. Part 3. Chemical Methods. Soil Science of America and American Society of Agronomy, Madison, pp.961-1010.

[25] Gatto, A., Barros, N. F., Novais, R. F., Silva, I. R., Mendonça, E. S. and Villani, E. M. A. 2009. Comparação de métodos de determinação do carbono orgânico em solos cultivados com eucalipto. Rev. Bras. Ciênc. Solo **33**(3):735-740 (in Portuguese).

[26] Cohen, S. Z., Wauchope, R. D., Klein, A. W., Eadsforth, C. V. and Graney, R. 1995. Offsite transport of pesticides in water: Mathematical models of pesticide leaching and runoff. Pure Appl. Chem. **67**(12):2109-2148.

[27] Gustafson, D. I. 1989. Groundwater ubiquity score:A simple method for assessing pesticide leachability. Environ. Toxicol. Chem. **8**(4):339-357.

[28] Rao, P. S. C., Hornsby, A. G. and Jessup, R. E. 1985. Indices for ranking the potential for pesticide contamination of groundwater. Soil Crop Sci. Soc. Fla. Proc. **44**(1):1-8.

[29] Spadotto, C. A., Hornsby, A. G. and Gomes, M. A. F. 2005. Sorption and leaching potential of acidic herbicides in Brazilian soils. J. Environ. Sci. Health. Part B: Pestic., Food Contam., Agric. Wastes **40**(1):29-37.

[30] Spadotto, C. A., Gomes, M. A. F. and Hornsby, A. G. 2002. Pesticide leaching potential assessment in multilayered soils. Pesticidas: R. Ecotoxicol. Meio Ambiente **12**:1-12.

[31] Paraíba, L. C., Cerdeira, A. L., Silva, E. F., Martins, J. S. and Coutinho, H. L. C. 2003. Evaluation of soil temperature effect on the herbicide leaching potential into groundwater in the Brazilian Cerrado. Chemosphere **53**(9):1078-1095.

[32]Weber, J. B., Wilkerson, G. G., 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., Talbert, R. E. and Peeper, T. F. 2000. A proposal to standardize soil/solution herbicide distribution coefficients. Weed Sci. **48**(1):75-88.

[33]FOOTPRINT 2014. Creating tools for pesticide risk assessment and management in Europe. University of Hertfordshire. http://sitem.herts.ac.uk/aeru/footprint/en/index.htm. (Accessed Mar 2014).

[34]EXTOXNET 2014. Pesticide information profiles. http://extoxnet.orst.edu/pips/ghindex.html. (Accessed Mar 2014).

[35]Gomes, J., Dick, D. P. and Souza, R. F. 2002. Sorção de atrazina em cambissolo húmico do Rio Grande do Sul sob vegetação nativa. Rev. Bras. Ciênc. Solo **26**(2):521-528 (in Portuguese).

[36]Oliveira, M. F., Colonna, I., Prates, H. T., Mantovani, E. C., Gomide, R. L. and Oliveira Jr., R. S. 2004. Sorção do herbicida imazaquin em Latossolo sob plantio direto e convencional. Pesqui. Agropecu. Bras. **39**(8):787-793(in Portuguese).

[37]Guerra, N., Oliveira Jr., R. S., Constantin, J., Oliveira Neto, A. M. and Braz, G. B. P. 2013. Aminocyclopyrachlor e indaziflam: Seletividade, controle e comportamento no ambiente. Rev. Bras. Herbic. **12**(3):285-295 (in Portuguese).

[38]Andrade, S. R. B., Silva, A. A., Queiroz, M. E. L. R., Lima, C. F. and D'Antonino, L. 2010. Sorção e dessorção do ametryn em argissolo vermelho-amarelo e latossolo vermelho-amarelo com diferentes valores de pH. Planta Daninha **28**(1):177-184 (in Portuguese).

[39]Hill, I. R. 1978. Microbial transformations of pesticides. In Hill, I. R. and Wright, S. J. L. (eds). Pesticide Microbiology. Academic Press, London, pp. 137-202.

[40]Oliveira Jr., R. S., Koskinen, W. C. and Ferreira, F. A. 2001. Sorption and leaching potential of herbicides on Brazilian soils. Weed Res. **41**(2):97-110.

[41]Procópio, S. O., Pires, F. R., Werlang, R. C., Silva, A. A., Queiroz, M. E. L. R., Neves, A. A., Mendonça, E. S., Santos, J. B. and Egreja Filho, F. B. 2001. Sorção do herbicida atrazine em complexos organominerais. Planta Daninha **19**(3):391-400 (in Portuguese).

[42]Arantes, S. A. C. M., Lima, J. M., Nóbrega, J. C. A., Guilherme, L. R. G., Julião, L. G. F. and Jesus, E. A. 2006. Sorção da atrazina em solos representativos da sub-bacia do Rio das Mortes - MG. Pesticidas: R. Ecotoxicol. Meio Ambiente **16**:101-110.

[43]Inoue, M. H., Oliveira Jr., R. S., Regitano, J. B., Tormena, C. A., Constantin, J. and Tornisielo, V. L. 2006. Sorption-desorption of atrazine and diuron in soils from southern Brazil. J. Environ. Sci. Health. Part B: Pestic., Food Contam., Agric. Wastes **41**(5):605-621.

[44]Carbo, L., Martins, E. L., Dores, E. F. G. C., Spadotto, C. A., Weber, O. L. S. and Freire, E. M. L. 2007. Acetamiprid, carbendazim, diuron and thiamethoxam sorption in two Brazilian Tropical Soils. J. Environ. Sci. Health. Part B: Pestic., Food Contam., Agric. Wastes **42**(5):449-507.

[45]Oliveira Jr., R. S., Alonso, D. G. and Koskinen, W. C. 2011. Sorption-desorption of aminocyclopyrachlor in selected Brazilian soils. J. Agric. Food Chem. **59**(8):4045-4050.

[46]Souza, M. D., Boeira, R. C., Gomes, M. A. F., Ferracini, V. L. and Maia, A. H. N. 2001. Adsorção e lixiviação de tebuthiuron em três tipos de solo. Rev. Bras. Ciênc. Solo **25**(4):1053-1061 (in Portuguese).

[47]Spadotto, C. A., Matallo, M. B. and Gomes, M. A. F. 2003. Sorção do herbicida 2,4-D em solos brasileiros. Pesticidas: R. Ecotoxicol. Meio Ambiente **13**:103-110 (in Portuguese).

[48]Semple, K. T., Morriss, A. W. J. and Paton, G. I. 2003. Bioavailability of hydrophobic organic contaminants in soils: Fundamental concepts and techniques for analysis. Eur. J. Soil Sci. **54**(4):809-818.

[49]Ferri, M. V. W., Gomes, J., Dick, D. P., Souza, R. F. and Vidal, R. A. 2005. Sorção do herbicida acetochlor em amostras de solo, ácidos húmicos e huminas de argissolo submetido à semeadura direta e ao preparo convencional. Rev. Bras. Ciênc. Solo **29**(5):705-714 (in Portuguese).

[50]Ferri, M. V. W., Vidal, R. A., Gomes, J., Dick, D. P. and Souza, R. F. 2002. Atividade do herbicida acetochlor em solo submetido à semeadura direta e ao preparo convencional. Pesqui. Agropecu. Bras. **37**(12):1697-1703 (in Portuguese).

[51]Matallo, M. B., Almeida, S. D. B., Costa, E. A. D., Luchini, L. C., Gomes, M. A. F., Spadotto, C. A., Cerdeira, A. L., Moura, M. A. M. and Franco, D. A. S. 2008. Sorption of *s*-triazines in Brazilian rainforest soils. Pesticidas: R. Ecotoxicol. Meio Ambiente **18**:17-26.

[52]Lavorenti, A., Rocha, A. A., Prata, F., Regitano, J. B., Tornisielo, V. L. and Pinto, O. B. 2003. Comportamento do diclosulam em amostras de um latossolo vermelho distroférrico sob plantio direto e convencional. Rev. Bras. Ciênc. Solo **27**(2):183-190 (in Portuguese).

[53]Dores, E. F. G. C., Spadotto, C. A., Weber, O. L. S., Carbo, L., Vecchiato, A. B. and Pinto, A. A. 2009. Environmental behaviour of metolachlor and diuron in a tropical soil in the central region of Brazil. Water Air Soil Poll. **197**(1-4):175-183.

[54]Barizon, R. R. M., Lavorenti, A., Regitano, J. B. and Tornisielo, V. L. 2005. Sorção e dessorção do imazaquin em solos com diferentes características granulométricas, químicas e mineralógicas. Rev. Bras. Ciênc. Solo **29**(5):695-703 (in Portuguese).

[55]Regitano, J. B. and Koskinen, W. C. 2008. Characterization of nicosulfuron availability in aged soils. J. Agric. Food Chem. **56**(14):5801-5805.

[56]Assis, E. C., Silva, A. A., Barbosa, L. C., Queiroz, M. E. L. R., D'Antonino, L. and Cruz, L. S. 2011. Sorption and desorption of picloram in soils under pastures in Brazil. Planta Daninha **29**(4):893-899.

[57]Regitano, J. B., Koskinen, W. C. and Sadowsky, M. J. 2006. Influence of soil aging on sorption and bioavailability of simazine. J. Agric. Food Chem. **54**(4):1373-1379.