

Estimating sorption of monovalent acidic herbicides at different pH levels using a single sorption coefficient

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Abstract

BACKGROUND: Monovalent acidic pesticide sorption can be determined for any soil pH if the dissociation constant of the compound is known, and sorption coefficients are available for at least two different pH values, measured in a wide enough range to enable estimating both neutral and anionic form coefficients. Sorption estimates have also been made from a single sorption coefficient available, assuming a non-compound specific value of the anionic form sorption coefficient or considering a generic ratio between sorption coefficients of the two forms. A compound-specific procedure for adjustment of parameters of the equation for estimating sorption of monovalent acidic herbicides at different pH levels, from a single sorption coefficient, is proposed and evaluated.

RESULTS: The quality of fits was good for sorption of all three herbicides studied, especially for 2,4-D and flumetsulam at pH above 5, even for diverse soils and experimental procedures and conditions. The best fits resulted in the following ratios of the theoretical maximum organic-carbon sorption coefficients for neutral and anionic forms ($K_{ocn}:K_{oca}$): 440:1 for 2,4-D; 132:1 for flumetsulam; and 55:1 for sulfentrazone.

CONCLUSION: The ratios of theoretical maximum sorption coefficients for neutral and anionic forms ($K_{ocn}:K_{oca}$) are compound-specific, thus this procedure should also be applied to pH-sorption datasets for other acidic pesticides to provide the respective ratio between the theoretical maximum sorption coefficients, instead of using generic assigned values. More calibration research is recommended and validation of this approach is required to demonstrate applicability of the method.

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Keywords: ionizable compound; acidic pesticide; soil; sediment; agricultural efficacy; environmental behavior

1 INTRODUCTION

Sorption affects different processes of pesticide fate and behavior in the environment (i.e., bioavailability, degradation and transport). Models that describe sorption are important in pesticide registration and environmental quality assessments.¹ Approximately a third of the active ingredients of pesticides currently used are ionizable (i.e., acidic, basic and amphoteric) compounds. It is noteworthy that many veterinary and human pharmaceuticals and personal care products are also ionizable compounds. Ionizable pesticides can exist in different proportions of neutral and ionic forms in soil and sediment, depending on pH. The ionized form behaves differently from the non-ionic molecule, severely limiting generalizations.^{2–7} Agricultural efficacy and environmental behavior of pesticides, especially soil-applied herbicides, depend on sorption.

Among the models frequently used in predicting environmental behavior and fate of pesticides, only a few have an option for ionizable pesticides; that is Root Zone Water Quality Model – RZWQM,⁶ Chemicals, Runoff, and Erosion from Agricultural Management Systems – CREAMS,⁸ Pesticide Leaching Model – PELMO⁹ and Pesticide Emission Assessment at the Regional and Local Scale – PEARL.¹⁰

The sorption coefficient of an ionizable pesticide is a combination of the sorptivity of both neutral and ionic forms. It is useful to assume two sorption coefficient limits that can be obtained when approximately the pesticide is as neutral molecule or charged species. Thus, the composite sorption coefficient can be estimated as the sum of the sorption of neutral and ionic forms.⁸ In the PEARL model, the Freundlich equation was modified to consider weak acids, using the organic-carbon sorption coefficient (K_{foc}) under acidic conditions and under basic conditions, respectively.^{10,11} The pH range that the overall sorption is measured should be sufficiently ample to allow estimation of both coefficients.¹² To determine whether this approach more accurately represents sorption changes with pH, further investigations

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are necessary, especially with data from sorption experiments performed at pH values below the pKa of the compound.¹

According to Wauchope *et al.*,^{6,7} when a default organic-carbon sorption coefficient (Koc) is available, RZWQM uses an approximation procedure to provide a correction for ionization, and requires values of sorption coefficients for individual neutral and ionic forms. Based on the observed sorption coefficient for strong-acidic pesticides, Koc for anions was assumed to equal 10². While within PELMO, the sorption coefficient of an ionizable compound is estimated by the weighted mean of neutral and ionic forms and differences in sorption at different pH values are related to the variation of the fraction of neutral form (pH-dependent). The organic-carbon sorption coefficient can be determined for any soil pH if the sorption coefficient is known for at least two different pH values.¹³ To determine sorption coefficients, two different built-in models can be utilized within PELMO: (i) where Koc is known at two different pH values – then all the information necessary is available to determine the sorption coefficient dependent on soil pH; and (ii) where the sorption coefficient is known at a single pH value only – then the determination of the sorption coefficient is only possible when assuming for anions of weak acids that their sorption coefficients are two to three orders of magnitude lower than the coefficient of non-ionic forms.¹⁴ Therefore, as noted by Klein,⁹ an assigned ratio of 10³:1 for sorption coefficients of the neutral form and the ionic form is considered to overcome the missing information. Based on this assumption, which is only a rough estimation, sorption coefficient can be determined for any given soil pH.

In summary, monovalent acidic pesticide sorption can be determined for any soil pH if the dissociation constant of the compound is known, and sorption coefficients are available for at least two different pH values, measured in a wide enough range to enable estimating both neutral and anionic form coefficients. However, databases and most of the literature report sorption data only at one pH in a soil or sediment. Thus, sorption of monovalent acidic pesticides has also been estimated from a single sorption coefficient available, assuming a non-compound specific value of the anionic form sorption coefficient or considering a generic ratio between sorption coefficients of neutral and anionic forms. In this paper, results of evaluating a proposed compound-specific procedure for adjustment of parameters of the equation for estimating sorption of monovalent acidic herbicides at different pH levels, from a single sorption coefficient, are presented and discussed.

2 MATERIALS AND METHODS

A theoretical basis and mathematical expression to estimate sorption of ionizable organic compounds in soils and sediments can be found in the literature.^{3,4,15–23} In all equations presented, sorption is largely influenced by the extent of dissociation or protonation of the compound. The overall sorption coefficient (Kd) of a monovalent acidic organic compound is the sum of contributions of the neutral form sorption (Kdn) and the anionic form sorption (Kda), and Kdn, Kda and, consequently, Kd are pH dependents. As noted by Franco *et al.*,²³ dissociation of monovalent acids can be determined based on the Henderson-Hasselbalch equation and is a function of the dissociation constant (pKa) and pH. Thus, Eqn 1 can be used to represent the pH dependence of monovalent acidic organic compounds sorption.

$$Kd = \frac{Kdn'}{1 + 10^{pH - pKa}} + \frac{Kda'}{1 + 10^{pKa - pH}} \quad (1)$$

where, Kdn' and Kda' are the theoretical maximum sorption coefficient for neutral and anionic forms, respectively, and neither varies with pH; Kd, Kdn' and Kda' have the same unit (L kg⁻¹).

Eqn 1 is based on Franco *et al.*,²³ however, according to Spadotto and Hornsby,²⁰ a different notation was used to clearly distinguish Kdn' and Kda' (non-pH-dependent sorption coefficients) from Kdn and Kda (pH-dependent sorption coefficients).

The ability of Eqn 1 to represent experimental datasets of Kd_(pH) values collected in the literature was assessed using parameter adjustments that minimize residuals for each herbicide–soil combination. Thus, a preliminary curve fitting of Eqn 1 was performed to evaluate the parameterized model performance and resultant Kdn':Kda' ratios.

A few datasets of sorption coefficient values for acidic pesticides at different pH levels – at least four data pairs, that is Kd_(pH), in a sufficiently wide modified pH range – for the same soil were found in the literature. In this study, data for 2,4-D,²⁰ flumetsulam,¹⁷ and sulfentrazone²⁴ were used. Flumetsulam and sulfentrazone are weak monovalent acids (pKa = 4.6 and 6.6, respectively), while 2,4-D is a strong monovalent acid (pKa = 2.8).

The Kd value at the highest pH level in the dataset of each herbicide–soil combination was assumed to represent the anionic form sorption (Kda). This was used to estimate Kda' (i.e., the non-pH-dependent coefficient for anionic form) using the second part of Eqn 1. This value, in turn, was held constant and the respective dataset was fitted to Eqn 1 to estimate the Kdn' value for specific herbicide–soil combination. This procedure allows the determination of the Kdn':Kda' ratios when Kda' values are estimated and kept constant.

The method of initially estimating and holding constant the sorption coefficient at the highest pH was also tested using larger datasets for diverse soils from literature. Sorption data reported by Spadotto and Hornsby,²⁰ Dubus *et al.*,²⁵ Duwig *et al.*,²⁶ Kah and Brown,²⁷ Bælum *et al.*,²⁸ and Prado *et al.*²⁹ for 2,4-D, by Fontaine *et al.*¹⁷ and Strebe and Talbert³⁰ for flumetsulam, and by Grey *et al.*²⁴ and Ohmes and Mueller³¹ for sulfentrazone were used.

Fitting Eqn 1 to the collected sorption datasets were made and evaluated using Microsoft Excel Analysis ToolPak™ (Solver and Data Analysis Tools) for regression statistics and analysis of variance (ANOVA). Goodness-of-fit was evaluated using the adjusted Coefficient of Determination (R²_{adj}), Probability Value (P-value) and ratio of the Root Mean Square of Error (RMSE) to the Standard Deviation of measured data (RSR).

RMSE represents the differences in measured and predicted values in proper units and, according to Legates and McCabe³² and Harmel *et al.*,³³ is an absolute error goodness-of-fit indicator. Based on Singh *et al.*,³⁴ Moriasi *et al.*³⁵ developed RSR, which, brings the benefits of statistical error indexes and includes the observations standard deviation as a scaling-normalization factor. RSR is considered low when it is less than 0.50 for datasets obtained using the same materials and method.

3 RESULTS AND DISCUSSION

Results of fitting Kd_(pH) datasets of each herbicide–soil combination to Eqn 1 are presented in Table 1. These results show a good fit for all herbicide–soil combinations as evidenced by low (< 0.50) RSR values, high R² (> 70%) and significant P-value (≤ 10%). These indicate that Eqn 1 has enough flexibility to be

Table 1. Results of fitting $K_{d(pH)}$ datasets composed of nine herbicide–soil combinations to Eqn 1

Herbicide	Soil	Kdn'	Kda'	R ² _(adj)	RSR
2,4-D ^a	Haplorthox	47.23	4.03	0.783***	0.43
Flumetsulam ^b	Appling ^c	3.48	0.00	0.889***	0.30
	Barnes ^c	27.15	0.00	0.958***	0.18
	Catlin	7.59	0.40	0.910***	0.27
	Webster	50.10	1.60	0.996***	0.05
Sulfentrazone ^d	Congaree	0.355	0.046	0.822*	0.34
	Decator	0.464	0.000	0.963**	0.20
	Dundee	0.611	0.340	0.721*	0.43
	Hiwassee	0.723	0.058	0.989***	0.09

Asterisks indicate the level of significance at 10% (*), 5% (**) and 1% (***). Kdn' and Kda' have units of L kg⁻¹.
^a Spadotto and Hornsby.²⁰
^b Fontaine *et al.*¹⁷
^c constraint Kda' ≥ 0.
^d Grey *et al.*²⁴

fitted to the datasets of pH dependence of sorption of all herbicide–soil combinations studied.

Haplorthox is a soil with high clay content, mainly kaolinite and minerals such as gibbsite, that also contains aluminum and iron hydroxides and oxyhydroxides that have variable surface charges. The Point of Zero Net Charge (PZNC) values of kaolinite and gibbsite are 5.25 and 9, respectively.³⁶ At pH values below PZNC, the mineral will have a net positive charge. In the fitting work, Kda' values different from zero indicate some sorption of anionic form of 2,4-D. The 2,4-D pKa is low (2.8), and its anionic form is prevalent at pH > pKa. At pH ≥ pKa + 2, it is expected that 2,4-D is in anionic form, under most environmental conditions (pH range 4–9). Experimental sorption data from Spadotto and Hornsby²⁰ were for a wide pH range (2.5–6.2) and, as expected, Kd values were low at pH > pKa + 2.

The fitted Kda' values for flumetsulam were low, even for the Appling series that consists of kaolinitic soil (kaolinite is variable charged clay mineral) having low clay and organic matter contents. The initial adjusted values of Kda' for the Appling and Barnes series were negative (–0.10 and –0.21, respectively), denoting low sorption or even repulsion of the anionic form by negatively charged soil colloids. A constraint of Kda' ≥ 0 was alternatively used for these soils in the fitting work to avoid negative values, with almost no effect on the estimated values of Kdn' or goodness-of-fit. Flumetsulam exists predominantly in the anionic form at pH > 4.6 and as an anion at pH ≥ 6.6. Both of these pH values are commonly present in the natural environment. Reported flumetsulam sorption data¹⁷ were for pH values below and above the pKa; it is expected that changes in pH between pKa – 2 and pKa + 2 result in differences in sorption, due to the variations in the proportion of neutral and anionic forms.

Fitted Kdn' and Kda' values for sulfentrazone were low, because overall Kd values were low. Even for kaolinitic soils such as the Decatur series (Kda' = 0) and Hiwassee series, with 35% and 30% clay content, respectively, Kda' values were low. Of these, the Decatur series soil has the highest clay to organic matter ratio (about 29:1), suggesting that a larger contribution from the anionic form to sorption on kaolinite clay (a variable-charge mineral) would be expected. However, the highest sulfentrazone Kda' value and the smallest Kdn':Kda' proportion (2:1) were in the

Dundee series soil. Reported sorption data for sulfentrazone²⁴ were at pH levels lower and a little higher (about pKa + 1) than the pKa of 6.6. Thus, even with predominance of the anionic form at pH > pKa, sulfentrazone is not completely found as an anion in the pH range studied. At pH < 6.6, this herbicide is mainly in the neutral form.

Table 2 presents results of initially estimating and keeping constant Kda' from a single Kd at the highest pH in the respective dataset and then adjusting only the Kdn' value to the Kd_(pH) dataset of each herbicide–soil combination to Eqn 1. This procedure also provided good qualities of fit and, as expected, improved the goodness-of-fit at higher pH levels. Thus, this is a practical alternative to adjusting parameters in modeling and estimating sorption of monovalent acidic organic compounds, especially in the environmental range of pH 4 to 9. Results presented in Tables 1 and 2 demonstrate that the Kdn':Kda' ratios were one or two orders of magnitude for all herbicide–soil combinations.

Sorption data for 2,4-D, based on soils collected from distinct locations in Australia, Brazil, Columbia, Denmark, England, France, Mexico, New Zealand, Israel, Italy and USA^{25–29} were added to the dataset of Spadotto and Hornsby.²⁰ Based on Pignatello,³⁷ only data for soils with organic carbon content higher than 0.1% were considered. The resulting dataset was used to test the method of initially estimating and holding constant the sorption coefficient at the highest pH. Data for different soils from the USA presented by Fontaine *et al.*¹⁷ for flumetsulam (Tables 1 and 2 of that paper) and by Grey *et al.*²⁴ and Ohmes and Mueller³¹ for sulfentrazone were used for testing the method.

As these data were derived from different soils, the sorption of the neutral and anionic forms was assumed to occur exclusively on organic matter, and Eqn 1 was modified to accommodate this assumption. As noted by Tülp *et al.*,³⁸ organic matter is the primary sorbent in soils, even for anionic forms of organic acids, with the exception of highly weathered tropical and subtropical soils with low organic matter content. The anionic forms of organic acids sorbs markedly less to organic matter than their related neutral form.³⁹ Results in Table 1 corroborate this statement.

Thus, Koca' was determined using the second part of Eqn 1, assuming that the respective Koca is equal to the highest-pH

Table 2. Results of fitting $K_{d(pH)}$ datasets of each herbicide–soil combination to Eqn 1, initially estimating K_{da}' from a single K_d at the highest pH level in the respective dataset

Herbicide	Soil	$K_{d(pH)}^a$	K_{da}^b	K_{dn}'	R^2	RSR
2,4-D	Haplorthox	0.40(6.2)	0.40	51.42	0.814***	0.52
Flumetsulam	Appling	0.19(6.4)	0.19	3.45	0.911***	0.32
	Barnes	0.56(6.8)	0.56	26.94	0.966***	0.19
	Catlin	1.05(6.8)	1.05	7.46	0.928***	0.30
	Webster	1.00(7.1)	1.00	50.28	0.997***	0.06
Sulfentrazone	Congaree	0.058(7.7)	0.063	0.351	0.882*	0.35
	Decator	0.052(7.5)	0.059	0.464	0.975**	0.20
	Dundee	0.370(7.5)	0.422	0.589	0.814*	0.60
	Hiwassee	0.119(7.5)	0.135	0.700	0.992***	0.20

^a K_d at the highest pH level available.

^b K_{da}' determined assuming K_d at the highest pH level as K_{da} , using the second part of Eqn 1. Asterisks indicate the level of significance at 10% (*), 5% (**), and 1% (***). K_d , K_{dn}' and K_{da}' all have the same unit ($L\ kg^{-1}$).

K_{oc} . In turn, K_{ocn}' was estimated by fitting each dataset to Eqn 1. Results are presented in Fig. 1.

The highest-pH K_{oc} values were $19\ L\ kg^{-1}$ at $pH = 8.3$ for 2,4-D; $5\ L\ kg^{-1}$ at $pH = 7.6$ for flumetsulam; and $1\ L\ kg^{-1}$ at $pH = 8.2$ for sulfentrazone. These values were used as the respective reference values. The quality of fit was good for all three herbicides, showing that the tested method was able to represent the datasets of sorption as a function of pH in different soils. It is worthy of note that, in the RZWQM database,⁶ default K_{oc} values are $20\ L\ kg^{-1}$ ($pH = 6$) for 2,4-D and $5\ L\ kg^{-1}$ ($pH = 8$) for flumetsulam, which when used as reference values resulted in good-quality fit for both herbicides [2,4-D ($R^2 = 0.660^{***}$; $RSR = 0.63$) and flumetsulam ($R^2 = 0.747^{***}$; $RSR = 0.50$)]. There are no data for sulfentrazone in the RZWQM database.

In the RZWQM database, based mainly on Hornsby *et al.*,⁵ a single K_{oc} value provides only a first-approximation estimate. The simplifying assumption that the anionic form of acidic pesticides is, like the neutral form, solely sorbed to soil organic matter was also made to build the RZWQM database. The default K_{oc} is at pH of the soil in which K_{oc} was measured. For many pesticides a source-soil pH of 6 was assumed.

2,4-D is expected to be an anion for most of the environmentally relevant pH range. This can account for the low experimental and predicted values of K_{oc} at $pH > 5$. It is not clear in Fig. 1 the sigmoidal shape (due to the acid dissociation function) of the adjusted curve for 2,4-D, because less sorption coefficient data are available at pH below 4.8 ($pK_a + 2$) for this herbicide and the lowest pH in the dataset (and in the adjusted curve) is higher than its pK_a . Sorption of 2,4-D seems to be consistently underestimated at intermediate pH levels, thus using results of the procedure here proposed in a leaching simulation make an estimation of groundwater contamination more conservative regarding environmental problems.

Flumetsulam is predominantly in the anionic form at $pH > 4.6$ and entirely as an anion at $pH \geq 6.6$, which can explain the low values and the smaller scatter of experimental K_{oc} data at $pH > 6$. Most reported sorption data for sulfentrazone are at pH levels between $pK_a - 2$ and $pK_a + 2$, which is the range where any change in pH results in change in sorption, because the proportion of neutral and anionic forms is varying. Along with the different properties of diverse soils, this can help explain the dispersion of experimental K_{oc} values.

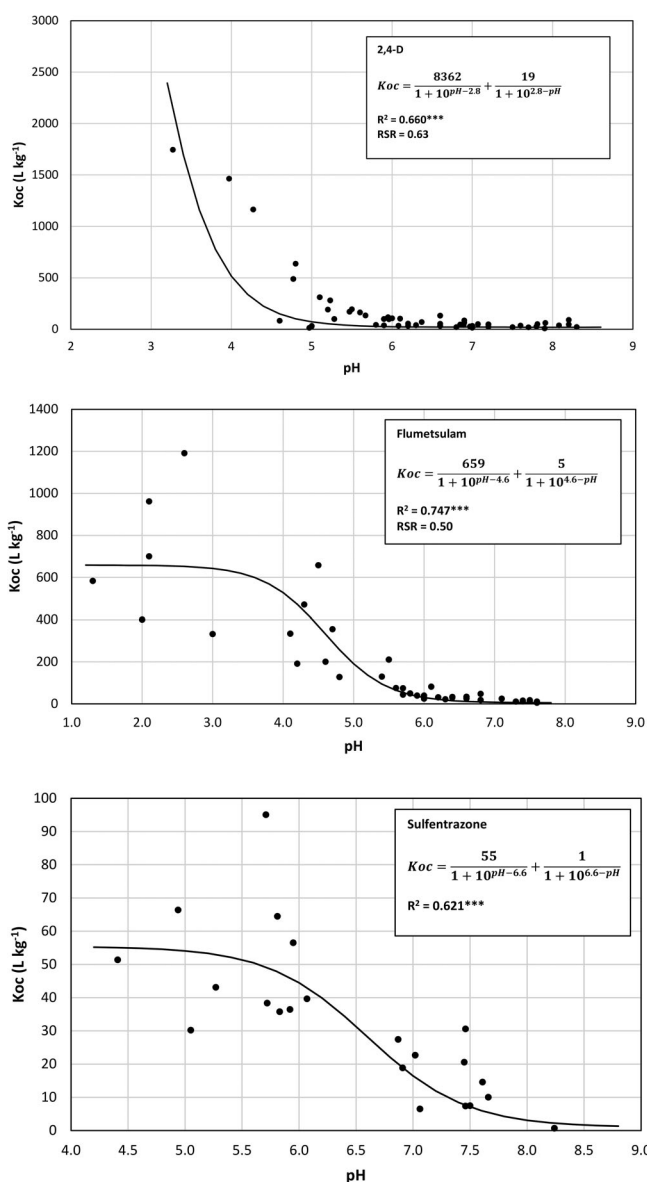


Figure 1. Curves generated using Eqn 1, starting with K_{oc} value at the highest pH level in the respective dataset (—) and the original datasets (●) for 2,4-D, flumetsulam and sulfentrazone.

The quality of fit was good for all three herbicides, considering that sorption data are for diverse soils with distinct properties, other than organic carbon content (e.g., type of decomposing material and stage of decomposition of organic matter, molecular structure of humic acid), and the fact that they were generated by using different experimental procedures and conditions (e.g., ionic composition and ionic strength of soil solution, electrolyte solution and soil: solution ratio for pH measurement).

As noted by Kah and Brown,²¹ differences in experimental methods sometimes complicate the interpretation and comparison of results relative to the influence of pH on sorption of ionizable pesticides in soils. According to the authors, standardization of experimental settings, description of methods used to determine soil properties, especially organic matter content and pH, and determination of pH at the surface of soil particles should improve comparisons of results from different studies.

Nonionic interactions seem to rule the partitioning of neutral and anionic forms to organic matter, however electrostatic interactions of anionic forms with organic matter are a less understood function of the acidic functional group type.³⁸ Discussing different mechanisms of sorption is beyond the scope of this paper. For further information, Kah and Brown²¹ offered a comprehensive review on sorption of ionizable pesticides.

From data used to generate curves in Fig. 1, the best fits resulted in the following ratios of theoretical maximum organic-carbon sorption coefficients for neutral and anionic forms (Kocn':Koca'): 440:1 for 2,4-D; 132:1 for flumetsulam; and 55:1 for sulfentrazone. Thus, for these three compounds, the Kocn':Koca' ratio was inversely proportional to the dissociation constant (pKa).

It is noteworthy that Nicholls¹⁴ stated that sorption coefficients of anions of weak acids (as flumetsulam and sulfentrazone) are two to three orders of magnitude lower than the coefficient of the neutral form and Klein⁹ assumed an assigned ratio of 10³:1 for sorption coefficients of the neutral form and the anionic form. Green and Karickhoff² assumed a Koc value for anions of strongly acidic compounds, as 2,4-D, equals to 10 L kg⁻¹; the Koca' value estimated here is 19 L kg⁻¹ (Fig. 1).

Sorption coefficient data (Kd) in the literature for all three herbicides are not enough for model validation. Other data for 2,4-D are only available at pH levels above 4.8 (pKa + 2), in the range that changes in sorption with pH are not large. There are few data in literature on sorption of flumetsulam and sulfentrazone, which were already used in the calibration effort.

The proposed method is intended to be applied primarily in the modeling-simulation context, as an alternative to estimate sorption of acidic pesticides at different pH levels. From a single sorption coefficient for each pesticide available in databases, approximate extrapolation is possible by using the compound-specific Kocn':Koca' ratio, if it was previously determined. Thus, the main purpose of this work was to develop a method to determine the Kocn':Koca' ratio for each compound, considering different soils. It can also be applied for a specific soil (or sediment), however, it is not to replace laboratory methods for determining sorption coefficients at various pH levels.

4 CONCLUSION

The described and tested procedure, named 'high-pH boundary estimation method', is a compound-specific method to adjust parameters for modeling and estimating sorption of monovalent acidic organic compounds, from a single sorption coefficient. The quality of fit was good for sorption of acidic herbicides, especially

for 2,4-D and flumetsulam at pH above 5. The ratios of theoretical maximum sorption coefficients for neutral and anionic (Kocn':Koca') are compound-specific, thus this procedure should also be applied to pH-sorption datasets for other acidic pesticides (and for other monovalent acidic organic compounds, in general) to provide the respective ratio between the neutral and anionic form theoretical maximum sorption coefficients, instead of using generic assigned values. Knowing this ratio for each monovalent acid compound will be useful for estimating the respective sorption at different pH levels, from a single coefficient. However, more calibration research with broader datasets is recommended and validation of this approach against independent data is required to demonstrate applicability of the method.

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