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Research article

Pesticide sorption and leaching potential on three Hawaiian soils

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ABSTRACT

On the Hawaiian Islands, groundwater is the principal source of potable water and contamination of this key resource by pesticides is of great concern. To evaluate the leaching potential of four weak acid herbicides [aminocyclopyrachlor, picloram, metsulfuron-methyl, biologically active diketonitrile degradate of isoxaflutole (DKN)] and two neutral non-ionizable herbicides [oxyfluorfen, alachlor], their sorption coefficients were determined on three prevalent soils from the island of Oahu. Metsulfuron-methyl, aminocylcopyrachlor, picloram, and DKN were relatively low sorbing herbicides (K_{oc} = 3–53 mL g^{-1}), alachlor was intermediate ($K_{oc} = 120–150$ mL g^{-1}), and oxyfluorfen sorbed very strongly to the three soils ($K_{oc} >$ 12,000 mL g^{-1}). Following determination of K_{oc} values, the groundwater ubiquity score (GUS) indices for these compounds were calculated to predicted their behavior with the Comprehensive Leaching Risk Assessment System (CLEARS; Tier-1 methodology for Hawaii). Metsulfuron-methyl, aminocyclopyrachlor, picloram, and DKN would be categorized as likely leachers in all three Hawaiian soils, indicating a high risk of groundwater contamination across the island of Oahu. In contrast, oxyfluorfen, regardless of the degradation rate, would possess a low and acceptable leaching risk due to its high sorption on all three soils. The leaching potential of alachlor was more difficult to classify, with a GUS value between 1.8 and 2.8. In addition, four different biochar amendments to these soils did not significantly alter their sorption capacities for aminocyclopyrachlor, indicating a relatively low impact of black carbon additions from geologic volcanic inputs of black carbon. Due to the fact that pesticide environmental risks are chiefly dependent on local soil characteristics, this work has demonstrated that once soil specific sorption parameters are known one can assess the potential pesticide leaching risks.

1. Introduction

On the Hawaiian Islands, where groundwater is the principal source of potable water, contamination of this key resource is of great environmental concern. Agrochemicals have been detected in Hawaii's groundwater as far back as 1979, when traces of dibromochloropropane (DBCP) were discovered, and various other contaminants have since been found including ethylene dibromide (EDB), trichloropropane, bromacil, hexazinone, and atrazine (Khan and Liang, 1989; Li et al., 2001; Miles et al., 1990; Oki and Giambelluca, 1987; Zhu and Li, 2002). Hawaii's plantation agriculture elicits the widespread application of pesticides for crop production. To prevent the pollution of groundwater by these agrochemicals, the Hawaii Department of Agriculture (HDOA) regulates the registration and use of pesticide products island-wide; however, knowledge of the pesticide's leaching potential is required to do this evaluation process effectively.

HDOA utilizes fate and transport models to assess the likelihood of a pesticide leaching and compromising groundwater quality (Dusek et al., 2010). The Tier-I model employed for registering new pesticides is based on the revised attenuation factor (AFR) approach proposed by Li et al. (1998). This approach uses reference chemicals to determine a pesticide's leachability classification (i.e. unlikely, uncertain, likely) and accounts for uncertainty of model parameters in its estimation (Stenemo et al., 2007). This index-based tool and others like it [e.g. groundwater ubiquity score (GUS), Gustafson, 1989] use physicochemical parameters to estimate the ranking of a pesticide's mobility in soil over large areas. However, these estimates require site specific data on the chemical's behavior which is

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typically assessed through field or soil column experiments (Oliveira et al., 2001). The most commonly used parameters to evaluate pesticide leaching are the chemical half-life ($t_{1/2}$) and the sorption/distribution coefficient (K_d, L kg^{-1}), or, in many models, the K_d value normalized to the soil organic carbon content (K_{oc}, L kg^{-1}) (Oliveira et al., 2001). Because pesticide fate and transport is largely controlled by a chemical's sorptive behavior, accurate site-specific K_d and K_{oc} values are essential for evaluating its leaching risk in soil.

The sorption of pesticides to soil is influenced by the physicochemical properties of the pesticide itself, as well as the properties of the soil. Through comparisons of chemically disparate pesticides, it has been observed that weak acid herbicides (which exist primarily in their anionic form at typical soil pH levels) are often sorbed less than nonionic and weak base herbicides on the same soils (Assis et al., 2011; Dyson et al., 2002; Hiller et al., 2008; Nicholls and Evans, 1991). Correlations with pesticide solubility and sorption have also been reported (Hiller et al., 2008; Laabs et al., 2002). In terms of soil characteristics, organic carbon (OC) content, clay content, clay mineralogy, and pH are known to affect the immobilization and degradation of pesticides (Barriuso et al., 1992; Hiller et al., 2008; Koskinen and Harper, 1990). The oxide character and content can also be influential, particularly in tropical soils such as those found in Hawaii (Assis et al., 2011; Shuai et al., 2012).

Local climatic conditions can strongly influence the aforementioned soil properties and in turn, the sorption of applied herbicides (Langenbach et al., 2001). Tropical soils, compared to temperate soils, are exposed to relatively high year-round temperatures and high rainfalls. For example, at an elevation of 500 m on the Hawaiian Island of Maui, the average air temperature is approximately 20 °C. Mean annual open sea rainfall around Hawaii ranges from 640 to 760 mm, with orographically driven rainfall between 250 and 11,140 mm on the islands (http://www2.hawaii.edu/~hikawa/mauinet/climate.html; accessed 10/22/2014). Soils under tropical conditions such as these typically have low organic matter, low pH, and high levels of aluminum and iron oxides (compared to temperate soils) (Oliveira et al., 2001; Sanchez, 1977). However, these distinct properties imply that sorption coefficient values from temperate climates cannot be readily extrapolated to tropical regions (e.g., Rao et al., 1974). To better understand differences in sorptive behaviors of pesticides in tropical versus temperate zones, a number of studies have focused on tropical soils in Brazil (Assis et al., 2011; Dores et al., 2009; Laabs et al., 2002; Langenbach et al., 2001; Oliveira et al., 2001). However, there is need to verify that information on pesticide mobility in Brazilian soils can accurately describe the movement of chemicals in other tropical soils, such as those in Hawaii. In addition, the volcanic origins of Hawaiian soils may confound pesticide sorption estimations based on other tropical soils.

The objective of this study was to characterize the sorption of four weak acid herbicides (aminocyclopyrachlor, picloram, metsulfuron-methyl, diketonitrile (DKN)) and two neutral nonionizable herbicides (oxyfluorfen, alachlor) on three Hawaiian soils. To determine their leaching potentials, the measured sorption coefficients of the herbicides were used to calculate the corresponding $t_{1/2}$ values required to qualify as a "leacher" (GUS index) (Gustafson, 1989). The leaching potentials of these chemicals were then assessed using the CLEARS leaching tool (Stenemo et al., 2007).

2. Materials and methods

2.1. Soils

Three Hawaiian soils from the island of Oahu were selected for this study: Poamoho, Manoa, and Waimanalo. At each location, soil was collected from the upper 20 cm, air-dried, and passed through a 2 mm sieve. Select properties of these soils are listed in Table 1. Analyses of soil texture, OC content, and total nitrogen (N) were performed by the University of Minnesota Soil Testing Laboratory (St. Paul, MN). Soil texture was determined using the hydrometer method. Soil OC content was determined by dry combustion at 900 °C and measurement of CO_2 evolution using a C/N Analyzer (VarioMAX; Elementar Americas, Inc., Mt. Laurel, NJ). Total N measurements were based on the Dumas Method (Lee et al., 1996) using a Nitrogen Analyzer (FP-528; LECO Corp, St. Joseph, MI). Soil pH was measured in 0.005 M $CaCl_2$ using a 1:1 soil:solution ratio.

2.2. Chemicals

Information regarding the 6 herbicides evaluated in this study is given in Table 2. Solutions were prepared for each herbicide with $CaCl_2$ (0.005–0.01 M) in the following concentrations: aminocyclopyrachlor (0.3 mg L^{-1}), picloram (1 mg L^{-1}), metsulfuron-methyl (0.4 mg L^{-1}), oxyfluorfen (0.03 mg L^{-1}), DKN (0.5 mg L^{-1}), and alachlor (1 mg L^{-1}). All solutions were spiked with the corresponding ^{14}C radiolabeled chemicals to give solution radioactivity levels between 75 and 400 Bq mL^{-1}.

2.3. Sorption

Sorption studies were performed in duplicate using the batch equilibration method. The ratio of soil to solution for the herbicides was selected independently to achieve measurable sorption of the original chemical. In glass centrifuge tubes with Teflon-lined caps, 15 mL of aminocyclopyrachlor solution was added to 10 g of soil, 20 mL of oxyfluorfen solution to 1 g, 10 mL to 10 g for DKN and alachlor, and 6 mL to 6 g soil for both the picloram and metsulfuron. The tubes were shaken approx. 18 hr, sufficient time for equilibration according to previous kinetics studies (data not shown). Samples were centrifuged for 30 min at 1280 × g and the supernatants were collected. One mL aliquots of the supernatant solutions were combined with 5 mL scintillation cocktail (EcoLite(+)™, MP Biomedicals, LLC, Solon, OH), vortexed, and analyzed for ^{14}C by liquid scintillation counting using a Packard 1500 Tri-Carb counter (Packard Instruments, Downers Grover, Il).

The difference between the initial herbicide concentration in solution and the concentration after equilibration was assumed to equal the amount of herbicide sorbed to the soil. The sorption coefficient, K_d (L kg^{-1}), was determined from the concentration sorbed (C_s) and the concentration remaining in solution after equilibration (C_w) according to the following relationship:

$$K_d = \frac{C_s}{C_w}. \tag{1}$$

K_d values were calculated for each soil-herbicide interaction and were normalized to the soil organic carbon content (*%OC*) to give the K_{oc} coefficient:

$$K_{OC} = \frac{K_d}{\%C_{org}} \times 100. \tag{2}$$

2.4. Leaching risk

The GUS index was used to evaluate the leachability of the herbicides in this study. This screening method uses the K_{oc} value and half-life ($t_{1/2}$, days) of an herbicide to rank the likelihood of it contaminating groundwater according to two extremes (Gustafson, 1989). An herbicide with a GUS score less than 1.8 is regarded as a

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Table 1
Physicochemical properties of soils.

Soils	Classification	Clay (%)	Silt (%)	Sand (%)	Texture	% OC	Total N (% N)	pH
Poamoho	Silty clay oxisol	88.9	11.1	<2	Clay	1.43	0.12	6.8
Manoa	Clay inceptisol	49.9	26.2	23.9	Clay	2.41	0.20	6.6
Waimanalo	Clay vertisol	78.7	21.3	<2	Silty clay	1.29	0.10	6.6

Table 2
Sorption coefficients for K_d and K_{oc}.

Herbicides *(chemical class)*	Initial solution concentration (mg L^{-1})	Soils	K_d (mL g^{-1})	K_{oc} (mL g^{-1})
Aminocyclopyrachlor *(pyrimidine carboxylic acid)*	0.3	Poamoho	0.09 ± 0.03	6.3 ± 2.1
		Manoa	0.44 ± 0.01	18 ± 0.4
		Waimanalo	0.57 ± 0.02	44 ± 1.6
Oxyfluorfen *(diphenol ether)*	0.03	Poamoho	333 ± 107	23,262 ± 7448
		Manoa	351 ± 25.0	14,583 ± 1038
		Waimanalo	166 ± 1.38	12,836 ± 107
Picloram *(pyridine carboxylic acid)*	1	Poamoho	0.25 ± 0.01	17 ± 0.7
		Manoa	0.64 ± 0.02	27 ± 0.8
		Waimanalo	0.69 ± 0.00	53 ± 0.0
Diketonitrile (DKN)[a] *(oxazole)*	0.5	Poamoho	0.12 ± 0.01	8.4 ± 0.7
		Manoa	0.22 ± 0.00	9.1 ± 0.0
		Waimanalo	0.16 ± 0.01	12 ± 0.8
Metsulfuron-methyl *(sulfonylurea)*	0.4	Poamoho	0.07 ± 0.04	4.9 ± 2.8
		Manoa	0.08 ± 0.01	3.3 ± 0.4
		Waimanalo	0.06 ± 0.02	4.7 ± 1.6
Alachlor *(chloroacetanilide)*	1	Poamoho	1.80 ± 0.05	126 ± 3.5
		Manoa	2.99 ± 0.05	124 ± 2.0
		Waimanalo	2.30 ± 0.05	178 ± 3.9

[a] DKN is an herbicidally active degradate of isoxaflutole.

"nonleacher," a value greater than 2.8 qualifies as a "leacher," and those between 1.8 and 2.8 are considered to be "transitional." The GUS index is calculated from the following relationship:

$$GUS = \log t_{\frac{1}{2}}(4 - \log K_{OC}). \tag{3}$$

The $t_{1/2}$ value required for each herbicide to be classified as a "leacher" and consequently present a threat to groundwater pollution in the three soils was calculated using the experimental K_{oc} values.

The Tier-I model (Stenemo et al., 2007) employed for registering new pesticides, based on the AFR approach proposed by Li et al. (1998), was used to estimate leaching potential of chemicals on selected Hawaiian Islands. AFR is defined as

$$AFR = \ln\left(\frac{d\,(RF)\,\theta_{FC}}{q\left(t_{\frac{1}{2}}\right)}\right) + k, \tag{4}$$

where d is the compliance or depth to groundwater (m), θ_{fc} is the water content at field capacity, q is the water flow (or recharge) rate through the soil (m d^{-1}), k is a constant ensuring AFR is greater than unity, and $t_{1/2}$ is the pesticide half-life (d). RF is the retardation factor defined as

$$RF = 1 + \frac{\rho(f_{OC})K_{OC}}{\theta_{fc}}, \tag{5}$$

where ρ_b is the soil bulk density (kg m^{-3}), f_{OC} is the fractional organic carbon content (0–1), and K_{OC} is the sorption coefficient (m^3 kg^{-1}).

The model, which was implemented in ArcGIS (ESRI, Redlands, CA) as a customized tool using Visual Basic script, allowed spatial analysis of soil vulnerability for the major islands of Hawaii. Soil (i.e., θ_{FC}, ρ_b, and f_{OC}) and recharge properties (i.e., q) previously updated for AFR and RF calculations (Stenemo et al., 2007) were used in this assessment. Sorption coefficients and half-life values of selected herbicides varied depending on different leaching scenarios (see Section 3.2). The tool also accounted for the uncertainty of model outputs from input parameters through first order uncertainty analysis. By comparing (the upper and lower) uncertainty bands of known reference chemicals (i.e., a leacher and non-leacher in Hawaii) to those of a chemical of interest, the leaching risk of selected herbicides was determined to be likely (leaching), uncertain (or intermediate), or unlikely (or low) in areas where soil information was available. For the leaching assessment, d is set to 0.5 m and herbicides were assumed to be uniformly applied to the soil surface for each island. Note that although the Tier-I tool is not specifically designed to address groundwater vulnerability, it is used as an initial indicator of whether or not a particular chemical is likely to contaminate shallow groundwater in Hawaii (Stenemo et al., 2007). The tool is particularly beneficial to areas with limited parameter information for simulations. More information on the leaching tool in Hawaii can be found in the previous study (Stenemo et al., 2007).

2.5. Biochar amendment

The influence of three biochar amendments on the sorption of aminocyclopyrachlor was also determined. The three biochars were prepared from wood pellets (650 °C), wood chips (~500 °C), and cornstover (490 °C). The same batch equilibration methods as previously outlined were used; however, 1.0 g of biochar was mixed with the 10 g soil prior to the addition of 15 mL 0.3 mg L^{-1} aminocyclopyrachlor solution.

3. Results and discussion

3.1. Sorption

The sorption of the six herbicides to the Poamoho soil, according to K_d values, increased in the following order: metsulfuron-

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methyl ≈ aminocycloprachlor ≈ DKN < picloram < alachlor << oxyfluorfen (Table 2). The Manoa and Waimanalo soils showed a similar ranking of the herbicides' sorption, metsulfuron-methyl < DKN < aminocylopyrachlor < picloram < alachlor << oxyfluorfen. Based on the K_d values reported in Table 2, metsulfuron, aminocylcopyrachlor and DKN are relatively low sorbing herbicides ($K_d < 1$ mL g^{-1}), while oxyfluorfen sorbs very strongly to the three soils. K_d values of aminocyclopyrachlor and picloram are consistent with those reported by Oliveira et al. (2013) ($K_d = 0.3$ and 0.37–0.45 mL g^{-1}, respectively) on Molokai soil, a Hawaiian Oxisol. The strong adsorption of oxyfluorfen has been observed in previous studies and attributed to the compound's high octagonal water coefficient (log $K_{ow} = 4.10$); it is accordingly considered to be a non-leacher (Kogan et al., 2007).

As expected, the observed sorption ranking, as it relates to herbicide chemistries, revealed that weak acid herbicides sorbed less than nonionizable compounds. The order did not increase according to pK_a values; however given the limited variability and low K_d values among the weak sorbing herbicides a clear pattern may be difficult to discern. The soil pH values in this study (6.6–6.8) exceeded the pK_a values of all of the ionizable herbicides (2.3–4.7), meaning the anionic forms of these compounds, which are less likely to adsorb to the negatively charged soil colloids, predominate (Assis et al., 2011; Nicholls and Evans, 1991). It has, however, been suggested that Fe^{2+} and Al^{3+} oxyhydroxides may sorb the anionic species of weak acid herbicides like aminocyclopyrachlor, as they do imazaquin, in low OC tropical soils (Oliveira et al., 2013; Regitano et al., 1997). We did not directly measure the Fe^{2+} and Al^{3+}forms, but these oxyhydrides are typically present in tropical soils (Ikawa et al., 1985).

Of the three soils used in this study, no single soil was found to consistently sorb the pesticides more or less than the others. This is not surprising due to the minimal variation among the properties of the three soils known to commonly affect sorption including OC, clay content and pH (Table 1). In fact, normalizing the sorption coefficients to soil OC did not affect the variability among the three soils. A previous study of pesticide sorption to Hawaiian soils by Dusek et al. (2010) ranked the Waimanalo soil as having an overall higher leaching potential than Poamoho; however, great variation was observed in the ranking of the soils for the six pesticides examined in the present study. The inconsistent sorption of the herbicides to one soil over another may also be a result of certain soil properties unequally impacting different classes of herbicides. For example, pH has a lesser impact on nonionizable herbicides than weak acids (Nicholls and Evans, 1991).

3.2. *Leaching risk*

The $t_{1/2}$ values calculated from the measured K_{oc} values for each herbicide assuming a GUS score of 2.8 (“leacher” classification) are listed in Table 3. In comparison to the calculated $t_{1/2}$ values, $t_{1/2}$ values previously reported for aminocyclopyrachor, metsulfuron-methyl, and picloram are longer (Table 4), indicating that they would be considered leachers. In contrast, some literature alachlor $t_{1/2}$ values are shorter and some are longer than those calculated from a GUS score equal to 2.8. When evaluating these $t_{1/2}$ values, however, one must bear in mind degradation rates of pesticides are not fixed values (Table 4).

Pesticide degradation rates are influenced by a blend of climatic conditions and soil properties. For many pesticides, degradation depends on the presence of a degrading population of soil microorganisms as well as the abundance and activity of the population, which are contingent on the soil and environmental characteristics. For example, in tropical regions the half-lives of various herbicides have been shown to decrease (compared to temperate), presumably due to enhanced microbial activity in the warm wet environment (Sethunathan et al., 1982). In the case of oxyfluorfen, however, the $t_{1/2}$ value was found to slightly increase in tropical soils (Sanchez-Bayo and Hyne, 2011). This longer half-life may in part be due to the higher rainfall regime in the tropics and the decreased photo-decomposition following its incorporation into the soil (Kogan et al., 2007). Because degradation values, like K_d values, are specific to each soil, they too must be known for a particular region to accurately evaluate leaching risks. In fact, Dyson et al. (2002) found that K_d and $t_{1/2}$ values must be “paired” (measurements from same soil) to properly assess the leaching potential of mesotrione, a weak acid herbicide. In this study by Dyson et al. (2002), mesotrione GUS values ranged 1.6-fold across 15 soils when calculated using “paired values”; while values ranged 4.6-fold when the adsorption/degradation correlation was disregarded, thereby broadening its leaching potential characterization.

As the state of Hawaii uses the Tier-1 leaching tool CLEARS (Stenemo et al., 2007) for the initial pesticide screening process, we developed leaching risk maps using this tool for three of the six chemicals, i.e., aminocyclopyrachlor (Fig. 1), metsulfuron-methyl

Table 3
Calculated $t_{1/2}$ values for GUS values of 2.8 and 1.8.

Herbicides	Soils	Calculated $t_{1/2}$ for GUS = 2.8 (days)	Calculated $t_{1/2}$ for GUS = 1.8 (days)
Aminocyclopyrachlor	Poamoho	7.5	3.6
	Manoa	10.5	4.5
	Waimanalo	15.5	5.8
Oxyfluorfen	Poamoho	–[a]	–
	Manoa	–	–
	Waimanalo	–	–
Picloram	Poamoho	10.4	4.5
	Manoa	12.2	5.0
	Waimanalo	17.1	6.2
DKN	Poamoho	8.1	3.8
	Manoa	8.3	3.9
	Waimanalo	9.2	4.2
Metsulfuron methyl	Poamoho	7.0	3.5
	Manoa	6.4	3.3
	Waimanalo	6.9	3.5
Alachlor	Poamoho	29.8	8.9
	Manoa	29.4	8.8
	Waimanalo	39.9	10.7

[a] Chemical with K_{oc} value over 10,000 would be classified as a non-leacher regardless of $t_{1/2}$.

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Table 4
Values of K_{oc} and $t_{1/2}$ obtained from different sources.

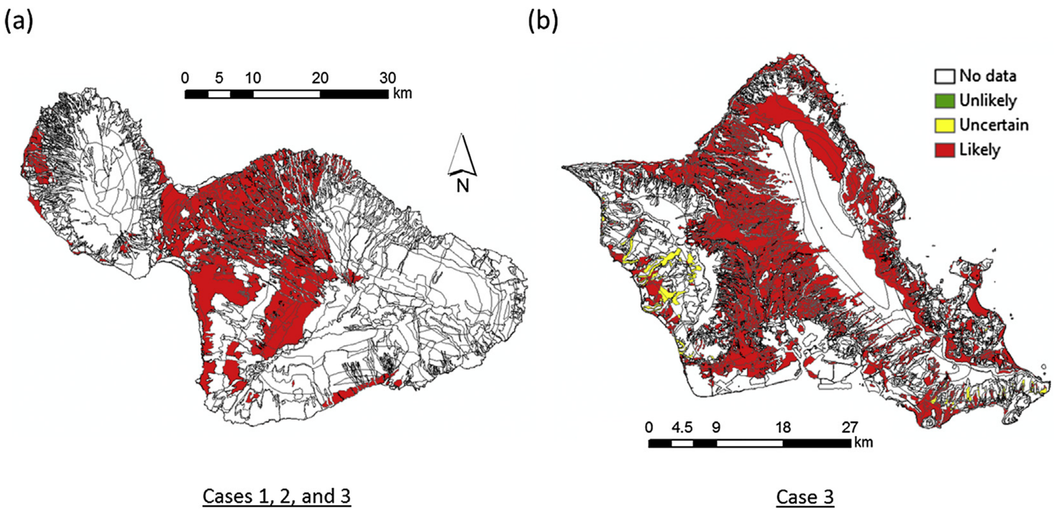
Herbicides	K_{oc} (mL g^{-1})			$t_{1/2}$ (days)			References
	Ranges	Mean	*n*	Ranges	Mean	*n*	
Aminocyclopyrachlor	2–55	29	2	11–103	41	5	University of Hertfordshire (2013)
Oxyfluorfen	2891–13,711	8056	3	31–438	136	7	University of Hertfordshire (2013)
Picloram	10–60	–	15	5–87	–	4	Biggar et al. (1978); Farmer and Aochi (1974); Fast et al. (2010); Grover (1967); Krzyszowska et al. (1994); Oliveira et al. (2013); Zhao et al. (2011)
DKN	4–60	–	9	13–239	–	18	Alletto et al. (2008); Koskinen et al. (2006); Papiernik et al. (2007); Rice et al. (2004)
Metsulfuron methyl	7–29	–	32	6–36	–	24	Barriuso et al. (1997); Baskaran et al. (1996); Ismail and Tet-Vun (2003); James et al. (1995)
Alachlor	57–457	–	21	8–200	–	13	Patakioutas and Albanis (2002); Sakaliene et al. (2007); Sonon and Schwab (1995); Stolpe and Shea (1995); Walker et al. (1996); Weed et al. (1995); Yen et al. (1994)

(Fig. 2), and oxyfluorfen (Fig. 3), on the major islands of Hawaii. Note that three leaching scenarios were developed and used for herbicide leaching assessment. This is because as described above, a significant difference was observed between K_{oc} values determined experimentally (Table 2) and those in literature (Table 4). The same applies to $t_{1/2}$ values estimated with GUS indices of 2.8 and 1.8 (Table 3), as well as the K_{oc} and $t_{1/2}$ values taken from the pesticide properties database (PPDB) of the European Union (Table 4, University of Hertfordshire (2013)). As no single source consistently provided higher values than others, we selected K_{oc} and $t_{1/2}$ that likely contributed to high, intermediate, and low leaching risk as the worst (for case 1), intermediate (for case 2), and best case scenarios (for case 3), respectively. For example, providing low K_{oc} and high $t_{1/2}$ values to the tool (for case 1) leads to a map showing a high risk of soil vulnerability, and vice versa.

Fig. 1 illustrates the leaching of aminocyclopyrachlor on two Hawaiian islands, (a) Maui and (b) Oahu, with scenarios based on different parameter values. Specifically, we used three scenarios for aminocyclopyrachlor leaching assessment as follows: experimental K_{oc} (22.9 mL g^{-1}) and $t_{1/2}$ (40.6 days) in PPDB for case 1 (i.e., the highest leaching scenario), both K_{oc} (28.5 mL g^{-1}) and $t_{1/2}$ (40.6 days) in PPDB for case 2 (i.e., the intermediate leaching scenario), and K_{oc} (28.5 mL g^{-1}) in PPDB and $t_{1/2}$ in 1.8 GUS index (4.6 days) for case 3 (i.e., the lowest leaching scenario). Note that these values are the average of experimental K_{oc} values and available literature $t_{1/2}$ values. As shown in Fig. 1a and b, aminocyclopyrachlor generally shows high leaching potential in Hawaiian soils regardless of the tested scenarios. In particular, aminocyclopyrachlor is likely to leach to groundwater in all agricultural soils on the islands of Maui (red area in Fig. 1a) and Hawaii (figure not shown). However, there are also some areas that are classified as uncertain (or less likely) in the lowest leaching scenario, which are observed in soils on the island of Oahu (yellow area in Fig. 1b) and the other islands (Kauai and Molokai, figures not shown). On Oahu, these areas appear to be related to relatively dry soil conditions.

We also estimated the leaching potential for metsulfuron-methyl (Fig. 2) and oxyfluorfen (Fig. 3) on the major Hawaiian Islands. For metsulfuron-methyl, we examined two leaching scenarios: experimental K_{oc} (4.3 mL g^{-1}) and $t_{1/2}$ in 2.8 GUS index (6.8 days) as case 1, and the experimental K_{oc} and $t_{1/2}$ in 1.8 GUS index (3.4 days) as case 2 (see Tables 2 and 3). The results of metsulfuron-methyl leaching for case 1 and 2 are shown in Fig. 2a and b, respectively. As observed in Fig. 2a (for Kauai) and b (for Molokai), there is a distinct difference in the leaching potential for metsulfuron-methyl between two cases. Similar leaching patterns for case 1 and case 2 were observed in the remaining islands (figures not shown). The figures show that with a lower GUS index, more areas become "uncertain" for leaching, and the areas showing high leaching potential are correspondingly reduced. These results indicate that the leaching tool is sensitive to the properties of metsulfuron-methyl. Therefore, these properties should be carefully considered in leaching assessments of metsulfuron-methyl.

For oxyfluorfen, we compared the leaching scenario of case 1 (i.e, experimental K_{oc} and $t_{1/2}$ in 1.8 GUS index) with that of case 2 (both K_{oc} and $t_{1/2}$ in PPDB) (Tables 2–4). This is because there is no significant difference between $t_{1/2}$ estimates for GUS indices of 2.8 and 1.8 (Table 2). Fig. 3 presents the leaching potential of oxyfluorfen on the island of Hawaii with two different scenarios. As can



Cases 1, 2, and 3

Case 3

Fig. 1. Leaching potential map of aminocyclopyrachlor on the islands of (a) Maui for all three cases (1, 2, and 3) and (b) Oahu for case 3. No data indicates soil information in the CLEARS tool is not available.

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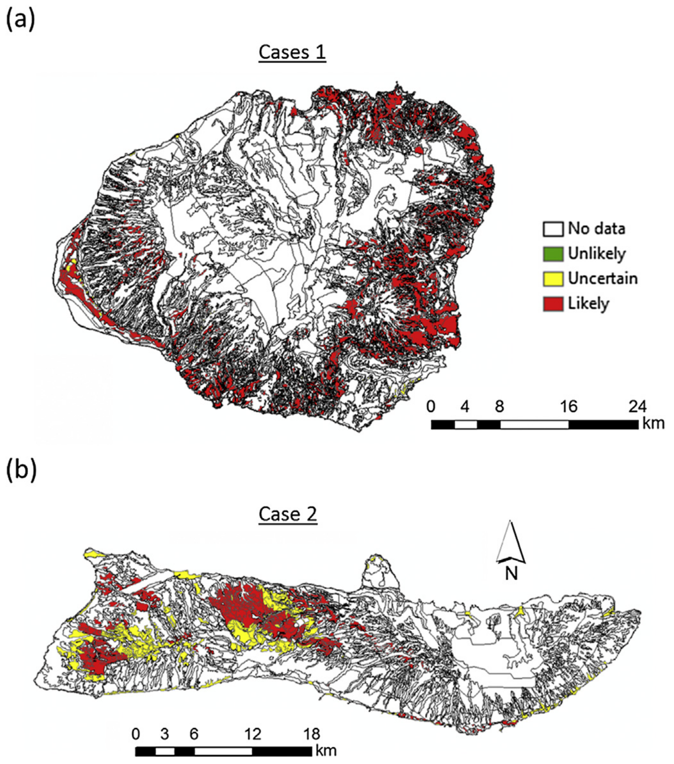

Fig. 2. Leaching potential map of metsulfuron-methyl on the islands of (a) Kauai for case 1 and (b) Molokai for case 2. No data indicates soil information in the CLEARS tool is not available.

be seen in Fig. 3a (for case 1) and b (for case 2), the difference in oxyfluorfen leaching is more apparent between these two scenarios than those of aminocyclopyrachlor and metsulfuron-methyl. The leaching potential of oxyfluorfen in Hawaiian soils is classified as “unlikely” for case 1 and “uncertain” for case 2. Note that the same patterns seen in these two cases are observed on the rest of islands (figures not shown). In accordance with above results, these findings also highlight the importance of chemical properties in groundwater vulnerability assessment.

Given its high sorptive capacity, the application of biochar to soils has been proposed as a strategy to prevent the leaching of some pesticides. The efficacy of this approach depends on the pesticide, biochar, and soil properties (Cabrera et al., 2011; Jones et al., 2011; Larsbo et al., 2013), as not all biochar amended soils have resulted in higher sorption (Rittenhouse et al., 2014). Furthermore, pesticide sorption could decrease if other soluble organic compounds are associated with the amendment, which then reduce active soil sorption sites (Cabrera et al., 2011). Given the high leaching potential of aminocyclopyrachlor under even the best case scenario, the ability of biochar to increase the sorption of aminocyclopyrachlor was tested. Of the three biochars tested, none succeeded in increasing the sorption of aminocyclopyrachlor when added to the different Hawaiian soils (Table 5). Based on this preliminary experiment, biochar does not appear to be an effective means of reducing aminocyclopyrachlor leaching in Hawaii. One potential explanation could be due to prior production of black carbon (charcoal) in these volcanic soils from carbonization of biomass by lava flows (Lockwood and Lipman, 1980).

4. Conclusion

Simplistic models such as GUS depend solely on key sorption and degradation data; therefore it is imperative that these input values be accurate for the soil and climate being assessed. Careful consideration is necessary when selecting the appropriate sorption coefficients to utilize in leaching models due to the wide range of values reported in the literature. A single pesticide can have considerably different sorption values on soils with varying physicochemical properties, and because sorption for many pesticides is concentration dependent, the sorption coefficient must reflect the application rate. Additionally, failure to account for hysteresis may lead to overestimation of leaching (Oliveira et al., 2013). When evaluating leaching potential it is also necessary to utilize the appropriate half-life, as also vary greatly. If degradation rates are not available for the specific soil and environmental conditions of interest, experimental values obtained in similar soils under

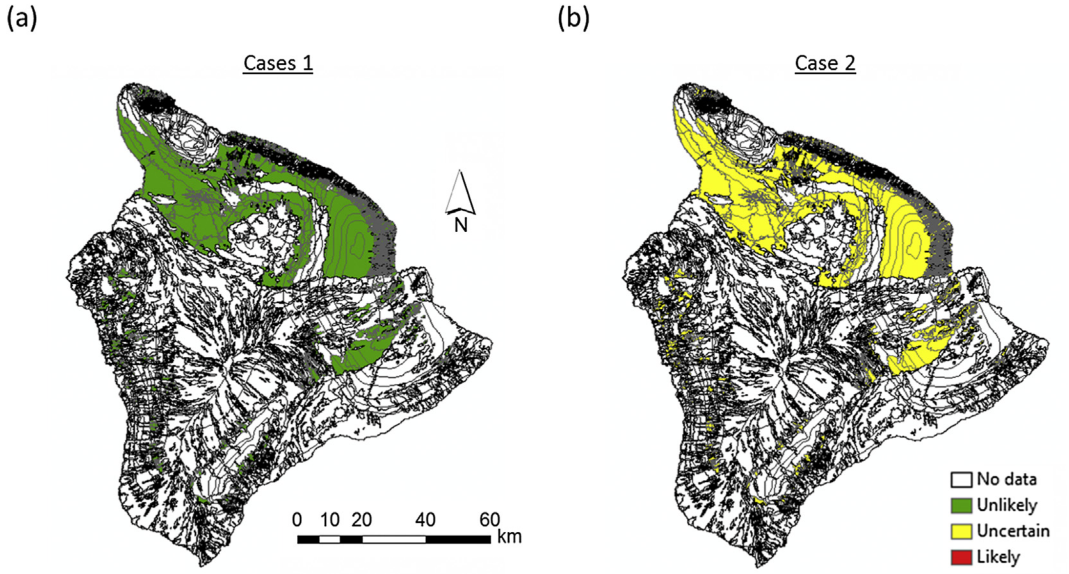

Fig. 3. Leaching potential map of oxyfluorfen on the island of Hawaii for (a) case 1 and (b) case 2. No data indicates soil information in the CLEARS tool is not available. Specifically, in Hawaii Island, these represent areas of volcanic activity.

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Table 5
Aminocyclopyrachlor (0.3 mg kg^{-1}) sorption to soils amended with biochars.

Amendments	Soils	K_d (mL g^{-1})	pH
Wood pellet biochar	Poamoho	0.14 ± 0.01	6.93 ± 0.19
	Manoa	0.38 ± 0.05	6.63 ± 0.06
	Waimanalo	0.44 ± 0.07	6.54 ± 0.08
Wood chip biochar	Poamoho	0.19 ± 0.03	6.78 ± 0.01
	Manoa	0.51 ± 0.02	6.51 ± 0.02
	Waimanalo	0.58 ± 0.08	6.40 ± 0.04
Corn stover biochar	Poamoho	0.20 ± 0.01	7.19 ± 0.01
	Manoa	0.47 ± 0.05	6.91 ± 0.02
	Waimanalo	0.45 ± 0.00	6.66 ± 0.21

representative temperature and moisture conditions can be used. As leaching models become increasingly complex, a pesticide's site-specific sorption coefficient and half-life will remain key parameters.

In spite of the aforementioned shortcomings, the GUS index provides an estimation for pesticide leaching potential, particularly when coupled with tools such as CLEARS, which combines spatial analysis. This would be especially beneficial for Hawaii where the spatial vulnerability of groundwater and the Islands' dependence on fate and transport models prompts regulators to use these tools and data for risk assessment. This in turn offers a more ecosystem level analysis of environmental risk.

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