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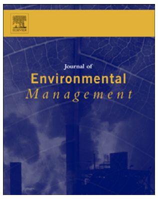

Research article

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 ($\mathrm{K_{oc}}$ = 120–150 mL g^{-1}), and oxyfluorfen sorbed very strongly to the three soils (K_{oc} > 12,000 mL g^{-1}). Following determination of $\mathrm{K_{oc}}$ 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