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Behaviour of ionic herbicides in different forestry soils derived from volcanic ash

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Abstract

Background: Weed control has been one of the most significant factors in forest establishment practices that can improve biomass production, and herbicides represent the most effective and convenient way to control weeds. The environmental concern about herbicides in this industry is because the herbicide-treated area is often located near water reservoirs or areas where rivers and creeks originate. This study aimed to determine the adsorption and degradation behaviours of seven ionic herbicides used in forestry production in five Chilean forestry soils and their relation to the leaching and to generate information to validate environmental predictive models.

Methods: Adsorption and degradation of ionisable herbicides such as simazine, terbuthylazine, hexazinone, metsulfuron-methyl, indaziflam, flazasulfuron and glyphosate were studied in Andisol, Ultisol, Inceptisol, Entisol and Alfisol forestry soils, to be related to their leaching in 100-cm high and 11-cm diameter soil disturbed lysimeters. Herbicides were quantified using high-pressure liquid chromatography and gas chromatography. Relationships between soil physicochemical properties, herbicide adsorption and degradation, and herbicide leaching were determined.

Results: In decreasing order, the herbicides were mobile in Entisol>Alfisol>Ultisol>Inceptisol>Andisol soils. On the other hand, the more leachable herbicides, from high to low, were: hexazinone, metsulfuron-methyl, simazine, glyphosate, terbuthylazine, flazasulfuron and indaziflam. The last two herbicides were not detected below 60 cm soil depth. In general, the maximum soil depth herbicide reached and the percentage mass leached up to 90 cm soil depth were inversely related to soil adsorption ($1/Kd$), soil porosity, humidity, silt, aluminium, and calcium soil content. Herbicide degradations were generally faster than referential published values.

Conclusions: The environmental coefficients of ionic herbicides were more related to soil properties than their physicochemical properties. Persistence of herbicides in soil was smaller than that commonly reported in other studies or international databases and soil adsorption averages were generally higher than international reference values. The stronger relationship between ionic herbicide behaviour and forestry soil properties endorses the requirement to determine the environmental herbicides parameters in situ, avoiding using parameters estimated in other soils.

Keywords: Adsorption, leaching, environmental risk, ionic herbicides.

Introduction

Weed control has been one of the most significant silvicultural practices that can improve the long-term growth of forest plantations, and herbicides represent the most effective and convenient way of managing weeds, being applied once or twice during the first two years after planting (Nambiar & Sand 1993; Kogan et al. 2002; Kogan & Alister 2011). Thus, environmental concerns about the use of herbicides in forestry is not related to their annual use rate but to large herbicide-treated areas, often located near water reservoirs (i.e., rivers and lakes) or areas in which rivers and creeks originate (Neary et al. 1993; Palma et al. 2004; Calder 2007).

Currently, industrial forest production operates under certified processes, resulting in a positive evolution towards using herbicides with better ecotoxicological profiles and an intrinsically lower environmental risk (Gutierrez et al. 2020; Wolf & Schweinle 2022). However, the use of lipophilic compounds ($LogK_{ow}$>3.0), or herbicides that are highly persistent (DT_{50}>90 days) and have low soil adsorption (K_{oc}<300 mL g^{-1}) or water solubility (>30 mg L^{-1}) has been criticised and some of them have been prohibited under some certifications programs, such as Forest Stewarship Council (FSC®) or Rainforest Alliance , diminishing the number of pesticides that can be used in forestry plantations (Zanucio et al. 2016; Forest Stewardship Council 2019; Rainforest Alliance 2023).

Soil leaching is one of the processes associated with the off-site movement of herbicide when applied to land under agricultural and forestry production, a factor which is affected, in a major or sometimes minor way, by their physicochemical properties and the pesticide-soil relationship (Sánchez-Camazano et al. 1996; Gao et al.1998; Yang et al. 2005; Kogan et al. 2007; Cao et al. 2008; Gámiz et al. 2019).

Chilean forestry uses soils principally derived from volcanic ash, with significant variations in pH, organic matter, clay-silt content, and subject to a Mediterranean climate, characterised by a cold and rainy winters and warm and dry summers. These productive conditions offer an extremely favourable scenario for weed growth (Rubilar et al. 2008; Kogan & Alister 2011). Therefore, developing sustainable forestry production under those conditions requires knowledge about herbicide-soil interactions and leaching potentials to safeguard and protect water resources.

This study aimed to determine the adsorption and degradation behaviours of seven ionic herbicides in five forestry soils, the consequences for leaching, and to generate information to be used to validate environmental predictive models.

Methods

Selected soils and herbicides

Andisol, Ultisol, Inceptisol, Entisol, and Alfisol soil groups samples were collected from *Pinus radiata, Eucalyptus globulus* and *E. nitens* plantation sites, in the 0 to 20 cm soil layer. In each soil group, 20 subsamples were collected using a steel shovel and samples were combined to obtain one 40 kg sample to be characterised and used in the sorption, degradation and leaching studies. Each soil sample was packed in a plastic bag and air-dried, sieved at < 2 mm, and characterised at Sidal Laboratory according to the methodology described by Kalra & Maynard (1991) (Table 1).

The herbicides were selected according to their present and future importance of use in forestry production. Therbuthylazine (Triazine, inh. PS II), simazine (Triazine, inh. PS II), and hexazinone (Triazinone, inh. PS II) corresponded to soil-active herbicides used for weed control in pine and eucalyptus plantations.

TABLE 1: Physicochemical properties of each selected soil. Analysis realisedaccording the methodology proposed by Karla & Mainard (1991). Values for each soil came from one combined sample collected from 0-20 cm soil layer.

Soil taxonomy	Textural class	pH	EC[1] (ms cm^{-1})	CEC[1] (meq 100 g^{-1})	OC[2] (%)	Sand (%)	Clay (%)	Silt (%)	Soil porosity (-)	S-DTPA[2] (mg kg^{-1})	Al-Ext[2] (mg kg^{-1})	S Cations[2] (mg kg^{-1})
Andisol	Sandy Loam	6.05	0.05	77.8	8.8	69.0	2.0	29.0	0.662	8.4	887	1,405.0
Ultisol	Clay	5.60	0.04	24.0	6.2	33.0	48.0	19.0	0.515	11.9	568	1,223.0
Inceptisol	Sandy Loam	5.10	0.08	32.6	4.0	53.0	18.0	29.0	0.550	35.7	564	1,192.0
Entisol	Sand	5.43	0.02	9.8	1.5	93.0	2.0	5.0	0.408	3.4	92	848.0
Alfisol	Sandy Clay Loam	4.96	0.08	42.7	10.8	51.0	22.0	27.0	0.542	35.4	653	1,155.0

[1] EC=Electrical conductivity; CEC=Cationic Exchange Capacity;

[2] OC=Organic Carbon; S-DTPA=Sum of available Copper, Iron, Manganese, and Zinc; Al-Ext=Extractable aluminium; S-Cations=Sum of Calcium, Potassium, Magnesium, and Sodium.

Indaziflam (Alkylazine, inh. cellulose synthesis) and Flazasulfuron (Sulfonylurea, inh. Acetolactate Synthasa enzyme) are the newest soil-active herbicides registered for forestry production, showing an appropriate environmental profile. Glyphosate (Glycine, inh. EPSPs enzyme) and metsulfuron-methyl (Sulfonylurea, inh. Acetolactate Synthasa enzyme) are the principal herbicides used to control emerged herbaceous and perennial weeds and are principally applied prior to planting. Application rates, formulations, commercial names, manufacturers and selected physicochemical properties of each herbicide are shown in Table 2.

Adsorption studies

Twenty milliliters of aqueous 0.01 M $CaCl_2$ solutions at a concentration of 3.0 mg kg^{-1} of simazine, terbuthylazine, and metsulfuron-methyl; 8.0 mg kg^{-1} of hexazinone, glyphosate, flazasulfuron, and 1.5 mg kg^{-1} of indaziflam, were prepared. Each herbicide solution was added to 10 g air-dried of each soil type in triplicated polypropylene centrifuge tubes (Three repetitions ofr each combination of soil x herbicide). Soil suspensions were shaken in darkness for eight hours at 180 rpm at 20±1°C. At the end, each tube was centrifuged at 5,000 rpm x 5 min, and 5 mL of each supernatant was removed to quantify herbicide concentrations. Control tubes with herbicide solutions without soil were included, and no herbicide losses were determined during the adsorption experiments. The amount of soil-adsorbed herbicide was calculated as the difference between the amount in the initial solution and the concentration remaining in the solution after tubes centrifugation.

Degradation studies

Six hundred grams of each soil were put on aluminium trays and applied with each herbicide at a concentration shown in Table 2, in a water volume equivalent to the content at field capacity. After herbicide application, each combination soil x herbicide was mixed in order to be homogenised, divided into two portions (two repetitions for each combination) of 300 g of soil each, and put in non-reactive plastic bags. Soil sample incubation was performed in a growth chamber set to maintain a day/night temperature of 14/8°C, relative humidity 75/90%, and daylight for 12 h, very similar to the annual average environmental conditions in the main Chilean forestry area. The incubation bags were almost closed, allowing gas exchange through a capillary tube. Every three days, all incubation bags were weighed and received the necessary water to maintain soil water at around 75% of their field capacity. Before soil sampling (0, 13, 32, 68, and 92 days after herbicide application), each incubation bag was mixed, and a 10 g soil sample was taken to determine the remnant herbicides.

Disturbed soil lysimeter studies

Duplicate 100-cm height and 11-cm diameter PVC cylinders for each soil were filled with to a height of 90 cm and mounted according to the procedure indicated by Alister et al. (2011). The soil columns were irrigated using a micro-sprinkler system, installed in the upper part of each one, until water percolation from the columns stopped (approximately 48 h). Mixtures of the herbicides were applied at maximum rates used in forestry production (Table 2), proportional to soil column area (0.01 m^2). Herbicide distribution over the soil column was carried out using a micropipette to dispense 10 mL of herbicide solution in 10 drops on a circular pattern on each column. Twenty-four hours after herbicide application 28 mm of simulated rainfall was applied and repeated seven times over two weeks. Each column was opened longitudinally 48 hours after water percolation stopped, and soil samples were taken at four depths to quantify herbicide concentrations (15, 30, 60, and 90 cm depth). Leachates were not sampled during these experiments. Preliminary work showed no effect in adsorption and leaching (0-20 micro-lysimeters) of the studied herbicides when were applied to the columns alone or a mixture of them (data not shown).

Herbicide extractions

Herbicides from each soil lysimeter layer were extracted from a 10 g soil sample and added to 50 mL centrifuge tubes with 16 mL of acetonitrile and 4 mL of water. The tubes were vortexed and shaken at 300 rpm for 90 min. Then 4 g $MgSO_4$, 1 g NaCl, 500 mg Na_2citrate, and 1 g Na_3citrate were added. The tubes were capped and immediately vortexed vigorously for 1 min and centrifuged for 5 min at 5,000 rpm. After that, 1.5 mL of the upper layer (acetonitrile) from each tube was transferred into a 1.5 mL glass vial and analysed using high-pressure liquid chromatography or gas chromatography with a mass detector, depending on the herbicide.

In the case of adsorption studies, the supernatants were filtered and transferred to 1.5 mL glass vials and analysed using high-pressure liquid chromatography with a diode-array detector.

Herbicide quantification

Simazine, terbuthylazine, hexazinone, indaziflam, and flazasulfuron quantifications were performed using gas chromatography with a mass detector unit (Shimadzu GCMS-QP2010 ultra) equipped with an RTX® 5-MS 30 m x 0.25 mm x 0.25 µm. The gas carrier was held at a flow rate of 1.2 mL min^{-1}, and the injector temperature was set at 280°C. Samples were injected at 1 µL with an autosampler in a splitless mode. The oven temperatures were 100 °C (2 min hold), then raised to 180 °C at 20 °C min^{-1} and afterward raised to 300 °C at 5 °C min^{-1}, and then raised to 310 °C at 5 °C min^{-1}.

Metsulfuron-methyl was quantified using high-pressure liquid chromatography with a diode-array detector (Hitachi LaChrom Elite Model L-2450) equipped with a Kromasil 100-5 C18, 5 µm column (250 mm length). The liquid phase was acetonitrile, formic acid 1% v/v, and water. Acetonitrile gradient was: 0 at 2 min 30%; 2 – 12 min 70%; 12 – 15 min 70%, and 15 – 25 min 30%. The column temperature was 25 °C, and the flow rate was 1 mL min^{-1}. The injection volume was 20 µL.

TABLE 2: Selected herbicides, chromatographic analytical parameters and selected physicochemical properties.

Herbicide[2]	**Maximum forestry rate (g ai ha^{-1})**	**Equivalent soil concentration (Degradation studies) (mg kg^{-1})**	**Chromatographic analytical parameters**			**Detector conditions**			**Selected herbicides physicochemical properties**[1]				
			Recovery (%)	**LD**[3] **(mg kg^{-1})**	**Rt**[3] **(min)**	**m/z**[3]	**λ**[3]	**Ex/Em**[3]	***pKa***[4]	**Solubility**[4] **(ppm)**	**Log Kow**[4]	**Vapor pressure**[4] **(mPa)**	**HK**[4] **(Pa m^3 mol^{-1})**
Simazine	4,500	3.00	95	0.010	10.473	201	--	--	1.62	5.0	2.30	8.1 x 10^{-4}	5.6 x 10^{-5}
Terbuthylazine	2,500	2.00	89	0.011	11.180	214	--	--	1.90	6.6	3.40	1.5 x 10^{-1}	2.3 x 10^{-3}
Hexazinone	2,700	2.00	104	0.012	22.237	171	--	--	2.20	33,000	1.17	3.0 x 10^{-5}	1.1 x 10^{-7}
Metsulfuron-methyl	29	0.04	85	0.012	12.183	--	224	--	3.75	2,790	-1.87	1.4 x 10^{-8}	2.9 x 10^{-6}
Indaziflam	75	0.06	116	0.011	23.757	158	--	--	3.50	2.8	2.80	2.5 x 10^{-5}	2.7 x 10^{-6}
Flazasulfuron	63	0.06	98	0.008	11.757	231	--	--	4.37	2,100	-0.06	1.3 x 10^{-2}	2.6 x 10^{-6}
Glyphosate[5]	2,160	1.30	78	0.022	19.510	57	--	--	5.60[6]	10,5600	-3.20	1.3 x 10^{-2}	2.1 x 10^{-7}

[1] Referential pesticide properties in: https://sitem.herts.ac.uk/aeru/ppdb/en/atoz_herb.htm and https://pubchem.ncbi.nlm.nih.gov/

[2] Simazine=Simazina 90 WG (ANASAC); Terbuthylazine=Terbutilazina 500 SC (SIPCAM OXON); Hexazinone=Hexazinone 750 WSG (ARYSTA LifeScience); Metsulfuron-methyl= Ajax® 50 WP (ANASAC); Indaziflam= Esplanade® 500 SC (BAYER); Flazasulfuron=Longrun WG (SYNGENTA); Glyphosate=Rango® 75 WG (ANASAC)

[3] LD= Limit of detection; Rt=Retention time; m/z=detector quantification ion mass; λ= detector wavelength; Ex/Em=Fluorescence detector excitation and emission energy.

[4] pKa= Dissociation constant; Solubility= Water solubility at 20°C; Log Kow= Octanol/water coefficient; Vapor pressure at 20°C; HK= Henry´s law constant at 25°C.

[5] Monoamonium salt.

[6] Four *pKa* values: pKa1=2.0; pKa2=2.6; pKa3=5.6 and pKa4=10.6.

TABLE 3: Adsorption coefficients (*Kd*) and soil degradation half-lives (DT_{50}) for the studied herbicides in the five forestry soils. Values corresponded to an average of three repetitions ± standard deviation.

Herbicide	**Soil type**									
	Andisol		**Ultisol**		**Inceptisol**		**Entisol**		**Alfisol**	
	K_d (mL g^{-1})	DT_{50} (days)	K_d (mL g^{-1})	DT_{50} (days)	K_d (mL g^{-1})	DT_{50} (days)	K_d (mL g^{-1})	DT_{50} (days)	K_d (mL g^{-1})	DT_{50} (days)
Simazine	1.93 (±0.10)	25.9 (±2.0)	1.09 (±0.06)	49.2 (±4.4)	2.37 (±0.12)	35.0 (±4.7)	0.26 (±0.07)	25.3 (±3.7)	3.40 (±0.18)	37.2 (±4.5)
Terbuthylazine	15.56 (±2.21)	33.2 (±3.7)	9.02 (±0.26)	55.5 (±4.0)	22.91 (±1.69)	37.9 (±3.4)	3.61 (±0.30)	15.8 (±3.2)	30.31 (±1.75)	38.8(±3.1)
Hexazinone	1.27(±0.01)	51.2 (±6.0)	0.73 (±0.02)	46.6 (±3.9)	1.63 (±0.19)	35.2 (±2.0)	0.35 (±0.04)	36.6 (±2.8)	2.27 (±0.10)	61.6 (±6.3)
Metsulfuron-methyl	1.53 (±0.13)	37.4(±3.5)	6.24 (±0.39)	28.6 (±2.9)	12.67 (±0.24)	32.7 (±3.0)	1.32(±0.19)	21.0 (±1.3)	14.23 (±0.33)	22.7 (±2.3)
Indaziflam	38.96 (±1.76)	77.9(±5.4)	35.56 (±1.88)	46.6 (±3.7)	20.59 (±1.71)	38.3 (±2.6)	10.09(±0.78)	43.1 (±3.0)	45.45 (±2.35)	36.7 (±3.2)
Flazasulfuron	8.30 (±0.84)	59.0(±4.8)	1.43 (±0.16)	42.2 (±2.9)	12.99 (±0.31)	27.9 (±2.0)	3.67 (±0.24)	22.1 (±2.5)	9.75 (±0.51)	51.2 ±2.6)
Glyphosate	692.2 (±38.5)	46.1(±4.3)	331.3 (±17.28)	57.2 (±4.7)	385.9 (±25.3)	40.5 (±4.5)	252.2(±27.57)	47.8 (±3.0)	511.9 (±44.8)	75.8 (±6.1)

Glyphosate FMOC derivatives (Catrinck et al. 2014) were determined using high-pressure liquid chromatography with a fluorescence detector (Hitachi LaChrom Elite Model L-2485) equipped with two Chromolith HighResolution RP-18e, 5 µm column (150 mm length) in tandem. The liquid phase used was acetonitrile and phosphoric acid 0.2% v/v. The acetonitrile gradient was: 0 at 16 min 45%; 16–25 min 45%; 25–30 min 10%, and 30–38 min 10%. The column temperature was 30 °C, and the flow rate was 1 mL min^{-1}. The injection volume was 10 µL. Recovery from spiked samples, detection limits, retention times, and detector conditions are shown in Table 2.

Data analysis

Equations for adsorption and degradation studies were fitted using non-linear regression analysis. Adsorption coefficients (*Kd*) were determined using Equation 1, where C_s (mg kg^{-1}) is the sorbed herbicide and *Ce* (mg L^{-1}) is the herbicide in solution after the equilibrium period. Equation 2 was used to estimate organic carbon adsorption coefficient (*Koc*), where *OC* corresponded to a percentage of soil organic carbon content.

$$C_s = Kd * Ce \quad [1]$$

$$Koc = Kd * 100/\%\ OC \quad [2]$$

Degradation rates (*k*) (1 day^{-1}) and half-lives (DT_{50}) (Days) were determined using Equations 3 and 4, where C_t (mg kg^{-1}) corresponded to herbicide concentrations at time *t* (days) and *Co* the herbicide concentrations at application time.

$$C_t = Co * e^{(-k*t)} \quad [3]$$

$$DT_{50} = Ln(2)/k \quad [4]$$

The relationship between physicochemical properties (soils and herbicides) and soil adsorptions, degradations, and leaching (soil depth movement and mass leached) were determined using Pearson correlation analysis.

Results

Soil adsorption and persistence

Herbicides soil sorption was variable depending on the soil. Simazine, terbuthylazine, hexazinone, metsulfuron-methyl, and indaziflam, showed the maximum *Kd* values in Alfisol soil; flazasulfuron showed higher *Kd* in the Inceptisol soil, and the highest glyphosate *Kd* was in Andisol soil (Table 3). On the other hand, the lowest *Kd* was determined in Entisol soil for all herbicides, except flazasulfuron, which showed a lower *Kd* in the Ultisol soil (Table 3). The average herbicide adsorption from higher to lower was: glyphosate > indaziflam > terbuthylazine > flazasulfuron > metsulfuron-methyl > simazine > hexazinone.

The correlation analysis between *Kd* and soil physicochemical properties only showed a relation with soil bulk density (r=0.6187; p<0.0001). On the other hand, correlation analysis between herbicide physicochemical properties and *Kd* showed a relation with *pKa* (r=0.6237; p<0.0001), *LogKow* (r=-0.5686; p<0.0001) and molecular weight (r=-0.4519; p<0.0001). Specific correlations with each herbicide and soil properties are shown in Table 4.

Persistence of herbicides was dependent on the type of soil. Thus, the highest persistence of simazine and terbuthylazine was found in Ultisol. In the case of indaziflam, flazasulfuron and metsulfuron-methyl, were more persistent in Andisol, and hexazinone and glyphosate in Alfisol (Table 3). Otherwise, simazine, terbuthylazine, metsulfuron-methyl, and flazasulfuron showed lower persistence in Entisol, hexazinone and glyphosate in Inceptisol and indaziflam in Alfisol (Table 3). Herbicide persistence, from high to low DT_{50}, was: glyphosate (53 d), Indaziflam (49 d), hexazinone (46 d), flazasulfuron (40 d), terbuthylazine (36 d), simazine (35 d), and metsulfuron-methyl (28 d). The incubation DT_{50} average and the degradation rate (*k*) (all soils x all herbicides) was 41.1±7.8 d and 0.019±0.004 mg day^{-1}, respectively.

No general correlations between soil-herbicide physicochemical properties and persistence were found, but some specific relations were obtained for each herbicide. Simazine and terbuthylazine DT_{50} were related to soil clay + silt content with a Pearson'**s** coefficient of 0.9120 (p<0.0001) and 0.9765 (p<0.0001), respectively. Hexazinone (r=0.9502; p<0.0001), flazasulfuron (r=0.9204; p<0.0001), and glyphosate degradation (0.6831; p=0.0295) soil degradation were related to OC. Indaziflam soil degradation was related to pH (r=0.9192; p=0.0002) and CEC (r=0.7866; p=0.0072), and in the same way, CEC was related to metsulfuron-methyl (r=0.7346; p=0.0155) and to flazasulfuron (r=0.8526; p<0.0001) soil degradation.

Herbicide soil-column leaching

In decreasing order, the maximum soil depth reached by herbicides was determined in Entisol, Alfisol, Ultisol, Inceptisol, and Andisol soils. According to the percentage of herbicide mobilised in depth in the different soil columns (90 cm), the higher amount was determined in Entisol, followed by Ultisol and Alfisol. In Andisol and Inceptisol, no herbicides were detected below 60 cm depth, in none of the soils (Table 5).

The average herbicide mass (quantified up to 90 cm of soil depth), in decreasing order, were: hexazinone (3.5%); metsulfuron-methyl (3.4%); glyphosate (1.1%); simazine (0.9%), and terbuthylazine (0.3%). Indaziflam and flazasulfuron were not detected below 60 cm of soil depth.

In general, the principal parameters related to maximum herbicide movement in soil were 1/*Kd* (r=0.7919; p=0.0338), soil porosity (r=-0.6509; p<0.0001), Al (r=-0.6469; p<0.0001), Ca (r=-0.6544; p<0.0001), silt (r=-0.5959; p<0.0001), and CEC (-0.5638; p<0.0001). Significant parameters with relation to herbicide mass quantified up to 90 cm soil depth were: silt (r=-0.5749; p<0.0001), Al (r=-0.5531; p=0.0001),

TABLE 4: Pearson correlation coefficients for *Kd* and relevant physicochemical soil properties. Significance value (p) between parenthesis.

Herbicide	**Physicochemical soil property**													
	pH	**EC**	**CEC**	**Al**	**Ca**	**Na**	**K**	**Cu**	**Fe**	**Zn**	**Mn**	**OC**	**Silt**	**Silt+Clay**
Simazine	*	0,9397 (0.0001)	*	0.6531 (0.0083)	0.5419 (0.0369)	*	*	0.9541 (0.0001)	0.8309 (0.0001)	0.6378 (0.0106)	*	0.7675 (0.0008)	0.8342 (0.0001)	0.5138 (0.0492)
Terbuthylazine	-0.5646 (0.0283	0.9568 (0.0001)	*	0.5607 (0.0297)	*	*	*	0.9577 (0.0001)	0.8921 (0.0001)	0.7052 (0.0033)	*	0.6787 (0.0054)	0.7910 (0.0004)	*
Hexazinone	-0.5192 (0.0473)	0.9381 (0.0001)	*	0.5958 (0.0191)	*	*	0.5253 (0.0443)	0.9485 (0.0001)	0.8584 (0.0001)	0.6529 (0.0083)	*	0.7308 (0.002)	0.7971 (0.0004)	*
Metsulfuron-methyl	-0.8401 (0.0001)	0.8865 (0.0001)	*	*	*	*	*	0.9232 (0.0001)	0.9321 (0.0001)	0.7568 (0.0011)	0.5520 (0.0329)	*	0.5487 (0.0341)	0.5932 (0.0197)
Indaziflam	*	*	0.6473 (0.0091)	0.8147 (0.0002)	0.6778 (0.0055)	0.5287 (0.0427)	*	0.6194 (0.0138)	*	*	0.5328 (0.0409)	0.9691 (0.0001)	0.6641 (0.0069)	0.6027 (0.0174)
Flazasulfuron	*	0.8461 (0.0001)	*	*	*	*	0.8419 (0.0001)	0.6856 (0.0048)	0.8247 (0.0002)	0.8871 (0.0001)	*	*	0.7198 (0.0028)	*
Glyphosate	*	*	0.9758 (0.0001)	0.8698 (0.0001)	0.9058 (0.0001)	*	0.6459 (0.0093)	*	*	*	*	0.7636 (0.0009)	0.7337 (0.0018)	*

*Non-significant correlation.

1/Kd (r=0.5141; p<0.0001), soil humidity (r=-0.5007; p<0.0001), and soil porosity (r=-0.4987; p<0.0001).

Simazine soil leaching (soil depth movement and mass quantified up to 90 cm) was higher than terbuthylazine in all soils, which was related to their difference in *Kd* values (Table 3). Terbuthylazine *Kd* was, in general, nine times higher than simazine *Kd* and both triazine herbicides soil leaching was highly related to 1/*Kd* and OC (p<0.0001). Terbuthylazine and simazine 1/*Kd* correlation values were 0.9546 and 0.9837; for OC, values were -0.7267 and -0.7174, respectively.

Hexazinone, the herbicide with the lower *Kd* values (Table 3), was the most mobile compound but showed limited soil movement in the Andisol soil (Table 5). Hexazinone soil leaching was highly correlated with 1/Kd (r=0.9173; p<0.0001), silt content (r=-0.9546; p<0.0001) and soil Al-Ext (r=-0.8909; p=0.0005).

Sulfonylurea herbicides (metsulfuron-methyl and flazasulfuron) showed different soil leaching under the same soils there, metsulfuron-methyl was more leachable than flazasulfuron (Table 5). Metsulfuron-methyl leaching was related to sand (r=0.9419; p<0.0001), silt + clay (r=-0.9386; p<0.0001), and 1/*Kd* (r=0.6856; p=0.0286), and flazasulfuron leaching was related to soil porosity (r=-0.8201; p=0.0037) and 1/*Kd* (r=0.6249; p=0.0489).

As flazasulfuron and indaziflam did not leach below 60 cm in any of the soils (Table 5) and their soil leaching was only related to Ca (r=0.7002; p=0.0242), total porosity (r=-0.6955; p=0.0255) and to the relation Al-Ext/Clay (r=0.9654; p<0.0001).

Glyphosate only reached the bottom of the lysimeters in the Entisol soil and in general, only 4% of the applied mass leached below 30 cm of soil depth (Table 5). Correlation analysis showed that glyphosate leaching was related to silt (r=-0.7415; p=0.0141), soil porosity (r=-0.6357; p=0.0482) and 1/*Kd* (r=0.6373; p=0.0475).

Discussion

Soil adsorption

The inverse relation obtained between *Kd* and herbicide molecular weight could be explained because small molecules diffuse easily through organo-clay particles and are adsorbed at higher rates than large molecules (Letey 1994; Liu et al. 2011).

It is widely accepted that herbicide *LogKow* coefficient is highly related to soil adsorption. Thus, pesticides with high *LogKow* will result in a high *Kd*, which is opposite to the correlation obtained in this work. However, the supposed direct relationship between *LogKow* and *Kd* could be the result of limited numbers of chemicals that have been used in some studies and also because they included mainly non-ionic or hydrophobic pesticides (Seth et al. 1999; Wauchope et al. 2002; dos Reis et al. 2013). On the contrary, in the present study, all herbicides corresponded to the ionic compounds category (Pesticides Properties Database 2024). Furthermore, the closeness between herbicide *pKa* and soil pH values (Tables 1 and 2) could increase the abundance of ionic

TABLE 5: Herbicide soil-depth movement in disturbed soil lysimeters after fifteen days of herbicides application*. Values corresponded to an average of two replications ± standard deviation.

Soil type	**Soil depth (cm)**	**Herbicide**						
		Simazine (mg kg^{-1})	**Terbuthylazine (mg kg^{-1})**	**Hexazinone (mg kg^{-1})**	**Metsulfuron-methyl (mg kg^{-1})**	**Indaziflam (mg kg^{-1})**	**Flazasulfuron (mg kg^{-1})**	**Glyphosate (mg kg^{-1})**
Andisol	15	2.673±0.260	1.793±0.131	1.858±0.217	0.036±0.001	0.059±0.011	0.057±0.020	1.215±0.040
	30	0.062±0.087	<0.011	0.058±0.020	0.022±0.004	<0.010	<0.011	0.178±0.003
	60	<0.010	<0.011	<0.012	0.022±0.011	<0.010	<0.011	<0.022
	90	<0.010	<0.011	<0.012	<0.012	<0.010	<0.011	<0.022
Ultisol	15	1.806±0.141	1.314±0.195	1.232±0.073	0.037±0.005	0.062±0.014	0.038±0.020	1.369±0.013
	30	0.479±0.165	0.090±0.066	0.366±0.072	0.011±0.002	0.005±0.007	0.022±0.005	<0.022
	60	0.121±0.061	<0.011	0.287±0.103	<0.012	<0.010	0.023±0.015	<0.022
	90	<0.010	<0.011	0.075±0.003	<0.012	<0.010	<0.011	<0.022
Inceptisol	15	1.835±0.157	1.337±0.098	1.605±0.049	0.034±0.002	0.053±0.014	0.033±0.004	1.156±0.097
	30	0.735±0.006	0.033±0.005	0.249±0.092	0.015±0.003	<0.010	0.023±0.004	0.067±0.022
	60	0.192±0.040	<0.011	0.015±0.022	0.011±0.001	<0.010	<0.011	0.043±0.002
	90	<0.010	<0.011	<0.012	<0.012	<0.010	<0.011	<0.022
Entisol	15	1.416±0.025	1.370±0.068	0.516±0.040	0.037±0.003	0.025±0.001	0.020±0.006	0.748±0.019
	30	0.492±0.015	0.278±0.023	0.669±0.147	0.025±0.003	0.023±0.001	0.020±0.004	0.267±0.016
	60	0.182±0.039	0.043±0.025	0.347±0.034	0.020±0.007	0.012±0.003	0.017±0.002	0.117±0.025
	90	0.082±0.003	0.026±0.001	0.139±0.110	0.017±0.002	<0.010	<0.011	0.085±0.041
Alfisol	15	1.553±0.128	1.126±0.018	0.912±0.118	0.040±0.005	0.042±0.005	0.029±0.002	1.061±0.050
	30	0.790±0.051	0.207±0.025	0.465±0.144	0.017±0.004	0.011±0.001	0.021±0.005	0.268±0.124
	60	0.121±0.008	<0.011	0.250±0.049	0.016±0.004	0.013±0.001	0.015±0.001	0.170±0.022
	90	0.049±0.002	<0.011	0.097±0.005	<0.012	<0.010	<0.011	<0.022

*After herbicides applications lysimeters received 225 mm of simulated rain in eight events each two days.

pesticide forms and increase soil adsorption (Stougaard et al. 1990).

Higher *Kd* values determined in the Alfisol and Inceptisol soils could be related to the presence of variable surface charges in both soils (Sollins et al. 1988; Qafoku et al. 2004; Escudey et al. 2007; Suffardi et al. 2020) and to their lower pH (Table 1). Therefore, low soil pH would produce a more positive net soil charge and an abundance of herbicide ionic forms. This relationship between ionic herbicides, soil surface variable charges and the low soil pH could explain why in the studied soils, basic herbicides, like simazine, terbuthylazine, or hexazinone were less adsorbed to soil matrices than acidic herbicides, such as glyphosate, metsulfuron-methyl, indaziflam, or flazasulfuron, contrary to the results obtained by Kah & Brown (2007).

Glyphosate did not show a relation with soil pH, in contrast to the published results that mention an inverse relation between pH and glyphosate adsorption (McConnell & Hossner 1985; Cáceres-Jensen et al. 2009; De Geronimo & Aparicio 2022). The present study determined the largest glyphosate *Kd* in the Andisol soil, which presented the highest pH (Table 1). Nevertheless, Andisol soil also showed higher CEC, Al-Ext, Mg, and Cu contents, which have been highly related to glyphosate soil adsorption (Mamy & Barriuso 2005; Tévez & Afonso 2015). Moreover, Chilean Andisol soils have a high phosphorus retention capacity, another soil characteristic related to the glyphosate sorption (Kogan et al. 2003; Cáceres-Jensen et al. 2009; De Geronimo & Aparicio 2022).

Soil persistence

In general, a low degradation variability was found between soils. These results could be a consequence of incubation temperature, soil humidity, and soil pH, which did not limit the biological and chemical degradation processes (Kaufman & Kearny 1970; Pons et al. 1998; Fernández et al. 2001; Sarmah & Sabadie 2002; Grey & McCullough 2012; Bento et al. 2016; Muskus et al. 2020).

As mentioned previously, a correlation analysis between soil properties and herbicide DT_{50} showed specific relations, confirming that pesticide degradation was related to soil properties and could not be extrapolated between molecules even with similar chemical properties. For example, Kah et al. (2007) found that DT_{50} of acidic compounds, such as metsulfuron-methyl, fluroxypyr, and dicamba, were highly correlated with OC, but DT_{50} of fluazifop-methyl, also an acidic herbicide, was related with pH**;** DT_{50} of flypyrsulfuron-methyl (acidic) was related to clay content, and that of 2,4-D (acidic herbicide) did not show significant correlations. On the other hand, DT_{50} of basic pesticides, such as pirimicarb and tebutryn, were related to OC and clay, but that of fenpropimorph (basic) was highly correlated only with pH. The same authors concluded that degradation is a complex phenomenon resulting from complex interactions between different processes and is complicated to predict.

Concordant with other studies, the relation between *Kd* and herbicide degradation was not significant because degradation can occur to herbicides present in the liquid phase, as well as when they are adsorbed (Guo et al. 2000; Park et al. 2001; Villaverde et al. 2008; Albers et al. 2009). Moreover, pesticide sorption equilibrium (*Kd*) will be more relevant in the late incubation phase but not before herbicides are degraded by around 50% of their initial soil concentration (Guo et al. 2000).

In general, the obtained DT_{50} values for all herbicides were lower than those reported in the peer-reviewed studies and databases (James et al. 1995; Giesy et al. 2000; Tejada et al. 2017; González-Delgado & Shukla 2020; Pesticides Properties Database 2024). Other studies have already reported reduced herbicide persistence in Chilean soils (Alister et al. 2005; Kogan et al. 2007; Alister et al. 2008; Kogan et al. 2012). In the present study, higher degradation rates could be explained by the incubation conditions, as mentioned previously, and also by the humic substance present in the studied soils. Alister et al. (2020) determined that Andisol, Ultisol, Inceptisol, Entisol, and Alfisol soils, the same soils utilised in this study, have a significant content of fulvic substances (8 to 37 % of its total soil OC), with a concentration of carboxylic groups between 12.7 to 61.4 meq g^{-1}.

It is well known that humic substances can interact with soil pesticide sorption, but they can have a significant effect on their dissipation, i.e., catalysing chemical processes such as hydrolysis or dealkylation, condensation and polymerisation reactions and photosensitisation (Khan 1980; Bollag et al. 1992; Kamiya & Kameyama 1998; Fava & Piccolo 2001; Salvestrini 2013). Specifically, fulvic acids increase pesticide solubility, reactivity, and mobility in the soil and also can generate light-induced radicals that react with pesticides, inducing degradation, i.e., triazine, sulfonylureas, and hexazinone herbicides (Stevenson 1972; Thompson et al. 1992; Sabadie 1997; Manzanilla-Cano et al. 2010; Rering et al. 2017; Pozdnyakov et al. 2018).

Herbicide soil-column leaching

Literature generally reports that herbicide soil leaching is highly related to soil sorption and water flux (Feng & Feng 1998; Dousset et al. 2004; dos Reis et al. 2017). Thus, an increase in water flux would reduce pesticide adsorption. The observed inverse relation, found in this study, between leaching and soil porosity could result from a high density of small pores, reducing the water flux and increasing the interaction time between herbicide and soil matrix (Cox et al. 1997).

Triazine (simazine and terbuthylazine) herbicide leaching was significantly influenced by clay type, soil pH, soil soluble organic matter, and humic and fulvic acid reactive group density (Dousset et al. 1994; Celis et al. 1997; Laird & Koskinen 2008; Alister et al. 2011; Alister et al. 2020). In the present work triazines soil leaching were highly related with OC.

The literature mentions that hexazinone soil leaching could be related to clay and OC soil contents (Koskinen et al. 1996; Mendes et al. 2016; dos Reis et al. 2017); however, our results showed that silt and Al-Ext were the only relevant soil factor affecting hexazinone soil leaching. Interactions between clay minerals and pesticides could be reduced when the soil presents a high OC content (Villaverde et al. 2008; Cáceres et al. 2010). The same authors indicate that strong interaction occurred with Clay mineral/OC relation near 30; in our study, this relation was between 3.5 and 11.9. Soils with high Al or Fe oxides could also contribute to ionic pesticides, such as hexazinone, increasing their adsorption to soil matrix and reducing leaching (Ghafoor et al. 2012).

Sulfonylureas soil adsorption and leaching are related to pH, OM, and texture (Sarmah et al. 1998; Oliveira et al. 2005; Berisford et al. 2006; Grey & McCullough 2012; Tejada & Benitez 2017; Kumari et al. 2020; Alister et al. 2020). No correlations between sulfonylureas leaching and soil pH were found, but this may be because soil pH variations from low to high were not higher than 1.09 units (Table 1). In most of the published data that have shown significant relationships between pH and leaching, degradation, or sorption, the utilised soils presented pH differences larger than 2.0 units between them (Stougaard et al. 1990; Oliveira et al. 2001; Saha & Kulshrestha 2002; Grey & McCullough 2012).

The limited soil movement of Indaziflam has been reported before in orchard soils (Jhala et al. 2012; Jhala & Singh 2012; Guerra et al. 2016; González-Delgado et al. 2015). Similarly to results obtained by González-Delgado & Shukla (2020), our study did not show a relationship between leaching and soil OC. Guerra et al. (2016) also did not find differences in Indaziflam soil leaching in two contrasting soils with similar variations in pH, texture and OC content to those in the soils used in the present study; however, the simulated rainfall applied by the above-mentioned authors was almost seven times lower than that used in our study.

Leaching studies under disturbed and undisturbed soil columns have reported glyphosate soil movement between 15 to 110 cm of depth (de Jonge et al. 2000; Fomsgaard et al. 2003; Strange-Hansen et al. 2004; Laitinen et al. 2006; Al-Rajab et al. 2008; Bergström et al. 2011). Glyphosate leaching is affected by soil adsorption, pH, soluble organic matter, texture, and hydraulic soil properties (Vereecken 2005; Borggaard & Gimsing 2008), which is very similar to the correlations found in this study, except for the correlation with pH. However, as well as in the case of sulfonylurea herbicides, slight soil pH variations between the Chilean forestry soils could explain why glyphosate leaching was not related to pH. One explanation for glyphosate soil leaching, despite its high soil adsorption, is a possible formation of complexes with water-soluble humic substances (Albers et al. 2009), and in the present work, the soils present an important concentration of humic substances (Alister et al. 2020).

Conclusions

Ionic herbicides' environmental coefficients were more related to forest soil properties than their physicochemical properties. specifically, herbicide physicochemical properties showed a relation only with the adsorption coefficient, with *pKa* and *LogKow* being most relevant. Otherwise, forestry soil properties, such as silt, OC, pH, CEC and porosity, were highly related to herbicide soil adsorption, persistence and leaching. However, silt content was the most relevant. Nevertheless the importance of the soil texture silt fraction is rarely mentioned as an important factor in the adsorption phenomenon.

Soil persistences determined for the herbicides in this study were smaller than those commonly reported in other studies or international databases and soil adsorption averages were generally higher than the international reference values.

The strong relationship between ionic herbicides behavior and forestry soil properties endorses the requirement to determine the herbicide environmental parameters in situ, avoiding using parameters estimated in other soils.

List of abbreviations

Inh= Inhibition
EC=Electrical conductivity.
CEC=Cationic Exchange Capacity.
SB=Sum of bases.
OC=Organic Carbon.
S-DTPA=Sum of available Copper, Iron, Manganese and Zinc.
Al-Ext=Extractable aluminium.
S-Cations=Sum of Calcium, Potassium, Magnesium and Sodium.
WG=Water-dispersible granules.
SC=Suspension concentrate.
DF=Dry flowable.
FG=Fine granule.
LD=Limit of detection.
Rt=Retention time.
m/z=ion mass.
λ=Wavelength.
Ex/Em=Energy of excitation /Energy of emission.
pKa= negative log base ten of the acid dissociation constant (Ka).
LogKow=Log base ten of relation octanol/water.
DT_{50}=Dissipation time for 50% of the herbicide applied amount.
k=Daily dissipation rate of herbicide residues.
Kd=Soil adsorption herbicide coefficient.
Koc=Soil adsorption herbicide coefficient normalised according to OC.
r= Pearson´s correlation value.
p=Correlation significance value.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

GV and KB conducted laboratory and lysimeter studies. MA performed chromatograpgic herbicide analyses. CA coordinated most of different stages of the study, made the statistical analyses and, together with MK wrote the paper. AZ as the Compañía Manufacturera de Papeles y Cartones (CMPC) counterpart participated in all the different part of the study. All co-authors accepted the final draft.

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