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Chapter

Herbicides Mechanisms Involved in the Sorption Kinetic of Ionisable and Non Ionisable Herbicides: Impact of Physical/ Chemical Properties of Soils and Experimental Conditions

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Abstract

Volcanic ash-derived soils (VADS, variable-charge soils) are predominant in some regions of the world, being of great importance in the agricultural economy of several emerging countries. Their amphoteric surface charge characteristics confer physical/chemical properties different to constant surface charge-soils, showing a particular behavior in relation to the herbicide adsorption kinetics. Volcanic soils represent an environmental substrate that may become polluted over time due to intensive agronomic uses. Solute transport models have contributed to a better understanding of herbicide behavior on variable- and constant-charge soils, being also necessary to evaluate the fate of herbicides and to prevent potential contamination of water resources. The following chapter is divided into four sections: physical/chemical properties of variable and constant-charge soils, kinetic adsorption models frequently used to obtain kinetic parameters of herbicides on soils, solute transport models to describe herbicide adsorption on VADS, and impact of experimental conditions of kinetic batch studies on solute transport mechanisms.

Keywords: variable-charge soils, constant-charge soils, kinetic adsorption, herbicides and solute transport mechanism

1. Introduction

Nature of soils is regulated by various soil-forming factors such as parent material, climate, vegetation, and time [1]. These factors vary widely among region, and also these vary in their properties. Volcanic ash-derived soils (VADS) are predominantly found in regions of the world with geochemical characteristics dominated by active and recently extinct volcanic activity. These have great importance in the agricultural economy of several emerging and developing countries of Europe, Asia, Africa, Oceania, and America. They are abundant and widespread in central-southern Chile (from 19° to 56° S latitude), accounting for approximately 69% of the arable land [2].

Agricultural practices developed in Chilean VADS have led to the very increased use of herbicides and also require frequent adjustments of soil pH and mineral fertilization [3–5]. Among these soils, andisols and ultisols are the most abundant, both presenting an acidic pH (4.5–5.5). Andisols are rich in organic matter (OM), with high specific surface area, P retention (>85%), and variable charge with low saturation of bases, low bulk density (<0.9 Mg m⁻³) associated with a high porosity, and a strong microaggregation of heterogeneous forms and a mineralogy dominated by short-range ordered minerals, such as allophane (Al₂O₃SiO₂ × nH₂O) [2, 6]. Allophane plays a key role in surface reactivity in andisols determining the availability of nutrients and controlling soil contaminant behavior [6]. Ultisols have a low amount of OM, relatively high amounts of Fe oxides in different degrees of crystallinity, low base saturation (<30%), high bulk density (0.8–1.1 Mg m⁻³), and high clay content (>40%) [2, 7]. This last component provides a finer texture that allows a greater cohesion with respect to andisols [2, 8].

Andisols present variable surface charge, originated in both inorganic and organic constituents. Inorganic minerals such as goethite (FeOOH), ferrihydrite (Fe₁₀O₁₅ × 9H₂O), gibbsite (Al(OH)₃), imogolite, and allophane contribute through the dissociation of Fe—OH and Al—OH active surface groups, while OM through the dissociation of its functional groups (mainly carboxylic and phenolic) and humus-Al and Fe complexes with amphoteric characteristics contributes too. For the other side, ultisols present little or no charge, because more crystalline minerals, such as halloysite and/or kaolinite dominate their mineralogy.

Several herbicide adsorption kinetic studies on VADS have indicated that the herbicide adsorption is a nonequilibrium process [5, 9]. Time-dependent adsorption can be a result from physical and chemical nonequilibrium and intrasorbent diffusion can occur during the transport of pesticides in soils [10]. In general, nonequilibrium adsorption has been attributed to several factors, such as: diffusive mass transport resistances, nonlinearity in adsorption isotherms, adsorption-desorption nonsingularity and rate-limited adsorption reactions [11]. The *intra-OM-diffusion* has been suggested to be the predominant factor responsible for the nonequilibrium adsorption of nonionic or hydrophobic compounds on VADS [9, 12]. The differences in the *intra-OM* adsorption kinetics of herbicides were due to soil constituents, such as organic carbon (OC) and mineral composition on VADS.

The adsorption-desorption behavior of pesticides is the principal process affecting the fate of these chemicals in soil and water. In general, adsorption-desorption processes are known to be important because they are time-dependent and with considerable ecosystem impact, influencing the availability of organic pollutants for plant uptake, microbial degradation, and transport in soil and consequently leaching potential. In this sense, the principal process that affects the fate of pesticides in soil and water is adsorption of pesticides from soil solution to soil particle active sites, which limit transport in soils by reducing their concentration in the soil solution. Therefore, adsorption kinetic studies provide important information for weed control, crop toxicity, runoff, and carryover events, serving as the foundation for estimating effects on biotic and abiotic environmental components. The kinetic parameters can be obtained by means of the application of two kinds of kinetic models: the ones that allow establishing principal kinetic parameters and modeling of the adsorption process and other models frequently used to describe adsorption mechanisms of organic compounds on soils. Such information is necessary in order to understand leaching of herbicides for preventing potential contamination of groundwater.

The aim of this chapter is to establish the differences of adsorption kinetics of ionizable and nonionizable herbicides (INIH) in Chilean VADS to investigate the

mechanisms involved of INIH adsorption on VADS by applying different solute adsorption mechanism models. Kinetic adsorption model description is also necessary in order to develop and validate computer simulation transport models on VADS to prevent potential contamination of water resources, considering model restrictions related to experimental conditions of kinetic batch studies on solute transport mechanisms.

2. Physical and chemical properties of variable-charge soils

Variable-charge soils are dominated by Al/Fe-humus complexes, by ferrihydrite, a short-range-order Fe hydroxide mineral, or by clay components characterized by the formation of short-range-order aluminosilicates, such as allophane and imogolite [13]. The clay fraction mineralogy of VADS is usually dominated by allophane with a minor content of kaolinite, gibbsite, goethite, and hematite [14]. Besides, these minerals contain 2:1 and 2:1:1 type minerals and their integrades, opaline silica and halloysite [13].

These distinctive physical and chemical properties are largely due to the formation of noncrystalline materials, biological activity, and the accumulation of OM [13, 15]. The soil OM represents a key indicator of soil quality, both for agricultural (i.e., productivity and economic returns) and environmental functions (i.e., carbon sequestration). Andisols are highly representative of VADS; their OC concentration is more associated with metal-humus complexes than with concentrations of noncrystalline materials. Nevertheless these materials with variable charge surfaces provide an abundance of microaggregates that permit to encapsulate OC, favoring their physical protection [13]. Other studies indicate that Al/Fe oxides/hydroxides in allophanic soils are linked to carboxylic and aromatic groups of soil OM being the last highly decomposed [1].

In general, andisols are soils rich in constituents with amphoteric surface reactive group being considered the most abundant variable charge soils in Chile [14]. The most striking and unique properties of these are: variable charge, high water-holding capacity, low bulk density, high friability, highly stable soil aggregates due to unstable colloidal dispersions, excellent tilth and strong resistance to water erosion [13], anion adsorption, high lime or gypsum requirement to achieve neutral pH, and considerable adsorption affinity for cations (Ca and Mg), which may form both inner- and outer-sphere complexes although the first are found to be more important [14].

Andisols are relatively young soils and cover about 0.84% of the world's land [13, 16], being a typical product of weathering increases in temperate and tropical environments with sufficient moisture [13]. In this sense, metastable noncrystalline materials are transformed to more stable crystalline minerals (e.g., halloysite, kaolinite, and gibbsite) allowing the alteration of andisols to Inceptisols, alfisols, or ultisols. Andisols are often divided into two groups based on the mineralogical composition of A horizons: allophanic andisols dominated by variable charge constituents (allophane/imogolite), and nonallophanic andisols dominated by both variable charge and constant charge components (Al/Fe-humus complexes and 2:1 layer silicates) [13]. Allophanic andisols form preferentially in weathering environments with pH values in the range of 5–7 and a low content of complexing organic compounds. Nonallophanic andisols form preferentially in pedogenic environments that are rich in OM and have pH values of 5 or less [13].

Allophanic andisols present allophane, imogolite, poorly crystalline Fe oxides (probably ferrihydrite), Al/Fe-humus complexes, volcanic glass (which is a mixture of aluminosilicates and traces of ferromagnesian minerals), and secondary Si minerals (opaline silica), resulting in pH-dependent variable charge, CEC and anion exchange capacity (AEC), and high phosphate retention >70% [1, 13]. Allophane,

the main component of the clay fraction of VADS, has short to mid-range atomic order and a prevalence of Si—O—Al bonding [17]. This aluminosilicate consists of hollow, irregularly spherical nanoparticles with an outside diameter of 3.5–5.0 nm, a wall thickness of 0.7–1 nm, and a specific surface area of 700–900 m² g⁻¹ with a chemical composition generally ranging from an Al:Si atomic ratio of 1:1–2:1 [13].

The presence of allophane in andisols provides excellent physical fertility properties for crop production, such as: high friability, stable aggregates, ease of root penetration, good drainage, high permeability, low bulk density at field-moisture water content <0.9 g cm⁻³, high porosity, and high air and water retention [13]. An unusually high amount of micropores in allophanic VADS is partially attributable to the intra- and inter-particle pores of allophane [15]. The development of aggregates in VADS is closely related to the retention of large amounts of plant-available water. The large volume of both mesopores/micropores relates with the high water-holding capacity of andisols. In this sense, young VADS have a greater amount of macropores larger than 100 μ m in diameter and a lesser amount of mesopores (0.4–6.0 μ m) and micropores (<0.4 μ m). In contrast, moderately weathered soils have a large amount of mesopores (0.4–6.0 μ m) and micropores (<0.4 μ m), contributing to the large plant-available water.

Based on their surface charge characteristics, VADS are characterized by a mixed charge system [14]. In this sense, the soil particles are of two different types: dual and variable-charge particles (phyllosilicates and allophane) and variable-charge particles (Fe/Al oxides). The surface charge density of variable-charge oxides depends on pH and ionic strength (IS) of the soil solution. The Fe/Al oxides have a surface reactive group with amphoteric properties; these groups are protonated and positively charged under acidic conditions (at a pH below the point of zero charge, PZC) or deprotonated and negatively charged under basic conditions (at a pH higher than the PZC). In general, the PZC of Al/Fe oxides are between 8 and 9. The Fe in VADS is present mostly in the form of noncrystalline hydroxides (ferrihydrite) and partly as Fe-humus complexes [13]. Ferrihydrite appears as individual spherical particles ranging in size between 2 and 5 nm. These particles form aggregates ranging from 100 to 300 nm in diameter [13].

Dual-charge particles, such as phyllosilicates and allophane, usually develop permanent and variable charge or only variable charge but with different magnitude an even different sign on different surfaces of the same particle. These inorganic minerals are abundant in VADS, controlling chemical properties of the bulk soil. The siloxane ditrigonal cavity of the phyllosilicate siloxane surfaces may develop a localized permanent negative charge as a result of isomorphic substitutions in their internal crystal structures regardless of ambient conditions. The magnitude of this permanent negative charge does not depend on pH and IS of the soil solution. In contrast, the edges of these particles develop variable charge.

The variable charge of allophane is the result of protonation and dissociation of Al—OH and Si—OH superficial functional groups, with Al—OH groups having negative, neutral, or positive charge and the more acidic SI—OH groups having either neutral or negative charge. As allophane is a dual-variable charge, VADS usually have a slightly acidic to acidic soil solution pH [14]. Under acidic conditions, the surfaces of these minerals are net positively charged. The variable positive charge results from protonation of surface inorganic soil constituents with Al—OH, Fe—O, and Fe—OH groups, while the variable negative charge results from dissociation of surface Si—OH and organic functional groups of organic soil constituents (e.g., carboxylic, phenolic, or amino reactive groups) [13]. The development of negative charge with increasing soil pH has been common to all andisols and has been strongly related to the amount of soil OM [13]. Soils with a large variable charge component required large additions of lime for pH amendment and were susceptible to leaching of cations when the soil pH decreased [13]. The CEC and AEC of variable charge

components on particle edges are pH- and IS-dependent of the soil solution. On the other hand, the most important mineralogical components in ultisols are: kaolinite (dual-charge minerals), hydroxy-interlayered vermiculite, muscovite, smectite, and Fe/Al oxides (quartz in the sand and silt fractions). Kaolinite is a 1:1 phyllosilicate with a relatively low specific surface area (between 5 and 39 m² g⁻¹) and presents the lowest surface charge (about 1–5 cmol (c) kg⁻¹) among common dual-charge clay minerals. The PZC of kaolinite is between 2.8 and 2.9 [14]. The kaolinite in A horizons has the same tubular morphology as the halloysite at depth suggesting that hydrated halloysite transforms to kaolinite upon dehydration. Halloysite is a 1:1 aluminosilicate hydrated mineral characterized by a diversity of morphologies (e.g., spheroidal and tubular), specific surface area, structural disorder, and physical-chemical properties (e.g., cation exchange capacity (CEC) and ion selectivity) [13].

3. Physical and chemical properties of constant-charge soils

There are different soil orders classified by soil formation, climates, and morphological features [18]. However, globally, most of the soil orders have constant charge. In general, these soils present a similar composition to the andisols, except for amorphous clays, metal oxides, oxyhydroxides, and hydroxides. In this sense, constant-charge soils are a simplification of andisols, what is expressed in a lower variety of adsorbent forms that result in a minor mechanistic variability of adsorption-desorption processes. The lack of Fe/Al oxides and allophane involves a surface without humus-Fe/Al, Fe/Al-mineral, and mineral-Fe/Al-humus complexes, reducing the combinations of possible surface-surface and herbicide-surface interactions, increasing the colloidal stability due to electrostatic repulsion between non-Fe/Al minerals and OM, both with surfaces dominated by anionic sites (S⁻).

A thorough analysis is required to study the adsorption kinetics with agricultural or remediation purposes. For example, histosols from peat or bog have a high OM content (>20%) [18], so the adsorption process can be simplified to the soil/solution partition coefficient normalized to the OC content (K_{oc}) or OM content (K_{om}) [19], and the stability of microaggregates by OM. Aridisols, developed in arid regions, have a high presence of clay and salts such as sodium, calcium carbonates, or gypsum, together with a low water content [18], so the adsorption process can be simplified to clay/solution partition coefficient, with high probability of equilibrium and/or precipitation of adsorbate under field conditions. Ultisols, with low base saturation but high clay content, OM and acidity, have humus as the main soil component that contributes to the little variable charge on these soils, controlling the pesticide adsorption mainly through hydrophobic and H-bonding.

Despite the diversity previously exposed, in all the cases, the adsorption sites are mostly neutral (S⁰, e.g., $OM_{aromatic,aliphatic}$) and anionic (S⁻, e.g., siloxane), and this implies adsorption of hydrophobic, polar, and cationic herbicides, where the dominance of siloxane and anionic organic surface groups generates a low PZC and negative surface charge, mostly pH-independent [20], which therefore implies small changes in CEC of minerals and negligible AEC at soil pH. So, the adsorption is independent of PZC for constant-charge soils. We will use ultisols as a constantcharge soil to show this and contrast with andisols.

3.1 Effect of MSM adsorption in PZC on ultisols and andisols

The curve of PZC versus pH for ultisol and andisol soils is shown in **Figure 1** [5]. As can be observed, a displacement of PZC to a higher pH was produced in both soil surfaces with adsorbed metsulfuron-methyl (MSM) confirming the contribution of



Figure 1.

Electrophoretic migration curves: (\blacktriangle) ultisol without MSM adsorbed; (Δ) ultisol with 15 µg mL⁻¹ of MSM adsorbed; (\bullet) and isol without MSM adsorbed; and (O) and isol with 15 µg mL⁻¹ of MSM adsorbed [5].



Figure 2.

Connection between adsorption parameters and mechanistic explanation from kinetic models in andisols and ultisols from **Figure 3** (S^+ , S^- , and S^0 : surface charge. X^+ , X^- , and X^0 : herbicide species. The green ovals are OM. pH_{soils} were measured in water at 1:2.5 soil:solution ratio).

charged surface sites to adsorption of anionic MSM through electrostatic and hydrophilic interactions on ultisols and andisols, respectively. The OM and active and free Fe/Al oxides will control the adsorption process in andisols mainly through hydrophilic on surface minerals, such as allophane, gibbsite, hematite, and goethite. In contrast, andisols present positive sites (S^+ , e.g., goethite at pH < 7.8) in addition to S^0 and S^- , that allow the anionic herbicide adsorption (X^- (hydr) and X^-) (**Figure 2**). Some intuitive mechanisms affected by pH, pK_a, and PZC are anionic and cationic exchange due to their electrostatic nature, but these kinds of adsorption are usually accompanied by other mechanisms.

4. Adsorption kinetics

The adsorption is characterized by a three-stage process: a rapid uptake on readily available adsorption sites (**Figure 2**, 1st stage), followed by slow diffusion-immobilization into mesopores, micropores, or capillaries in the sorbent's internal structure through mechanisms controlled by *intraparticle diffusion* (*IPD*), with small adsorbed amounts appearing on the external surface [9] (**Figure 2**, 2nd stage). The third stage (**Figure 2**), which is controlled by mass transfer mechanisms, involves rapid uptake of the solute in the inner surface of the sorbent. Adsorption processes are known to be important because they are time-dependent with considerable ecosystem impact, influencing the availability of organic pollutants for plant uptake, microbial degradation, and transport of pesticides in the soil environment during the short-term and consequently affecting their leaching potential [4, 9, 12, 21]. Adsorption kinetic studies may provide important information related to weed control, crop toxicity, runoff, and solute transport mechanisms [9, 22].

4.1 Kinetic adsorption models frequently used to estimate kinetic parameters of herbicides on soils

The *pseudo-second order* (*PSO*) model (**Figure 3A**) has been the best adsorption kinetic model to establish principal kinetic parameters and modeling of the adsorption process of INIH on ultisols and andisols [9, 12, 23]. In the **Figure 3A**, q_t is the adsorbed quantity ($\mu g g^{-1}$) at any soil-solution contact time t (min) for kinetic adsorption experiments. The higher value of the overall rate constant k_2 of MSM with respect to DI adsorption on andisols indicates that this value reflects contributions from the favored electrostatic interactions considering both a retarded *IPD* as well as *intra-OM-diffusion*.

4.2 Mechanistic kinetic models to describe herbicide adsorption on ultisols and andisols

Figure 3B and **C** show a different transport mechanism for glyphosate (GPS, $pK_a = 0.8; 2.23; 5.46; 10.14$), metsulfuron-methyl (MSM, $pK_a = 3.3$) and diuron (DI) on ultisol and andisols [9, 12, 23]. The *IPD* or Weber-Morris model (**Figure 3B**) is one of the most used models to describe solute transport mechanisms of organic compounds in different adsorbents intended for remediation purposes [9, 12, 23]. Nevertheless, the *two-site nonequilibrium* (*TSNE*) *model* (**Figure 3C**) has been the



Figure 3.

(A) PSO model for adsorption kinetics of GPS on ultisol (\blacksquare) and andisol (\square), MSM on ultisol (\blacktriangle) and andisol (Δ) and DI on ultisol (\bullet) and andisol (O). (B) IPD model for GPS adsorption kinetics on ultisol (\blacksquare) and andisol (\square); MSM on ultisol (\blacklozenge) and andisol (Δ); and DI on ultisol (\bullet) and andisol (\square); MSM on ultisol (\blacklozenge) and andisol (Δ); and DI on ultisol (\bullet) and andisol (\square). (C) TSNE model plots for GPS adsorption on ultisol (\blacksquare) and andisol (\square), MSM adsorption on ultisol (\blacklozenge) and andisol (Δ) and DI adsorption on ultisol (\blacklozenge) and andisol (\square), PSM adsorption on ultisol (\blacklozenge) and andisol (\square), MSM adsorption on ultisol (\blacklozenge) and andisol (Δ) and DI adsorption on ultisol (\bullet) and andisol (O) [9, 12]. pH_{ultisol} = 5.2 and pH_{andisol} = 4.1.

best kinetic model to describe INIH transport mechanisms on VADS [9, 12]. In **Figure 3C**, C_t is the solute concentration at any time (μ g mL⁻¹) and C_{in} is the initial added solute concentration (μ g mL⁻¹). As an advantage, the *TSNE* model allows obtaining the soil/solution partition coefficient (K_d), percentage of instantaneous adsorption (F), and first-order desorption rate constant (k_{des}) from the time-dependent adsorption sites (100 – F).

Time-dependent adsorption can be a result of physical and chemical nonequilibrium [12]. The nonequilibrium adsorption on soils has been attributed to several factors, such as: diffusive mass transfer resistances, nonlinearity in adsorption isotherms, adsorption-desorption nonsingularity, and rate-limited adsorption reactions [11]. The rate-limited diffusion of the adsorbate from bulk solution to the external surface of the sorbent and rate-limited diffusion within mesopores and micropores of the soil matrix will occur before the equilibrium is reached. The adsorption process first occurs within the boundary layer around the sorbent being conceptualized as a rapid uptake process on readily available adsorption sites. The intercept of the first adsorption step (C_1) by the *IPD* model has been related to the extent of the boundary layer effect, namely, the diffusion of solute molecules through the solution to the external surface of the adsorbent [21]. In this regard, C_1 is the initial solute adsorption (mg/g) [24] being proportional to the thickness of the boundary layer.

When $C_1 = 0$, the rate of adsorption is controlled by only *IPD* for the entire adsorption period (Figure 2, 1st stage and Figure 3B) [9, 12, 21]. In this regard, an external mass transfer of the solute from the bulk solution to the soil particle surface exists. This can be seen in the initially steeper linear (*kint*₁) (**Figure 2**, 1st stage), where the MSM adsorption on ultisols was controlled exclusively by *IPD* (C_1 close to 0) (**Figure 3B**). A low value for C_1 has been related with the heterogeneity of the adsorbent, enhanced by the colloidal stability of ultisols, implying a high meso- and micro-porosity with a complex pore morphology. In this regard, the intercept also decreases with the increasing surface heterogeneity of the soils, indicating a small film resistance to mass transfer surrounding the adsorbent particle. This can be seen in the initially steeper linear (*kint*₁) (**Figure 2**, 2nd stage), where the mass transfer across the boundary layer and IPD were the two mechanisms to control the MSM adsorption on andisols. The last mechanisms were observed for GPS and DI adsorption on ultisols and andisols (**Figure 3B**), where GPS presented the same initial adsorption on both kinds of soils. A large value for c_1 indicates that the adsorption proceeds via a more complex mechanism consisting of both surface adsorption and *IPD*. In this regard, the highest C_1 values for DI correspond to large film diffusion resistance due to the greater boundary layer effect surrounding the particles for DI [24, 25] indicating a rapid adsorption in a short time and highest initial DI adsorption on andisols with a wide distribution of pore sizes. This was associated with the macroporosity of andisols due to aggregates composed by humus-Al/Fe complexes with low colloidal stability. If andisols have high OM content, these complexes could generate a preferential flow, increasing the transport of herbicides by the remaining colloidal or dissolved OM, increasing the leaching potential of DI.

The second (*kint*₁) and (*kint*₂) third stage describe the gradual adsorption stage (**Figure 2**, 2nd and 3rd stage), where *IPD* through macropores is rate limiting [21] followed by slow diffusion-immobilization in micropores or capillaries of the sorbent's internal structure. The rate-controlling step may be controlled by *film diffusion* and *IPD* [26]. In this sense, the adsorption process proceeds in the liquid-filled pore (external mass transfer (EMT)) steps or along the walls of the pores of the sorbent (internal mass transfer (IMT)) steps. It is assumed that the external resistance to mass transfer surrounding the solute is significant only in the early stage of adsorption [27]. This can be seen in the initially steeper linear (*kint*₁) (**Figure 2**, 2nd

stage), where the *IPD* model indicated that mass transfer across the boundary layer and *IPD* to control the GPS and DI adsorption on ultisols and andisols (**Figure 3A**). The molecules of GPS diffuse quickly through the macropores of the andisols. MSM adsorption on ultisols was controlled exclusively by macropore *IPD* (**Figure 3A**) and MSM adsorption on andisols occurred on two stages ($kint_1 \approx kint_2$) being controlled by *EMT* and *IPD*.

The 3rd stage (**Figure 2**) is the adsorption of the particle in the inner surface of the sorbent through mass-action-controlled mechanisms where a rapid uptake occurs or mechanism of surface reaction which consider the interactions between functional groups of solute and surface (as a chemisorption) [9, 12, 24]. In this regard, this stage is observed in the second linear portion (kint, Figure 2, 2nd stage and Figure 3B) being the gradual adsorption stage in which *IPD* dominates [27]. The second line (Figure 2, 3rd stage and Figure 3B) will depict micropore diffusion with the IMT occurring during the retention of INIH. In general, INIH present a highest adsorption capacity (q_{max}) on andisols. In this regard, the OM contributes to the ionic adsorption through the dissociation of its functional groups (mainly carboxylic and phenolic) and Al/Fe-humus complexes with amphoteric characteristics. And also, the organic colloids have an important role in hydrophobic pesticide transport [28], due to their small size ($<0.45 \,\mu$ m) and high affinity to nonpolar functional groups. This could have implications for the management of soils and pesticides in relation to the release of organic colloids into solution, especially in rainy areas or organic soils. The exogenous and endogenous water-extractable OM (WEOM) can influence the pesticide transport on soils, through formation of WEOM-pesticide complexes or competition between WEOM and pesticides for the adsorption sites, and thus, the retention and transport of the pesticides decrease and increase, respectively [29]. In this regard, Thevenot et al. [29] found that on a sandy-loam soil with low DI and WEOM adsorption capacity, the application of organic amendments with high WEOM content could increase DI leaching and, consequently, ground-water contamination risks.

While inorganic minerals such as goethite, ferrihydrite, gibbsite, imogolite, and allophane contribute through the dissociation of Si—OH, Fe—OH, and Al—OH active surface groups [21], kaolin clays could contribute to the adsorption in ultisols through Si—OH and (Al—OH—Si)^{+0.5} from the exposed edge kaolinite of the octahedral and tetrahedral basal surfaces having a hydrophilic and hydrophobic character, respectively [21].

For the case of ionizable herbicides, such as MSM, a negative correlation has been found between adsorption capacity and pH on acidic andisols (pH_{soils} between 4.49–6.46) from southern China [30] and acidic ultisols (pH_{soils} acidic 4.7–5.2) and acidic andisols (pH_{soils} acidic 4.1–6.2) from Chile [5, 31]. This behavior could be related to the adsorption mechanism of neutral pesticide species (X⁰) on OM at low pH (S^{0...*}X⁰, with S⁰ = hydrophobic or polar OM) and the increase of repulsion between S⁻ and X⁻ at high pH (**Figures 1** and **2**, 1st stage). In addition, a positive correlation between adsorption capacity and CEC and amorphous and free Al/Fe content even at low pH implies a significant electrostatic adsorption mechanism on S⁺, probably anionic exchange (S^{+...*}X⁻(hydr)) (**Figures 1** and **2**). The presence of two mechanisms explains the variations on K_{oe} value, and the reversibility of anionic exchange explains the lower hysteresis at higher pH.

For the case of amphoteric herbicides, such as imazaquin, Weber et al. studied the imazaquin adsorption ($pK_a = 1.8$ for $-NH^+$, 3.8 for $-COO^-$, and 10.5 for $-N^-$) in Cape Fear soil [32]. In this acidic ultisol ($pH_{soil} = 4.7$), the authors found a positive correlation between adsorption capacity and presence of cationic (X^+) and neutral imazaquin, attributed to cationic exchange, an electrostatic mechanism opposite to anionic exchange observed for MSM in andisols ($S^{-...*}X^+$ (hydr)) instead of $(S^{+...}X^{-}(hydr))$, while the inverse correlation with the anionic species was explained by electrostatic repulsion with negative charge surfaces. In this sense, the different surface charge of both soil orders (predominance of S⁻ for ultisols and S⁺ for andisols) plays an important role in herbicide-soil speciation that should be considered together with molecular properties to explain the mechanistic behavior of adsorption.

On the other hand, the OM, humic substances, and clay content increased the adsorption and reduced the mobility of imazaquin at low pH, due to the inverse relationship between adsorption and transport [32]. But this trend involves the adsorption on negatively charged sites, then andisols could exhibit a different behavior affected by positive charges and their interactions with herbicides $(S^{+...}X)$ and OM $(S^{+...}S^{-})$. For the case of a nonionizable herbicide, such as metolachlor, the OM plays a fundamental role for specific and nonspecific adsorption mechanisms. In this regard, Weber et al. studied the adsorption of metolachlor in Cape Fear soil [32], comparatively to imazaquin. In general, metolachlor was adsorbed by physical binding with soil. The proposed mechanisms were hydrophobic bonding to lipophilic sites of OM and humic substances $(X^{0...*}S^0)$, charge-transfer mechanisms, van der Waals forces, and H-bonds on polar surfaces of clay minerals, with a greater adsorption than imazaquin, similar to DI in Chilean soils (Figure 2, 1st stage and equilibrium) [9]. Additionally, the adsorption process could be dependent on mass transfer instead of soil-herbicide affinity. In this sense, the adsorption mechanisms depend on chemical and physical properties of soil and herbicide, including the interaction between soil components. This was observed for atrazine adsorbed on OM [33], in which hydrophobic interactions were dominant in aliphatic C of the inner sites of humic self-associated aggregates for ultisols, while for andisols the adsorption occurred on the surface of aromatic C stabilized by allophane and therefore becomes more easily desorbed [33]. This effect on conformational rigidity of organic and Fe/Al-humus sorbents is interesting to predict the environmental fate of organic nonionizable herbicides, where the formation of stable Fe/Al-humus complexes becomes OM less heterogeneous in andisols, which plays an important role in controlling the reversibility of adsorption processes. The effect of soil-solution interaction on hydrophobic adsorption of acetamiprid ($pK_a = 4.16$) was studied by Murano et al. [34]. The adsorption of neutral acetamiprid at pH 6.5 (neutral specie) increased when Al⁺³ or Fe⁺³ was added to humic substances because of hydrophobicity enhanced by cation bridging in the formation of humic substance-metal complexes $(S^{-...*}M^{+3...*}S^{-}$ and $3S^{-...*}M^{+3}$, where M=Al⁺³/Fe⁺³), changing the surface charge, conformational structure of humic substances, and accessibility to reactive sites. The TSNE model (Figure 3C) indicated that MSM adsorption on andisols presented an initial phase with a fast trend to equilibrium, where \sim 50% (F \sim 50%) of sites account for almost instantaneous equilibrium, while for ultisols, great part of sites corresponded to the time-dependent stage of adsorption (91%, F ~ 10%) (Figure 2, 1st stage). As F is related to irreversible adsorption, this parameter acts as an indirect indicator of hysteresis. So, high F values imply low desorption. The instantaneous adsorption on andisols was associated to OM-pesticide complexes, more stable and irreversible than clay-pesticide complexes, which was consistent with low k_{des} values. On the other hand, F on ultisols was related to a pore deformation mechanism due to the hysteresis water sorptivity in hydrated minerals, such as halloysite.

The DI adsorption on andisols presented an initial phase with a fast trend to equilibrium, where between 10 and 50% of sites account for very fast adsorption (**Figure 2**, 1st stage). Again for ultisols, most of the sites corresponded to the time-dependent stage of adsorption (90%) (**Figure 2**, 1st stage). The adsorption of nonionic or hydrophobic compounds on VADS has been described as a two-site equilibrium-kinetic process, where *intra-OM-diffusion* has been suggested to be

the predominant factor responsible for the nonequilibrium adsorption [9]. In this sense, the OM is the governing factor for NIH adsorption on andisols (OC content higher than 4.0%). The presence of crystalline minerals, such as kaolinite, halloysite, and Al/Fe oxides will be significant in the *IPD* mechanism in ultisols [5, 35]. The way minerals, present on VADS, are interrelated or chemically spatially distributed, either being freely distributed throughout the soil mass or coating silt and clay grains, is determinant on their chemical role in the whole ion adsorption-desorption mechanisms [7]. The different mineral composition of VADS will have an impact on their different physical behavior, influencing the INIH adsorption rate, the adsorption mechanism involved, and the INIH adsorption capacity. All of the above must be taken into account to evaluate the potential leaching of INIH in VADS.

4.3 Impact of experimental conditions of kinetic batch studies on solute transport mechanisms

The adsorption mechanism is strongly related to the experimental conditions established to carry out the adsorption kinetic study. Considering previous examples of herbicide adsorption kinetics on ultisols and andisols exposed in **Figure 3**, the pH can affect the speciation of MSM and GPS [4, 12]. Similarly, pH can significantly affect the fraction of different soil sites for adsorption $(S^+, S^- \text{ and } S^0)$ in and sols. In this sense, the variability in q_{max} due to changes in adsorption mechanisms for the pH effect will be MSM and GPS in andisols > MSM and GPS in ultisols > DI in andisols > DI in ultisols. In addition, the cations and anions in solution, related with IS and ionic composition, can affect the CEC and AEC of soil, including the ionic exchange mechanism for MSM and GPS by (i) competition, such as GPS versus phosphate, with affinity for the same S⁺, or (ii) cooperativity, such as GPS and Ca²⁺ by cation bridge adsorption in S⁻ (S^{-...²Ca^{2+...}GPS⁻). To evaluate (i), initial status of soil must} be known, e.g., the natural or anthropogenic P content in agricultural soils. The same driving factors mentioned above could modify the structure and porosity of soils, changing the transport mechanism of pesticides. Interactions such as $S^{+...}S^{-}$ in Al/ Fe-humus complexes or $S^{-...*}M^{+...*}S^{-}$ and $S^{+...*}X^{-...*}S^{+}$ for the solution composition can explain the difference between kint₁ and kint₂, especially for GPS adsorption in andisols, due to the joint effect between a high content of macropores and a low molecular size. In all previous cases, different stoichiometric coefficients may be related to the same mechanism, depending on herbicide and soil properties. If we describe the adsorption rate based on the adsorption capacity only, a simple case will be the anionic exchange of GPS^- and GPS^{2-} (e.g., phosphonate group) on S⁺ and 2S⁺, respectively, where $GPS^- + S^+ \rightarrow GPS$ -S is a pseudo-first order (*PFO*) reaction with respect to soil $(v \propto [S^+])$ and GPS $(v \propto [GPS^-])$, while $GPS^{2-} + 2S^+ \rightarrow GPS-S_2$ is a *PSO* reaction with respect to soil $(\mathbf{v} \propto [S^+]^2)$ but *PFO* reaction with respect to GPS $(\mathbf{v} \propto [GPS^-])$. In this sense, it will be important to consider the experimental conditions. For example, for high soil:solution ratios, both cases will be represented by a PFO reaction (variation on [GPS⁻] or [GPS²⁻]), while an excess of herbicide or low soil:solution ratios will be represented by a *PFO* (variation on $[S^{2+}]$) or *PSO* reaction (variation on $[S^{+}]$).

5. Conclusions

The surface charge amphoteric characteristics of VADS confer them physical/ chemical properties absolutely different to constant charge-soils, where soil composition (i.e., SOM), mineralogy, and variable charge are key components of most VADS controlling soil INIH adsorption, representing an environmental substrate that may become polluted over time due to intensive agronomic uses. The *PSO* and *TSNE* models have been the best to describe kinetics and solute transport mechanisms of INIH on VADS. These models are also necessary in order to develop and validate *QSAR* models to predict INIH adsorption on VADS to prevent potential contamination of water resources and predict environmental risks. The complex adsorption mechanisms of INIH on VADS and the diversity of soil mineralogy, texture, OC structure, and content make it necessary to consider them in *QSAR* model applications, not only to predict INIH adsorption but also to contribute to a better understanding behavior of INIH on VADS.

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Conflict of interest

The authors certify that they have no conflict of interest with the subject matter discussed in this chapter.

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