Impact of Physical/Chemical Properties of Volcanic Ash-Derived Soils on Mechanisms Involved during Sorption of Ionisable and Non-Ionisable Herbicides

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Abstract

Volcanic ash-derived soils (VADSs) are of great importance in the agricultural economy of several emerging and developing countries. The surface-charge amphoteric characteristics will confer physical/chemical properties absolutely different to constant-charge soils. This surface reactivity will confer to them a particular behaviour in relation to the herbicide sorption, representing an environmental substrate that may become polluted over time due to intensive agronomic uses. Sorption is a key parameter to evaluate the fate and behaviour of herbicides in volcanic soils. Sorption type and kinetic sorption models are also necessary in order to develop and validate QSAR models to predict pesticide sorption on volcanic soils to prevent potential contamination of water resources. The use of solute sorption mechanism models and QSAR models for pesticide sorption in soils has contributed to a better understanding of the behaviour of pesticides on volcanic soils. This chapter is divided into five sections: Physical/chemical properties of volcanic ash-derived soils; Ionisable and non-ionisable herbicides’ fate and behaviour in soil; Kinetic sorption: mechanisms involved during sorption of ionisable and non-ionisable herbicides on VADS; Sorption of ionisable and non-ionisable herbicides on VADS; and Physical/chemical properties in QSAR models: a mechanistic interpretation.

Keywords: volcanic ash-derived soils, herbicides kinetic, herbicides sorption, solute transport mechanisms, mechanistic interpretation of QSAR models

1. Introduction

The nature of soils is regulated by various soil-forming factors such as parent material, climate, vegetation, relief and time [1]. These factors vary widely among region, and also vary in their properties. Volcanic ash-derived soils (VADSs) are predominantly found in regions of the world with geochemical characteristics dominated by
active and recently extinct volcanoes. 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 (ChVADS) have led to the very increased use of pesticides and also frequent adjustments of soil pH and mineral fertilisation [3–5]. Among these soils, andisols and ultisols are the most abundant and present an acidic pH (4.5–5.5). Andisols are characterised by their high organic carbon (OC) content, high specific surface area and a mineralogy dominated by short-range-ordered minerals such as allophane (Al₂O₃·SiO₂·nH₂O). Ultisols have lower OC than andisols, but higher total iron oxide content. Andisols present variable surface charge, originated in both inorganic and organic constituents. Inorganic minerals 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 organic mineral (OM) contributes through the dissociation of its functional groups (mainly carboxylic and phenolic), and humus-Al and Fe complexes with amphoteric characteristics. Nevertheless, ultisols present lower variable surface charge than andisols, because more crystalline minerals such as halloysite and/or kaolinite dominate their mineralogy.

Several sorption kinetic studies of herbicides on VADS have indicated that herbicide sorption is a non-equilibrium process [5]. Time-dependent sorption (or non-ideal sorption) can be a result of physical and chemical non-equilibrium and intra-sorbent diffusion that can occur during the transport of pesticides in soils [6, 7]. In general, non-equilibrium sorption has been attributed to several factors such as diffusive mass transport resistances, non-linearity in sorption isotherms, sorption-desorption non-singularity and rate-limited sorption reactions [8]. Intra-OM diffusion has been suggested to be the predominant factor responsible for the non-equilibrium sorption of non-ionic or hydrophobic compounds on VADS [7, 9]. It has been found that differences in sorption kinetic of herbicides were due to soil constituents, such as OC and mineral composition on VADS.

In general, sorption 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 the sorption of pesticides from soil solution to soil particle active sites, which limit transport in soils by reducing their concentration in the soil solution.

The kinetic parameters can be obtained by means of the application of two kinds of kinetic models: the ones that allow to establish principally kinetic parameters and modelling of the sorption process and other models frequently used to describe sorption mechanisms of organic compounds on soils. Such information is necessary in order to understand leaching of pesticides, such as herbicides for preventing potential contamination of groundwater.

The aim of this chapter is to establish the sorption kinetics of ionisable and non-ionisable herbicides (INIH) in ChVADS to apply different solute sorption mechanism models, considering the models’ restrictions and VADS properties to investigate the mechanisms involved in INIH sorption on VADS. These kinetics studies, complemented with ‘batch’ sorption studies of INIH on VADS, allow the identification of sorption characteristics. Sorption type and kinetic sorption models description are also necessary in order to develop and validate computer simulation transport models on VADS or to increase the quality of sorption data to develop reliable models, such as QSAR models, and to predict pesticide sorption on VADS to prevent potential contamination of water resources.
2. Physical/chemical properties of volcanic ash-derived soils

In general, VADSs are soils rich in constituents with amphoteric surface reactive groups; Although andisols and ultisols are the most important in Chile, oxisols, alfisols and spodosols are also considered variable charge soils [10]. The nature of soils is regulated by various soil-forming factors such as parent material, climate, vegetation, relief and time [1]. These factors vary widely among regions, also affecting their properties. The most striking and unique properties of these are variable charge, high water-holding capacity, low bulk density, high friability, highly stable soil aggregates, excellent tilth and strong resistance to water erosion [11], high anion sorption, high lime or gypsum requirement to achieve neutral pH and considerable sorption affinity for cations (Ca and Mg), which may form both inner- and outer-sphere surface complexes although the first is found to be most important [10].

These distinctive physical and chemical properties are largely due to the presence of non-crystalline materials, biological activity and the accumulation of OC [11, 12]. The soil organic matter (SOM) represents a key indicator of soil quality, both for agricultural (i.e. productivity and economic returns) and environmental functions (i.e. carbon sequestration). The OC concentrations in andisols are more strongly associated with metal-humus complexes than with concentrations of non-crystalline materials; nevertheless, inorganic materials with variable-charge surfaces provide an abundance of microaggregates that permit to encapsulate OC, favouring their physical protection [11]. Other studies indicate Al/Fe oxides/hydroxides in allophanic soils are linked through carboxylic and aromatic groups present in SOM being the SOM highly decomposed [1].

VADSs are dominated by Al/Fe-humus complexes, by ferrihydrite, a short-range-order Fe hydroxide mineral or by short-range-order clay components (amorphous aluminosilicates), such as allophane and imogolite [11]. The VADS clay fraction mineralogy is usually dominated by kaolinite, gibbsite, goethite and hematite [10]. Besides these minerals, they contain 2:1 and 2:1:1-type minerals and opaline silica, halloysite, etc. occasionally in substantial or dominant amounts. Halloysite is a 1:1 aluminosilicate hydrated mineral characterised by a diversity of morphologies (e.g. spheroidal and tubular) [11].

Andisols are relatively young soils and cover about 0.84% of the world’s land [11, 13] being typical products of weathering increases in both temperate and tropical environments with sufficient moisture [11]. In this sense, metastable non-crystalline 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, with allophanic andisols dominated by variable-charge constituents (allophane/imogolite), and non-allophanic andisols dominated by both variable-charge and constant-charge components (Al/Fe-humus complexes and 2:1 layer silicates) [11]. Allophanic andisols form preferentially in weathering environments with pH values in the range of 5–7 and a low content of complexing organic compounds. Non-allophanic andisols form preferentially in pedogenic environments that are rich in OM and have pH values of 5 or less [11].

Allophanic andisols of Southern Chile derive from holocenic volcanic ash, presenting dates less than 12,000 years old. Chilean andisols are rich in OM, with high specific surface area and a mineralogy dominated by short-range-ordered (amorphous) minerals such as allophane, high P retention (>85%), low saturation of bases, presence of clay, high variable charge, low bulk density (<0.9 Mg m$^{-3}$) associated with a high porosity and a strong microaggregation of heterogeneous forms [2, 14]. The variable surface charge in Chilean andisols is originated in both
organic and inorganic constituents. The OM contributes through the dissociation of its functional groups (mainly carboxylic and phenolic) and Al/Fe-humus complexes with amphoteric characteristics; 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 [15]. Furthermore, allophane plays key roles in surface reactivity such as determining the availability of nutrients and controlling soil contaminant behaviour [14].

2.1 Agricultural implications of Chilean volcanic ash-derived soils

The importance of VADSs is due to the ability to manipulate their surface charge characteristics in order to control the retention of cations and anions [10]. Chilean andisols have higher total P concentrations than ultisols, and significant amounts of the accumulated P are from the organic forms (organic P) (>45% of the total P), similar to allophonic soils in other parts of the world [4, 5]. The inorganic P fraction has been associated with Fe and Al in uncultivated Chilean andisols, and organic P has been strongly correlated with OC content, being considered an important P source for crops through mineralisation. But generally, they have low available P resulting in reduced fertility [2, 4, 5, 16, 17]. The availability of P decreases or increases in relation to the development of the soil, the decrease of P availability with increasing soil development due to incorporation of P into organic forms and P fixation by non-crystalline Al and active Al/Fe components making it sparingly available for plant uptake [12]. On the other hand, P is often a growth-limiting nutrient for agricultural crops grown on relatively young soils where its availability is relatively high due to rapid weathering of apatite, and its retention is low due to low concentrations of active Al/Fe [11].

At their original acidic pH range (4.5–5.5), VADSs require frequent adjustments of soil pH, replenishment of exchangeable Mg and P applications to remain productive [4]. In relation to adjustments of pH, the increase of soil pH has been shown to reduce phytotoxic levels of exchangeable acidity (Al<sup>3+</sup>) and increase the ability of soils to retain nutrient ions and potential toxic heavy metals [10]. The exchangeable Al often dominates exchange sites, controls soil acidity and buffering capacity on ultisols, resulting in heavy reliance on liming practices to optimise soil acidity/ fertility for plant growth [18].

Although P fertiliser application has been proposed as a management tool to increase the Cation-exchange capacity (CEC) of volcanic charge soils (VCS), large quantities of P fertiliser are required to cause a significant increase in CEC [10]. P fertiliser applied to andisols is rapidly sorbed by active Al/Fe components and changes to less available forms with time [11]. In general, ChVADS presents a high capacity to retain P due to its specific phosphate sorption [2]. Also, specific and preferential sorption of phosphate by variable-charge minerals can modify the soil surface to be more negative [17]. In such cases, it could result in the enhanced mobility of ionisable herbicides, because of increased competition with inorganic anions for positively charged sites and could modify the charge on the oxide surface, changing their speciation. Moreover, the strong influence of pH and phosphate addition in its sorption on ChVADS are conditions that are known to favour excessive transport of sulfonylurea herbicides (SHs), such as metsulfuron-methyl (MSM) [5]. A displacement of the isoelectric point (IEP) of an allophanic andisol towards a higher pH would be a most favourable condition for electrostatic interaction between anionic MSM and free or active Fe/Al oxides. The SH anionic forms predominate in solution for most soils, which is more soluble in water, being less susceptible to hydrolysis but favouring the herbicide transport. This situation is aggravated when considering that ChVADSs are relatively shallow (<15 m) in relation to groundwater.
Therefore, the lower sorption of MSM at higher pH was attributed mainly to the decrease of available active sites, despite its high maximum sorption capacity of phosphate. Maximum phosphate sorption capacity for ultisols (mainly attributed to kaolinite content) was 1.7 times lower than for andisols, so a lower amount of common sites will be also available for MSM sorption. In this sense, intensive soil fertilisation and liming are the most probable scenarios for leaching potential of ionisable herbicides in VADS as a consequence of decreasing soil sorption. The extensive use of glyphosate (GPS) on Chilean andisols may result in enhanced sorption and, consequently, reduced availability of phosphate [4]. Moreover, on Chilean ultisols, GPS may be immobilised with no effect on the phosphate sorption, suggesting a different mechanism involved during GPS and phosphate sorption on VADS. In this sense, the long-term use of GPS may therefore have different effects on the retention and availability of soil P. The continuous input of P fertiliser for VADS may subsequently decrease sorption of post-applied carboxylic acid herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and desorb previously applied 2,4-D [19]. In this sense, Chilean andisols are generally cropped to maize (Zea mays L.) and their management includes the application of liquid cow manure (LCM) at rates higher than 100,000 L ha⁻¹ and the application of atrazine for broad leaf weed control [14].

3. Ionisable and non-ionisable herbicides fate and behaviour in soil

Herbicides are the dominant pesticides used to control weeds in agricultural production. The total amount of pesticides used in the world exceeded 39.4 billion USD in 2007, of these, herbicides accounted for the largest amount (40%) [20]. The physical, chemical and biological characteristics of soil, as well as the chemical properties of herbicides, will influence their fate and behaviour in soils [1, 19, 21, 22]. And also, sorption processes are an important physicochemical characteristic on use herbicides, which are used considering their specific biological activity on target species.

Even more, although sorption-desorption processes are dynamic, where molecules are continually transferred between the bulk liquid and solid surface, an excess of herbicide sorption may result in unavailability of herbicide to targeted pests as well as uneven distribution around the plants. In this sense, sorption is a key parameter to evaluate the fate and behaviour of herbicides in soils, controlling the bioavailability, distribution and transport to other environmental compartments. In this regard, the main processes of herbicides in soils, such as sorption, degradation, biodegradation, bioavailability and transport, are commonly studied and evaluated [22].

Soil sorption is characterised by a partition coefficient, K, conventionally written with a subscript d (‘distribution’). The distribution coefficient (Kd) is the most common and accepted quantitative measurement of pesticide soil sorption [23, 24]. Moreover, it is considered as a unique property or constant of pesticides, which is used to describe the equilibrium distribution of a pesticide between a soil, sediment or particles and the aqueous phase that it is in contact with [25]. Several mathematical models have been developed to describe equilibrium sorption of pesticides on soils, such as Linear, Freundlich and Langmuir models. A linear model assumes that the relationship between the amount adsorbed and concentration at equilibrium of the chemicals is proportional which is often only valid at trace levels, for example, below half solubility. The Freundlich model assumes that the solid matrix has an infinite sorption capacity, thus sorption increases indefinitely with the solute concentrations in a non-linear way [26]. At low pesticide concentration levels, this model has been widely applied describing adequately the sorption behaviour of
Sorption

INIH on VADS (Figure 1). *Freundlich* model with \((1/n) < 1\) (L-type) indicates a heterogeneous sorption site, a strong adsorbent affinity for the adsorbate, diversity of sorption mechanisms and strong concentration dependence of sorption for the sorption sites [4, 14, 15, 19]. Isotherms with \((1/n) > 1\) (S-type) indicate competition between solvation water and adsorbate for the sorption sites [19]. The *Langmuir* model assumes: (1) sorption occurs on planar surfaces that have a fixed number of sites that are identical and the sites can hold only one molecule; thus, only monolayer coverage is permitted, which represents maximum sorption; (2) sorption is reversible; (3) there is no lateral movement of molecules on the surface and (4) the sorption energy is the same for all sites and independent of surface coverage (i.e. the surface is homogeneous), and there is no interaction between adsorbate molecules (i.e. the adsorbate behaves ideally) [26].

4. Kinetic sorption: mechanisms involved during sorption of ionisable and non-ionisable herbicides on VADS

Sorption processes are known to be important because they are time-dependent processes with considerable ecosystem impact, influencing the availability of organic pollutants for plant uptake, microbial degradation and transport in soil and consequently the leaching potential. Sorption kinetic studies may provide important information related to weed control, crop toxicity, runoff, sorption mechanisms, solute transport mechanisms and its applied use in decontamination, such us remediation [7, 22]. This process occurs within the boundary layer around the sorbent, being conceptualised as a rapid uptake process to readily available sorption sites and proceeds in the liquid-filled pores (external mass transfer steps; (EMT)) or along the walls of the pores of the sorbent (internal mass transfer steps (IMT)) followed by slow diffusion-immobilisation in micropores or capillaries of the sorbent’s internal structure (intra-particle diffusion, IPD), except for small sorbed amounts that appear on the external surface, and can occur during the transport of pesticides in soils. The third stage is the sorption of the solute in the inner surface of the sorbent through mass-action-controlled mechanisms where a rapid uptake occurs or surface reaction through interactions between solute and surface functional groups (such as chemisorption) [7, 9, 27].

The herbicide-VADS interaction is a time-dependent process that often progresses rapidly over the short term (minutes or hours), and it may also take a short time to reach equilibrium on VADS (Figure 1). Sorption process has influence on the transport of pesticides in the soil environment during the short term [4, 7, 9, 15]. The *pseudo-second-order* model has been the best sorption kinetic model to establish principal kinetic parameters and modelling of sorption process of INIH on VADS (Figure 1). On the other hand, the *Weber-Morris* model is one of the most used models to describe solute transport mechanisms of organic compounds in different sorbents intended for remediation purposes. Nevertheless, the *two-site non-equilibrium* (TSNE) model has been the best kinetic model to describe INIH transport mechanisms on VADS (Figure 1B; Table 1).

**Figure 1A** and **B** shows different transport mechanisms of MSM and diuron (DI) on ultisol (Collipulli soil, COLL) and andisol (Nueva Braunau soil, NBR). The *Weber-Morris* model indicates that the mass transfer across the boundary layer and IPD control DI sorption on all ChV ADSs (Figure 1A; Table 1). The non-ionic or hydrophobic herbicide sorption 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 non-equilibrium sorption on andisols. In contrast, the MSM sorption on ultisols was controlled exclusively by IPD; thus, the
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first line (at shorter time) will depict macropore diffusion in the boundary layer, with the EMT occurring at short contact times during the retention of MSM into macropores and the second line (at longer time) accounts for the gradual sorption

| Pesticide-VADS | Kinetics sorption description and/or model | Ref. |
|----------------|------------------------------------------|------|
| AT-Andisol (Southern, Chile) | AT approached equilibrium in about 12 h | [14] |
| AT-acidic andisols and ultisols (Southern Chile). Soils presented negative net charge at $p_H$ | AT sorption on VADS was controlled by instantaneous equilibrium followed by a time-dependent phase. Andisols: two rate-limited phases were established; the first one related to intra-sorbet diffusion in OM and second one related to slow IPD in the organo-mineral complex. Ultisols: only one rate-limited phase attributed to kaolinite associated to slow and progressive sorption | [15] |
| GPS-acidic ultisol and andisol (Southern Chile) | GPS sorption kinetics on ChV ADS followed a pseudo-second-order model with an apparent equilibrium reached in 10–120 min. The faster GPS sorption of andisol was related to higher OC content. The slower GPS sorption kinetic on ultisols was controlled by IPD | [4] |
| T-non-allophanic (Central Chile) and allophanic soils (Southern Chile). Soil pH range: 6.3–7.4 | A rapid adsorption was observed during the first few minutes, followed by a slower process that in all cases reached an apparent equilibrium within 2 h. The order of the kinetic reaction was two. The slow process may be attributed to the diffusion of MBT within the porous of the soil matrix. On the sorption kinetic for non-allophanic soils, OM amendment increased the $S_{max}$ values and decreased the rate constant, pointing out a higher porosity of the soil matrix | [33] |
| MSM-acidic ultisols and andisols (Southern Chile) | MSM sorption kinetics on ChV ADS followed a pseudo-second-order and the Weber-Morris model, indicating that the mass transfer across the boundary layer and IPD are the two mechanisms controlling MSM sorption on andisol, whereas in ultisols, the rate was controlled exclusively by IPD into macropores/micropores. The two-site nonequilibrium (TSNE) model was the best kinetic model to be applied to VADS. Andisol presented an initial phase with a fast trend to equilibrium, where ~50% of sites accounted for instantaneous MSM sorption. Most ultisol sites corresponded to the time-dependent stage of sorption | [9] |
| DI-acidic ultisols, inceptisol and andisol (Southern Chile) | The pseudo-second-order model was able to describe DI sorption at all time intervals for all soils. The Weber-Morris model indicated that mass transfer across the boundary layer and IPD were the two processes controlling sorption kinetics of DI in all ChV ADS, being corroborated by the Boyd model. An initial phase, with a fast trend to equilibrium, was established for the andisols through the TSNE model, whereas ~51% of sites account for instantaneous sorption on andisols. For the ultisols, most of the sites corresponded to the time-dependent stage of sorption | [7] |

| Pesticide-VADS | Sorption description model | Ref. |
|----------------|----------------------------|------|
| AT-Andisol (Southern Chile) | AT sorption on ChVADS was well described by the Frendlich model ($K_f = 1.19 \text{ mg}^{(1-\gamma)} \text{ L} \text{ kg}^{-1}; R^2 = 0.98$), exhibiting non-linear isotherms of L-type ($N_f < 1$) and a concentration-dependent AT solid-solution distribution. The mechanisms involved are hydrogen bonding and charge transfer. AT in acidic soil, for its weak basic nature, presents a partial protonation of amine groups, which are involved in the hydrogen bonds with carboxyl and carboxyl groups of soil. These contribute to its protonation, forming a partial positive charge in the aromatic ring | [14] |
| AT-acidic andisols and ultisols (Southern Chile). Soils presented negative net charge at $p_H$ | Sorption data were well described by the Freundlich model ($K_f$ between 2.2 and 15.6 $\text{ mg}^{(1-\gamma)} \text{ L} \text{ kg}^{-1}$; $R^2 \geq 0.993$). The highest sorption was observed on andisols being adsorbed mainly through hydrophobic interactions or van der Waals forces at the phenolic groups of OM (humic acid and humin fraction). AT was weakly sorbed on soil with permanent negative charge (ultisols) through a hydrophobic bonding at the silanol surface sites of the tetrahedral sheets present on clays, such as chlorite, gibbsite, goethite/hematite and kaolinite | [15] |
## Sorption Kinetics sorption description and/or model

| Pesticide-VADS | Kinetics sorption description and/or model | Ref. |
|----------------|------------------------------------------|------|
| BSM-acidic and ultisols (Southern Chile) which presented negative net charge at pH\text{\textsubscript{\text{H0}}} | BSM sorption on ChVADS was well described by the \textit{Freundlich} model ($R^2 > 0.995$), exhibiting non-linear isotherms of L-type. BSM was weakly sorbed on soil with permanent negative charge (ultisols). A multifactorial influence of several properties of soils was demonstrated, through a partial least squares regression model (P value = 0.0042) by use of % OC, % Fe and surface area. The BSM sorption on mineral (AlSi-Fe) and mineral-organic complexes (AlSi-Fe-HA) confirmed the participation of variable-charge materials present in VADS, both with a high sorption capacity, demonstrating the effect of BSM sorption on charge of both sorbents. The distribution of SOH, SOH$^-$ and SO$^-$ sites was better characterised for AlSi-Fe-HA | [16] |
| GPS-acidic ultisol and andisol (Southern Chile) | GPS sorption on ChVADS over the extended range of concentrations was well described by \textit{Freundlich} model ($K_f$ between 1480 and 3764 $\mu g^{1-1/\nu} mL^{1/\nu} g^{-1}$; $R^2 \geq 0.99$). The highest sorption was observed on andisols being adsorbed to Fe/Al oxides and allophane by ligand exchange through its phosphonic acid moiety or by hydrogen bonding reacting with polyvalent cations adsorbed on SOM between GPS and humic substances (metal-GPS OM complex). GPS was adsorbed strongly and specifically to kaolinite on ultisol | [4] |
| AT, CPF, CTL, DZN, GPS and MSM, DEA, AMPA, TCP and IMHP-acidic ultisol and andisol (Southern Chile). All soils present a negative net charge at pH\text{\textsubscript{\text{H0}}} | Data fitted to the \textit{Freundlich} model with $R^2 > 0.97$. All herbicides and metabolites (except GPS) showed a markedly higher sorption on allophanic soil exhibiting a non-linear isotherm of L-type ($N_i < 1$) with a trend to the saturation of sorption sites at higher concentrations. The exceptionally high sorption of GPS on ultisols (with lower OM, Al$\text{\textsubscript{total}}$, and Fe$\text{\textsubscript{ox}}$ contents than andisols; $K_f > 1500 \mu g^{1-1/\nu} mL^{1/\nu} g^{-1}$) was related to kaolinite contents and acidic pH, posing the need to establish its possible contamination | [3] |
| MBT-non-allophanic (Central Chile) and allophanic (Southern Chile) soils. The pH values of natural soils (6.3–7.4) | The isotherms fit the \textit{Freundlich} model ($K_f$ between 5.3 and 82.1 cm$^3$ g$^{-1}$; $R^2 \geq 0.998$) exhibiting a non-linear isotherm of L-type ($N_i < 1$). The MBT sorption was markedly higher on allophanic soils with OM being the principal component responsible for MBT sorption. The clay and smectite contents on non-allophanic soils were considered the most important factors governing the MBT sorption. The interaction was predominantly by physical bonding (van der Walls forces or hydrogen bonding) between the amino hydrogen of MBT and hydroxyl groups of humic acids of SOM, or through the carbonyl group, which could act as a strong donor to hydrogens of the alcoholic and phenolic groups on the humic acid of SOM. The presence of MBT in surface waters in Chile would be produced only by losses from the sediment-adsorbed MBT through runoff process | [33] |
| MSM-ultisol and andisol (Southern Chile) | The \textit{Freundlich} model described MSM sorption in all ChVADSs ($K_f$ values between 3.1 and 14.4 $\mu g^{1-1/\nu} mL^{1/\nu} g^{-1}$; $R^2 > 0.992$). The lower MSM sorption capacity on low variable-charge soils (Chilean ultisols) was attributed to the low OM content. The kaolinite mineral group as major constituent of the inorganic fraction of ultisols and minerals, such as allophane, gibbsite, hemateit and goethite, contributed to MSM sorption mainly through hydrophilic interactions. The OM and active/free Fe/Al oxides controlled the MSM sorption in andisols mainly through hydrophilic rather than hydrophobic interactions | [5] |
| 2,4-D-oxisols (Brazil), andisols (South Korea), ultisols (Costa Rica), and alfisols (Toronto) | Linear sorption model fitted to isotherms measured from CaCl$_2$, CaSO$_4$, Ca(H$_2$PO$_4$)$_2$ and KCl systems ($K_f$ values between 1.28 and 18.5 L Kg$^{-1}$; $R^2 > 0.96$). The higher 2,4-D sorption was obtained on CaCl$_2$, reflecting both effects of inorganic anion in terms of competition and cation in terms of bridging interactions. 2,4-D sorption via Ca-bridging took place on silanol edges (Si-OH) of kaolinite or silicate edges | [17] |
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stage, where the molecules of MSM diffuse through the smaller pores of the soil (IPD) (Figure 1A; Table 1). On the other hand, the mass transfer across the boundary layer and IPD were the two mechanisms to control MSM sorption on andisol (Figure 1A; Table 1).

Time-dependent sorption (or non-ideal sorption) can be a result of physical and chemical non-equilibrium [9]. Non-equilibrium sorption on soils has been attributed to several factors, such as: diffusive mass transfer resistances, non-linearity in sorption isotherms, sorption-desorption non-singularity and rate-limited sorption reactions [8]. The rate-limited diffusion of the sorbate 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 TSNE model (Figure 1B; Table 1) indicated that MSM sorption on andisol presented an initial phase with a fast trend to equilibrium, where about 50% of sites accounted for the instantaneous stage and the great part of sites on ultisols corresponded to the time-dependent stage of sorption (90%). In contrast, the sorption of non-ionisable herbicide (DI) on andisols presented an initial phase, with a fast trend to equilibrium,
where ~20% of sites accounted for instantaneous sorption on andisol. For the ultisols, most of the sites corresponded to the time-dependent stage of sorption (90%).

The higher value in the overall rate constant, \( k_2 \), of MSM on andisols with respect to DI in the same soil indicates that this value reflects contributions from the favoured electrostatic interactions considering both a retarded IPD as well as intra-OM diffusion. 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 of their chemical role in the whole ion sorption-desorption mechanisms [28]. In this sense, the OM content is the principal component to control the pesticide sorption on andisols, as much by instantaneous equilibrium as by IPD, the presence of kaolinite, halloysite and Al/Fe oxides in Ultisols will be significant in the IPD mechanism. According to this analysis, ultisols present a potential risk of ionisable herbicide transport. The different mineral composition of ultisols impacts on their different physical behaviour, influencing the slowest INIH sorption rate, the sorption mechanism involved and the lowest INIH sorption capacity. All of the above must be taken into account to evaluate the potential leaching of INIH in these kinds of soils.

5. Sorption of ionisable and non-ionisable herbicides on VADS

The retention and mobility of herbicides in soil are determined by the strength and extent of sorption reactions [14]. The soil particles (adsorbent) may adsorb herbicides (adsorbate) weakly or strongly depending on the adsorbent-adsorbate interactions. In this sense, herbicides can be adsorbed in soil through different mechanisms such as physical sorption (van der Waals and H bond interactions) and chemical sorption. Physical sorption is fast and usually reversible, due to small energy requirements [21].

The physical and chemical interactions between herbicides and other organic molecules on the soil particles surface depend on the physical and chemical properties of the soil and herbicide. The nature of surface charge may vary with the chemical properties of VADS. The surface charge amphoteric characteristics will confer to VADS chemical and physical properties absolutely different from those exhibited in soils of constant charge. This surface reactivity of VADS confers to them a particular behaviour in relation to the retention of herbicides, representing an environmental substrate that may become polluted over time due to intensive agronomic uses.

There are only a few reports on the behaviour of INIH in VADS despite being important to agricultural systems of many regions (Figure 1). A higher sorption capacity of several herbicides has been reported for allophanic soils (Figure 1). In this regard, the herbicide sorption on VADS will be affected by soil properties (SOM content, allophane, clay, pH, IS, particle size distribution, moisture content and variable charge) and herbicide chemical properties (molecular structure, molecular size, electrical charge, ionisability, aqueous solubility, hydrophobicity (K\(_{ow}\)), volatility, reactivity with soil constituents and longevity in the environment) [29]. Environmental conditions may also affect INIH sorption and mobility on VADS.

5.1 Sorption of ionisable herbicides and non-ionisable herbicides on VADS

The ion sorption rate in VADS depends on the surface area, CEC, the proportion of Fe/Al oxides or oxyhydroxides present as the surface coating of clay and silt particles [28]. Oxides have also been found to enhance the deprotonation of organic acids and, therefore, increase the activity of the anionic species at a given is expected to be at a maximum if the ratio of the mineral to the OC fractions is more than 30, regardless of the mineral content [7, 9, 19].
At soil pH, both Fe/Al oxides and amorphous Fe oxide surfaces on VADS are positively charged. This property is considered effective in the retention of different SH at pH$_{\text{soil}}$ > ZPC, oxides and amorphous Fe oxide surfaces on VADS has been considered the most effective condition for the retention of different SH at pH$_{\text{soil}}$ > zero point of charge (ZPC), where the anionic herbicide will be present (Figure 1), due to the strong dependence of pH in sorption of this kind of compound. Caceres et al. [5] studied the effect of the sorption of MSM on VADS. These researchers observed a change in the behaviour of both soils’ surface charge (andisol and ultisol) when MSM was sorbed. At pH lower than ZPC, hydrogen bonding has been suggested as interaction mechanism through the protonation of pyrimidine nitrogen moiety of SH and subsequent with the surface hydroxyls on the amorphous Fe oxide (positively charged), and also, these important adsorbents on VADS can retain SH through electrostatic attraction and ligand exchange.

In general, as the pH comes closer to the pK$_a$ of herbicides, the sorption increases due to the hydrophobicity of their neutral form. It was also suggested that the hydrophobic part of the organic anion might sorb to a hydrophobic surface, with its polar end oriented towards the more polar aqueous phase. In VADS, a decrease in soil pH increases the net positive charge on the surface [30], at low pH the negatively charged chlorophenols are adsorbed onto the positive sites through electrostatic attraction. The Ca-bridging can take place between anionic SOM functional groups (e.g. carbolic and phenolic groups) or negatively charged sites on constant/variable-charge mineral surfaces and anionic pesticides (Table 1) [17, 31].

A large part, but not all, of the variation in herbicide sorption coefficients between different soils can be eliminated by expressing sorption on OC basis rather than on a total soil mass basis [24]. In this sense, $K_d$ is usually normalised to the OC content of the soil ($K_{OC} = K_d/OC$) or to the OM content of the soil ($K_{OM} = K_d/OM$) [25, 31]. The $K_d$ for a particular organic compound changes significantly from one soil to another, and generally increases as the OC content of the soil and the hydrophobicity of the chemical increases. In this sense, the OM has a high affinity for many non-polar pesticides and dominates their sorption in soils with more than 3% OM (Table 1). It reflects the fact that OC is the major sorption domain for non-ionisable herbicides on soils [32], whereas poorly crystalline minerals attract polar organic molecules.

6. Physical/chemical properties in QSAR models: a mechanistic interpretation

QSAR modelling is a useful technique to predict the activity of chemicals, such as pesticides in a short time and with low cost, establishing a statistical relationship between the activity of chemicals and their structural and physicochemical properties [34–37]. The development of QSAR models with regulatory purposes is based on precaution, while their application facilitates prevention. In this regard, the member countries of the organisation for economic co-operation and development (OECD) have developed a set of five guiding principles, enabling the practical application of QSAR modelling as a reliable tool in the regulatory context, which have been adopted by the European Union and United States [38–40]: (i) a defined endpoint; (ii) an unambiguous algorithm; (iii) a defined domain of applicability; (iv) an appropriate measure of goodness-of-fit, robustness and predictivity and (v) a mechanistic interpretation. The QSAR models are based on the assumption that chemicals are able to reach and interact with the target site by similar mechanism, related to their similar physicochemical properties [40].
6.1 QSAR models for sorption of pesticides in soils

The recent developments in QSAR models for the estimation of soil sorption coefficients of organic pesticides will be reviewed, taking into account the literature related to QSAR and its mechanistic interpretation. The aim of this section is to examine the descriptors used in the prediction of $K_{oc}$ values on soil by means of QSAR models, which according to principle (v) should be associated with a ‘mechanistic interpretation’. In this regard, two approximations have been used for the mechanistic basis of the models: (i) statistical approach and (ii) mechanistic approach. In the ‘mechanistic approach’, the descriptors selection can be guided by the modeller’s a priori knowledge of the physicochemical properties involved in the mechanism proposed for the studied activity. Thus, presumed mechanistic meaning can be assigned to some molecular descriptor used; then, the modeller selects it personally from a limited pool of potential modelling variables, which are largely employed (for instance: $\log K_{ow}$, $\log P$, $\log D$, $pK_a$, OC, etc.). However, as the sorption mechanisms of pesticides on soils and especially on VADS are quite complex, their understanding is only possible at certain levels of approximation. The a priori selection of one (or more) physicochemical variable(s) for their mechanistic meaning, in relation to one assumed mechanism, is very risky. In this sense, important variables influencing other mechanisms, participating in such a response, could remain ignored.

6.2 Statistical approach: a posteriori mechanistic interpretation

The European joint research centre (JRC) QSAR models database provides information on the recent developments in QSAR models that can be used for purposes of regulatory assessment of chemicals (e.g. REACH registration). In this database, four detailed QSAR models to predict the sorption partition coefficient are normalised to the OC content of the soil ($K_{oc}$, $K_{oc} = K_d/OC$ or $K_{oc} = K_f/OC$). The QSAR Model Reporting Format (QMRF) documentation for all QSAR models is available in the JRC’s QMRF Inventory [41–44]. All these models were developed by statistical approach, wherein no mechanistic basis for their descriptors selection was set a priori. The first was published few years ago [44]. In this study, QSAR model was developed using $K_{oc}$ values of 142 non-ionic organic pesticides (34 split for the validation set). The $K_{oc}$ data for 20 other chemicals were used as external validation set. The QSAR model developed in this study is represented by Eq. (1):

$$\log K_{oc} = 0.96 - 0.26 \text{ Polarity parameter (AM1)/distance} + 1.07^{-0.02} \text{ALFA polarizability (DIP)(AM1)} - 1.99 \text{Max net atomic charge (AM1) for C atoms} + 1.30^{-0.02} \text{WNSA1 Weighted PNSA} \left( \frac{\text{PNSA1} \times \text{TMSA}}{1000} \right) \text{(Zefirov)}$$

where ‘ALFA polarizability (DIP) (AM1)’ and ‘WNSA1 Weighted PNSA (PNSA1 × TMSA)1000 (Zefirov)’ are descriptors that quantify the molecular size related to charge distribution. The ‘Max net atomic charge (AM1) for C atoms’ and the ‘Polarity parameter (AM1)/distance’ are descriptors related to charges and to charge distribution.

Recently, Mansouri and Williams [41] published a new reliable QSAR model for estimating the $K_{oc}$ of heterogeneous organic chemicals. This is freely available as an open-source, command-line application called OPERA (OPEn structure–activity/property Relationship App) [45]. The model was generated using 729 curated outlier-free experimental $K_{oc}$ data, which were divided into training (545 compounds) and
validation sets (184 compounds). The descriptors’ selection consisted of coupling genetic algorithms (GAs) with the weighted $k$NN algorithm, which allows building a model with 12 molecular descriptors, related to logP and water solubility. These descriptors were calculated using the free and open-source software PaDEL [46]. The model has potential to correctly predict the Log$_K$ values of organic pesticides since the predictivity-statistics obtained by external validation was quite significant, i.e. $R^2 = 0.71$ and RMSD = 0.61.

In both QSAR models exhibited above, compounds with large molecular size tend to have higher soil sorption than compounds with small molecular size, due to their lower water solubility. For electronic descriptors related to charges and charge distribution, the presence of active functional group adjacent to carbon allows a high charge on this atom, which together with likewise higher polarity leads to better water solubility. In the first, the minus sign in the QSAR equation (Eq. (1)) on these descriptors indicates that the higher the values, the lower the soil sorption. In the last update published by Gramatica et al. in JRC QSAR Model Database, QSAR Eq. (2) [43, 47] and Eq. (3) [42, 47], QSAR models were generated using the $K_oc$ experimental data of 643 heterogeneous organic compounds obtained from literature. The median of the $K_oc$ values was used when more than one value was available for a single compound.

\[
\text{Log } K_{oc} = 0.87 + 0.26 \text{ VP} - 0.23 n\text{HBAcc} + 0.08 n\text{AromBond} - 0.19 \text{MAXDP} \quad (2)
\]

where $N = 643$ (nTr = 93, nPred =550); $R^2 = 0.79$; $Q^2_{\text{LOO}30\%} = 0.79$; CCC (correspondance correlation coefficient) = 0.89; RMSE = 0.54

\[
\text{Log } K_{oc} = -1.92 + 2.07 \text{VED}_1 - 0.31 n\text{HBAcc} - 0.31 \text{MAXDP} - 0.39 \text{CIC}_0 \quad (3)
\]

where $N = 643$ (nTr = 93, nPred =550); $R^2 = 0.79$; $Q^2_{\text{BOOT}} = 0.79$; CCC (correspondance correlation coefficient) = 0.88; RMSE = 0.55.

The model described by Eq. (2) and Eq. (3) takes into account two different ways to describe a potential intermolecular adsorbate-adsorbent interaction. First, $n\text{HBAcc}$ (Eq. (2) and Eq. (3)) is related to electronegative atoms of molecules that form hydrogen bond indicating a potential mechanism. Second, the MAXDP descriptor (Eq. (2) and Eq. (3)) related to molecule electrophilicity supposed a possible sorption mechanism of charge transfer between adsorbate and adsorbent. These mechanisms have been suggested for pesticides where amine and/or heterocyclic N atoms (e.g. AT) act as electron donors to acceptor structural groups of humic acid [48]. Moreover, Briceno et al. [14] conclude that the mechanisms involved in the AT soils’ sorption are both hydrogen bonding and charge transfer (Table 1). The other two descriptors in each QSAR equation, Eq. (2) (VP - 0 and nAromBond) and Eq. (3) (VED1 and CIC0), are related to molecular size and have positive signs. Models indicate in general that the larger compounds are more sorbed than leached. Consequently, the ability of these models in estimating the $K_oc$ values of pesticides is restricted to sorption of non-ionised chemicals on permanent charge soils, which were widely represented in the calibration sets as well as in validation sets. Moreover, a mechanistic interpretation of molecular descriptors for non-ionisable pesticides was provided a posteriori, after modelling, by interpretation of the final model in view of an association between the descriptors used and the soil sorption predicted.

6.3 Mechanistic approach: polyparameter linear free energy relationships

In the last decade, the concept of polyparameter linear free energy relationships (PP-LFERs) has been widely used for the prediction of sorption coefficients of neutral organic chemical, because of its important mechanistic basis and good
prediction power [49–53]. PP-LFERs are multiple linear regression (MLR) models that employ several solute- or sorbate-specific descriptors as independent variables and their fitting coefficients are denoted as they describe system-specific, solute-independent properties. In this sense, descriptors and their coefficients quantitatively describe the energetic contribution of different types of sorption coefficients [53, 54]. The major advantages of the PP-LFER approach are its solid mechanistic grounds and the use of uniformly measured calibration data.

In the last decade, different PP-LFER models for organic contaminants sorption on soil estimation have been proposed. Endo et al. [52] proposed two PP-LFER models at environmentally relevant concentrations. However, these models lack reliable PP-LFER descriptors for environmentally relevant chemicals (e.g. pesticides, pharmaceuticals and highly polar compounds, acids, bases, and ionic compounds). This deficiency also has been identified for PP-LFER models developed for high sorbate concentrations previously reported [55]. The PP-LFER models’ reviews up to now mainly have been calibrated estimating logKoc data of classical pollutants such as PCBs and PAHs and also of organic compounds that have chemical structure comparatively simple than chemicals of current environmental concern. These are often multifunctional or complex organic chemicals like pesticides and pharmaceuticals. The first reliable PP-LFER model for soil-water partitioning was calibrated with data from 79 polar and non-polar compounds that cover a more diverse and wider range of chemical classes than other PP-LFERs published. The model of Bronner and Goss [49] was validated using the experimental data for about 50 pesticides and pharmaceuticals not involved in the calibration set. This has potential to correctly estimate the Koc data for multifunctional or complex organic chemicals like pesticides and pharmaceuticals. However, Sabljic and Nakagawa [53] suggest still important drawbacks to the general applicability of the developed model. In view of the scope of this section, we recommend the review made by Sabljic and Nakagawa [53] around this topic.

On the other hand, little attention has been paid to the general applicability of the calibrated PP-LFERs for predicting sorption to soils considering the diversity of soil mineralogy, variable surface charge, OC structures and their interactions [51]. The evaluation of possible applications of PP-LFERs in the study of partitioning of ionic organic chemicals is a subject of ongoing research [56, 57].

6.4 Mechanistic approach: QSAR models for sorption of ionisable pesticides

In the last decade, different authors developed equations to predict the sorption of ionisable and non-ionisable compounds in soils or sediments [25, 58–61]. Several models have expanded their applicability domain including soil properties and ionisation effects [48, 58, 59]. Franco et al. carried out a surface acidity correction, because the two units proposed by Bintein and Devillers [59] are dependent on soil properties, related to the surface potential of the colloid [25]. These researches suggest a general non-linear equation based on LogKow for neutral and ionic species (a fragmentation of LogD) and the speciation of monovalent acids, monovalent bases and amphoteric species. Franco et al. aimed to predict pH-dependent Kd values of organic acids, considering speciation as a function of soil pH and species-specific partition equilibrium [60]. This modification of their previous models by replacing their constant terms pHopt by a varying pH range allowed that the modified model performs significantly better than the original model for organic acids [25]. The two molecular descriptors, pKa and logPn, and the two soil descriptors, OC and pH, used in the model have a major impact on the sorption of ionisable chemicals. Nevertheless, it was not successful to develop the analogous modified model for bases due to the contradictory effect of pH on the total sorption.
6.5 Physical/chemical properties of VADS: considerations for a mechanistic approach

In general, VADS are rich in OM, possess high specific surface area, variable surface charge and consequently pH-dependent CEC and AEC (anion-exchange capacity (AEC)). In this way, they have significant differences with regard to soils with mineralogy dominated by constant charge minerals [2]. These differences in the physicochemical properties make difficult the $K_c$ prediction for organic ionisable compounds using generic QSAR models or also published PP-LFER models. In this regard, the descriptors selection to a mechanistic interpretation of pesticide-VADS system must be related to the type of organic compound (e.g. non-ionisable, ionisable, acid, base, etc.) and to physicochemical properties of VADS.

According to physical/chemistry characteristics of VADS, in these soils, the pH is a critical parameter when ionisable pesticide-VADS interaction is considered, because the sign and magnitude of total VADS surface charge depends on $\text{pH}_{\text{equilibrium}}$. The total VADS surface charge is defined by the $\text{ZPC}_{\text{Soil}}$. The total VADS surface charge, at a given pH, could be negatively charged if $\text{pH}_{\text{equilibrium}} > \text{pH}_{\text{ZPC}}$ affecting the pesticide-VADS interaction (i.e. andisol and ultisols), which is particularly important for ionisable pesticides. The Fe/Al oxide content is an important variable for ionisable pesticide sorption on positively charged active sites at $\text{pH}_{\text{equilibrium}} < \text{pH}_{\text{ZPC}}$ and also in the remaining oxide sites that exhibit positive charge even at pH higher than ZPC [4, 17, 48]. Additionally, it is necessary to consider the relationship between these oxides and OM due to blockage of specific sorption sites, and between oxides and pH due to the presence of pH-dependent sorption sites and the speciation of ionisable pesticides [48, 62]. In this regard, Hyun et al. [63, 64] demonstrated that anion exchange in VCS is significant for pentachlorophenol and prosulfuron. Moreover, the extent of anion exchange correlated well to the ratio of pH-dependent AEC to CEC (i.e. AEC/CEC) as well as the ratio of AEC to the total number of soil surface charge (AEC + CEC) (i.e. AEC/(AEC + CEC)). Caceres-Jensen et al. [5] studied the effect of MSM sorption on total VADS surfaces observing a change in total VADS surfaces produced when the highest MSM concentration was sorbed. A displacement of IEP$_{\text{Soil}}$ to a higher pH was established for the soils. These results confirmed the contribution of charged surface sites on VADS to the sorption of anionic MSM through electrostatic interactions. Finally, soil composition, mineralogy (e.g. amorphous (hydro)oxides, Fe/Al oxide content), texture (e.g. silt, sand or clay content), surface area of colloids, OM, AEC and its relation with CEC (i.e. AEC/CEC, AEC + CEC, AEC/(AEC + CEC), ZPC$_{\text{Soil}}$ and $\text{pH}_{\text{equilibrium}}$ are potential modelling VADS descriptors; due to these descriptors, the $K_c$ magnitude is strongly influenced by physicochemical properties of VADS, sorption sites and specific surface area [2, 17, 19, 63].

According to the type of organic compound, special attention has been given to ionisable organic compounds. With changes in the pH, the speciation of soil active sites and of the ionisable pesticide also change, affecting the sorption. For ionisable pesticides, $\log D$ could be a good descriptor for the variation in hydrophobic interactions. Also, pesticide $pK_a$ values are possible descriptors that take into account dissociation in order to describe the interactions for pesticides on VADS considering the soil pH. This molecular property is determinant of hydrophilic interactions for polar compounds [17, 48].

7. Conclusions

The surface charge amphoteric characteristics will confer to VADS physical/chemical properties absolutely different to constant-charge soils, where soil
Sorption composition (i.e. SOM), mineralogy and variable charge are key components of most VADS, controlling soil sorption of INIH, representing an environmental substrate that may become polluted over time due to intensive agronomic uses. The pseudo-second-order model and TSNE have been the models that best describe the kinetics parameter and solute sorption mechanism, respectively, of INIH on VADS. These models are also necessary in order to develop and validate QSAR models to predict pesticide sorption on VADS to prevent potential contamination of water resources and predict environmental risks. In this regard, the last section of this chapter illustrates briefly some of the advances of QSAR models established for predicting the soils' sorption of pesticides with a focus on the mechanistic interpretation. In the generation of QSAR models, the statistical approach is the most used with a posteriori mechanistic interpretation, possibly due to complex sorption mechanisms of pesticides on soils. In the mechanistic approach (a priori mechanistic interpretation), few studies have paid attention to the diversity of soil mineralogy, texture, variable surface charge, OC structures and their implication on sorption of ionisable pesticides. Finally, the use of solute sorption mechanism models and QSAR models for pesticide sorption in soils will contribute to a better understanding of behaviour of pesticides 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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Sorption

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