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ABSTRACT

Specific pedoclimatic conditions in tropical environments have a considerable impact on pesticide fate. Tropical volcanic soils result from specific pedogenesis processes linked to successive volcanic projections; they are characterised by acidic conditions, high organic matter content, a specific mineralogical composition and the presence of organo-mineral complexes. The retention of pesticides in these soils is therefore often high but variable depending on the associated molecules and soil properties. Nevertheless, knowledge of pesticide sorption in these soils remains limited, and knowledge of the desorption process is scarce. The objectives of this work were to study the variability of the sorption and desorption coefficient of four pesticides currently used in banana and sugarcane crops on a set of representative tropical soils developed on volcanic ash (Guadeloupe, French West Indies). Adsorption and desorption isotherms were analysed for three ionizable pesticides (2,4-D, mesotrione, glyphosate) and a hydrophobic pesticide (difenoconazole) on ten soil samples from five soil profiles: one silandic andosol, one vitric andosol, two nitisols and one ferralsol. For ionizable pesticides, soil pH appears to be a first-order discriminating factor of the sorption capacity, and the organic carbon content appears to have a lesser impact on 2,4-D. For a strongly hydrophobic pesticides such as difenoconazole, the organic carbon content plays a major role in sorption. Desorption hysteresis has been observed regardless of the soils and the molecules considered, and tropical volcanic soils seem to be conducive to adsorption but show low to moderate release. The silandic andosol, which has the greatest sorption, buffers the dissemination of pesticides towards surface and groundwaters but also increases the risk of long-term contamination in the case of molecules that degrade slowly. Moreover, our results highlight that agronomic practices, such as liming, have a major impact on the sorption coefficient of pesticides and must be considered for when predicting sorption in a tropical volcanic context.

1. Introduction

In tropical contexts, intensive agricultural production systems are subject to high pest pressure because environmental conditions are favourable for the proliferation of insects, weeds and pathogens on crops (Lewis et al., 2016). As a result, the use of plant protection products remains an important means of control, but these products can contaminate nontarget environments, including soils and water (e.g., Cabidoche et al., 2009; Rawlins et al., 1998; Dusek et al., 2010; Charlier et al., 2009; Dores et al., 2016; Crabit et al., 2016). In a review of the current state of knowledge on pesticide fate in tropical conditions, Lewis et al. (2016) warned that it is difficult to extrapolate knowledge and results from well-documented temperate environments to tropical

environments because the processes involved in pesticide fate are highly dependent on pedoclimatic conditions.

Tropical volcanic islands such as the French West Indies are a relevant case studies in this respect. These islands are particularly affected by the risks of environmental contamination by pesticides due to their land use, which consists mainly of intensive crops such as banana and sugarcane, and due to intense rainfall that leads to pesticide leaching (Saison et al., 2008). Severe soil and water pollution issues are thus observed on these islands (e.g., Cabidoche et al., 2009; Crabit et al., 2016; Voltz et al., 2023). Moreover, soils of volcanic origin have specific physical and physicochemical characteristics, such as low bulk density, high organic matter content, high cation exchange capacity and high phosphate adsorption, which are rare in other types of soils (Shoji et al.,

1993). The sorption of pesticides on the soils of these tropical volcanic islands is still less well documented than that in temperate regions, although knowledge about sorption is an essential prerequisite for analysing the risks of contamination of various ecosystem compartments by pesticides.

Tropical volcanic soils result from pedogenesis closely linked to successive volcanic projections and are influenced by intense rainfall regimes. These soils are generally acidic in nature and have a high organic matter content and a mineralogical composition consisting of organo-mineral complexes and mineral compounds such as oxy-hydroxides of iron, aluminium and silica in amorphous or crystallised forms (Racke et al., 1997; Daam et al., 2019), the proportions of which vary according to the degree of weathering. Depending on pH, the sur-face charges of these soils can vary: at pH levels below the isoelectric point, soils develop positive surface sites and possess anion exchange capacity, and the opposite occurs at pH levels above the isoelectric point (Qafoku et al., 2004). Accordingly, it has been shown that pH is an important factor that is negatively correlated with the retention of pesticide molecules on these soils, especially ionic molecules, due to the influence of pH on the surface charges of both the molecules and mineral constituents (Cáceres-Jensen et al., 2009). In addition, the ionic strength of the soil solution also influences the distance over which surface charge has an impact; the greater the ionic strength is, the smaller the distance of influence. The retention of pesticides in these soils is there-fore often high but variable depending on their properties and on the composition of the volcanic soil (Cáceres-Jensen et al., 2009; Duwig et al., 2006; Fernández-Bayo et al., 2013). The allophane and organic carbon (OC) contents of volcanic soils are recognised as major factors that can increase the retention of molecules (e.g., Kogan et al., 2003; Rocha et al., 2006; Duwig et al., 2006; Fernández-Bayo et al., 2013). For ionic pesticides, which are prone to ionic exchange with charged sites at the soil surface, retention also depends on the electrolyte composition of the soil solution, which is influenced by management practices, namely fertilisation and soil amendment. Accordingly, some studies point to the possible effect, in these soils, of a decrease in the retention of ionic pesticides, such as 2,4-D, prosulfuron and glyphosate, due to competi-tion with phosphate for potential adsorption sites (e.g. Vasudevan and Cooper, 2004; Hyun and Lee, 2004; Kogan et al., 2003; Dotor-Robayo et al., 2022). However, to our knowledge, no model predicts the reten-tion properties of pesticide molecules in volcanic soils as a function of their composition. Moreover, only a few studies, limited to a small number of molecules and soils, have investigated both adsorption and desorption on volcanic soils. These studies report a marked hysteresis between adsorption and desorption (Cáceres-Jensen et al., 2009; Olvera-Velona et al., 2008; Fernández-Bayo et al., 2013; Dotor-Robayo et al., 2022), except for cadusafos, whose behaviour differs according to the soil properties (Fernández-Bayo et al., 2013).

In this context, the main objectives of this paper are to study the range and factors of variation of the adsorption and desorption co-efficients of four pesticides on the main volcanic soils of the island of Basse-Terre in Guadeloupe and to discriminate between the pesticide sorption properties of the different types of volcanic soils. The four studied pesticides, three ionizable pesticides (2,4-D, mesotrione, glyphosate) and a hydrophobic pesticide (difenoconazole), are commonly used in banana and sugarcane crops, which are the major crops in the French West Indies. The soils studied, namely andosols, nitisols and ferralsols, are derived from the same volcanic environment but differ greatly in their mineralogical compositions, due to differences in the age of the volcanic material from which they formed and in the weathering intensity. Our hypothesis is that the pedological variability present in tropical volcanic soils, indicated by variations in pH, OC content and mineralogical composition, may be involved in the signifi-cant variation in the sorption coefficients of the studied molecules in relation to their physicochemical properties.

2. Materials and methods

2.1. Soils, sampling and analysis of soil properties

Soils were sampled from five sites located on the island of Basse-Terre (16°N, 61°W), which were the subject of an experimental study on the fate of pesticides in banana and sugarcane field plots (Ponchant et al., 2020). These sites were selected from a 1:20000 soil map of Guadeloupe (Colmet Daage, 1969) to sample the main soil types developed from the volcanic ash found on Caribbean volcanic islands (Colmet-Daage and Lagache, 1965). According to the Colmet Daage (1969) soil map, the five sites correspond to, according to the local soil classification in force at the time of the map's establishment, an andosol, an andic brown soil, a rusty brown soil with halloysite and a ferralitic soil, of which the first two are classified in the FAO soil classification (WRB, 2014) as andosols and the next two as nitisol and ferralsol. These soil types are differentiated according to the age of the volcanic deposits from which they originated. For the recent deposits near the Soufrière volcano in Basse-Terre, the soils are organised on the slopes according to a climatosequence ranging from andosol to nitisol, with the following mineralogical transformations: ash → gibbsite, allophane → halloysite (Colmet-Daage and Lagache, 1965; Ndayiragije, 1996; Ndayiragije and Delvaux, 2003). The rainfall gradient, with average annual rainfall exceeding 5000 mm at an altitude of 500 m and approximately 2500 mm at sea level, is the origin of this progressive sequence of mineralogical alteration. The highest rainfall at the top of the slope allows significant leaching of silica and bases, leading to the formation of amorphous oxyhydroxides and organomineral complexes (Mizota and Van Reeu-wijk, 1989; Chadwick et al., 2003; Henriet et al., 2008), while the lower rainfall at the bottom of the slope allows for the maintenance of silica availability, which favours the formation of 1:1 clay minerals such as halloysite (Parfitt et al., 1983; Dahlgren et al., 2004). Ferralsols formed in the older deposits located north of the Soufrière volcano. Theses soils underwent more marked alteration than the soils in the previous cli-matosequence, resulting in the formation of iron hydroxides or halloy-site (Colmet-Daage and Lagache, 1965; Dupuits-Bonin et al., 2015). The location of each site is shown in Table 1. The first four sites, As, Av, N_M and N_P, are part of the andosol to nitisol climatosequence, while the fifth site annotated F represents ferralsols developed on ancient deposits.

For the characterisation of the physicochemical properties of the five soils, soil at two depths (H1 = 0–10 cm and H2 = 20–30 cm) was sampled at each site and analysed at the CIRAD soil analysis laboratory (Montpellier, France), which is ISO 9001 certified for the performance of soil physicochemical analyses. The samples were prepared according to NF ISO 11464 (X31–412), which includes air-drying and 2 mm sieving. For the two andosol sites, As and Av, the samples were preserved and analysed at their initial moisture state to avoid any irreversible modi-fication of certain soil properties, notably texture, due to drying (Baize and Girard, 2008). The properties measured were i) pH H_2O and pH KCl in a volume ratio of 1/5 and with a KCl concentration of 1 mol.L^{-1} (NF ISO 10390: 2005); ii) the granulometry of 5 fractions by sedimentation (AFNOR NF X 31–107), where for the granulometric determination of andosols, the dispersion of mineral colloids is known to be difficult due to strong organomineral bonds which require a specific post treatment process to dissolve amorphous iron, aluminium and silica oxyhydroxides with ammonium oxalate at pH = 3 according to the recommendations of Baize (2018); iii) the organic matter and nitrogen contents after dry combustion (NF ISO 10694 and NF ISO 13878); iv) cations exchangeable with ammonium acetate at pH = 7 (Ca^{2+}, Mg^{2+}, K^+ and Na^+); and v) exchangeable cation capacity (CEC) according to the Metson method and calculation of the saturation rate (TS). Mineralogical complexes were evaluated by selective dissolution of Al, Fe and Si compounds (Parfitt and Wilson, 1985; Blakemore et al., 1987). The organomineral complexes were quantified after extraction with a sodium pyrophos-phate solution; the forms of iron oxyhydroxides, aluminium oxy-hydroxides and amorphous silica were quantified after extraction with

Table 1
Soil properties.

Soil	Location WGS84 UTM zone 20 N - EPSG32620	Average altitude m	Soil horizon	pH H$_2$O	pH KCl %	Sand %	Silt %	Clay %	Organic carbon %	CEC mequiv/100 g	Ca^{2+} mequiv/100 g	Saturation rate %	Alox* %	Feox* %	Siox* %	Alp* %	Fep* %	FeCBD* %	Allophane** %
Silandic Andosol (As)	Concession 16.059771; -61.609136	281	AsH1	5.9	5.4	35.2	34.3	30.4	6.50	44.5	11.58	37.5	7.94	4.01	2.86	0.98	0.81	3.8	20.3
			AsH2	6.4	5.9	24.4	35.4	40.3	5.62	48.5	11.20	28.0	10.43	6.67	3.76	0.99	0.95	5.2	26.7
Vitric Andosol (Av)	Bomba 16.06133; -61.590132	170	AvH1	7.5	7.0	9.1	17.2	73.7	3.54	30.2	20.61	91.1	1.01	1.15	0.14	0.24	0.50	6.8	1
			AvH2	5.1	4.2	8.8	15	76.2	2.13	28.1	4.45	27.0	0.70	0.48	0.039	0.29	0.54	7.5	< 1
Nitisol (N_M and N_P)	Morne d'Or 16.058650; -61.581710	82	N_MH1	4.6	4.1	10.6	21.9	67.5	1.51	16.3	1.97	23.0	0.54	0.93	0.029	0.27	0.48	5.9	< 1
			N_MH2	4.8	4.1	9.6	24.4	66.1	1.02	13.7	1.72	19.9	0.58	0.93	0.05	0.20	0.34	6.7	< 1
	Cassaverie 16.0308; -61.3414	48	N_PH1	6.3	5.7	24.7	30.4	46.6	2.66	28.7	16.79	76.1	0.57	0.54	0.14	0.12	0.060	3.99	1.0
			N_PH2	5.3	4.3	13.2	24.8	50.5	1.46	23.6	4.22	26.6	0.71	0.44	0.16	0.16	0.047	4.05	1.2
Ferralsol (F)	Fenneteau 16.1856161; -61.6257848	145	FH1	5.3	4.8	12.7	38.2	49.1	2.95	20.8	4.04	35.5	0.70	1.04	0.070	0.28	0.72	5.8	< 1
			FH2	5.4	4.8	11.8	41.1	47.1	2.39	17.4	2.91	30.6	0.69	0.57	0.039	0.21	0.50	7.6	< 1

* ox for ammonium oxalate extraction for amorphous forms, p for sodium pyrophosphate extraction for organo-mineral complexes, CBD for Dithionite-Citrate-Bicarbonate extraction for crystallised forms of iron oxyhydroxide.

** The allophane content is estimated by the formula proposed by Parfitt and Wilson (1985): allophane = 7.1 x Siox, where Siox is the Si content after extraction with oxalate. The relationships Alp/Alox et Alox + ½ Feox are used as an indicator for the classification of andosols reflecting a degree of alteration of volcanic glasses according to a more or less marked character in allophane or organo-aluminium complex (Shoji et al., 1993).

an ammonium oxalate solution (Tamm's method); and finally, the crystallised forms of iron oxyhydroxides were analysed by extraction with citrate-bicarbonate-dithionite (Mehra-Jackson method).

The main characteristics of the soil horizons are presented in Table 1 and were used to refine their FAO classification. Two of the five sites have horizons characteristic of andosols; the highest site is similar to a silandic andosol (As), and the lower site is similar to a less developed vitric andosol (Av). Two sites have nitisol properties, with three dystric horizons (N_MH1, N_MH2 and N_PH2) characterised by an S/T ratio of <50% and one eutric horizon (N_PH1), with an S/T ratio of >50%, where S represents the sum of exchangeable cations and T represents the CEC. Finally, the two horizons FH1 and FH2 are characteristic of a ferralsol profile.
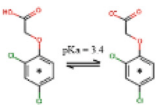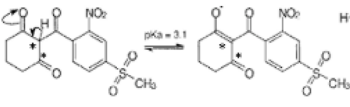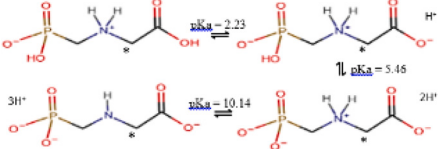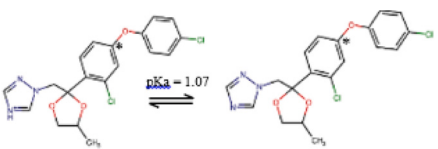
2.2. Pesticides

The main properties of the molecules are listed in Table 2. 2,4-D and mesotrione are weak acids; they are present mainly in the anionic form in the pH range of the studied soils and have high solubility. According to their pKa values and the pH of each studied soil, the percentages of the neutral forms of 2,4-D and mesotrione were estimated to range from 0 to 6% and 0 to 3%, respectively, across the soils. Notably, the hydrophobicity of 2,4-D, represented by log Kow, evolves over the pH range of the soils studied: under acidic conditions, 2,4-D is slightly hydrophobic (log Kow > 0), and it progressively becomes hydrophilic as the pH increases. Mesotrione is slightly hydrophobic over the whole pH range of the studied soils. Glyphosate is a very hydrophilic zwitterion, which results in very high aqueous solubility. Notably, its negative charge increases with pH across the pH range of the soils studied. Difenoconazole is classified as a hydrophobic compound (log Kow > 3) with low solubility in water. Given that the pKa of difenoconazole is close to 1, we concluded that this molecule is present only in its neutral form over the pH range of the soils.

All experiments were conducted with a mixture of unlabelled and C^{14}-labelled molecules. The unlabelled molecules were obtained from Sigma-Aldrich (France). Labelled mesotrione, [1,3-cyclohexanedione-2-14C] (with a specific activity of 1691 MBq.mmol^{-1} and a radiopurity of 97%) and 2,4-D, [RING-U-14C] (with a specific activity 1136 MBq. mmol^{-1} and a radiopurity 98%) were supplied by the Institute of Isotopes Co., Ltd. (H-1121 Budapest), and glyphosate, [glycine-2-14C] (with a specific activity of 1850 MBq.mmol^{-1} and a radiopurity 98%) and difenoconazole, [4-chlorophenyl ring-14C(U)] (with a specific activity of 2390.2 MBq.mmol^{-1} and a radiopurity 97%) were supplied by the company Isobio (Belgium).

2.3. Measurement of the sorption coefficients

Sorption isotherms were obtained by batch experiments and were designed following the OECD guidelines n°106 (OECD, 2000). Pesticide solutions were prepared in a 0.01 M CaCl$_2$ solution and 200 mg.L^{-1} NaN$_3$ as a biocidal agent, except for glyphosate for which only a NaN$_3$ solution was used to avoid an artificial increase in sorption as a result of cationic bridging in the presence of CaCl$_2$ as proposed by previous studies (e.g., De Jonge and de Jonge, 1999; De Jonge et al., 2001; Mamy and Barriuso, 2007; Dollinger et al., 2015). Adsorption isotherms were determined for 5 concentrations: 5, 50, 200, 500 and 1000 µg.L^{-1} for 2,4-D, mesotrione and difenoconazole and 5, 10, 50, 100 and 1000 µg. L^{-1} for glyphosate. The solid/liquid ratio was 2:10 (g/mL) for 2,4-D, mesotrione and difenoconazole, and 1:10 (g/mL) for glyphosate. To maintain moisture conditions close to the in situ conditions, the soil samples were initially stabilised at pF2 by equilibration on pressure plates. The soils were then maintained for 24 h at 20 ± 2 °C in contact with the pesticide solutions in glass tubes and mechanically shaken at 150 rpm. Subsequently, the tubes were centrifuged for 10 min at 3000 rpm (centrifuge 3-16PK Sigma, Osterode an Harz, Germany) to separate the soil from the supernatant. Blank tubes containing the background

Table 2
Physicochemical properties of the molecules studied.

Pesticide	Dominant molecular formulas in the soil pH range	Molecular weight (g. mol^{-1})[a]	Water solubility at 20 °C (mg. L^{-1})[a]	Log Kow	pKa[a]	Vapour pressure at 20 °C (mPa)[a]	Laboratory DT50 at 20 °C (j)[c]
2,4-D		221.04	3390 at pH 4–24,300 at pH 7	0.81 at pH 4.5[b] −0.8 at pH 6.5[b]	3.4	0.009	4.4
Mesotrione		339. 32	2200 at pH 5	1.09 at pH 4.5[b] 0.98 at pH 6.5[b]	3.12	5. 70*10^{-3}	19.6
Glyphosate		169.07	10,500 at pH 2	−3.2 from pH 5 to 9[a]	2.23 5.46 10. 14	0.0131	16.11
Difenoconazole		406.26	15 at pH 7	4.36 from pH 4.5 to 6.5[a]	1.07	3.33*10^{-5}	130

*C^{14} radiolabelled.

[a] Values from the ANSES Agritox database, updated on 21/11/2022.

[b] Values calculated by Chemicalize.

[c] Values from PPDB (Pesticides Properties DataBase, University of Hertfordshire).

solution and pesticide without soil, were included to check that the sorption of each compound onto the glassware could be neglected. For each pesticide, adsorption isotherms were obtained in triplicate for each soil-concentration pair. After centrifugation, 1 mL of the supernatant was removed with a micropipette and added to 4 mL of scintillation liquid to measure the amount of radiolabelled pesticide in the supernatant after adsorption; thus, the concentration of pesticide in the solution at equilibrium was determined: C_e (μg.L^{-1}). Radioactivity was measured in duplicate by liquid scintillation counting using a Tri-Carb 2800TR liquid scintillation counter with Ultima Gold as scintillation liquid (PerkinElmer, Waltham, USA). The amount of pesticide adsorbed on the solid matrix, C_s (μg.kg^{-1} of soil dried at 105 °C), was calculated from the difference in concentration between the initial concentration of pesticide in solution, C_0, and C_e:

$$C_s = \frac{(C_0 - C_e)V}{m_s} \tag{1}$$

where V is the volume of solution in the tube, corresponding to the sum of the volume of aqueous solution of radiolabelled pesticide added and the volume of water initially contained in the soil, and m_s is the mass of dry soil in the adsorption tube.

The sorption isotherms were fitted by a linear equation:

$$C_s = K_d C_e \tag{2}$$

and the Freundlich equation:

$$C_s = K_f C_e^{n_{ads}} \tag{3}$$

where K_d is the sorption coefficient (L.kg^{-1}), K_f the empirical Freundlich sorption coefficient (g$^{(1-n)}$.kg^{-1}.L^n) and n_{ads} is the Freundlich exponent of the adsorption isotherm.

Following the adsorption phase at 1000 μg. L^{-1}, five-step desorption was performed. For each tube, the supernatant was removed (approximately 8 mL) and replaced with 8 mL of a solution containing 0.01 M

CaCl$_2$ and 200 mg. L^{-1} NaN$_3$ for 2,4-D, mesotrione and difenoconazole and 8 mL of NaN$_3$ solution for glyphosate. The tubes were then mechanically shaken at 150 rpm for 24 h at room temperature (20 ± 2 °C). Finally, the tubes were centrifuged for 10 min at 3000 rpm and the concentration of pesticide in the solution was determined as described above. This desorption procedure was repeated five times in succession. The desorption isotherms were described by the Freundlich equation:

$$C_s = K_{f,des} C_e^{n_{des}} \tag{4}$$

where $K_{f,des}$ is the empirical Freundlich desorption coefficient (g$^{(1-n)}$. kg^{-1}.L^n) and n_{des} is the Freundlich exponent of the desorption isotherm.

The hysteresis index, H, was calculated using the following equation as suggested by Barriuso et al. (1994), and later taken up in the literature (e.g, Mamy and Barriuso, 2007; Cáceres-Jensen et al., 2009; Fernández-Bayo et al., 2013; Mendes et al., 2016; Cáceres-Jensen et al., 2021):

$$H = \frac{n_{des}}{n_{ads}} \tag{5}$$

where n_{des} and n_{ads} are the exponents of the Freundlich equation for the desorption and adsorption isotherms, respectively. As H decreases, the hysteresis between adsorption and desorption increases, indicating lower desorption. Hysteresis is generally considered significant when H < 0.7 (Barriuso et al., 1994).

2.4. Data analysis

The Freundlich equation (Eqs. (3) and (4)) is linearized by applying the decimal logarithm, and adjustment of Kf and n was then obtained by linear regression. Linear regression for adjustment of sorption coefficient Kd or Kf and n, confidence interval using the Student's t distribution and PCA analysis on soil and sorption properties were conducted using Xlstat (version 4.1.0). Pearson correlations between sorption coefficients and soil properties and associated *p* values were calculated using the Cor function in R software (version 3.6.0). A stepwise multiple

linear regression with backward elimination was performed with the lm function in R software (version 3.6.0.) to identify the set of soil properties that significantly influence the sorption coefficients. Backward elimination was performed by iteratively suppressing the predictors whose *t*-test p value was >5%.

3. Results

3.1. Soil properties

Table 1 shows the soil properties measured for the soil samples. For all sites and horizons studied, the OC contents are high but decrease from the topsoil to the subsoil. The silandic andosol site at the top of the slope (As) has the highest OC content, above 5.5% for both of its horizons. The other soils had OC contents between 3.5% and 1.5% in the topsoil horizons and between 2.4% and 1% in the subsoil horizons. The contents of organo-mineral complexes containing iron and aluminium as well as the amorphous forms of iron, aluminium and silica oxyhydroxides are systematically greater in the As profile than in the other soil profiles. Conversely, the crystallised form of iron oxyhydroxide is less abundant in the As profile than in the other soil profiles. Therefore, as expected, the As profile presents both partial crystallisation of oxyhydroxides and a large quantity of organic matter, which is related to the fact that amorphous mineral forms such as allophanes are known to have a protective effect on organic matter by promoting its stabilisation and accumulation (Shoji et al., 1993). The allophane, amorphous

oxyhydroxide and OC contents in the vitric andosol (Av) soils are much lower than those in the silandic andosol soils and are similar to those in the other soils.

The soil profiles studied are predominantly acidic, with a pH H_2O between 4.6 and 6.4, and there are small differences between the topsoil and the subsoil. However, the pH values of the vitric andosol Av and the nitisol N_P are one to two units greater in their surface horizons than in their deep horizons; this can be explained by the liming that took place sometime before the samples were collected. For the two horizons affected by liming, one consequence is also to significantly increase the content of exchangeable cations, particularly Ca^{2+}. For all soils, the difference between the pH KCl and the pH H_2O is consistently negative, indicating potential soil acidity through a reserve of hydronium cations stored in the CEC. The correlations among the soil variables (MS Table S1) show that the OC content is correlated with many of the other soil parameters, especially CEC and the different forms of aluminium, iron and silica. The presence of the two As profile horizons partly determines these correlations due to their high OC content and mineralogical specificities. The relationship between the OC content and pH (see MS Fig. S1) is, however, not statistically significant if all soils are considered but becomes significant only if either the two silandic andosol horizons or the two limed horizons are excluded (without As: $r = 0.807$ and p value = 0.015; without the limed horizons: $r = 0.872$ and p value = 0.005). When interpreting the correlations between the sorption coefficients of molecules and soil properties, possible confounding effects due to the correlations between soil properties must be

Table 3
Sorption coefficients.

MA	Soil	Kf $g^{(1-n)}.kg^{-1}.L^n$	n ads	R^2	Kd $L.kg^{-1}$	R^2	% adsorbed	Kf, des $g^{(1-n)}.kg^{-1}.L^n$	n des	R^2	H	% desorbed
2,4-D	AsH1	8.7	0.95	1.00	6.8	1.00	51	499	0.31	0.94	0.33	49
	AsH2	7.0	1.00	1.00	7.1	1.00	51	863	0.23	0.90	0.23	37
	AvH1	1.9	0.96	1.00	1.5	1.00	17	388	0.15	0.90	0.16	52
	AvH2	3.9	0.98	1.00	3.3	1.00	33	229	0.34	0.99	0.35	35
	N_MH1	5.1	0.93	1.00	3.3	1.00	35	168	0.38	0.99	0.41	70
	N_MH2	5.0	0.94	1.00	3.5	1.00	35	185	0.38	0.99	0.40	68
	N_PH1	3.5	0.95	1.00	2.5	1.00	29	274	0.28	1.00	0.29	61
	N_PH2	7.5	0.90	1.00	4.2	1.00	43	209	0.39	0.98	0.43	63
	FH1	5.7	0.94	1.00	3.8	1.00	37	290	0.33	0.98	0.35	62
	FH2	6.6	0.94	1.00	4.6	1.00	43	221	0.38	0.99	0.41	64
Mesotrione	AsH1	8.5	1.00	1.00	8.2	1.00	60	834	0.23	0.97	0.23	39
	AsH2	8.6	1.00	1.00	8.5	1.00	55	1112	0.20	0.99	0.20	37
	AvH1	2.0	0.98	1.00	1.7	1.00	23	578	0.10	0.88	0.10	39
	AvH2	12.3	1.00	1.00	12.3	1.00	71	395	0.38	0.96	0.38	47
	N_MH1	18.0	1.00	1.00	17.1	1.00	78	369	0.43	0.86	0.43	42
	N_MH2	21.5	1.00	1.00	21.0	1.00	81	382	0.44	0.88	0.44	40
	N_PH1	2.7	0.97	1.00	2.1	1.00	30	435	0.18	0.96	0.18	49
	N_PH2	13.2	0.98	1.00	11.5	1.00	72	461	0.34	0.87	0.35	44
	FH1	9.8	0.97	1.00	7.3	1.00	56	481	0.31	0.97	0.32	51
	FH2	12.9	1.02	1.00	14.2	1.00	73	355	0.42	0.96	0.41	48
Glyphosate	AsH1	11.3	1.01	1.00	12.4	1.00	56	1351	0.22	0.97	0.22	46
	AsH2	13.1	1.01	1.00	14.2	1.00	58	1750	0.20	0.98	0.20	41
	AvH1	21.1	1.02	1.00	25.7	1.00	73	4620	0.07	0.94	0.07	19
	AvH2	9.0	1.01	1.00	9.7	1.00	49	1505	0.18	0.96	0.18	45
	N_MH1	7.9	1.01	1.00	8.6	1.00	47	1397	0.18	0.98	0.18	46
	N_MH2	9.4	1.00	1.00	9.8	1.00	51	1321	0.20	0.97	0.20	47
	N_PH1	11.7	1.02	1.00	12.5	1.00	58	1714	0.16	0.81	0.16	44
	N_PH2	11.5	1.01	1.00	12.0	1.00	56	1000	0.27	0.99	0.27	50
	FH1	8.7	1.02	1.00	10.4	1.00	50	1081	0.25	0.98	0.24	52
	FH2	8.8	1.00	1.00	8.6	1.00	46	1350	0.19	0.97	0.19	46
Difenoconazole	AsH1	211.7	1.01	1.00	228.5	1.00	98	3946	0.06	0.96	0.05	4
	AsH2	187.0	0.97	1.00	178.9	1.00	97	4673	0.07	0.89	0.08	5
	AvH1	97.9	1.01	1.00	99.4	0.99	97	2511	0.06	0.97	0.06	6
	AvH2	51.3	0.96	1.00	43.9	0.99	92	1954	0.12	0.98	0.12	12
	N_MH1	49.4	0.97	1.00	43.0	0.99	93	2054	0.09	0.94	0.10	10
	N_MH2	21.4	0.93	0.99	14.4	0.97	80	935	0.20	1.00	0.22	26
	N_PH1	105.0	1.04	1.00	113.9	1.00	97	3324	0.02	0.99	0.02	3
	N_PH2	75.5	0.96	0.99	57.2	0.97	94	2573	0.08	1.00	0.08	9
	FH1	103.4	0.99	1.00	100.1	1.00	96	3065	0.03	0.87	0.04	4
	FH2	61.4	0.98	1.00	57.3	0.99	94	2181	0.10	0.95	0.10	9

considered.

3.2. Adsorption and desorption isotherms

3.2.1. Adsorption

The linear and Freundlich models show equivalent performance in predicting the adsorption coefficients of the four molecules on the different soils (Table 3, MS Fig. S2). Indeed, the Freundlich exponent n_{ads} is either not statistically significantly different from 1 or only slightly different from 1 (MS Table S2). Thus, for simplicity, only the

variability of the Kd coefficients is analysed below. The Kd values cover a wide range of variation, from 1.5 to 230 L.kg^{-1}, and are ordered according to the molecules as follows: 2,4-D < mesotrione - glyphosate < difenoconazole. 2,4-D exhibited the lowest adsorption, with Kd values between 1.5 and 7.1 L.kg^{-1}, and presented moderate variation according to the different soil horizons. Glyphosate and mesotrione also show moderate variation with similar orders of magnitude but higher adsorption coefficients than 2,4-D, ranging from 1.7 to 21 L.kg^{-1} and from 8.6 to 25.7 L.kg^{-1} respectively. Difenoconazole exhibited the highest and most variable adsorption coefficients, ranging from 14.4 to
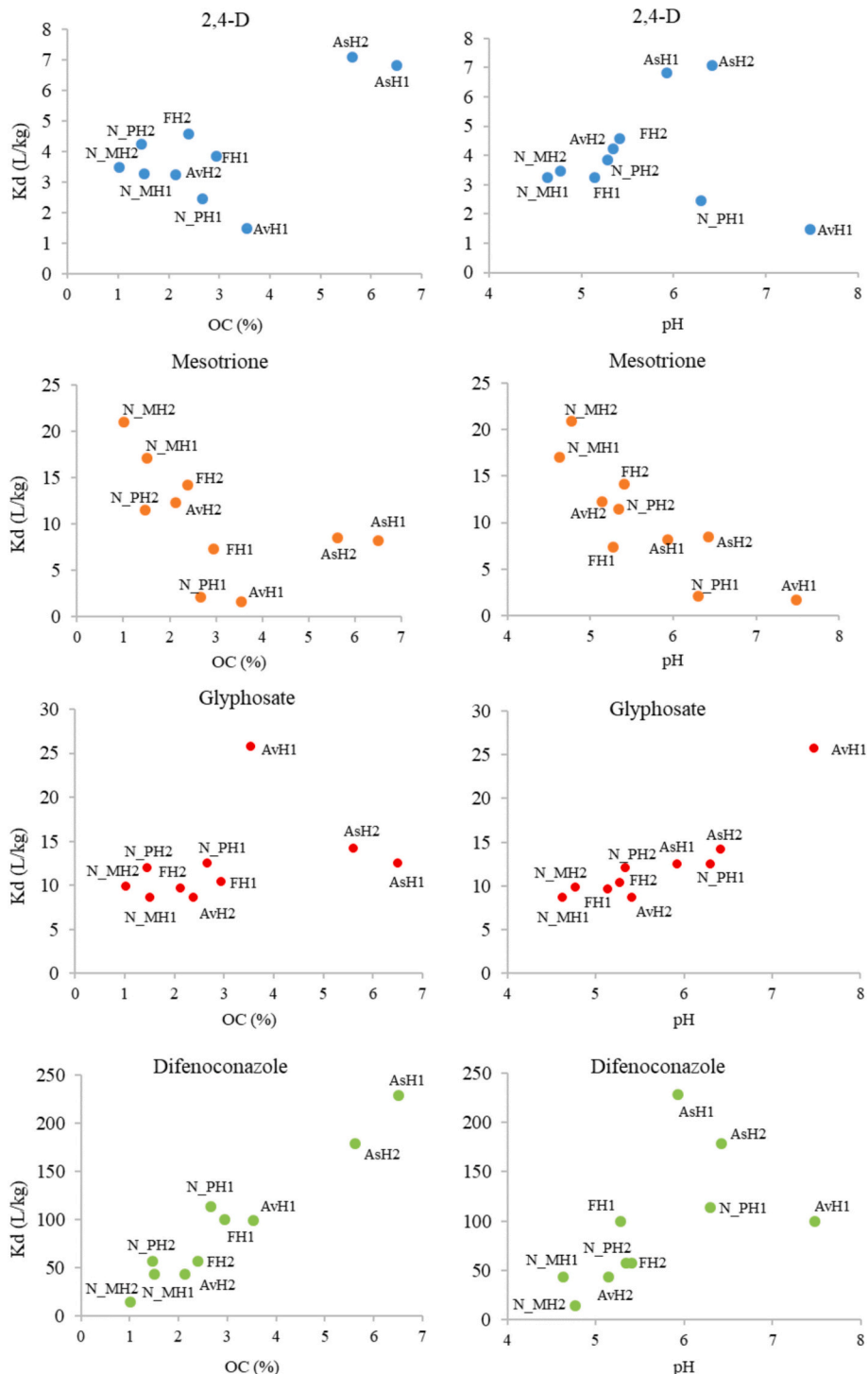

Fig. 1. Sorption coefficients as a function of pH and soil organic carbon content.

228.5 L.kg^{-1}. The amounts of pesticides adsorbed after 24 h, characterised by the percentage adsorbed (Table 3), evidently follow the same classification between molecules but vary largely between soils: 2,4-D exhibits the lowest percentages adsorbed (from 17% to 51% with a mean of 37.4%), followed by glyphosate (from 46% to 73%, with a mean of 54.4%) and mesotrione (from 23% to 81%, with a mean of 59.9%), whereas difenoconazole exhibits the largest percentages (from 80 to 98% with a mean of 93.8%).

Fig. 1 present the observed adsorption coefficient (Kd) for each molecule as a function of the soil OC content and pH, which are usually considered major factors influencing sorption in the literature. In addition, principal component analysis (PCA) provides an easy visualization of the entire dataset and allows for the identification of three distinct groups: soils with high organic matter and allophane content (As), limed soil horizons (N-PH1 and AvH1), and the remaining samples (MS Fig. S3). The correlations between the adsorption coefficients and soil properties are summarised in MS Table S3. This complementary approach enhances the overall interpretation of the data structure and relationships among soil properties. For 2,4-D, the apparent relationship between Kd and OC content or pH changes drastically depending on whether the silandic andosol is considered or not. When considering all soils, the correlation between the adsorption coefficients Kd and the OC content was significant and positive ($r = 0.67$ and p-value $= 0.033$), whereas the correlation between Kd and soil pH was not significant ($r = -0.09$ and p-value $= 0.813$). In contrast, without the two As horizons, the correlation between Kd and pH became significant and negative ($r = -0.75$ and p value $= 0.033$), whereas the correlation with OC content became negative but no longer significant ($r = -0.53$ and p value $= 0.177$). Moreover, stepwise multiple regression revealed that both OC content and pH were significant predictors when all soils were considered, but only pH was a predictor when the two As horizons were not considered (Table 4). Thus, for non allophanic soils, 2,4-D adsorption decreases when the pH increases. This result was expected given the increase in negative surface charges with pH, both on the soil particle surfaces and on the molecule. However, when including allophanic silandic andosol, the correlation with pH is blurred, and the positive influence of the high OC content of this soil needs to be considered.

For mesotrione, which is also an ionizable molecule, the correlation patterns are more stable regardless of whether the presence of a silandic andosol is considered. For all soils, the adsorption coefficient Kd exhibited a significant negative correlation only with pH (pH: $r = -0.84$ and p value $= 0.002$, OC: $r = -0.51$ and p value $= 0.129$), which was confirmed by the stepwise multiple regression that retained only pH as a predictor (Table 4) and by the PCA (MS Fig. 3). When the silandic andosol were excluded, negative correlations of Kd with both pH and OC were observed (pH: $r = -0.85$ and p value $= 0.007$; OC: $r = -0.87$ and p value $= 0.005$). The negative correlation observed with OC is surprising since adsorption is expected to increase with OC content for molecules exhibiting some hydrophobicity. This result can be explained by the positive correlation between pH and OC within the soil samples (Fig. S1 in MS). Indeed, the linear regression analysis confirmed the redundancy of pH and OC as predictors of mesotrione adsorption since none of them were significant when they were both included as predictors in the multiple regression, and each of them led to similar prediction performance when included as a single predictor (Table 4). Therefore, similar to 2,4-D, soil pH appears to be the main factor affecting the variation in adsorption, but unlike to 2,4-D, the soil pH of the silandic andosol does not differ from the other soils.

With respect to glyphosate, contrary to the previously studied molecules, an increase in the adsorption coefficient with pH and, to a lesser extent, with OC is observed for all soils. In this case, only the AvH1 horizon differed somewhat from the trend observed for the other horizons by exhibiting a high adsorption coefficient in association with a neutral pH. For all soils together, the correlation was significant for pH ($r = 0.90$ and p value <0.001) and not significant for OC ($r = 0.35$ and p value $= 0.329$). If the AvH1 horizon is excluded, the correlation with OC becomes significant ($r = 0.67$ and p value $= 0.05$). The stepwise multiple regression, conducted with and without AvH1, indicates, however, that pH is the only significant predictor retained, suggesting that any correlation with OC is again related to the underlying correlation between pH and OC (Table 4).

For difenoconazole, there was a very clear and strong positive linear correlation between the adsorption coefficient Kd and the OC content, whereas the correlation of Kd with pH was not significant (OC: $r = 0.97$ and p value <0.0001; pH: $r = 0.55$ and p value $= 0.10$). Moreover, in contrast to the previously investigated molecules, no obvious outliers were identified. Given the electrically neutral form and hydrophobic nature of difenoconazole over the pH range of the studied soils, it was expected that the preferential adsorption factor would be organic matter (Kah and Brown, 2006). This hypothesis is supported by the stepwise multiple regression, which identified only OC as a significant predictor of the difenoconazole adsorption coefficient (Table 4).

3.2.2. Desorption

All desorption isotherms are described by the Freundlich equation with coefficients of determination $R^2 \geq 0.81$ (Table 3, MS Fig. S2). Regardless of the molecule or soil considered, the desorption isotherm at 24 h showed a shift with respect to the adsorption isotherm at 24 h, which was reflected by a H value markedly lower than 0.7 and desorption coefficients one to three orders of magnitude greater than the adsorption coefficients.

The values of the desorption coefficients and the intensity of the hysteresis of the molecules rank similarly and follow the order of the adsorption coefficients: 2,4-D and mesotrione < glyphosate <

Table 4
Multiple linear regression for adsorption prediction.

Pesticide		Estimation of the sorption coefficient by linear regression	Adjusted R^2	p-value	RMSEP
2,4-D	All soils	Kd = 8.85–1.40 pH* + 1.05 OC**	0.71	0.0057	0.22 (6.6%)[a]
	Without As	Kd = 7.67–0.78 pH*	0.47	0.0355	0.20 (5.9%)
Mesotrione	All soils	Kd = 44.28–5.98 pH**	0.68	0.0020	0.98 (9.4%)[b]
	Without As	Kd = 26.33–7.00 OC**	0.71	0.0055	1.14 (10.4%)[b]
		Kd = 45.89–6.32 pH**	0.69	0.0066	1.17 (10.74%)[b']
Glyphosate	All soils	Kd = −16.84 + 5.16 pH***	0.80	0.000513	0.68 (5.5%)[c]
	Without AvH1	Kd = −2.453 + 2.384 pH* + 0.112 OC	0.63	0.0207	0.32 (2.9%)[c']
Difenoconazole	All soils	Kd = −13.10 + 35.85 OC***	0.93	< 0.0001	4.94 (5.3%)[d]

*p-value <0.05; ** p-value <0.01; ***p-value <0.001.

[a] RMSEP expressed as a percentage of the average value of Kd (4.04 L.kg^{-1}).

[b] RMSEP expressed as a percentage of the average value of Kd (10.37 L.kg^{-1}).

[b'] RMSEP expressed as a percentage of the average value of Kd (10.88 L.kg^{-1}).

[c] RMSEP expressed as a percentage of the average value of Kd (12.39 L.kg^{-1}).

[c'] RMSEP expressed as a percentage of the average value of Kd (10.91 L.kg^{-1}).

[d] RMSEP expressed as a percentage of the average value of Kd (93.66 L.kg^{-1}).

difenoconazole. That is, the molecules with the highest adsorption co-efficients are also those with the highest desorption coefficients. 2,4-D and mesotrione show the most moderate hysteresis, with similar H values between 0.16 and 0.43 and between 0.1 and 0.44, respectively, and with Freundlich desorption coefficient values between 160 and 1200 $g^{(1-n)}.kg^{-1}.L^n$ (Table 3). Glyphosate exhibits greater hysteresis, with H values between 0.07 and 0.27, and higher Freundlich desorption coefficients between 1000 and 4600 $g^{(1-n)}.kg^{-1}. L^n$. Finally, difenoconazole, similar to glyphosate, has high desorption coefficients between 950 and 4600 $g^{(1-n)}.kg^{-1}. L^n$ and the most marked hysteresis with the lowest H values were mostly between 0.02 and 0.12, except for the N_MH2 site at 0.22. Thus, the percentages of pesticides desorbed after

the 5 desorptions rank inversely to the percentage adsorbed: difenoconazole has the lowest average percentage desorbed (from 3% to 26% with a mean of 8.8%), followed by glyphosate (from 19% to 52%, with a mean of 43.6%) and mesotrione (from 39% to 51%, with a mean of 43.6%), and finally 2,4-D (from 35% to 70%, with a mean of 56.1%).

For each of the four molecules, Fig. 2 shows the evolution of H as a function of the OC content and soil pH. The correlations between H and the soil properties are summarised in MS Table S3. For 2,4-D and mesotrione, there was a clear negative linear correlation between H and pH with very high significance (2,4-D: $r = -0.92$ and p value = 0.0002; mesotrione: $r = -0.95$ and p value <0.0001). No significant correlation was detected between H and the OC content (2,4-D: $r = -0.58$ and p
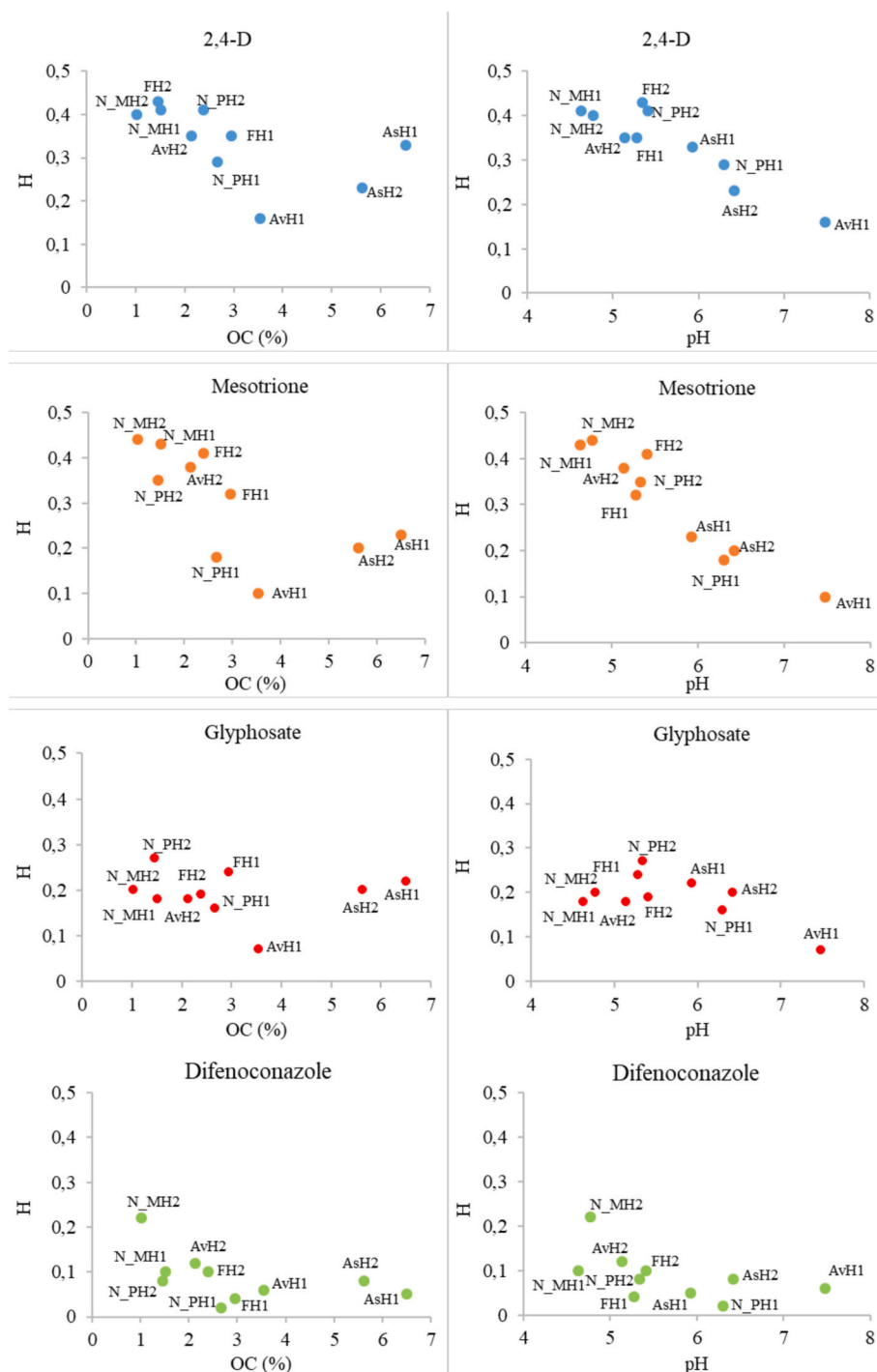

Fig. 2. Variation of the desorption hysteresis H-index as a function of organic carbon content and soil pH.

value = 0.08; mesotrione: $r = -0.65$ and p value = 0.04). However, when the silandic andosol was excluded, the correlation between H and OC content became significant for both molecules (2,4-D: $r = -0.81$ and p value = 0.014; mesotrione: $r = -0.80$ and p value = 0.017). Nevertheless, the predominant importance of pH in the variation in H was confirmed by stepwise multiple linear regression, which retained only this factor as a predictor (Table 5).

For glyphosate, the hysteresis is quite high and shows less variation than that of the two previous molecules. Accordingly, there were no significant correlations between H and pH or OC (pH: $r = -0.63$ and p value = 0.051; OC: $r = 0.05$ and p value = 0.89). The AvH1 horizon deviates again slightly from those of the other soil samples, but excluding it from the correlation analysis does not lead to significant correlations (pH: $r = -0.10$ and p value = 0.80; OC: $r = 0.06$ and p value = 0.88). The stepwise multiple linear regression retains only pH as a predictor variable and its prediction performance is small, with an R-squared of only 0.33 (Table 5).

In the case of difenoconazole, the H values were the lowest and decreased with increasing OC content and pH. The decrease is nonlinear since with a soil OC content >3% or a pH >6, the H value no longer decreases. Consequently, the linear correlation coefficients between H and OC content or pH were not significant (OC: $r = -0.49$ and p value = 0.147; pH: $r = -0.54$ and p value = 0.108), and the stepwise multiple regression did not reveal any significant predictors (Table 5). Here, none of the soil samples does markedly deviated from the cloud of points.

4. Discussion

4.1. Soil factors involved in the variation in the sorption coefficients

As expected, the soil factors controlling the variation in sorption between the studied volcanic soils vary according to the type of molecules.

For weak acids (2,4-D and mesotrione), soil pH appears to be a first-order factor of sorption. Current pedotransfer functions developed for 2,4-D (Weber et al., 2004; Boivin et al., 2005) and mesotrione (Dyson et al., 2002; Mendes et al., 2016) have shown that soil pH is negatively correlated with the adsorption coefficient. Our observations, however, additionally show that, for weak acid, adsorption on volcanic soils with low pH is not only more important but also more reversible than for soils with higher pH; this suggests that at low soil pH values, there are indeed more retention sites, but desorption from these sites is easier than at increasing pH values. The pH dependence of sorption of ionizable pesticides originates mainly from the changes in both the anionic exchange capacities of the soil solid phase and hydrophobic interactions with pH. In variable-charge soils, the anion exchange capacity and thereby the sorption capacity are increased by the increase in the positive surface charges of the soil matrix with decreasing soil pH (Qafoku et al., 2004). Hydrophobic interactions also increase with decreasing pH. For weak acids, neutral forms are more frequent when the pH is low; they exhibit greater hydrophobicity and are more strongly sorbed than anionic forms since they do not experience repulsion from the negative soil surface charges (Kah and Brown, 2006). However, for mesotrione and 2,4-D, the neutral forms represented only a few percent. Another source of the increase in hydrophobic interactions with decreasing pH can be the protonation of the humic acids present in organic matter (Barriuso et al., 1992), which increases the number of retention sites with significant hydrophobicity (Kah and Brown, 2006). The fact that desorption is more difficult at higher pH values suggests that, although the retention sites may be less abundant, soil-pesticide interactions are stronger on average. It is not possible to identify from our experiments what types of interactions are involved. However, it may be speculated that the proportion of hydrophobic interactions, known to be of low energy (Table 3 in Kah and Brown, 2006), decreases more than other types of interactions, such as anion or ligand exchange, when the pH increases. Concerning the influence of organic matter on the adsorption of weak acids, our results are quite variable, as are those from the literature. While some studies have shown a positive correlation between the adsorption coefficient and the OC content (e.g., Boivin et al., 2005; Duwig et al., 2006; Kah and Brown, 2007; Rocha et al., 2006), other studies have not show any specific link (e.g., Barriuso et al., 1992; Mendes et al., 2016). In fact, although 2,4-D and mesotrione may form, at low soil pH, hydrophobic interactions with OC through their aromatic structure (Benoit et al., 1996), it is likely that any relationship is difficult to interpret given the predominant influence of soil pH variation on adsorption in our dataset. Eventually, it is worth noting the increase in the adsorption coefficients of the weak acids for allophanic soil As. This increase may be explained by the high contents of both OC and iron and aluminium oxyhydroxides in the As horizons, which both promote adsorption. In addition to the hydrophobic interactions between the soil OC and the aromatic structures of the molecules, already mentioned above, several papers have reported on the potential interactions between the positively charged sites of iron and aluminium oxyhydroxides and the carboxylate hydrophilic group of 2,4-D (Barriuso et al., 1992; Duwig et al., 2006; Baskaran et al., 1996; Dubus et al., 2001; Cáceres-Jensen et al., 2021) and the anionic form of mesotrione (Mendes et al., 2016).

For glyphosate, our results show an unexpected positive relationship between the adsorption coefficient and the pH of the soils studied. This relationship is inconsistent with most of the literature, which agrees with a decrease in glyphosate sorption with pH (e.g., De Jonge and de Jonge, 1999; Mamy and Barriuso, 2005; Gimsing et al., 2007; Cáceres-Jensen et al., 2009; Gerónimo et al., 2018). Indeed, an increase in pH favours an increase in the negative surface charges of the soil and

Table 5
Multiple linear regression for the prediction of the desorption hysteresis index.

Pesticide		Estimation of the desorption hysteresis index by linear regression	Adjusted R^2	p-value	RMSEP
2,4-D	All soils	H = 0.86–0.093 pH***	0.82	0.000196	0.010 (3.1%)[a]
	Without As	H = 0.84–0.089 pH**	0.81	0.00155	0.012 (3.4%)[a']
Mesotrione	All soils	H = 1.04–0.13 pH***	0.90	< 0.0001	0.011 (3.5%)[b]
	Without As	H = 1.03–0.13 pH***	0.90	0.000233	0.014 (4.1%)[b']
Glyphosate	All soils	H = 0.41–0.039 pH*	0.33	0.0493	0.012 (6.5%)[c]
	Without AvH1	H = 0.232–0.00537 pH	0.01	0.796	0.011 (5.2%)[c']
Difenoconazole	All soils	H = 0.24–0.023 pH – 0.0083 OC	0.32	> 0.05	0.0135 (15.6%)[d]

*p-value <0.05; ** p-value <0.01; ***p-value <0.001.

[a] RMSEP expressed as a percentage of the average value of H (0.34 L.kg^{-1}).
[a'] RMSEP expressed as a percentage of the average value of H (0.35 L.kg^{-1}).
[b] RMSEP expressed as a percentage of the average value of H (0.30 L.kg^{-1}).
[b'] RMSEP expressed as a percentage of the average value of H (0.33 L.kg^{-1}).
[c] RMSEP expressed as a percentage of the average value of H (0.19 L.kg^{-1}).
[c'] RMSEP expressed as a percentage of the average value of H (0.20 L.kg^{-1}).
[d] RMSEP expressed as a percentage of the average value of H (0.09 L.kg^{-1}).

glyphosate, resulting in greater electrostatic repulsion (e.g., Wauchope et al., 2002; De Jonge and de Jonge, 1999). In our case, the observation of a positive relationship is likely related to the influence of other soil properties strongly correlated with pH in the samples of soils studied. Two potential factors may be mentioned. First, the divalent cation Ca^{2+} content exhibited a positive relationship with the glyphosate adsorption coefficient ($r = 0.83$ and p value $= 0.003$). In the two limed surface horizons (N_PH1 and AvH1), the content of divalent cations (Ca^{2+}) following liming was between 2 and 20 times greater than that in the other deep horizons. The presence of divalent cations is known to favour glyphosate adsorption because of the cationic bridging of phosphate functional groups with ligand exchange and complexation sites (e.g. De Jonge and de Jonge, 1999; De Jonge et al., 2001). Second, the Fe and Al oxyhydroxide contents also exhibited a positive relationship with the glyphosate adsorption coefficient after excluding the two limed surface horizons (Alox: $r = 0.84$ and p value $= 0.009$; Feox: $r = 0.81$ and p value $= 0.016$). Indeed, their presence favours the creation of interactions by ligand exchange between the surface hydroxyl groups (Fe-OH and Al-OH) and the phosphonate functional group of glyphosate (e.g., Borggaard and Gimsing, 2008; De Jonge et al., 2001; Mamy and Barriuso, 2005; Gimsing et al., 2007). Both high divalent cation contents and amorphous and Al and Fe oxyhydroxides favour the creation of strong interactions with little reversibility based on exchanging ligands with phosphonate functional groups and cationic bridging with carboxylates, as mentioned in previous studies (De Jonge et al., 2001; Cáceres-Jensen et al., 2009); this may explain why glyphosate desorption was observed to be small for all soils, particularly for the limed AvH1 horizon.

The behaviour of difenoconazole is similar to that of other hydrophobic molecules, whose adsorption is already known to be governed by hydrophobic interactions with soil organic matter (e.g., Von Oepen et al., 1991; Wauchope et al., 2002). Thus, the adsorption coefficient of difenoconazole varies according to the OC content of the different types of soil studied. Our results agree well with those of Fernández-Bayo et al. (2013), who showed that for the same soil types (andosol and nitisol) there was a strong correlation between the adsorption coefficients of two strongly hydrophobic neutral molecules, cadusafos and chlordecone, and the OC content of the soils. Moreover, the hydrophobic interactions with soil organic matter for the adsorption of difenoconazole do not appear to be very reversible, implying that strong interactions that limit desorption are sufficient. Overall, in our study, the soils with the highest adsorption rates of difenoconazole had the lowest desorption rates (Table 3). This relationship is the opposite of that observed for the ionic molecules 2,4-D and mesotrione: the greater the adsorption is, the greater the desorption, especially after excluding the silandic andosol. Similarly, in a study of the desorption of two hydrophobic and nonpolar pesticides cadusafos and parathion from tropical soils, Olvera-Velona et al. (2008) described the same behaviour, i.e., a more marked hysteresis when the adsorption capacity is high.

4.2. Variation in pesticide sorption features among tropical volcanic soils

The potential risks of nearby surface and groundwater contamination by pesticides vary not only according to the pesticide properties but also according to the soil types on which the pesticides were applied. Sorption is recognised as one of the major factors in regulating the mobility of pesticides through runoff and leaching (e.g. Farenhorst, 2006; Tang et al., 2012). The adsorption coefficient for a given pesticide and soil provides an indication of whether the pesticide is more or less mobile in that soil. In this respect, to compare the sorption behaviours between soil horizons, we computed for each pesticide the ratios of its adsorption and desorption coefficients on every soil horizon to the average of the values of its adsorption and desorption coefficients over all soil horizons (Fig. 3 and MS Fig. S4). Most observed ratios belong to the same cloud and are within an approximate range of 0.5 to 1.5 times of the average ratio per pesticide, which indicates limited variation in pesticide mobility between most soil horizons. However, in agreement
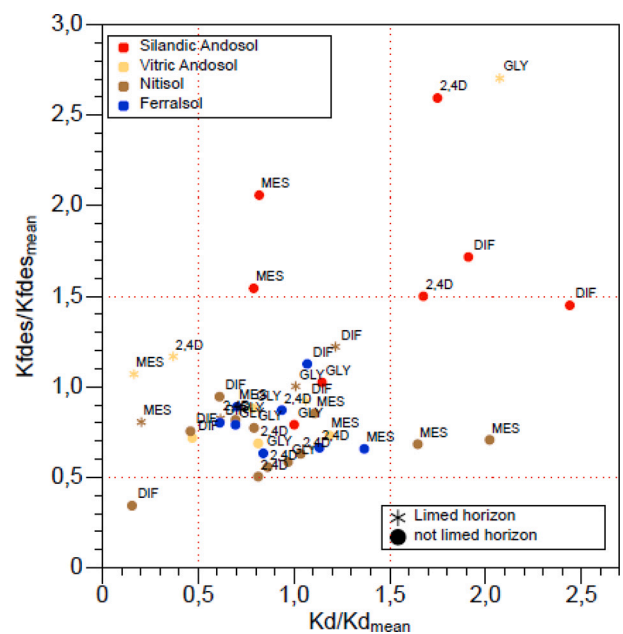

Fig. 3. Variation between the observed sorption coefficients of adsorption (K_d) and the Freundlich desorption coefficient ($K_{f,des}$) with respect to the average pesticide sorption values.

with the soil clustering of the PCA (MS Fig. S3), there are outliers to the cloud that are caused by three types of soil horizons whose behaviour differs markedly from the average behaviour of the soils.

The first are the silandic andosol horizons, which exhibit markedly higher sorption coefficients than the other horizons, for two out of four pesticides during adsorption and for three out of four during desorption. The specific mineralogical composition of the silandic andosol explains its generally high sorption properties for both hydrophobic and ionic pesticides. Previous studies involving andosols similar to the present silandic andosol indicated that andosols are privileged soil for adsorption (Duwig et al., 2006; Cabidoche et al., 2009; Fernández-Bayo et al., 2013) given their particularly high OC contents compared to those of other tropical volcanic ash soils (Sierra and Causeret, 2018) and their binding capacities with Fe and Al oxides (Baskaran et al., 1996; Kogan et al., 2003; Duwig et al., 2006; Cáceres-Jensen et al., 2009). Two exceptions must be noted. One is the adsorption of mesotrione, which is not greater for As than for the other soils. This could be linked to electrostatic anionic repulsion, which is more pronounced for this pesticide in As given the only slightly acidic pH of the As horizons (Dyson et al., 2002; Mendes et al., 2016). However, the desorption coefficient of mesotrione is still much larger for As than for other soils, which indicates the strength of the bonds between the pesticide and this soil. The other exception is glyphosate, which shows similar sorption on As as on other soils and whose sorption coefficients remain in the range of sorption values. However, apart from these exceptions, among the soils studied, the silandic andosol soils retain and limit the most, which is likely to buffer the dissemination of pesticides towards surface and groundwaters but also increase the risk of long-term contamination in the case of molecules that slowly degrade. This has already been shown for chlordecone, an organochlorine insecticide used on banana plantations until 1993 (Cabidoche et al., 2009). Moreover, the specific results obtained for the silandic andosol indicate that with respect to pesticide sorption properties, andosols do not exhibit unique behaviour. Indeed, vitric andosols (Av) are shown to have quite different sorption coefficients, similar to those described for nitisol and ferralsol if we exclude the limed topsoils. A clear distinction within andosols thus needs to be made according to their allophane and organic carbon contents.

The second kind of particular horizon is the limed horizons (N_PH1

and AvH1). Here, the two limed horizons exhibit either low sorption capacities, in the case of the ionic molecules 2,4-D and mesotrione, or some of the highest sorption capacities, as in the case of glyphosate. At high pH levels, ionic molecules are almost completely anionic, resulting in significant repulsion with the solid matrix, which is also negatively charged as the pH increases. For glyphosate, an increase in the concentration of divalent cations (Ca^{2+}) strongly favours sorption processes. These results are consistent with the literature, with liming significantly reducing the sorption capacity of weak acid molecules (e.g., Barriuso et al., 1992) and increasing that of glyphosate (e.g., De Jonge and de Jonge, 1999). These authors highlighted the importance of agricultural practices on the sorption properties of ionic molecules.

Last, it can be noted that the nitisol horizons cover a large range of sorption values in adsorption but not in desorption, for which their $K_{f,des}$ values are almost all in the range of those included in the fixed cloud limits. We attributed the relatively lower adsorption of hydrophobic molecules (difenoconazole) to the low OC content, and the greater adsorption of weak acids (mesotrione) to the acidic pH condition.

5. Conclusion

The present study identified the main soil factors involved in the variation of the adsorption and desorption coefficients of several ionizable and hydrophobic pesticides in acidic and variable-charge volcanic soils in the French West Indies. Reciprocally, this approach allowed us to illustrate the specific behaviour of each of the studied volcanic soils, namely, silandic and vitric andosols, nitisols and ferralsols, as well as the impact of liming on pesticide mobility.

The results obtained show that the main soil factors involved in sorption vary according to the type of compound. For weakly acidic compounds, such as 2,4-D and mesotrione, soil pH is the first-order factor of sorption since it plays a regulatory role in the electrostatic charge of the soil matrix and in the chemical dissociation of ionic molecules controls both the electrostatic charge of the soil matrix and the chemical dissociation of weak acids, favouring the possibility of ionic interactions. At low pH, the OC content is an additional factor because it favours hydrophobic interactions with the aromatic structure of weak acids. Eventually, the adsorbed amount of the weak acids is not only more important but also more reversible when the pH is low than when it becomes higher. For glyphosate, a zwitterion, the adsorption is clearly guided by the variation in pH induced by liming, which contributes to the increase in divalent Ca^{2+} cations, or by the amount of iron and aluminium oxyhydroxides in the soils, which is very high in silandic andosols. In both cases, interactions may occur with little reversibility. Finally, for difenoconazole, a hydrophobic molecule, adsorption is regulated by hydrophobic interactions and closely correlated with the OC content. This suggests a sufficiently intensive interaction that limits desorption. The obtained dataset allows us to propose multiple linear regressions to estimate both the adsorption coefficients and desorption hysteresis indices based on meaningful and easily available pedagogical predictors, e.g., pH and/or OC content. The regressions need, however, to be confirmed by a larger set of data since we noticed possible confounding effects between soil pH and OC content variables in the present dataset.

Considering the studied range of volcanic soils, the silandic andosol soils exhibited markedly greater adsorption and desorption coefficients than did the other soils for both hydrophobic and ionic pesticides. Thus, silandic andosols are among the volcanic soils that retain pesticides and limit their mobility the most; on the one hand, this attenuates the spread of pesticides towards surface water and groundwater, but on the other hand, it can increase the risk of long-term contamination, particularly in the case of slowly degrading molecules. In addition, based on the sorption coefficients of silandic and vitric andosols, we observed clearly different behaviours, which must be distinguished in terms of the risk of pesticide mobility. Therfore, this study enables us to refine our knowledge of sorption coefficients specific to the tropical volcanic context, and

thus more accurately estimate the risks of contamination of the soil and water compartments.

Finally, this study illustrated the effect of liming on the sorption properties of volcanic soils. Indeed, liming increases the pH and divalent cation (Ca^{2+}) content, which directly influences the sorption of ionic molecules. In the agricultural context of the French West Indies, because of the acidic soil pH condition, liming is a common practice for preventing aluminium toxicity and guaranteeing plantation survival (e.g., Sansoulet et al., 2007; Sierra et al., 2015). Accordingly, when estimating soil sorption properties, soil management practices should be considered, as should basic soil properties. This phenomenon appears to be particularly important for surface horizons whose properties are the most influenced by soil treatments and management practices.

Moreover, since soil pH and OC content are correlated and present a confounding effect, a specific protocol measuring sorption coefficients at varying pH levels or after a soil treatment to remove OC would be appropriate to better explore pesticide-soil interactions. This approach could aid in proposing more efficient soil management strategies to enhance pesticide retention through sorption processes.

CRediT authorship contribution statement

Pauline Campan: Conceptualization, Investigation, Writing – original draft, Data curation, Methodology. **Anatja Samouelian:** Conceptualization, Investigation, Validation, Writing – review & editing, Project administration, Funding acquisition, Methodology. **Antoine Richard:** Conceptualization, Investigation, Validation, Writing – review & editing, Project administration, Funding acquisition, Methodology. **Sandrine Négro:** Methodology, Data curation. **Manon Lagacherie:** Data curation. **Marc Voltz:** Conceptualization, Investigation, Methodology, Validation, Writing – review & editing, Supervision.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geodrs.2024.e00830.

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