Water repellency of volcanic ash soils from Ecuadorian páramo: effect of water content and characteristics of hydrophobic organic matter

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Summary

Water repellency of volcanic ash soils from the Ecuadorian páramo was studied by a combination of extraction and analysis of water-repellent products, Molarity Ethanol Droplet values, water contact-angle measurements by capillary rise, and N2 adsorption isotherms. The undried samples studied are hydrophilic, but exhibit water repellency after moderate drying (48 hours at 30°C). The advancing water contact-angle measured by capillary rise varies from 78° to 89°. These water contact-angles decrease strongly after extraction of organic materials by an isopropanol–water mixture. Elemental analysis, infrared spectra and gas chromatography-mass spectrometry analyses were used to characterize the extracts. The results show that long-chain fatty acids and more complex non-polar alkyl components (waxes) are the main water-repellent materials. The deposition of such extracted materials onto hydrophilic sand leads to the rapid increase of water contact-angle until values close to those measured on the soil samples are achieved. Assuming a coating of the mineral surface by organic hydrophobic products and using Cassie’s law, the water contact-angle of extracted materials was computed. The values ranged from 100° to 157°. Nitrogen specific surface areas of the soils studied were very small, indicating a low adsorbent–adsorbate interaction on hydrophobic surfaces. These results partially validate the hypothesis of water-repellent materials that occur as coatings at least after a drying process.

Introduction

Occurrence of water repellency has been extensively reported in many countries and soil types (e.g. the reviews of DeBano, 1981, 2000 and Doerr et al., 2000) and in a wide range of soil textures and amounts of organic matter, as follows: peat soils (Valat et al., 1991; Michel et al., 2001), sandy soils (Miller & Wilkinson, 1977; Dekker & Ritsema, 1994; Franco et al., 1995) or clayey soils (Dekker, 1998; de Jonge et al., 1999; Doerr et al., 2000). Although some studies have shown the occurrence of water repellency in soils of high water content (King, 1981; Jex et al., 1985; de Jonge et al., 1999) most studies indicate that soils are most repellent when dry and least repellent or non-repellent (hydrophilic) when moist (e.g. DeBano, 1981, 2000; Dekker & Ritsema, 1994; Dekker, 1998; Doerr & Thomas, 2000; Michel et al., 2001). However, the reported critical soil moisture thresholds demarcating water-repellent and non-repellent conditions vary widely (e.g. Tschapek, 1984; Dekker & Ritsema, 1994; Doerr & Thomas, 2000) and the exact relationship between hydrophobicity and soil moisture remains far from understood.

On the other hand, the development of water repellency in soils is largely related to the content and the composition of soil organic matter (see Doerr et al., 2000, and references therein). Various authors have emphasized the role of humic substances, such as humic acids (Savage et al., 1969; Tschapek et al., 1973; Jouany, 1991) and fulvic acids (Miller & Wilkinson, 1977), on the development of hydrophobic behaviour. Other studies have provided evidence of the role played by more specific organic materials in water repellency in soils, such as lipids (Ma’shum et al., 1988; Capriel, 1997; Horne & McIntosh, 2000), waxes (Franco et al., 1995) or the global aliphatics soil fraction (Savage et al., 1972; Capriel et al., 1995). Further research on the relationships between water content, water repellency and...
organic matter has led to suggestions that at least two types of soil hydrophobicity development are linked with organic matter during drying.

The first type of soil hydrophobicity has been attributed to conformational changes of the organic macromolecules which coat soil particles and microaggregates. During the drying process, the polar groups of the organic coatings should interact through hydrogen bonds. This forces the organic macromolecules into a micellar microstructure with their polar groups attached to the mineral surfaces (inner surface micelle microstructure) and their non-polar groups orientated outwards (outer surface micelle microstructure), rendering these organic coatings water repellent (Tschapek, 1984; Ma’shum & Farmer, 1985; Valat et al., 1991). The second type, clearly shown by Franco et al. (1995) after heating, involves a redistribution of waxes already present in the soil matrix as interstitial globules. In both cases, the drying process involves both change of soil structure and organic matter.

The soils belonging to the Andisol order of soil taxonomy (Soil Survey Staff, 1999), and particularly the non-allophanic ones, are known to be among the richest in soil organic matter (Batjes, 1996). On the other hand, the complete and irreversible change of physical structure and hydric properties with drying is one of the classical characteristics of these soils. However, water repellency occurrence with drying in Andisols, and particularly in volcanic ash Andisols, is not currently described (see, e.g., Nanzyo et al., 1993). Clothier et al. (2000) have recently reported water repellency in an unsaturated New Zealand Andisol, using a combination of solute transport and continuous TDR measurements, but these results demonstrate the occurrence of initial hydrophobicity.

In the high-altitude grasslands of Ecuador, Poulenard et al. (2001) have observed, under simulated rainfall, strong erosion of the topsoils by floating of aggregates on very dry, recently bare fallow Andisols. This behaviour was explained by the potential water repellency of the dry Andisol aggregates. Thus, in this environment, currently submitted to intense change of land use, the development of water repellency of dry topsoils can have a major impact on the erosive and hydrodynamic behaviour of the soil. The aim of this paper is therefore to study the interactions between potentially hydrophobic organic matter and soil moisture on the hydrophobic behaviour of a range of Andisol topsoils derived from volcanic ash in the Ecuadorian páramo.

This study involved the estimation of the degree of water repellency by the Molarity Ethanol Droplet method and measurements of water contact-angle by capillary rise, the extraction and characterization of water-repellent organic materials, and the measurement of N₂ adsorption isotherms where N₂ acts as a polar microprobe of the soil surface.

**Materials and methods**

**Soil samples**

The paper deals with the A1 horizons of five profiles characteristic of the range of Andisols occurring in the high-altitude grassland ecosystem of Ecuador known as ‘páramo’ (Poulenard, 2000). Table 1 lists on the one hand the classification of these profiles according to Soil Survey Staff (1999), and, on the other, some physical and chemical properties of the topsoil horizons selected for this study. As shown in Table 1, our samples differ mainly by their carbon and volumetric water contents, and consequently by their bulk density values. More details concerning the GEL, CUE and AZO samples can also be found elsewhere (Poulenard et al., 2003).

Disturbed and undisturbed samples of these topsoils were collected in January 1998. Disturbed samples taken at moisture contents very close to their field capacity were stored in plastic bags at 4°C. Undisturbed samples were collected as large

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**Table 1** Main properties of the soil samples studied

<table>
<thead>
<tr>
<th>Profile name</th>
<th>Soil classification³</th>
<th>Topsoil horizon depth /cm</th>
<th>Bulk density /g cm⁻³</th>
<th>Organic carbon /g kg⁻¹</th>
<th>Allophane content³ /g kg⁻¹</th>
<th>Al-humus content³ /g kg⁻¹</th>
<th>Volumetric water content of dried samples /cm³ cm⁻³</th>
<th>Moist samples /cm³ cm⁻³</th>
<th>48 hours at 30°C /cm³ cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHI</td>
<td>Typic Melanudand</td>
<td>0–30</td>
<td>0.65</td>
<td>86</td>
<td>17.0</td>
<td>52</td>
<td>0.76</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>PIC</td>
<td>Tha´plic Hapludand</td>
<td>0–20</td>
<td>0.82</td>
<td>125</td>
<td>1.4</td>
<td>20</td>
<td>0.47</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>GEL</td>
<td>Hydric Pachic Melanudand</td>
<td>0–30</td>
<td>0.39</td>
<td>212</td>
<td>2.8</td>
<td>90</td>
<td>0.68</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>CUE</td>
<td>Hydric Melanudand</td>
<td>0–30</td>
<td>0.35</td>
<td>233</td>
<td>5.0</td>
<td>256</td>
<td>0.81</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>AZO</td>
<td>Hydric Pachic Melanudand</td>
<td>0–15</td>
<td>0.33</td>
<td>180</td>
<td>2.1</td>
<td>110</td>
<td>0.75</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

³Soil classification according to Soil Survey Staff (1999).

⁴Allophane content was assessed according to the formula: allophane = 7.1 Si₀, where Si₀ is the ammonium oxalate-extractable Si (Parfitt & Wilson, 1985).

⁵Al-humus was assessed according to the formula: Al-humus = 7.5 Alp, where Alp is the pyrophosphate-extractable Al (Poulenard & Herbillon, 2000).

⁶Water content with reference to the oven-dried samples (48 hours at 105°C).

recording the speed of water capillary rise in the soil. By definition, when $\theta > 90^\circ$, capillary rise cannot occur, so this method does not permit the measurement of contact-angles larger than $90^\circ$.

**Extraction and characterization of water-repellent materials**

Extractions of water-repellent materials were performed according to Ma’shum *et al.* (1988). Ten grams of soils were extracted by 200 ml of isopropanol:water (7:3 by volume) mixture during 16 hours using a Soxhlet apparatus. The extracts were dried, weighed, and kept for further analysis. After extraction, excess of isopropanol was removed under vacuum, and the water repellency measured by the advancing contact-angle using the capillary rise technique after the soil had air-dried.

Elemental analysis (C, H, N) of the dried extracts was made by dry combustion using a CHN autoanlyser (Carlo Erba 1108). The analysis of the chromatogram of the analyser shows the absence of sulphur. Oxygen was calculated assuming $C + H + N + O = 100\%$. The fact that P was not included in the equation has a low impact on the O/C atomic ratio as P is $<1\%$ of the average composition of soil organic matter (Ballock & Nelson, 2000). Infrared (IR) spectra were obtained with a Bruker Vector 22 IRTF spectrophotometer (1 mg samples dried over $P_2O_5$ and compressed with 200 mg KBr at 10 t pressure). Gas chromatography-mass spectrometry analyses (GC-MS) were carried out on a Varian 3400 CX GC coupled with a Varian ION TRAP Saturn III MS. Compounds were separated by He-flow on a 30-m DB5 MS column (0.25 mm internal diameter and 0.25 $\mu$m film thickness) programmed from 70°C to 280°C at 5°C min$^{-1}$. Samples (1 $\mu$l of material dissolved in dichloromethane) were injected using a programmable sample injector mode. Operating conditions of the MS were: electron energy 70 eV, source temperature 200°C, scanning from 40 to 650 m/z. Part of the materials was analysed directly and part was first methylated before analysis. Before the GC-MS determination, the methyl esters of fatty acids were prepared using a rapid esterification method with BF3–methanol mixture (Knapp, 1979).

**Effect of extracted material on the water contact-angle of quartz**

Isopropanol–water-extracted materials from the GEL topsoil were dissolved in dichloromethane (100 ml of dichloromethane per 100 $\mu$g of extracted materials). Various volumes (5, 10, 15, 25, 50 and 75 ml) of this solution were added separately to 35 g of hydrophilic quartz (Fontainebleau sand). The Fontainebleau sand is characterized by a narrow particle-size distribution between 0.1 and 0.4 mm (median located at 0.22 mm) and a large degree of purity (97–99% quartz). After mixing, the solvent was evaporated under vacuum and the sand air-dried. The advancing water contact-angle was determined on the quartz
with and without adsorbed GEL water-repellent materials, following the procedure described previously.

N₂ specific surface area measurements

Nitrogen gas adsorption isotherms at liquid nitrogen temperature (77 K) were obtained with a custom-made, volumetric apparatus equipped with a Datametrics 0–1000 Torr pressure gauge. The 30°C-dried soil samples were degassed overnight at 20°C at 0.03 Torr. Total and micropore specific surface areas were calculated from the BET equation and the t-plot procedure, respectively (Rouquerol et al., 1999).

Results and discussion

Effect of drying on water repellency

Molarity Ethanol Droplet (MED) values for moist samples (data not shown) were zero for all the samples showing hydrophilic behaviour of the topsoils before drying. During the drying process, the MED value of the sample CHI remained at zero. Figure 1 presents the relation between the water repellency estimated by MED value and the moisture content for the four other samples during the drying process. There is a clear increase in water repellency as moisture content decreases. The relationship appears to be linear for three samples (GEL, CUE, AZO) and the slope of the relation is seen as a relevant index to the susceptibility to repellency after drying. The PIC sample shows two-stage behaviour. During the first part of drying there is high development of water repellency while at low water content, the slope is greatly reduced.

Water contact-angles, θ, of the moist and 30°C-dried topsoils, computed from capillary rise experiments, are listed in Table 2. Water contact-angle of moist samples ranges between samples from 0° to 71° and it is noticeable that with θ > 70°, the MED value was zero. This large discrepancy between the methods comes mainly from the high porosity of the moist samples (see the low bulk density values in Table 1) leading to rapid infiltration of pure water even if the water contact-angle is > 0. The water contact-angle of 30°C-dried samples was large, with a narrow range from 85° to 89° for most soils studied. This characterizes strong hydrophobic behaviour, very near the point where water repellency prevents capillary rise (θ ≥ 90°). The CHI dried sample had a water contact-angle of 78°, but the MED value is zero. Thus, we oppose water contact-angle < 78° with hydrophilic behaviour (moist samples and CHI dried samples) and > 78° with hydrophobic behaviour (all the other dried samples) (Table 2). This simple criterion appears here more relevant than the material classification of Van Oss (1996) in which all the moist and dried samples were considered as ‘partially hydrophobic’ with 54° > θ > 90°.

These results confirmed previous studies that reported that soils are most repellent when dry and least repellent or non-repellent (hydrophilic) when moist (DeBano, 1981, 2000; Dekker & Ritsema, 1994; Dekker, 1998; Doerr & Thomas, 2000; Michel et al., 2001). Furthermore, these results confirm the field observation of strong water repellency on highly dried

![Figure 1](image-url) Relationships between MED values recorded during drying at 30°C and the volumetric water content for the four water-repellent samples.
paramos soils (Podwojewski et al., 2002). The drastic erosion by the unexpected process of flotation of aggregates shown by Poulenard et al. (2001) on highly dried, bare fallow plots in the high grassland of Ecuador is probably due to the water repellency of such topsoil aggregates. The degree of drying, controlling the intensity of water repellency, can therefore be a key point for the erosion intensity by flotation on former-cultivated paramos Andisols.

Extraction and characterization of water-repellent materials

The amounts and characteristics of materials extracted by isopropanol–water are given in Table 3. First, they are similar in moist and dried samples of each topsoil. These amounts of extracted materials were also nearly 10 times larger than those found in an Australian water-repellent soil studied by Ma’shum et al. (1988), with the same extraction procedure. Extracted carbon represented 3.5–5.5% of the total soil organic carbon.

Second, the more organic is the soil, the greater is the mass extracted. The GEL, CUE and AZO mature Andisols, rich in organic matter (Table 1), contained much more water-repellent organic material than the CHI and PIC young Andisols (Table 3). Conversely, the O/C and the C/N atomic ratios of the materials extracted by isopropanol–water either decreased or increased, respectively, as a function of the amount of extracted materials (Table 1). Again, there was a distinction between the GEL, CUE and AZO mature Andisols (O/C and C/N atomic ratio ranges of 0.29–0.32 and 84.7–118.2, respectively) and the two CHI and PIC young Andisols (O/C and C/N atomic ratio ranges of 0.37–0.43 and 57.7–69.4, respectively).

In contrast, the large H/C atomic ratio of 1.7–1.8 was nearly constant, whatever the soil (Table 3). This shows the large degree of aliphaticity of all the materials extracted. The atomic ratios of the extracted material plotted according to Van Krevelen (H/C versus O/C; results not shown) was very close to the position of soil lipids extracted with benzene or diethyl ether and analysed by Jambu et al. (1978). However, soil lipids are more a convenient analytical group than a specific type of compound, being a mixture of fatty acids and compounds with a complex molecular structure such as waxes, terpenes, sterols and resins (Dinel et al., 1990). All these compounds have large aliphatic units as well as hydrophilic groups.

The IR spectra of the organic materials extracted by isopropanol–water (Figure 2) confirmed that the materials extracted were lipids with a high degree of aliphaticity and small amounts of nitrogen groups. The two strong IR peaks at 2920 and 2860 cm\(^{-1}\) correspond to the aliphatic CH\(_3\) and CH\(_2\) radicals, respectively. We also found the asymmetric deformations of the same aliphatic groups at 1460–1450 cm\(^{-1}\) and at 1380 cm\(^{-1}\), respectively. The wide IR band which

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Before isopropanol–water extraction</th>
<th>After isopropanol–water extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet samples</td>
<td>30°C-dried samples</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>CHI</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PIC</td>
<td>52.5</td>
<td>13.3</td>
</tr>
<tr>
<td>GEL</td>
<td>69</td>
<td>1.8</td>
</tr>
<tr>
<td>CUE</td>
<td>60.5</td>
<td>2.2</td>
</tr>
<tr>
<td>AZO</td>
<td>71</td>
<td>2.7</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Extracted materials</th>
<th>Wet /g kg(^{-1}) of soil</th>
<th>Dried</th>
<th>C (% of extracted material)</th>
<th>N</th>
<th>H</th>
<th>O</th>
<th>EC/TC(^a)</th>
<th>O/C</th>
<th>C/N</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHI</td>
<td>5.5</td>
<td>5.5</td>
<td>57.6</td>
<td>0.97</td>
<td>8.58</td>
<td>32.8</td>
<td>3.7</td>
<td>0.43</td>
<td>69.4</td>
<td>1.81</td>
</tr>
<tr>
<td>PIC</td>
<td>8.8</td>
<td>9.2</td>
<td>60.3</td>
<td>1.22</td>
<td>8.69</td>
<td>29.8</td>
<td>4.4</td>
<td>0.37</td>
<td>57.7</td>
<td>1.71</td>
</tr>
<tr>
<td>GEL</td>
<td>13.5</td>
<td>14.5</td>
<td>64.0</td>
<td>0.88</td>
<td>9.60</td>
<td>25.5</td>
<td>4.4</td>
<td>0.29</td>
<td>84.7</td>
<td>1.80</td>
</tr>
<tr>
<td>CUE</td>
<td>13.3</td>
<td>13.0</td>
<td>62.8</td>
<td>0.64</td>
<td>9.63</td>
<td>26.9</td>
<td>3.5</td>
<td>0.32</td>
<td>114.4</td>
<td>1.84</td>
</tr>
<tr>
<td>AZO</td>
<td>11.9</td>
<td>15.5</td>
<td>63.5</td>
<td>0.62</td>
<td>9.56</td>
<td>26.3</td>
<td>5.5</td>
<td>0.31</td>
<td>118.2</td>
<td>1.81</td>
</tr>
</tbody>
</table>

\(^a\)EC, extracted carbon; TC, total carbon.
centred at 3400 cm\(^{-1}\) was attributed to the O–H of carboxylic acids, alcohols and/or phenols. The ratio between the 2800–3000 cm\(^{-1}\) aliphatic area of the IR spectra and the amount of organic carbon was very large. In agreement with Capriel (1997), this indicates that the materials extracted were very hydrophobic in permanent grass ecosystems. The IR peak at 1710–1700 cm\(^{-1}\) was attributed to the vibration of C=O of carboxylic acids and ketones. Two neighbouring small IR peaks at 1630 cm\(^{-1}\) (vibration of C=O in quinones and amides) and at 1040 cm\(^{-1}\) (the vibration of C–O of alcohols) were also identified. The materials were therefore characterized by both hydrophobic groups (CH\(_3\)-CH\(_2\)) and hydrophilic ones (OH, C=O, C–O). The features of the IR spectra in Figure 2 are also quite similar to those of previously published IR spectra of water-repellent organic materials (Giovannini et al., 1983; Ma’shum et al., 1988).

The GC-MS analysis of non-methylated extracts indicated the presence of large amounts of vanilline, a compound typically attributed to residues of lignin degradation abundant in high-altitude grasslands (Serve et al., 1983). The GC-MS analysis of the methylated extracts (Figure 3) showed the presence of 121 products, with a predominance of \(n\)-fatty acids ranging from C\(_8\) to C\(_{28}\). When the 74 m/z ion was monitored as specific to methylated fatty acids we did not observe the dominance of any particular type of fatty acid as Ma’shum et al. (1988) reported for an Australian soil water-repellent material. In contrast, a large number of fatty acids, from C\(_{14}\) to C\(_{28}\), and an abundance of long-chain fatty acids (with C > 19) were observed (Figure 3). Terpenes, sterols and waxes were also identified in the extracts, but not quantified. The involvement of long-chain fatty acids in water repellency has been reported previously by different authors (Savage et al., 1972; Ma’shum et al., 1988; Dinel et al., 1990). Moreover, Coulibaly (1984) has shown that for the same amount of products deposited on soil, long-chain fatty acids have more effect on water repellency than small-chain fatty acids.

The question now arises as to the origin of the lipid fraction in the topsoils of this study. In the páramos, as well as in other mountain regions where vegetation is adapted to cold alpine conditions, the amount of lipids in plants is high (Körner,
Amongst the eco-physiological adaptations of alpine plants, thick plant cuticles is one of the most frequently reported (Körner, 1999). Cuticles are known to be rich in long-chain (C > 19) fatty acids (Jambu et al., 1978; Dinell et al., 1990) such as those quantified here in the isopropanol–water extracts (Figure 3). They are known to be more resistant to biodegradation than small-chain (C < 19) fatty acids, whose origin is mainly cellular. The thickness of the cuticle, linked with the alpine conditions prevalent in the páramos, is therefore one of the factors that explains the larger number of long-chain fatty acids (C > 19) occurring in the organic fraction of the topsoils studied. The other main factor is the low carbon mineralization due to the cold climatic conditions. Dinell et al. (1990) have shown that lipids are generally more recalcitrant to microbial decomposition than other organic compounds such as cellulose, hemicellulose or proteins. This leads to a relative accumulation of lipids (Capriel, 1997) and explains the relatively large lipid/total organic matter ratios found in this study (Table 3).

**Effect of extracted materials on water repellency**

As shown in Table 2, the water contact-angle of the soils clearly decreased after extraction by isopropanol–water, ranging from 20° to 74° for the AZO and GEL dry topsoils, respectively. This result confirms that the amphiphilic solvent (H-bonding) reduced soil water repellency as shown by Ma’shum et al. (1988) or more recently by Roy & McGill (2000). However, the extraction led to hydrophilic behaviour for all those dried topsoils with a water contact-angle below the threshold value of 78°. Further, although the data are scattered, we observed a slight positive relationship between the water contact-angles and the amounts of materials extracted by isopropanol–water (Figure 4). Except for the GEL topsoil, the water contact-angle after extraction decreased significantly as a function of the amount of material extracted (Figure 4). However, we also validated the crucial effect of the extracted organic products on soil hydrophobicity by recording the water advancing contact-angle of quartz (Fontainebleau sand) as a function of adsorbed organic materials, previously extracted with isopropanol–water from the GEL topsoil (i.e. the sample where the role of the extracted products seems the lowest). The results showed that the water contact-angle of the coatings ranged from 100.5° (GEL topsoil) to 157° (AZO topsoil), contact-angle of the organic coatings using Cassie’s law (Cassie & Baxter, 1944), as follows:

$$\cos \theta_{\text{(before extraction)}} = \cos \theta_{\text{(after extraction)}} + \cos \theta_{\text{of the organic coatings.}}$$

The results showed that the water contact-angle of the coatings ranged from 100.5° (GEL topsoil) to 157° (AZO topsoil),

(2)
indicating that the assumed organic coatings, extracted by isopropanol–water, were strongly water repellent (Figure 6). In addition, except again for the GEL dried topsoil, the calculated contact-angle of the organic coatings increased as a function of the amount of materials extracted by isopropanol–water (Figure 6).

**N₂ specific surface area**

Table 4 reports the values of the specific surface area (SSA) measured by applying the BET equation to the N₂ adsorption isotherms of the different topsoils of this study, as well as the values of the part of these SSA associated with their micropores. Clearly, both sets of values were extremely small. Moreover, the data did not show any positive relationship with the clay contents of the samples (Table 1). On the contrary, the topsoil with the largest clay content (AZO: 550 g kg⁻¹) exhibited a SSA more than four times smaller than the soil (CHI) having only 180 g kg⁻¹ of clay. However, all the topsoils with SSA < 5 m² g⁻¹ were also very rich in organic carbon (Table 1). As discussed by Theng *et al.* (1999), the inconsistencies between the results reported in Table 4 and Table 1 are not really surprising. Indeed, it has often been reported that the BET-N₂ method is inherently unable to provide realistic SSA values (and thus realistic SSA values of micropores) for soil samples rich in organic matter. This observation has been explained by different mechanisms (e.g. de Jonge *et al.*, 2000), but all of them are related to the fact that, at the boiling temperature of N₂, these molecules are restricted from covering surfaces where strong interactions take place between organic and mineral colloids.

In the framework of the present study, the results listed in Table 4 can therefore be taken as an indirect indication that the increasing hydrophobic behaviour observed after drying (Table 2) is due to coating of minerals by water-repellent organic materials. In the same way, these results also justify our attempt to assess the extent of the organo-mineral interactions by applying Cassie’s law to the samples of this study.

Our results should be partly explained using the hypothesis that air-drying increases the exposure of water-repellent substances at the interface between organic matter coatings and interstitial pore fluids. Following Ma’shun & Farmer (1985) and Roy & McGill (2000), we hypothesized that removal of water promotes interactions between polar functional groups, which in turn increase the exposure of non-polar alkyl chains. This change in conformation in organic matter coatings is due to the fact that non-polar moieties of water-repellent substances exposed at the interface between solid and fluid phases in soil are structurally flexible (Roy & McGill, 2000). Shrinkage, which is particularly pronounced in the volcanic soils studied (Poulenard *et al.*, 2002), should also explain the capillary rise data from wet to dry soils.

<table>
<thead>
<tr>
<th></th>
<th>Total BET surface area</th>
<th>Micropore surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHI</td>
<td>7</td>
<td>1.5</td>
</tr>
<tr>
<td>PIC</td>
<td>2.2</td>
<td>0.25</td>
</tr>
<tr>
<td>GEL</td>
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<td>0.11</td>
</tr>
<tr>
<td>CUE</td>
<td>2.6</td>
<td>0.5</td>
</tr>
<tr>
<td>AZO</td>
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</tr>
</tbody>
</table>

*Figure 6* Computed contact-angles (θ) of the organic coatings as a function of the mass of extracted organic materials.
sorptivity being a function, in a complex way, of porosity, initial water content and liquid-pore contact-angle (e.g. Benavente et al., 2002).

Conclusions

The combined application of extraction and analysis of water-repellent products, capillary rise measurements and N₂ adsorption isotherms leads to a consistent approach to the water repellency phenomena in the Ecuadorian páramos soils. The development of water repellency follows the decrease of water content on drying. This result, linked to the dramatic erosion, by flotation of water-repellent topsoil aggregates observed by Poulenard et al. (2001), shows the need to prevent strong drying processes on the surface of páramos soils.

After moderate drying, the water contact-angle determined from capillary rise was large, within a narrow range from 85° to 89° for most soils studied. This characterizes strong hydrophobic behaviour, except for the CHI topsoil which was partially hydrophobic (θ = 78°). These water contact-angles decrease strongly after extraction of organic materials by isopropanol–water. The abundance of long-chain fatty acids and waxes in topsoil horizons contributes to the development of water repellency after drying. Part of the variability of the hydrophobic behaviour seen between samples comes from differences in the lipid content. Nitrogen specific surface area data and the application of Cassie’s law suggest that these water-repellent organic materials occur as coatings. The results presented are insufficient to permit the identification of the respective effect of hydrophobic organic matter and soil moisture on the hydrophilicity/hydrophobicity balance of these soils. Nevertheless, they emphasize the strong relationships between the contribution of aliphatic organic compounds to water repellency and the drying process, at least for very porous and very organic-rich Andisols.

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References


