

Organo-mineral clay and physical properties in COST 622 European volcanic soils[†]

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Introduction

The particle-size distribution is undoubtedly a basic soil characteristic as useful in soil classification as it is in agronomy. Nevertheless, it is now well documented (see, e.g. the reviews of Nanzyo et al. 1993, Mizota and van Reeuwijk 1993) that Andosols (WRB 2001) fail to disperse completely when submitted to the dispersion agents that are utilized with success with other soils (e.g. sodium hexametaphosphate which is the recommended dispersant agent following the ISO international standards of soil particle-size analysis). The fact that sodium hexametaphosphate is not completely effective in obtaining dispersion should be attributed to the strong affinity of this dispersing agent for allophane, leading to edge to edge flocculated aggregates. Also, clay dispersability decreases when wet volcanic ash soils are dried. This is due to irreversible structural and mechanical changes occurring during drying (e.g. Kubota 1972, Nanzyo et al. 1993). Therefore, the common laboratory determined particle-size analysis of allophanic Andosols shows a low to very low clay content as compared with field determination (Ping et al. 1989), and particle-size/mineralogy modifiers such as ashy, medial and hydrous, based on 1500 kPa water retention, are used to replace the names of particle-size classes for Andisols in Soil Taxonomy (ST 1999).

The first aim of this study is therefore to adapt and develop the Na-resin method, without destruction of organic matter or/and poorly-ordered minerals, for obtaining most of the organo-mineral clay fraction. This Na-resin method was already recommended for strongly aggregated soils such as Oxisols and Andisols (Bartoli et al. 1991, Churchman et al. 1999).

The second aim of this study is to relate amounts of organo-mineral clay to physical soil properties such as bulk density, capillary porosity obtained by capillary rise, and total volumetric shrinkage of wet undisturbed soil cores at the end of controlled 40°C drying kinetics. As a matter of fact,

[†] This chapter is dedicated to the memory of late Gérard Burtin, co-author, who died in January 2004.

mineral, organic and organo-mineral colloidal soil constituents interact to give organo-mineral clay fractions (soil micro-property). In turn, organo-mineral clay coats and bridges coarser soil particles (soil aggregation) leading to soil structural features which vary with clay content and control soil macro-properties (enaulic coarse/fine related distribution pattern and granular microstructure, water retention and transport, aggregate stability and mechanical properties, shrinkage etc.).

This type of sequential scaling relationships has been widely reported for temperate cultivated soils, leading to, e.g., pedotransfer functions (prediction of water retention and hydraulic conductivity characteristics from particle-size data). Some of these expected relationships were already reported for Japanese volcanic ash soils: e.g., a linear relationship between retained water at 1500 kPa or liquid limit and organo-mineral clay content, mostly obtained by ultrasonication and pH adjustment (Nanzyo et al. 1993). However, such relationships have not been fully explored in volcanic soils, mostly because of the difficulty to disperse these strongly aggregated soils. In addition, European volcanic soils were much less studied than their American, Asian and New-Zealand counterparts.

Materials and methods

The following wet reference soil horizon samples (see the relevant Book Section 2 chapters) were analysed for particle-size distributions after Naresin, sodium hexametaphosphate, or water treatment:

- EUR01 (Gauro Volcano, near Naples, Italy): *Humi-Tephric Regosol (Eutric)* (WRB 2001), *Ashy, glassy, nonacid, thermic Vitrandic Xeropsamment* (ST 1999): A_p (0–16 cm)*, B_{w1} (16–54 cm)*, B_w 2 (54–95 cm), BC (95–125 cm)
- EUR02 (Gauro Volcano, near Naples, Italy): *Hyposodi-Humic Cambisol* (WRB 2001), *Ashy, glassy, mesic Vitrandic Haploxerept* (ST 1999): O_e + O_a (0.3–1 cm), A_h (1–6 cm)*, B_w (6–26 cm)*, BC1 (26–41 cm)
- EUR03 (Vico Volcano, near Rome, Italy): *Fulvi-Silandic Andosol (Dystric)* (WRB 2001), *Ashy, amorphous, mesic Eutric Fulvudand* (ST 1999): A_{h1} (2–24 cm)*, 2 B_{w1} (72–100 cm)*, 2 B_{w2} (100–127 cm)
- EUR04 (Vico Volcano, near Rome, Italy): *Fulvi-Silandic Andosol (Dystric)* (WRB 2001), *Ashy, amorphous, mesic Eutric Pachic Fulvudand* (ST 1999): A_{h1} (2–10 cm)*, B_{w1} (45–72 cm)*, B_{w2} (72–125 cm)
- EUR05 (Faial Island, Azores, Portugal): *Hyperdystric-Silandic Andosol* (WRB 2001), *Medial, amorphous, mesic Typic Hapludand* (ST 1999):

- A_h1 (0–10 cm)*, 2 A_hb (30–45 cm)*, 2 B_wb (45–65 cm)*, 2 B_wb/2C (65–90 cm)
- EUR06 (Pico Island, Azores, Portugal): *Hydri-Silandic Andosol (Umbric and Acroxic)* (WRB 2001), *Hydrous, amorphous, mesic Acrudoxic Hydrudand* (ST 1999): A_h (0–37 cm)*, AB (37–45 cm), 2AB (45–65 cm), 2 B_wb (65–98 cm)*, 2 B_w2 (98–125 cm), 2 B_w 3 (125–140 cm)
 - EUR07 (NW Iceland): *Orthidystri-Vitric Andosol* (WRB 2001), *Ashy, amorphous Pachic Fulvicryand* (ST 1999): A_h (5–17 cm)*, AC (17–38 cm)*, 2CB (38–65 cm)*, 3BC (65–73 cm), 3CB (73–82 cm), 4 B_w (82–95 cm)
 - EUR08 (N Iceland): *Dystri-Vitric Andosol* (WRB 2001), *Ashy, amorphous Typic Vitricryand* (ST 1999): A_h1 (3–15 cm)*, B_w1 (24–30 cm)*, 2 B_w2 (30–40 cm)
 - EUR09 (SW Iceland): *Umbri-Vitric Andosol (Pachic and Orthidystri)* (WRB 2001), *Ashy, amorphous Pachic Fulvicryand* (ST 1999): A_h (0–55 cm)*, 3H (60–95 cm)*
 - EUR10 (Tenerife Island, Canary, Spain): *Umbri-Silandic Andosol (Hyperdystric)* (WRB 2001), *Ashy, amorphous, mesic Humic Udivitrans* (ST 1999): A_h (0–45 cm)*, B_w (45–88 cm)*,
 - EUR 17 (Cantal, France): *Aluandi-Silandic Andosol (Umbric and Acroxic)* (WRB 2001), *Medial, amorphous, mesic Pachic Fulvudand* (ST 1999): A_h2 (8–32 cm)*, 2 B_w (50–90 cm)*

Asterisks (*) indicate that also wet undisturbed soil cores of 28.6 cm³ (2.7 cm diameter, 5 cm height) have been sampled using rigid plastic pipes with bevelled edges to ease insertion. The core samples were capped at both ends with two parafilm sheets to minimize soil and evaporative loss and stored at 4°C until analysis.

Bulk density, field volumetric soil moisture and capillary porosity were estimated as follows. After removal of the two parafilm sheets, each wet soil core sample was weighed and placed on a brass sieve (height 70 mm, diameter 60 mm, mesh size 200 µm), which was placed on a PVC grid (mesh size 2×20 mm) located 10 mm above the bottom of a rectangular PVC box. Demineralised water was added to a height of 12 mm (2 mm of water above the lower limit of the soil cores) and the PVC box was closed by a PVC box top to avoid evaporation. Capillary rise occurred for 48 hours. Soil cores were weighed thereafter and wet soils were oven-dried at 105°C for 26 hours, allowing estimation of bulk density (weight of 105°C dried soil/core volume ratio), capillary porosity (volumetric water content after capillary rise calculated as the difference between weight of the wet soil core after capillary rise and after drying at 105°C, normalised to the soil core volume) and field volumetric soil moisture (difference in weight

of the field-wet soil core and that of the 105°C dried core, normalised to the soil core volume).

After the capillary rise experiments, a set of wet undisturbed soil cores (water-filled capillary porosity) was submitted to controlled 40°C drying for 39 to 51 h. During this 40°C drying, regular (mostly each hour) measurements of both total soil volume and volumetric soil moisture were carried out. Total volumetric shrinkage of wet undisturbed soil cores (water-filled capillary porosity) was estimated at the end of the 40°C drying period.

Mean aggregate water-stability (3 replicates) was estimated for both the field-wet aggregates and their 40°C dried aggregate counterparts using a home-made sieving machine and a methodology as described by Bartoli et al. (1991). Samples of either 4 g of wet aggregates or 2 g of 40°C dried aggregates were added to 200 ml demineralised water in this sieving machine (nine brass sieves), each sieve (diameter 60 mm, mesh size 200 µm) being immersed 20 mm deep in 200 ml demineralised water. Oscillations were sinusoidal, with an amplitude of 2 cm and a frequency of 98 oscillations/min; the time of disaggregation in water was 6 h. The water-stable aggregates were expressed as a fraction of the 105°C dried soil, after correction of the real coarse sand fraction determined in triplicate on each sample.

The bulk wet soil samples were used for particle-size distribution analyses, as follows:

First, the amount of total organo-mineral clay was determined by Na cation-exchange resin, which is the recommended dispersant for strongly aggregated soils such as Oxisols and Andosols (Bartoli et al. 1991, Churchman et al. 1999). A specific methodology was designed for the reference COST 622 soils, as follows: 1.5 to 3 g of field wet soil (equivalent to 1 g of 105°C-dried soil) was added to 200 ml demineralised water (resistivity of 18 microSiemens) and the soil suspension was ultrasonicated (3 708 J g⁻¹ 105°C-dried soil using the North' method (1976) for ultrasonic energy calibration), and successively wet-sieved over 200 and 50 µm thereafter. The <50 µm soil suspension was added to 200 ml of Na Amberlite IR-120 resin (500 µm mesh, CEC of 2 eq l⁻¹ or of 250 mol kg⁻¹) and shaken for 16 hours in an end-over-end shaker at 40 rpm. The resin was collected by wet-sieving over 200 µm whereas the <50 µm soil suspension was transferred to a 1 l beaker and made up to a volume of one liter with demineralised water.

Second, the ISO standard soil dispersant sodium hexametaphosphate (HMP) was used as follows: ten g of field wet soil sample was added to 25 ml HMP solution (124 g l⁻¹) and 175 ml demineralised water and shaken

for 16 hours in an end-over-end shaker at 40 rpm. After sieving over 200 and 50 μm , the suspension was transferred to a 1 l beaker and made up to a volume of one liter with demineralised water.

Third, dispersion in demineralised water was used as a reference as follows: ten g of field wet soil sample was added to 200 ml demineralised water and shaken for 16 hours in an end-over-end shaker at 40 rpm. After sieving over 200 and 50 μm , the suspension was transferred to a 1 l beaker and made up to a volume of one liter with demineralised water.

At the end of each of these three treatments, amounts of coarse silt (20–50 μm), fine silt (2–20 μm) and clay (<2 μm) were determined using the Robinson pipette method. All the aggregate and particle-size fractions were expressed as fractions of 105°C dried soil. Proportions of clay obtained after HMP or water treatment were also calculated as fractions of total organo-mineral clay (ultrasonic and Na-resin sequential treatment, often called Na-resin treatment for simplification).

Finally, bulk soil samples were air-dried for Al, Si and Fe oxalate-extraction and analysis, pH-H₂O and pH-KCl N (1/2.5 soil/solution ratio) and elementary organic analysis by dry combustion of the ground <2 mm air-dried soil using a Carlo Erba 1500 auto-analyser. All the results were also expressed with respect to 105°C dried soil.

Results and discussion

Aggregate and particle-size distributions as a function of the dispersion treatment

Figure 1 shows aggregate and particle-size distributions determined after each of the three dispersant treatments (water, sodium hexametaphosphate, ultrasonic and Na-resin sequential treatment) for representative vitric soil or Andosol wet samples (A_h and B_w horizons). As a complement, Figure 2 shows how clay content varied as a function of both the dispersant treatment and the andic index $\text{Al}_0 + \frac{1}{2}\text{Fe}_0$.

All the soil suspensions were flocculated in water (Figures 1 and 2), being mainly composed of sandy and silty water-stable aggregates (Figure 1). In contrast, their soil suspension counterparts were relatively well dispersed after the Na-resin treatment (Figures 1 and 2). In the present study, the pH values of the soil-water suspensions varied from 4.3 to 6.9 whereas the range of the pH values of the soil suspensions was relatively narrow after the Na-resin treatment, from 5.8 to 7.0. Sodium hexametaphosphate (HMP) was also an efficient dispersant agent for the wet samples of the

vitric Andosols, so that similar aggregate and particle-size distributions were obtained after HMP and Na-resin treatment. By contrast, in the other wet Andosols samples, the HMP treatment disrupted only the sandy aggregates into fine silty aggregates, with low to very low clay dispersion (Figures 1 and 2). All the values of Na-resin clay content are included in the data base itself included in the accompanying CD of the present book (*physico-chemical data base.xls*).

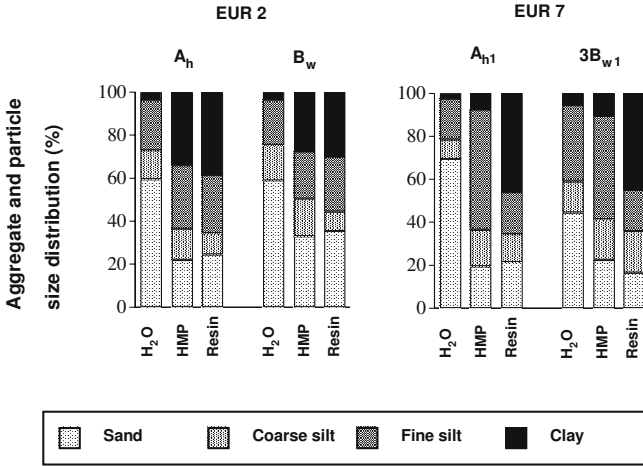


Figure 1. Aggregate and particle size distribution after dispersion by water (H₂O) or sodium hexametaphosphate (HMP) or by an ultrasonic and Na-resin sequential treatment (Resin) done on A_h and B_w horizon wet samples of two representative European vitric soil (Italy) and non-vitric Andosol (Iceland).

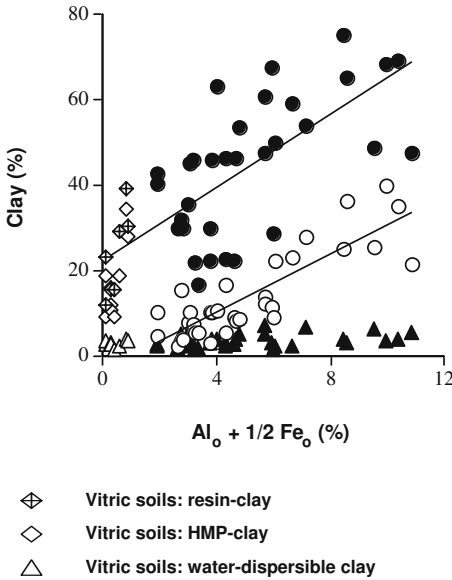


Figure 2. Relationships between amount of clay (dispersed, from wet soil samples, by Na-resin (resin), sodium hexametaphosphate (HMP), or water) and the andic index $Al_0 + 1/2 Fe_0$ for a range of European volcanic soil samples (8 vitric soil and 31 Andosol samples).

The very positive dispersant effect of the resin was already discussed by Bartoli et al. (1988, 1991) and by Churchmann et al. (1999), as follows. The maximum internal pressure due to air trapped in soil aggregates increases with soil wettability from hydrophobic soil to Na-resin hydrophilic soil. Na resin would be more efficient than Na salts for cation exchange, particularly for hydrated cations strongly hydrogen-bonded on the surfaces. The cation exchange process should also be rather stoichiometric with the Na-resin whereas the standardized HMP concentration would be too high, leading to larger solute concentration and flocculation of clay. However, the role of the resin is complex because three processes occur: cation exchange (with an increase of affinity from monovalent to trivalent cations), Donnan equilibrium, and resin swelling.

Total organo-mineral clay

Figure 2 shows that the Na-resin and HMP clay contents were very similar for the wet samples of vitric soils, but very different for the other wet Andosol samples, with a much better clay dispersion after the Na-resin treatment than after the HMP treatment.

Figure 2 also shows two positive but scattered linear relationships ($p < 0.001$) between the Na-resin clay content (all volcanic soil samples) or the HMP clay content (only the non vitric Andosol samples) and the andic index $Al_0 + \frac{1}{2}Fe_0$. This suggested that allophane, organo-aluminium associations and ferrihydrite are dispersed and part of the clay fractions. The more 'andic' the Andosol sample, the more statistically clayey it is. Most B_w horizons were then richer in total clay than the overlying horizons.

Na-resin clay content would therefore be as good a weathering and andic indicator, as the andic index $Al_0 + \frac{1}{2}Fe_0$. For example, the EUR06 Andosol samples from the Pico Island (Azores) were more andic and clayey than the EUR07 and 08 Andosol samples from Iceland (Figure 3a). The climate of Pico Island is rather warm (monthly temperature range from 9 to 20°C) and very wet (mean annual rainfall of 2500 mm), leading to an intense weathering of the volcanic ash. By contrast in Iceland, a cryic temperature regime (-8 to 9°C and many freeze-thaw cycles in winter, particularly for the EUR08 reference pedon with frost and snow cover for 6–9 months and 3–7 months, respectively) and relatively dry udic moisture regime (mean annual rainfall of 550 mm and 800 mm for the EUR07 and 08 reference pedons, respectively), lead to moderate amounts of allophane and ferrihydrite.

On the other hand, the fact that most of the EUR06 Andosol samples (Pico Island) were more clayey than the EUR05 Andosol samples (Faial

Island) (Figure 3a) should be attributed to (i) a larger mean annual rainfall in the Pico Island (2500 mm) than in the Faial Island (1600 mm) and (ii) older pyroclastic materials and longer soil development in Pico Island (10,000 to 50,000 years BP) than in Faial Island (1600 to 5500 years BP).

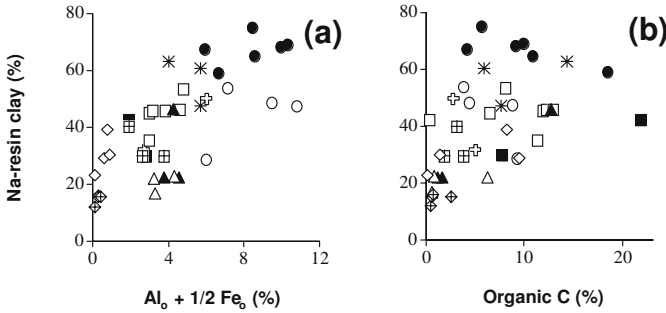


Figure 3. Relationship between Na-resin clay content and either the value of the andic index $Al_o + 1/2 Fe_o$ (a) or organic carbon content (b) for a range of European volcanic soil samples (8 vitric soil and 31 Andosol samples).

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	▣	EUR 8	■	EUR 9	⊕	EUR 10	*	EUR 17		

Finally, Na-resin clay is a fine organo-mineral soil fraction, as indirectly shown by the positive relationships between Na-resin clay content and either $Al_o + 1/2 Fe_o$ content (Figures 2 and 3a), allophane + ferrihydrite content (results not shown) or organic carbon content (Figure 3b, showing a positive but very scattered linear relationship). Previously, Nanzio et al. (1993) reported a similar relation between (allophanes + imogolite + ferrihydrite) content and organo-mineral clay content.

The Na-resin clay fractions of the representative EUR10 A_h and B_w samples (Tenerife Island, Canary) were analyzed in detail. They had 86 to 92% of total organic carbon, and 77 to 86% of total oxalate-extractable Al, Si and Fe (31.9 and 49.9% of total soil for the A_h and B_w samples, respectively). Most of the mineral, organic and organo-mineral colloids of the European reference volcanic soils should therefore be concentrated in the Na-resin clay fractions. Therefore, Na-resin clay content could be a useful indicator of weathering, organo-mineral interactions and soil development. However, further study on mineralogy and organic matter characteristics of the organo-clay fractions are needed to explain Figures 2 and 3.

Water-dispersible clay

Although clay was highly flocculated, it was possible to relate the proportion of organo-mineral clay dispersed by water to both soil organic matter and soil surface charges, as follows. The ratio Water-dispersible clay / Na resin clay decreased non-linearly as a function of organic carbon content ($p < 0.001$, shown on Figure 4) whereas it decreased linearly with increasing ΔpH ($p < 0.001$, see Figure 5).

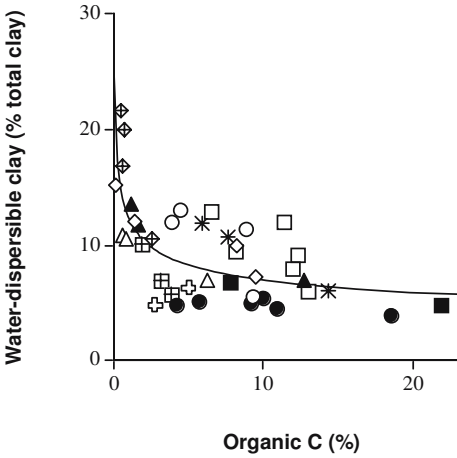


Figure 4. Relationship between water-dispersible clay / Na resin clay percentage ratio and organic carbon content for a range of European volcanic soil samples (8 vitric soil and 31 Andosol samples).

◊	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

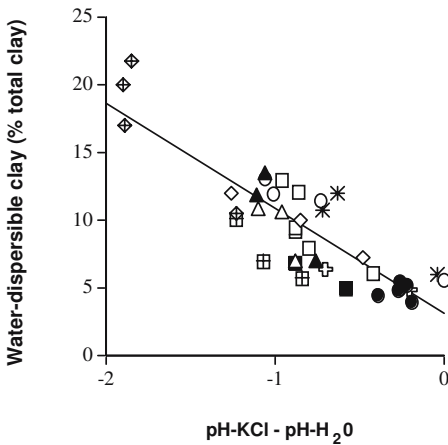


Figure 5. Relationship between water-dispersible clay / Na resin clay percentage ratio and ΔpH for a range of European volcanic soil samples (8 vitric soil and 31 Andosol samples).

◊	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

ΔpH ($\text{pH-KCl N} - \text{pH-H}_2\text{O}$) is related to negative and positive surface charges of soil constituents (e.g. Mekaru and Uehara 1972). The relationship between water-dispersible clay and ΔpH indicates that in the studied soils intra-aggregate bonding is mainly electrostatic, as was previously reported for Oxisols (e.g. Gillman 1974, Gillman and Bell 1976, Tessens 1984, Bartoli et al. 1992, Koutika et al. 1997).

As shown in Figure 5, most of the soil samples had a moderate net negative charge (ΔpH values from 0 to -1.2) and were relatively flocculated (only 6 to 16% of total clay was water-dispersible). The neutral to slightly negatively charged samples of EUR06 were most strongly flocculated whereas the negatively charged samples of the vitric soil EUR02 were most dispersed (Figure 4). Auxtero et al. (2004) recently characterized the surface charges of selected Andosols from Faial and Pico Islands (Azores). They found similar ΔpH values, mostly ranging from -0.2 to -0.9 (slightly to moderately negatively charged soil samples). The corresponding pH values of the point of zero net charge ranged from 4.2 to 5.7 and were positively correlated to both pH-KCl and allophane content.

Finally, we compared clay water-dispersability of the studied European Andosols to that of the also strongly aggregated Oxisols. Both Andosol and Oxisol B_w horizons are strongly flocculated in water whereas the studied Andosol A_h horizons are more flocculated (4–16% of total clay were water-dispersed, this study) than the Oxisol A_h horizons (often 20–40% of total clay were water-dispersible: Gillman and Bell 1976, Tessens 1984, Bartoli et al. 1992, Koutika et al. 1997). This discrepancy should be attributed to the stronger colloidal character of the allophanes, ferrihydrite and organo-aluminium associations of the Andosols (e.g., very large specific surface areas, partly due to the microporosity of allophanes), as compared to that of the rather rigid and coarser kaolinite, gibbsite and goethite of the Oxisols. Organo-mineral interactions should also be stronger and more complex in Andosols than in Oxisols, often leading to specific hydrophobic properties (Poulenard et al. 2004).

Soil structure and water retention

Figure 6 shows a significant ($p < 0.001$) but scattered power-law relationship between field soil moisture (weight %) and Na-resin clay content, with often larger soil moisture values (up to 250–280% for some Andosol samples particularly rich in organic and organo-aluminium colloids) than those measured in other soil types where soil moisture values mostly range from 5 to 60%.

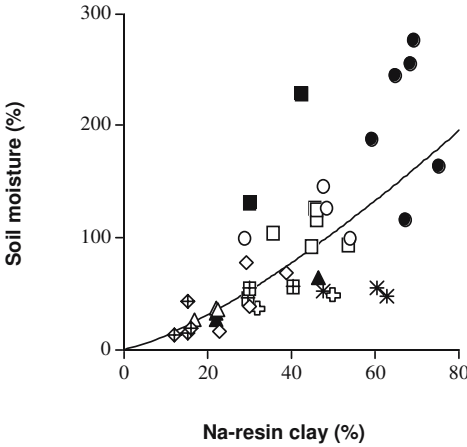


Figure 6. Relationship between proportion of field soil moisture (weight %) and organo-mineral clay content for a range of European volcanic soil samples (8 vitric soil and 31 Andosol samples).

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

Maeda and Soma (1985), Warkentin et al. (1988) and Nanzyo et al. (1993) clearly point out that, besides allophanes, organic colloids also influence bulk density and soil water retention. Mizota and van Reeuwijk (1989), Pinheiro et al. (2001) and Poulenard et al. (2003) have described organic matter-rich, non-allophanic Andosols (*Hydric Melanudands* according to ST 1999) characterized by 1500 kPa water contents close to or far exceeding 100%.

However, interpretation of these authors, as most soil scientists who studied volcanic soils, are constituent-based and not physical-based. We have to keep in mind the causal relation between soil constituents to soil structure and then to soil hydric properties. This is why field volumetric soil moisture (soil plots not reported) or capillary porosity (Figure 7) and Na-resin clay content show significant ($p < 0.001$) but scattered linear relationships.

The more clayey the soil, the larger its microporosity, and the more water it retains in its capillary porosity. This explains why most B_w horizons had higher water contents than the corresponding topsoils. However, water retention in the field is also controlled, in a complex way, by the various climatic, vegetative and pedoclimatic conditions occurring at the time of sampling. We will first focus on capillary and total porosity before coming back to field volumetric soil moisture.

The extremely large capillary porosity values of the studied volcanic soils (mostly from 0.6 to 0.8 $\text{cm}^3 \text{cm}^{-3}$, Figure 7) are similar to those of

Histosols but are much larger than those of other soil types, which range mostly from 0.1 to 0.4 cm³ cm⁻³.

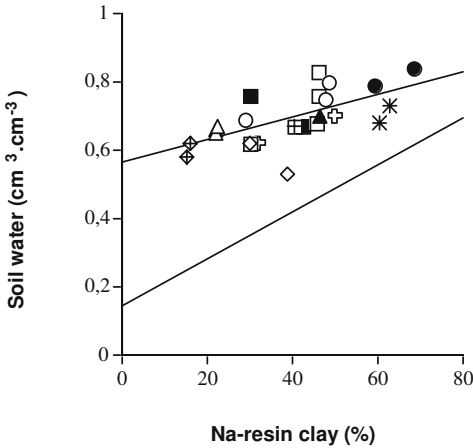


Figure 7. Relationships between capillary porosity (full line) or volumetric field soil moisture (dashed line without data plots) and organo-mineral clay content for a range of European volcanic soil samples (4 vitric soil and 20 Andosol A_n and B_w samples). Same symbols as those used in Figure 6.

This is mainly attributed to soil aggregation by the very reactive organo-mineral clay fraction which coated and bridged coarser particles, as shown indirectly by the capillary porosity *vs* organo-mineral clay relationship (Figure 7) and, directly, by soil micromorphology (Stoops and Gérard this book). Capillary porosity is also partly attributed to microporosity of pumice and ash, particularly for the vitric soils (as also described by Stoops and Gérard this book) and for a very small part, by the microporosity of allophane (quantified by nitrogen adsorption and use of the t-plot procedure allowing to estimate the volume and surface area of the micropores of diameters less than 1 nm, results not shown).

The question arises whether we can quantify the capillary porosity within the void network space. We can estimate total porosity from bulk density, ρ_b , and particle density, ρ_s (total porosity = $1 - \rho_b / \rho_s$). We measured bulk density and computed particle density from the linear relationship between particle density (measured by helium pycnometry) and organic carbon content which was recently obtained by Poulenard et al. (2003) on a wide range of allophanic and non-allophanic Andosols ($\rho_s = -0.004$ organic C + 2.678, $p < 0.001$).

First, the measured bulk density decreased as a function of Na-resin clay content (Figure 8, showing a significant, $p < 0.01$, but very scattered relationship).

Conversely but with a better physical meaning, a positive but scattered relationship between calculated total porosity and Na-resin clay content was identified (results not shown, also $p < 0.01$). Calculated total porosity

varied from 0.69 to 0.74 cm³ cm⁻³ for the vitric soil samples and from 0.72 to 0.87 cm³ cm⁻³ for the non-vitric Andosol samples. Similar high total porosity values of 0.7 to 0.85 cm³ cm⁻³ have been reported previously for Japanese Andosols (e.g. Nanzyo et al. (1993).

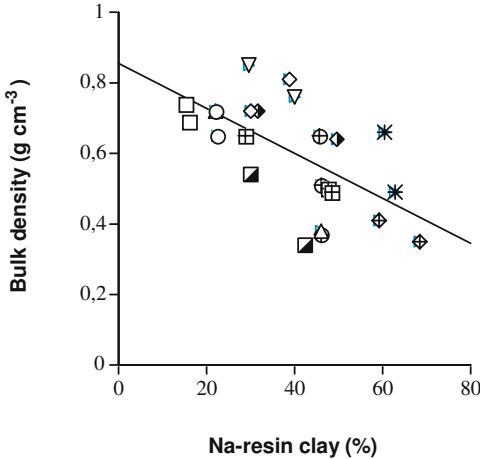


Figure 8. Relationship between bulk density and organo-mineral clay content for a range of European volcanic soil samples (4 vitric soil and 20 Andosol A_h and B_w samples).

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

The key result is that capillary porosity represents 87–97% of total porosity for most non-vitric Andosol samples, with a negligible macroporosity, but 75–85% of total porosity for the vitric soil samples (Figure 9). For most other soil types, capillary porosity represents only 40–70% of total porosity, leading to the well-known hierarchical and bimodal porosity (e.g. Brewer 1964).

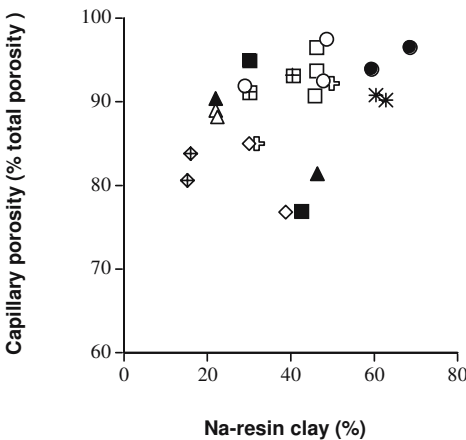


Figure 9. Relationship between proportion of total porosity that corresponds to capillary porosity and organo-mineral clay content for a range of European volcanic soil samples (4 vitric soil and 20 Andosol A_h and B_w samples). Same symbols as those used in Figure 8.

Let us now analyse again the results obtained on volumetric field soil moisture. Figure 10 shows that the H1 horizon sampled from the EUR09 *Umbri-Vitric Andosol (Pachic and Orthidystric)* (WRB 2001) was the only soil sample where capillary porosity was saturated. This validates field observation on this hydromorphic peaty soil horizon.

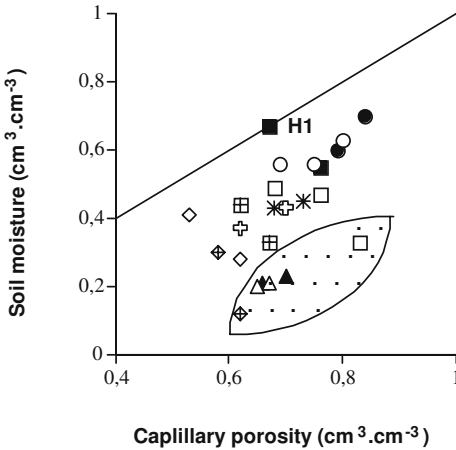


Figure 10. Relationships between volumetric field soil moisture and capillary porosity for a range of European volcanic soil samples (4 vitric soil and 20 Andosol A_n and B_w samples). Three categories of soil samples have been distinguished: the EUR09 H1 Andosol sample, with a data plot located on the saturation line (saturation of capillary porosity), the relatively dry soil samples with data plots located within the closed dotted area, and the relatively wet soil samples in between.

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

In most samples, 45–83% of the capillary porosity was filled by water, while in EUR05 and EUR06 samples the capillary porosity was filled for 75–83%. In the vitric soil samples these values were much lower and only amounted to 45–72% (Figure 10). This shows the high capacity of volcanic soils to retain water (particularly under the wet oceanic climate occurring in the Azores Islands) within their very large capillary porosity. By contrast, only a few samples were relatively dry at the time of sampling (Italian EUR03 and EUR04 Andosol samples, EUR07 topsoil sample and EUR01 vitric soil B_w horizon: Figure 10). For most of the studied soil samples, except the driest ones, the values of volumetric soil moisture from the field were also similar to those estimated from drainage at a suction value of 33 kPa as reported by Basile et al. in the next chapter of the present Book Section (results not shown).

A final question arises about the similarity between capillary porosity properly estimated by capillary rise (present study) and that estimated at a suction value of 33 kPa (see, e.g. the review of Nanzyo et al. 1993). Volumetric soil water of volcanic soils is often subdivided into three categories:

hygroscopic water (water content values at suction values more than 1500 kPa mainly referred to hygroscopic forces, micropores), capillary water available to plants (water content values at suction values from 1500 to 33 kPa mainly referred to capillary forces, mesopores) and gravitational water (water content values at suction values from 33 to 0 kPa mainly referred to gravitational forces, macropores). Nanzyo et al. (1993) reported water content values of nearly 30–35 vol%, 25 vol% and 30–10 vol% for hygroscopic, capillary and gravitational water, respectively, in the A_h and B_w horizons of a representative Andosol (*Alic Melanudand* according to ST 1989). This leads to 33 kPa capillary porosity values of nearly 0.55 to 0.6 $\text{cm}^3 \text{cm}^{-3}$ which appear to be underestimates when compared to those measured by capillary rise on wet undisturbed soil cores 0.6 to 0.8 $\text{cm}^3 \text{cm}^{-3}$ (this study).

It is therefore strongly recommended to estimate the capillary porosity by capillary rise on wet undisturbed soil cores rather than by measurement at a suction value of 33 kPa. The key result is that capillary porosity represents 87–97% of total porosity. This is exceptionally high for soils and has key consequences for physical properties of these volcanic soils. In a complex way, capillary porosity regulates water retention and also all processes in which capillary forces are involved, such as is shrinkage of fine-grained soils on drying.

Shrinkage

Despite previous work, shrinkage of Andosols has not been fully explored. The main results of the 40°C drying kinetics were as follows.

First, the studied soil samples were subdivided into two categories: those which dried without (or very moderate) shrinkage (e.g., EUR01 and 02 vitric soil samples from Italy, EUR08 Andosol samples from Iceland) and those which shrank, (often intensively, e.g., EUR05 and 06 Andosol samples from the Azores Islands) when submitted to controlled drying. Above a specific Na-resin clay content (20%) threshold value, total shrinkage increased as a function of either Na-resin clay content ($p < 0.001$: Figure 11). The maximum shrinkage of 60–80% is exceptional for soils. The more clayey a volcanic soil, the more microporous it is and the more it shrinks upon drying. This is why the B_w horizons shrank more than the corresponding topsoils (Figure 12).

The relation between total shrinkage and initial capillary porosity ($p < 0.001$: Figure 13) is physical-based. A similar relation between total shrinkage (40–75%) and initial void ratio was reported by Poulenard et al. (2002) for a range of Andosols from Central America, Japan and West Indies. The relation between total shrinkage and Na-resin clay ($p < 0.001$:

Figure 11), however is an indirect relation, because soil aggregation is controlled by Na-resin clay (e.g. Figure 7).

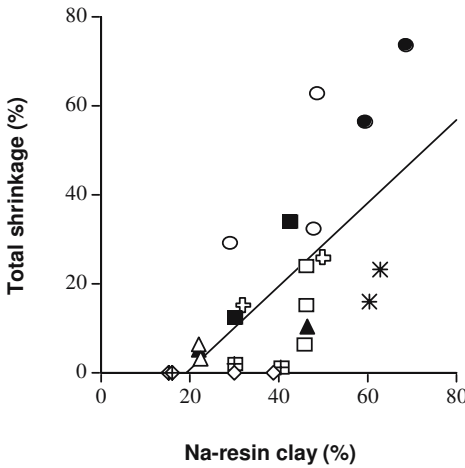


Figure 11. Relationship between total volumetric shrinkage at 40°C and Na-resin clay content for a range of European volcanic soil samples (4 vitric soil and 20 Andosol A_h and B_w samples).

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

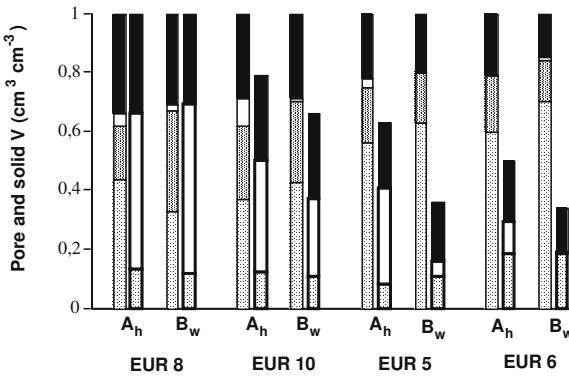


Figure 12. Void and solid volumes after water-filling of capillary porosity (initial state) and at the end of the controlled 40°C drying (final state) for a range of European Andosol A_h and B_w samples. Towards the right the samples show both larger clay content and stronger shrinkage. Capillary porosity - fw = field air-filled capillary porosity.

▨	field soil water (fw)	▩	capillary porosity - fw	□	air (macroporosity)	■	solid
▧	final soil water	▪	final air	■	final solid		

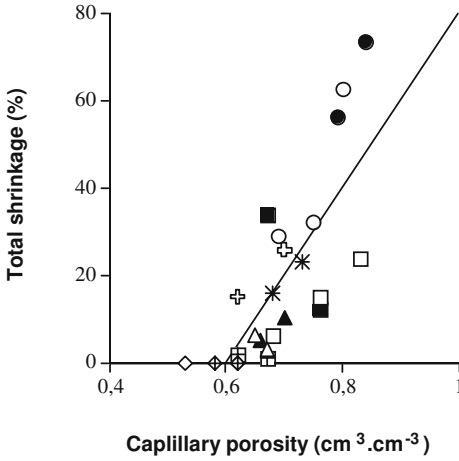


Figure 13. Relationship between total volumetric shrinkage at 40°C and capillary porosity for a range of European volcanic soil samples (4 vitric and 20 Andosol A_h and B_w samples).

◆	EUR 1	◇	EUR 2	△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6
□	EUR 7	⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

Figure 14 shows a typical shrinkage curve of a strongly shrinking sample. The drying starts at upper right. The first stage is a short loss of water without change in total volume. (the structural shrinkage domain of the Three Straight Lines Model described, e.g., by Poulenard et al., 2002). This stage is followed by an intense combined water loss and shrinkage process with data points often located on the saturation line (Figure 14). This emphasizes the exceptional predominance of capillary porosity within the total solid and void volume of the studied samples (Figure 12), capillary porosity controlling such intense shrinkage. As a matter of fact, shrinkage of fine-grained and highly microporous Andosols on drying is caused by movement of microaggregates as a result of pore-water tension developed by capillary menisci.

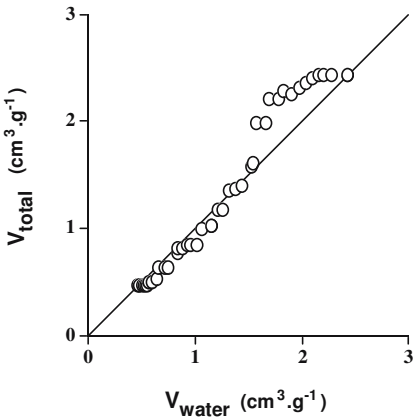


Figure 14. Shrinkage as change in total volume versus soil water volume for the undisturbed EUR06 2B_w,b core (capillary porosity preliminarily filled by water by capillary rise for 48 h) during its controlled 40°C drying.

Many changes in physical properties are associated with this change of void volume. For example, the increase in water-stable aggregates upon drying was proportional ($p < 0.001$) to volumetric shrinkage (Figure 15).

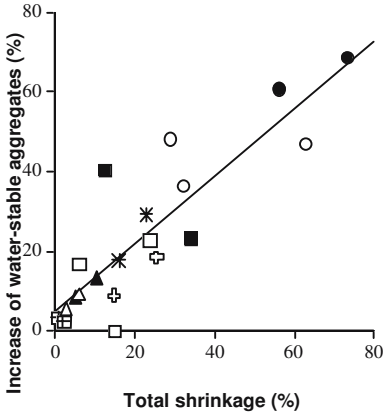


Figure 15. Relationships between the increase of mean proportion of water-stable aggregates occurring during drying and total volumetric shrinkage for a range of European Andosol A_h and B_w samples ($n=20$).

△	EUR 3	▲	EUR 4	○	EUR 5	●	EUR 6	□	EUR 7
⊞	EUR 8	■	EUR 9	⊕	EUR 10	✱	EUR 17		

The more shrunken the soil, the more water-stable are the $>200 \mu\text{m}$ aggregates. Such irreversible mechanical changes caused by drying have been previously reported for Japanese Andosols (e.g. Kubota 1972). The exceptional increase in the proportion of water-stable aggregates of 40–70% (of 105°C dried soil) estimated for the most clayey Andosol samples was attributed to the strong reduction of porosity occurring upon drying. This reduction in porosity is itself related to high values of initial capillary porosity (Figure 13). Further, the proportion of water-stable aggregates of the 40°C -dried soil was negatively related to its initial porosity, whereas this relationship was only a tendency for the wet samples (results not shown). We assume that capillary forces related to menisci of the residual water located between the solid phases are very high.

Conclusion

The main conclusions from the analyses carried out on a range of European volcanic soil samples can be summarised as follows:

Ultrasonic and Na resin sequential treatment, a recommended methodology for clay dispersion

The Na-resin method without destruction of organic matter or/and poorly-ordered minerals was specifically adapted for Andosols for obtaining most of the organo-mineral clay fractions. This relatively new methodology is recommended for characterizing particle-size distribution in Andosols. This opens new perspectives in this area, because many Andosols fail to disperse completely with sodium hexametaphosphate, as we clearly reported in this study. Na-resin clay content is a useful combined indicator of weathering, organo-mineral interactions and soil development.

Water-dispersible clay

Even with highly flocculated clay, a negative relation was found between the proportion of organo-mineral clay dispersed by water and soil surface charge estimated by ΔpH ($\text{pH-KCl N} - \text{pH-H}_2\text{O}$). The studied Andosol A_h horizons were more flocculated (4–16% of total clay were water-dispersible) than Oxisol A_h horizons previously studied elsewhere (often 20–40% of total clay were water-dispersible). This difference should be attributed to the much more colloidal character of the allophanes, ferrihydrite and organo-aluminium associations occurring in Andosols, as compared to that of the rather rigid and coarser kaolinite, gibbsite and goethite occurring in the Oxisols. Organo-mineral interactions should also be stronger and more complex in the Andosols than in the Oxisols.

Organo-mineral clay and water retention

The more clayey the soil, the more microporous it is and the more water it retains in its capillary pores. This explains why most B_w horizons were wetter than the related topsoils.

The very large capillary porosity of the studied soils (mostly from 0.6 to 0.8 $\text{cm}^3 \text{cm}^{-3}$) are similar to those of Histosols but are much more larger than those of other soil types (mostly from 0.1 to 0.4 $\text{cm}^3 \text{cm}^{-3}$). This is mainly attributed to soil aggregation by the very reactive organo-mineral clay fraction which coats and bridges coarser particles leading to frequent granular microstructures for the non-vitric Andosols (Stoops and Gérard this book). Capillary porosity is partly attributed to pumice and ash microporosity, particularly for the vitric soils and, for a very small part, to the microporosity of allophane.

Capillary porosity represents 87–97% of total porosity for most Andosol samples – with a rather negligible macroporosity – but 75–85% of total porosity for the vitric soil samples. The high capacity of volcanic soils to retain water is clearly related to their very large capillary porosity. For most of the other soil types, capillary porosity represents only 40–70% of total porosity, leading to the well-known hierarchical and bimodal porosity.

Capillary porosity determined by capillary rise: a recommended methodology in the study of soil structure and water retention

It is recommended to estimate the physical-based capillary porosity by capillary rise on wet undisturbed soil cores rather than by the classical estimate at a suction value of 33 kPa (underestimation of capillary porosity).

Drainage and shrinkage on drying

The studied soil samples were subdivided into two categories: those which drained without (or very moderate) shrinkage and those which shrank, often intensively, when submitted to controlled 40°C drying. Moreover, above a specific Na-resin clay content (20%) or capillary porosity ($0.6 \text{ cm}^3 \text{ cm}^{-3}$) threshold value, total shrinkage increased as a function of either Na-resin clay content or initial capillary porosity. The maximum shrinkage values of 60–80% are exceptional for soils. Thus, the more clayey a volcanic soil, the more microporous it is and the more it shrinks upon pronounced drying. This is why B_w horizons shrank more than topsoils.

For the most shrunken Andosol samples, the shrinkage curve typically began by a very short-time predominance of water loss, followed by an intense combined drying and shrinkage process with data points often located on the saturation line. This emphasizes the exceptional predominance of capillary porosity within the total solid and void volume of the studied horizons, capillary porosity controlling such intense shrinkage caused by movements of microaggregates as a result of pore-water tension developed by capillary menisci.

An increase in the proportion of water-stable aggregates occurred when the wet soils were 40°C dried. This was positively correlated to total volumetric shrinkage. The exceptional increase in the proportion of water-stable aggregates of 40–70% (of 105°C dried soil) estimated for the most clayey Andosol samples from the Azores Islands was attributed to the strong reduction of porosity occurring from the wet to the 40°C dried state, itself related to exceptional values of initial capillary porosity.

General conclusion

To summarise, the sampling and methods used to characterise soil texture, soil structure and physical properties on a range of European volcanic soils enabled a much wider range of scales to be considered than is often the case. In particular, we related amounts of organo-mineral clay to physical soil properties such as bulk density, capillary porosity obtained by capillary rise and total volumetric shrinkage of wet undisturbed soil cores (with water-filled capillary porosity) at the end of controlled 40°C drying kinetics. We therefore validated that mineral, organic and organo-mineral colloidal soil constituents interact between them to give organo-mineral clay fractions (soil micro-property) and that, in turn, organo-mineral clay coats and bridges coarser soil particles (soil aggregation) leading to soil structural features which vary as a function of clay content and control soil macro-properties (capillary porosity, water retention, shrinkage, irreversible structural and mechanical changes upon drying).

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