A self-consistent quantification of contributions to differential-TGA results of Volcanic soils samples

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Introduction

Volcanic soils have very peculiar water-binding properties. Adsorbed water can reach up to 400% of dry mass of the mineral fraction in some allophane-rich soils, but the pore-size distribution of the soils may still cause a very limited supply of plant-available moisture. Volcanic soils also have a relatively high amount of structural water, in various crystalline and amorphous components. Although water binding properties in the range of pF=0 to pF=4.2 and their effect on aggregation have been studied extensively, very little is known about binding of water and structural water content of different amorphous phases. The aim of this work is to analyze not only the amounts of Si,Al,Fe-oxides that are extracted by acid-oxalate from the amorphous fraction but also the corresponding extracted amounts of structural water by a sequence of thermogravimetric analyses (differential TGA). The sum of extracted oxides and structural water quantifes the total amount of amorphous phases extracted.

The results were used to analyze to what extent the observed variations characterize the differences in water binding of different volcanic soils. A tentative model which splits the results into contributions of ten different soil constituents gave a good description of measured water binding. The model may be useful for prediction of water binding.

Materials and methods

Soil profiles were sampled in two different climatic zones, three on Sicily (Italy) and three on Terceira (Azores Islands, Portugal) in order to include different soils. The three profiles on Sicily Island have developed in lava flows with tephra on the western slope of Mount Etna, at different altitudes and under different type of vegetation (*Fagus sylvatica* at 1623 m, *Quercus ilex* at 1440 m, and *Quercus pubescens* at 1200 m a.s.l.). Annual precipitation and temperature are estimated to be 1060 mm and 14 °C, respectively. The three profiles on Terceira Island were also selected at different altitudes and under different type of vegetation (Queimada at about 450 m, Veredas at about 300 m, and Vinha Brava at about 150 m a.s.l.). Correspondingly, yearly precipitation values are estimated to be 2000 mm, 1600 mm, and 1300 mm.

We produced a 32x34 data matrix for 28 samples plus 4 duplicates, based on fine-earth sample mass at air-dry, sample mass at 105 °C-dry before and after H_2O_2-oxidation and also after consecutive double acid-oxalate extraction and washing the residue on a glass-fiber filter, LOI in three steps (105-200 °C, 200-400 °C, and 400-950 °C) for the same three sequential sample-states, C and N analysis (using Element Analyzer) for the first two sequential sample-states, and AAS-analysis of Si_o, Al_o, and Fe_o. Further, undisturbed core samples were taken from a selection of sampled horizons, and used for measuring bulk density and water adsorption at field-moist conditions and after equilibration at pF0 and pF2. The reference state for reporting all results is 105 °C-dry.

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Results and conclusion

TGA results were plotted as three curves per sample that show the mass-loss steps of each sample-state from air-dry to 950 °C-ignited and also the mass loss at 105 °C upon oxidation and upon extraction . The relative positions of the three curves are known at 950 °C: same level before and after oxidation, and lower level after extraction because of extraction of the summed oxide-masses known from Si_o, Al_o, and Fe_o. The different segments of the three curves show mass losses that are generally seen as combinations of the mass losses of chemical components that decompose in specific temperature ranges.

Approximately, the following contributions may play a role in our samples:
from air-dry to 105°C-dry, mass loss from desorption of internal-surface-bound water (in micropores, interlayers, organic matter (OM), and aggregates)

- from 105 to 200°C, mass loss mainly from loss of structural water of amorphous sesquioxyhydroxides and alumino-silicates and from partial decomposition of OM
- from 300 to 400°C, from OM and ferrihydrite; in addition gibbsite looses structural water above 300°C
- from 400 to 950°C, mass loss from OM and crystalline phyllosilicates

Overlap of the contributions of these chemical and mineralogical components makes it difficult to distinguish or to quantify them. Factor analysis combined with direct optimization (Meijer and Buurman, 1997) is a powerful statistical method to decompose the TGA curves and other soil properties in terms of a mixture of soil constituents, which are tentative entities which model the (micro)aggregates that build up these soils. We derived the properties of ten of such soil constituents that describe 93% of the total variance of all available data. This soil model enables prediction of bulk density and water adsorption from at least ten other experimental properties (with maximal uncertainty) or from all other experimental properties (with minimal uncertainty). Figure 1 is a simulation of the last option in which modeled values for specific bulk volume VOL (inverse of dry bulk density BD) and water adsorption at saturation (Ads_{sat}), at field-capacity pF2 (ADS_{fc}), and at field-moisture conditions (ADS_{fm}), have been calculated from all other properties within the *same* data set.

We conclude that a relation between water binding and other properties has been established via the soil constituents mixing-model. Of course, this relation must be evaluated for *other* data sets.
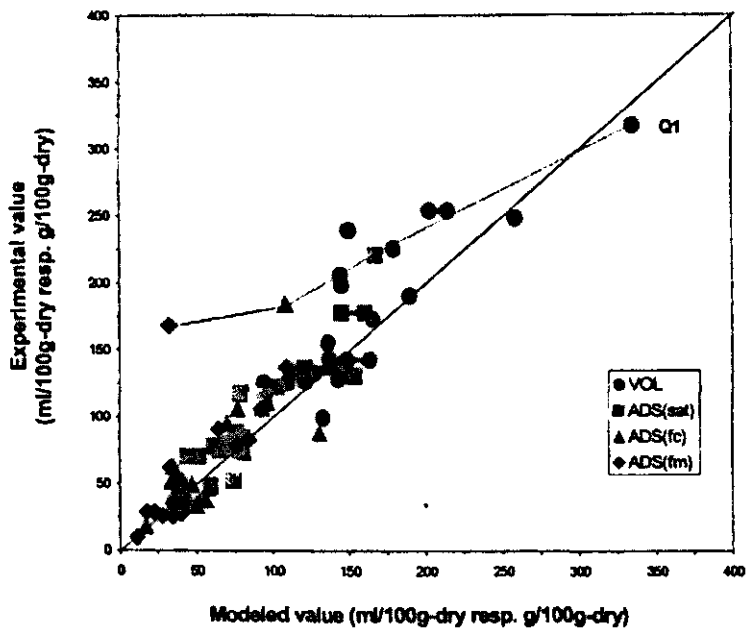
Figure 1 Experimental values of 100/BD and water adsorption at pF0, pF2, and field-moist conditions, versus values calculated from other measured properties (differential-TGA from air-dry to 950 °C, extracted Si_o, Al_o, and Fe_o, gravimetric mass losses upon oxidation and extraction, C and N contents before and after oxidation, etc.).

Meijer, E.L., Buurman, P., 1997. Factor analysis and direct optimization of the amounts and properties of volcanic soil constituents. Geoderma 80, 129-151.

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