



Water composition in the unsaturated zone at Sete Cidades central volcano (S. Miguel, Azores, Portugal)

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A field study was developed at Sete Cidades, the westernmost of the three active composite volcanoes that dominate the geology of São Miguel, the largest of the nine islands from the Azores archipelago. Research methodology comprehends the characterization of soil-water composition at several depths, sampled by means of ceramic suction cups. Previously to their installation, cups were all submitted to several stages of washing, first in the laboratory with supra pure water, until aliquot conductivity stabilizes, and after in the field.

This study was planned in order to study the water pollution due to agriculture, one of the main economic activities in the Azores, as shown by the gross value added to regional product. The negative effects of groundwater pollution due to agriculture have been reported in the majority of the nine islands, reflected by high contents of nitrogen species, derived from the inadequate use of synthetic and organic fertilizers, as well as from animal wastes leaching, or also by microbiology parameters. The relation between water pollution and agriculture results in some cases in the failure to comply regarding EU and national water quality regulations, through quality deterioration and compromising groundwater as strategic natural resource in the Azores.

The studied area corresponds to Sete Cidades volcano caldera, a 5 km-diameter circular shaped depression, contoured by steep walls from 30 m high up to 400 m. In order to characterize unsaturated water composition in the caldera floor, five pasture locations were selected and monitored, as well as one site with the same physical conditions, but without agricultural activity. From the 5 pasture lands we discuss further results obtained in the so-called Pavão I (Pa I), which corresponds to the most extensive data set. On this site, 6 suction cups were installed, at depths 0.35 m, 0.7 m, 1 m, 1.3 m, 1.6 m and 1.9 m. In the site without agricultural activity, in the vicinity of Sete Cidades village, two cups were there installed, at 0.25 and 0.5 m depths.

Unsaturated water at the Sete Cidades village site present a pH range between 5.45 and 8.44, without major variations been observed in depth. Electrical conductivity ranges from 40 to 495 $\mu\text{S}/\text{cm}$, and the maximum value at 0.25 m depth (495 $\mu\text{S}/\text{cm}$; median=90.5 $\mu\text{S}/\text{cm}$) is higher than the measured at 0.50 m depth (292 $\mu\text{S}/\text{cm}$; median=78 $\mu\text{S}/\text{cm}$). Values in summer period are generally higher, suggesting the effect of salts leaching after precipitation episodes. Instead, during winter leaching occurs all along the period. Water types are mainly Cl-Na and Cl content is generally higher at 0.25 m depth, showing the influence of sea salts deposition by precipitation. The SiO_2 content shows the contribution of hydrolysis (median=29.1 mg/L at 0.25 m; median=43.01 mg/L at 0.50 m), comparable to median value estimated for groundwater discharging from perched-water bodies.

Waters sampled at cups in the Pa I site are mainly from the HCO_3 to $\text{HCO}_3\text{-Cl}$ types in the anionic field and with a Ca-Mg trend for cations. Cl and HCO_3 content is higher at cups near the surface, showing the effects of the sea salts deposition and CO_2 dissolution at the upper layers. The in-depth decreasing trend of pH, from a median value of 8.25 at 0.35 m to median values between 6.99 and 7.15, from the 0.70 m depth to the water table, where median value is equal to 6.88, suggests acid neutralization by means of silicate weathering, which also explains the high SiO_2 content. Seasonal effect of salt washing by precipitation episodes during the dryer period is also shown.

From the results is possible to characterize the evolution of soil water, with a shift from a Mg-Ca cationic composition to Na-dominated waters, which is suggested to be influenced by cation exchange at the more superficial suction cups.

Comparing NO_3 contents from the pasture and the village sites is possible to show a marked difference, due to several applications of inorganic fertilizers, as well as the leaching of animal wastes. The median values in the village site at 0.25 m and 0.50 m depth are respectively 1.15 mg/L and 1.40 mg/L. In the Pa I pasture land NO_3 content ranges between 1.95 and 87.67 mg/L, and at the suction cup installed at 1.9 m depth median value is equal to 39.4 mg/L.