

ANNEX 2 (doi: 10.4401/ag-6760)

TRACE ELEMENTS MOBILITY IN SOILS FROM THE HYDROTHERMAL AREA OF NISYROS (GREECE).

Daskalopoulou, K., et al.

A.1. ANALYTICAL TECHNIQUES

All soil samples were air dried, thoroughly mixed and split into subsamples for analysis. Particular care was taken using a Riffle-type sample splitter to ensure that representative subsamples were obtained. All analyses were made after sieving the soil samples through a 2-mm sieve and, except for pH determination, ground with an agate mortar.

XRD analysis was carried out for all soil samples with the use of XD Diffractometer Bucker (Siemens) D5005, fully equipped with the software Diffract^{plus} of Bucker (Siemens). pH values were measured using a specific combination electrode on soil suspensions made with deionized water with a soil/solution weight ratio of 1/2.5 (Thomas, 1996).

Samples were treated for chemical determinations, using HNO₃ + HCl (closed microwave digestion) in order to determine the pseudo-total composition and with ultrapure water (leaching extraction) to determinate the soluble fraction. The first case, about 100 mg (precision ±0.1 mg) of the sample dried at 40 °C overnight was dissolved in a Teflon vessel with 4 ml HNO₃ (Merck Suprapur), 2 ml HCl (Panreac Suprapur) and 9 ml milliQ water using a microwave oven. After cooling down, the solution was filtered (0.45 µm) and diluted with milliQ water to 50 ml.

The reproducibility of the chemical analysis was verified by using repetition of several random samples. For most of the elements the reproducibility was in the order of 2-5 %, except for Be, Cr, Ni, Zn about 10%. The reliability of results was checked analysing four certified references materials (CRM) and quality control was assessed by comparing our results with the certified values. The recovery values,

that are a measure of the difference in percentage between measured and certified values for each element, for most of the elements were in the range between 80 and 120 %. Several replicates of the CRM and random samples confirmed a good reproducibility of analytical procedures (microwave digestion and chemical analysis) between about 5 to 15 % difference, depending on the element.

A second oven-dried sample aliquot was leached with milliQ water with a sample/water weight ratio of about 1/50 for 4 hours with constant stirring. The solution was subsequently centrifuged and filtered through 0.45 µm filter. Method blanks and duplicate samples were analysed too but certified standard was available for such kind of treatment.

Method blank values were subtracted from the raw concentrations of all samples.

All the solutions were analysed for major and trace element contents by inductively plasma spectrometry (ICP-MS and ICP-OES).

Trace elements (Al, As, B, Be, Bi, Ba, Cd, Co, Cr, Cs, Cu, Fe, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Te, Th, Ti, Tl, U, V, Y and Zn) were analyzed by ICP-MS using an Agilent 7500ce instrument. The instrument was equipped with a standard peristaltic pump, a Micro Mist concentric nebulizer, a Peltier-cooled spray chamber, the Plasma Forward Power, the Shield Torch System, and a Collision/Reaction Cell system. An autosampler (ASX 520, Cetac Technologies) was employed to introduce the samples into the plasma of the ICP-MS. Introduction was done with a Micro Mist concentric nebulizer and Scott-type quartz glass spray chamber. Helium was used as the collision gas for As, Co, Cr, Cu, Fe, Mo, Ni, Ti and Zn analyses while Hydrogen was used as a reaction gas only for Se analysis. No cell gas was used for the other elements. The instrumental setting were optimized to minimize both oxide levels and double charges (CeO⁺/Ce⁺ ratio < 1.5% and Ce⁺⁺/Ce⁺ ratio <3%).

Calibration solutions of all investigated elements were prepared daily by appropriate dilution of 100 mg l⁻¹ and 1000 mg l⁻¹ stock standard solutions (Merck) with 0.14 mol l⁻¹ high-purity nitric acid. The accuracy of the method was checked analysing certified reference materials of natural waters (Nist 1643e, Environment Canada TM-24.3 and TM-61.2, Spectrapure Standards SW1 and SW2) at regular intervals during sample analysis. The experimental concentrations determined in this study agreed well with these certified values (within ±5%). Matrix induced signal suppressions and instrumental drift were corrected by internal standardization. Indium was used for elements up to mass 138 (Ba¹³⁸), and rhenium was used for heavier elements. Major elements (Al, Ca, Fe, K, Mg, Na, S and Si) were measured with ICP-OES (Jobin Yvon Ultima2).

REFERENCES

[Thomas, G.W., 1996] Thomas, G.W. (1996). Soil pH and soil acidity. In: Methods of soil analysis – Part 3 Chemical methods (Sparks D.L. ed.). Soil Science Society of America Book Series n. 5, 475-490.