



Distribution of water-soluble inorganic ions in the soils of Cyprus



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ABSTRACT

The water-soluble anion content of soils reflects variable input of geogenic and anthropogenic influences, and is an important indicator of soil fertility, the existence or risk of salinization and effects of other pollutants. A rapid ion chromatography method has been used to determine the concentration of water-soluble F^- , Cl^- , NO_3^- and SO_4^{2-} on a suite of 3771 top soil samples collected as part of the geochemical atlas of Cyprus project. Excluding areas with salt flats and beach deposits, the average soil concentrations in Cyprus are 193 mg/kg for Cl^- , 17 mg/kg for F^- , 67 mg/kg for NO_3^- and 866 mg/kg for SO_4^{2-} . Parent lithology (especially sedimentary environment) and the effects of seawater are the dominant controls on F^- and Cl^- , whereas SO_4^{2-} and NO_3^- display a mix of geogenic and anthropogenic influences (including the effects of agriculture and mining of the basalt-hosted sulphide deposits). They display distinct fractal population characteristics that can be related to different sources of anions.

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1. Introduction

Analysis of the water-soluble inorganic ion concentrations in soils is important in both environmental management and the assessment of the suitability of areas for various agricultural activities (Jackson, 2000). Some of the more critical threats to soils, such as salinisation and desertification, are closely linked to increased concentrations of inorganic ions and related salts (Soil Atlas of Europe, 2005). Although salinisation primarily originates from the weathering of minerals or interaction of groundwater with palaeo-salt deposits, there can also be anthropogenic sources such as irrigation, municipal runoff and fertiliser application (Bloem et al., 2008).

Geochemical atlases, such as the GEMAS mapping of agricultural soils in Europe (De Vivo et al., 2013), provide a reference to measure spatial changes in the distribution of chemical species in the natural environment, assist in determining factors that control regional geochemical variations, and provide a basis for setting environmental targets and policies in different areas (Barth et al., 2009; Darnley et al., 1995; Reimann and Garrett, 2005; Salminen et al., 2005). The high sampling density soil geochemical atlas of Cyprus (Cohen et al., 2011) provides an opportunity to examine the effects of variation in geology, land use and other environmental factors on inorganic ions at the regional scale.

The island of Cyprus lies in the north-eastern Mediterranean Sea and covers an area of 9251 km². The geology of Cyprus (Fig. 1) may be divided into a number of distinct terranes, including the mafic-ultramafic Troodos ophiolite complex (TOC) in the centre of the island and the

carbonate-dominated circum-Troodos sedimentary sequence (CTSS). There are a series of Cyprus-type sulphide deposits in the basalts with extensive historical mining activity. The soil characteristics of Cyprus reflect the terrane. On the ridges and peaks of Troodos, up to 1 m of Fe-rich, organic-rich A and residual B horizon soils overlie a C horizon. The carbonate-rich CTSS units that flank Troodos produce massive chalky soils (calcisols) on hill slopes and terra rossa (chromic luvisols) over exposed limestones in areas with flat topography (Hadjiparaskevas, 2005). In coastal areas there are thick colluvium and alluvium deposits and saline lake deposits on the Akrotiri Peninsula and near Larnaca. Cyprus has a typical Mediterranean climate, with hot and dry summers from mid-May to mid-September and rainy winters from mid-November to mid-March.

Land use in Cyprus can be subdivided into the following major classifications:

- (i) Undeveloped forests that cover much of central and north-western Troodos Massif,
- (ii) Scrubland (garique–maquis) and degraded land that occupies much of eastern Troodos and the southern Troodos flanks as far as the coast (excluding parts of the Polis Valley and coastal fringe around Pafos and Lemesos) with some valleys heavily terraced,
- (iii) Cropping areas that are mainly found in the eastern end of the island between Kokkinochoria and the edge of the Troodos Mountains. The principal crop is wheat, followed by olives, vineyards and citrus fruits. There is intense farming with irrigation and use of fertilisers in areas such as the Kokkinochoria, west of Lemesos on the Akrotiri Peninsula east of Paphos and in the valley south from Polis. Historically, most of the irrigation water was obtained from ground water resources. Groundwater

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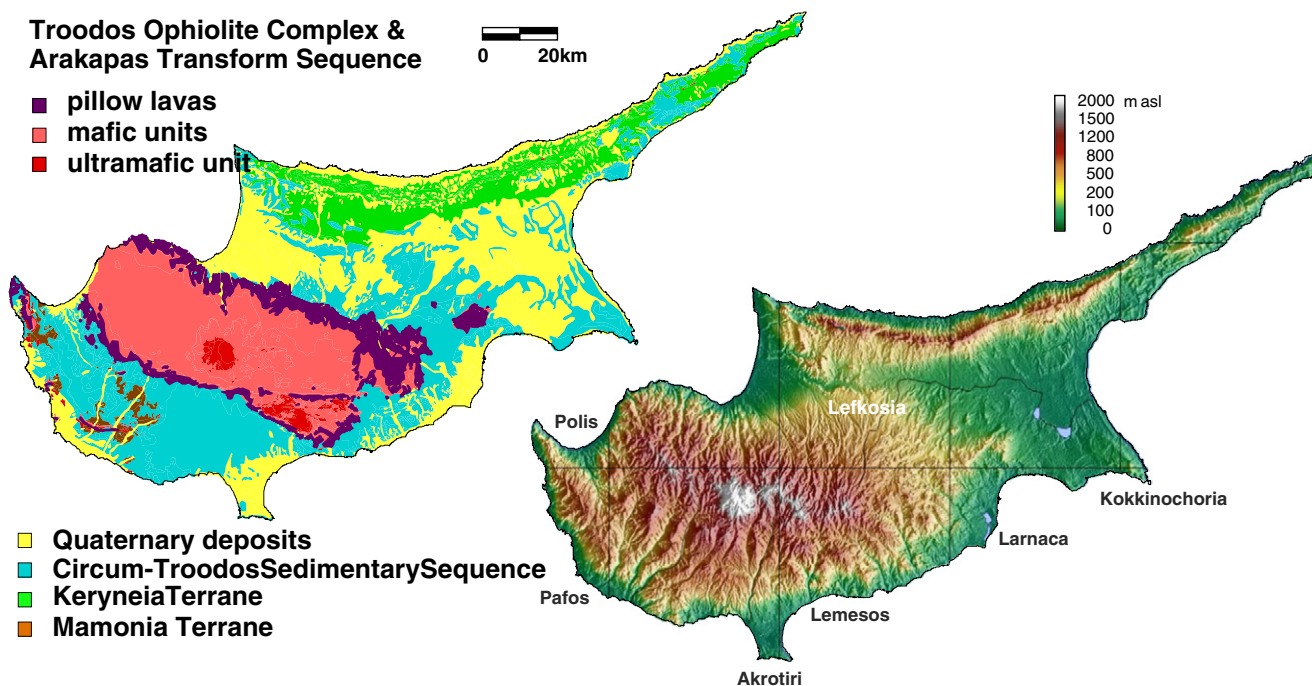


Fig. 1. Simplified geology and topography of Cyprus.

aquifers have been highly overexploited over the years with piezometric levels decreasing rapidly with concurrent aquifers' deterioration – quantity and quality – seawater intrusion (especially in the east of the island). Today irrigation water in cropping areas is supplied mainly from dams, to a lesser extent from ground water and also from tertiary treatment of sewage effluent. Irrigation water is distributed through an open channel and pipe network. Modern irrigation systems such as drippers, mini sprinklers and low capacity sprinklers have been used in Cyprus agriculture for the last 30 years. Most fertilisers applied in Cyprus soils are mineral or chemical fertilisers.

- (iv) Urban areas that incorporate industrial, commercial and residential areas.
- (v) Mining areas, for which the greatest environmental impact is derived from the (historical) copper mines and processing operations that ring Troodos in the pillow basalts. Cyprus has a very long history of mining which spans over 4000 years. Over 200 Mt of mine wastes are estimated to have been produced since the early 1900s (Demetriades et al., 2006).

2. Sampling and analysis

Sampling for the atlas involved collection of top soils (0–25 cm depth) and sub-soil (50–75 cm) on a 1 km × 1 km grid (Cohen et al., 2011). The samples were sieved to <2 mm mesh, air-dried and milled (95% passing < 75 μm sieve) using a Cr-steel mill. A typical sample size was 1 kg of soil depending of the topography of the sampling site. All samples were analysed for metals via both aqua regia extraction induced coupled plasma mass spectrometry (ICPMS) and total metals by instrumental neutron activation analysis (INAA). Soil pH and electrical conductivity (EC) were measured on 1:5 soil:water slurries.

Ion chromatography (IC) has proved to be a useful technique in the past for measuring inorganic ions in water samples such as underground, surface and seawater (Carrozzino and Righini, 1995; Gros and Gorenc, 1997; Jackson, 2000; Morales et al., 2000; Rowland et al., 1995). The method has also been applied for the measurement of inorganic ions in soils but to a lesser extent (Park et al., 2002). Ideally, solutions injected for ion chromatography analysis should be low in organic materials such as organic solvents, pollutants, strong acids, and soluble

salts; hence, many of the traditional methods used for the extraction or digestion of soils are not compatible with ion chromatography (Tabatabai and Basta, 1982). When it comes to regional geochemical mapping of soils the methods of analyses have to be rapid and practical because of the large number of samples processed. We have developed a method designed for this kind of application where within less than 4 h of laboratory work (including sample preparation) fit for purpose results could be obtained.

As part of this study, the effects of changing the sample mass to (18.2 MΩ/cm) deionized water ratio (solid–solution ratio) and leach time on extraction levels were tested using a bulk soil sample (CYP-A), derived from a calcareous marl in Cyprus milled to <75 μm and homogenised. The various combinations of parameters and extraction levels are summarised in Fig. 2. The results indicated that higher concentrations of inorganic ions were extracted as the dilution factor and the shaker time was increased.

Prior to analysis, all solutions were filtered through a 0.45 μm membrane to remove larger particulate matter. Conductivity of the filtrate was measured using a Mettler Toledo MC226 meter. Samples of electrical conductivity greater than 600 μS/cm or subsequently found to have anion concentrations exceeding the calibration range were diluted.

Chromatographic analysis was carried out using a Shimadzu ion chromatograph (model SCL-10Asp) with 50 μL sample loop. The system components consisted of one anion guard column Shim-pack IC-SA2(G) and a separator column Shim-pack IC-SA2 (250 mmL × 4.0 mm) for the simultaneous separation of anions, an anion self-generating suppressor package HK-10Asuper, a pulsed electrochemical detector CDD-10Asp and an advanced gradient pump LC-10ADsp. The eluents were delivered to the columns by a Shimadzu eluent degasser module DGU-14A and the above setup was used in combination with the SCL-10Asp system controller. Calibration curves for each anion were obtained using certified single element calibration solutions with concentrations 1.000 ± 0.002 g/L (Table 1). All the calibration curves had squared correlation coefficient R^2 greater than 0.99.

For every batch of 25 samples an internal QC (CYP-A) was run. For every run of the QC sample the whole extraction process and analysis were applied and therefore reproducibility estimates incorporate extraction and analytical variance. The coefficient of variance (CVR) was estimated from the QC results as a percentage giving the total variance

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