Journal of Geochemical Exploration 158 (2015) 22–33

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Geochemistry of serpentine agricultural soil and associated groundwater chemistry and vegetation in the area of Atalanti, Greece

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ARTICLE INFO

Article history:
Received 13 November 2014
Revised 11 May 2015
Accepted 28 June 2015
Available online 2 July 2015

Keywords:
Ni contamination
Cr contamination
Weathering
Geochemical mapping
Serpentine agricultural soil

ABSTRACT

The soil geochemistry was studied in the area of Atalanti, Greece, an area characterized by presence of mafic and ultramafic rock members of an ophiolite complex. The objectives of the study were to evaluate their impact on soil chemistry and to establish the geochemical baseline of soil with respect to elements derived from the ophiolite rocks. A total of 118 agricultural soil samples were collected and found to be enriched in Ca (7.6%), Co (31 mg/kg), Cr (230 mg/kg), Cu (37 mg/kg), Mg (2.9%) and Ni (330 mg/kg) relative to the median values of both European and Greek soils. Soil baseline concentrations of the ophiolite derived elements (Cr, Ni, Co) were estimated within two sub-areas and the variation in their concentration was assessed along two toposequences characterized by different intensities of weathering of parent rock. Differences in groundwater chemistry were also demonstrated for the aquifers developing within the two subareas. The results of this study can be utilized in future studies on serpentine soil in temperate climate by providing an objective basis for setting realistic threshold values for pollution assessment and remediation.

1. Introduction

The term “serpentine soils” is used to describe any soil derived from ultramafic rock or serpentinite (metamorphosed ultramafic rock). Although these rocks and soils cover minimal area of the earth's surface, they are present in populated areas within the Circum-Pacific margin and the Mediterranean (Oze et al., 2004a). The study of such areas is of particular interest to environmental geochemistry because soil, groundwater and sometimes vegetation near ultramafic rocks are known to contain high concentrations of potentially harmful elements (PHEs) including Cr, Ni, Co and Mn (Brooks, 1987; Cheng et al., 2011; Gasser and Dahlgren, 1994; Gough et al., 1989; Kabata-Pendias and Mukherjee, 2007; Oze et al., 2004a,b, 2008).

Due to the wide geographical occurrence and distribution of serpentinites and serpentine soils, weathering processes differ from location to location due to varying climatic conditions and nature of the parent material as well as other factors including topography, biota, time and tectonic activity (Chardot et al., 2007; Garnier et al., 2013; Hseu and Iizuka, 2013; Proctor and Nagy, 1992; Sadegh et al., 2012). As a result, the chemistry of these soils, groundwater and vegetation will differ from site to site and might represent, in varying degree, a geogenic source of elements with possible health implications for humans (Cox et al., 2013; Kabata-Pendias and Mukherjee, 2007; Kelepertzis and Stathopoulou, 2013; Selinus et al., 2005). Ranges in natural geochemical variability combined with bioaccessibility and ecotoxicological studies may then provide an objective basis for setting appropriate risk-related regulatory levels in such areas.

In Greece, mafic and ultramafic rocks of ophiolitic sequences cover large areas (Pe-Piper and Piper, 2002). This is reflected on the elevated geochemical background of Cr, Ni and Co in soil observed over the whole country in the FOREGS (Salminen et al., 2005) and GEMAS (Reimann et al., 2014) Geochemical Atlases of Europe. Studies have been conducted in order to estimate the impact of PHEs from the ultramafic rocks on soil and water (Kelepertzis et al., 2013; Megremi, 2010; Megremi et al., 2012; Vardaki and Kelepertsis, 1999), the environmental availability of these geogenic elements in affected areas (Economou-Eliopoulos et al., 2011; Kelepertzis and Stathopoulou, 2013; Megremi, 2010) and baseline soil mapping of such areas (Kanellopoulos and Argyraki, 2013). Recent publications on Cr(VI) contaminated areas (Dermatas et al., 2012; Economou-Eliopoulos et al., 2011; Moraetis et al., 2012) highlight even more the need of establishing such baselines in order to provide an objective basis for decision making and selection of appropriate mitigation measures.

This paper presents the results of a soil geochemical survey in the agricultural area of Atalanti, central Greece, which is characterized by outcropping ultramafic rocks and genetically related agricultural alluvial soil. The objectives of the study were: (a) to evaluate the impact of ultramafic rocks on soil chemistry including groundwater chemistry

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http://dx.doi.org/10.1016/j.gexplo.2015.06.013
0375-6742/

and characteristic annual plant species as ancillary data and (b) to establish the local geochemical baseline of soil with respect to geogenic elements derived from the ultramafic rocks.

2. Study area

2.1. Geographical location and land use

The study area is located in central Greece between latitudes 38° 69′ and 38° 55′ and longitudes 22° 97′ and 23° 08′ and covers 64 km^2 (Fig. 1). Its topography is characterized by an alluvial valley, opening to the sea on the east, surrounded by rocky mountains on the south and west. Intensive agricultural activities take place in the area while some livestock farming and small industrial units also exist. Atalanti town with population of ~6000, is located on the western part of the study area.

2.2. Geological setting

The studied area geologically belongs to the sub-Pelagonian geotectonic unit (Jolivet et al., 2013; Mountrakis, 1986). The Valley of Atalanti consists of post-Alpine deposits (Fig. 1) comprising mainly Quaternary-alluvial sediments, consisting of weathered material from the surrounding hills. Neogene lacustrine sediments including marl, clay, gravel, sandstone, conglomerate and marly limestone outcrop in the periphery of the valley. Rocky mountains to the south of the valley are composed of Cretaceous flysch, comprised of shale, sandstone, conglomerate and intercalated limestone; Cretaceous limestone and a shale-chert formation. Serpentinized peridotite, dolerite and gabbro are found within this layer. The rocks from the ophiolitic sequence in the area also outcrop south of the valley at higher topographic locations, near the village of Kirtoni. They comprise mostly ultramafic rocks consisting of peridotite, dunite, pyroxene–peridotite and olivinite. The degree of serpentinization varies from slight alteration to complete serpentinization (IGME, 1965). Diabase, dolerite, igneous basic tuff, pillow lava and spilite are also present towards the lower topographic parts. The ophiolitic rocks are tectonically overthrusted on Jurassic carbonate and clastic rocks, also intercalated by ophiolites. Weathered peridotite also outcrops on the north-northwest of the alluvial valley. The Chlomo Mountain, rising on the south west of the alluvial valley is built of Triassic compacted dolomite. Permo-carboniferous layers occur on the southwest part of the valley, near Atalanti town. This volcanic–clastic formation consists of graywacke, conglomerate, quartzite, violet shale, marly sandstone, green keratophyric tuff and thin layers of dark limestone.

2.3. Soil description

The soil type within the valley is Calcaric reflecting the composition of the surrounding mountains which are built mostly of carbonate rocks. However, samples collected near ultramafic rocks are characterized as Chromic. Calcaric Fluvisols develop in the central and eastern parts of Atalanti Valley. In the mountainous southern part of the studied area the soil horizon is usually shallow (Calcaric and Chromic Leptosols). Chromic Luvisols, enriched in clay and iron-bearing minerals appear on the south-western edge of Atalanti Valley, NW of Megaplatanos.

3. Materials and methods

3.1. Soil sampling and analysis

A total of 118 soil samples were collected from 64 sites in the field (Fig. 1). A sampling grid of 1 × 1 km covered the area within the Atalanti Valley. Additional samples were collected along a north–south transect extending south of the valley up to Kirtoni area, cutting through the mafic and ultramafic rocks that appear in higher elevation. This allowed the study of elemental variation in the shoulder, backslope and footslope along the toposequence.

At each sampling site, the surface of the soil was cleared of superficial debris, vegetation and the O-soil horizon material before taking a 3 fold composite sample using an Edelman type hand auger. Sixty four soil samples were collected from a 0–25 cm depth and 54 samples were collected at a depth of 25–50 cm wherever this was possible.

After collection, the samples were dried in an oven at a temperature of 40 °C, disaggregated with a porcelain pestle and mortar and sieved through nylon screens of 2 mm. The finer fraction (<2 mm) was homogenized and pulverized to <0.075 mm in an agate mill. Soil samples were digested with a mixture of $HClO_4$–HNO_3–HCl acids and were analyzed for a series of elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Vista-PRO Simultaneous) at the Natural History Museum of London, UK and by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce) at the Department of Biology and Environmental Science, University of Sussex, UK. It should be noted that perchloric–nitric–hydrochloric is a partial extraction method and is not very effective on spinels (e.g., chromite) or ilmenite, leading to underestimation of total Cr, Ti, V and other resistant mineral associated elements. Analytical data quality was assured by introduction of internal standards, use of certified (NIST SRM 2709, 2710, 2711) and house reference material samples in randomized positions within the analytical batch and by blank and duplicate analysis of a proportion of the samples (Ramsey et al., 1987). Analytical bias and precision were subsequently calculated and found to be within acceptable limits (<10%) for the following elements: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Se, Sr, Ti, U, V, and Zn. Thus, data analysis and interpretation was focused on this group of elements.

The soil mineralogy was studied in order to explore the relationship between the source (parent rock) of inorganic compounds and their weathering products within the soil matrix. The mineralogical composition of soil was investigated by powder X-ray diffraction (XRD) and microprobe analysis. The XRD study was carried out at the Laboratory of Economic Geology and Geochemistry, University of Athens using a Siemens 5005 X-ray diffractometer, operating with Cu Ka radiation at 40 kV, 40 nA, 0.020° step size and 1.0 s step time. Soil samples were finely ground in an agate mortar and pressed into pellets for XRD analysis. The XRD patterns were evaluated using the EVA 2.2 program of the Siemens DIFFRAC and the D5005 software package.

Polished sections were prepared by impregnating soil in epoxy resin, and examined by reflected light microscopy and scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS). Microprobe analyses and SEM imaging were carried out at the Laboratory of Economic Geology and Geochemistry, University of Athens, using a JEOL JSM 5600 scanning electron microscope, equipped with an automated energy dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 s and beam diameter 1–2 mm. The spectra were processed using the ZAF program (3 iterations).

3.2. Groundwater sampling and analysis

A total of 13 groundwater samples were collected from wells, springs and boreholes used for urban water supply or for agricultural activities (Fig. 1). Unstable parameters including pH, temperature, electrical conductivity, and total dissolved solids were measured in the field, using portable apparatus. For the chemical analysis, the samples were collected in polyethylene bottles. 1 L of sample was vacuum-filtered through 0.45 μm pore size membrane filters and stored in a polyethylene container. Another 200 mL portion of each sample was vacuum-filtered with the same membrane filters and acidified to a final concentration of about 2% nitric acid and stored in a polyethylene container. All samples were preserved in a refrigerator.

Sulfate, nitrate, phosphate and chloride were measured spectrophotometrically, using a Hach DR/2000 apparatus. Bicarbonate was measured