Science of the Total Environment 651 (2019) 656–667

Contents lists available at ScienceDirect

Science of the Total Environment

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

Spatial diversity of Cr distribution in soil and groundwater sites in relation with land use management in a Mediterranean region: The case of C. Evia and Assopos-Thiva Basins, Greece

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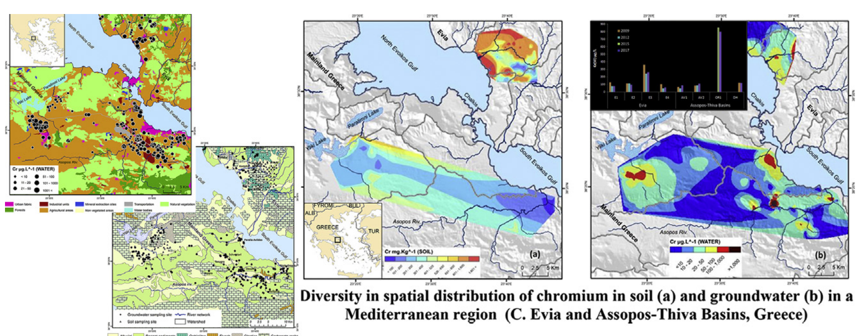
HIGHLIGHTS

- Spatial distribution of Cr and other elements in an area of Greece investigated
- Maps of land use and element contents in soil and groundwater were developed.
- GIS and multivariate statistics were applied to assess the origin of Cr contamination.
- Maps help distinguish Cr of geogenic and anthropogenic origin and salinization.
- These provide information for sustainable land management.

GRAPHICAL ABSTRACT



Diversity in spatial distribution of chromium in soil (a) and groundwater (b) in a Mediterranean region (C. Evia and Assopos-Thiva Basins, Greece)

ARTICLE INFO

Article history:
Received 4 July 2018
Received in revised form 14 September 2018
Accepted 14 September 2018
Available online 15 September 2018

Editor: Mae Mae Sexauer Gustin

Keywords:
Chromium
Nitrate
Salinization
GIS
Land use
Euboea

ABSTRACT

The present study compiles new and literature data in a GIS platform aiming to (a) evaluate the extent and magnitude of Cr contamination in a Mediterranean region (Assopos-Thiva and Central Evia (Euboea) Basins, Greece); (b) combine spatial distribution of Cr in soil and groundwater with land use maps; (c) determine geochemical constraints on contamination by Cr; and (d) provide information that will be useful for better management of land use in a Mediterranean type ecosystem in order to prevent further degradation of natural resources.

The spatial diversity of Cr distribution in soils and groundwater throughout the C. Evia and Assopos-Thiva Basins is considered. It is attributed to both natural Cr sources (Cr-bearing peridotites, affecting primarily soil) and human (industrial) activities (the dominant source of groundwater contamination).

A combination of the spatial distribution of metals in soil and land use maps was used to define the specific areas of agricultural land use with elevated heavy metal contents.

Furthermore, the combination of the spatial distribution of Cr in groundwater and land use maps allows for definition of specific areas of industrial land use with elevated Cr concentrations (Inofita, south Assopos-Thiva Basin). Despite the good correlation ($r = 0.75$) between Cr(VI) and the strong oxidant NO_3^- in C. Evia, the lower standard potential (E^0) values for NO_3^- compared to those for $Cr_2O_7^{2-}$ (the latter is a stronger oxidant than the former) suggest that NO_3^- is not an oxidant of Cr.

This detailed assessment and presentation of the available analytical data for soil and groundwater in Assopos-Thiva and C. Evia Basins on a land use map provides information for land management decision makers.

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https://doi.org/10.1016/j.scitotenv.2018.09.186
0048-9697/

1. Introduction

Current knowledge based on the European Soil Data Centre indicates that metals are frequent soil contaminants (Liedekerke et al., 2014). The term ‘Contaminated Site’ refers to a well-defined area where the presence of soil contamination has been confirmed, and this presents a potential risk to humans, water, ecosystems or other receptors. The term ‘Potentially Contaminated Site’ refers to sites where unacceptable soil contamination is suspected, but not verified, and where detailed investigations need to be carried out to determine whether there is an unacceptable risk of adverse impacts on receptors (Liedekerke et al., 2014). The most abundant species of chromium (Cr) in nature are Cr(III), that is a required nutrient, and the highly toxic and very soluble oxidized Cr(VI), which causes serious health problems in the form of chromate oxyanions such as CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$ (ATSDR, 2000; Losi et al., 1994; Shock et al., 1997).

Soil management, food, and water security are among the currently major issues of the ongoing Land Degradation and Restoration Assessment (LDRA) (Keesstra et al., 2016). The provision of the irrigation water is of global significance, since the amount of 92% of freshwater is of agricultural use (Hoekstra and Mekonnen, 2012). Water resources of proper quality are crucial for irrigation of crops, and for water supply in areas of increasing urbanization and growing tourism. The need to protect groundwater in the European Union, including Greece, has been recognized though the Water Framework Directive on groundwater. Council Directive 98/83/EC has established a maximum permissible limit for various potentially toxic elements. Among them Cr_{total} in drinking water, is regulated in a maximum permissible limit of 50 μg/L or ppb.

Soil contamination by Cr, and the consequent contamination of groundwater, is a risk in many countries of Europe, due to industrial activities and/or natural processes, related to Cr-bearing minerals and ores (Salunkhe et al., 1998; Eliopoulos and Economou-Eliopoulos, 2000; Fantoni et al., 2002; Oze, 2003; Becquer et al., 2003; Ball and Izbicki, 2004; Oze et al., 2004, 2007, 2016). Untreated or poorly treated industrial wastes from approximately 700 industrial plants, (concerning activities such as the production of chromic acid, Cr-pigments, leather tanning, corrosion control) in the Assopos-Thiva Basin, and the widespread occurrence of ophiolites and Fe-Ni-laterite deposits in C. Evia (Euboea) are considered to be the major contamination sources of Cr for soil and water, and in other regions in Greece (Giannoulopoulos, 2008; Vasilatos et al., 2008, 2010; Megremi, 2009, 2010; Megremi et al., 2013; Economou-Eliopoulos et al., 2011, 2012, 2013, 2014, 2016, 2017; Dermatas et al., 2015; Dimitroula et al., 2015; Dokou et al., 2015).

This work combines measurement of the spatial distribution of Cr and other potentially toxic elements with land use maps for soil and groundwater in a Geographical Information System (GIS). A Hot Spot Analysis for Cr distribution in soils and groundwater, in C. Evia and Assopos-Thiva Basins was applied. The main scope was (a) to evaluate the extent and magnitude of Cr contamination in those Basins, and (b) to contribute to a sustainable management of land use in Mediterranean type ecosystems (prevention of soil from further degradation and protection of local water resources in respect to the established agricultural activities and human consumption).

2. Methods of investigation

Hundreds of soil samples (N = 254) were collected from the Assopos-Thiva Basins and C. Evia, Greece (Fig. 1), during the period 2007 to 2012, and data reported for previous studies during this time are presented here. The elements Al, B, Ba, Cr, Cu, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, V, and Zn in soils were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS), at ACME Analytical Laboratories in Canada, after Aqua Regia digestion. Detection limits and the results for the quality control samples, the precision of the analyses of the minor and trace elements is in good agreement with international standards (<10%) (Supplementary table). Also, the mineralogical composition and mineral chemistry of representative soil samples have been investigated using reflected light microscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) analysis, at the National and Kapodistrian University of Athens (Megremi, 2009, 2010, Economou et al., 2011, Economou et al., 2012; Atsarou and Economou-Eliopoulos, 2012; Theodoratou and Economou-Eliopoulos, 2012).

Almost two hundred groundwater samples (N = 204) were collected from domestic and irrigation wells covering the C. Evia and Assopos-Thiva Basins (Fig. 1), during the period from 2007 to 2017, and analyzed for major and trace elements by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) (Giannoulopoulos, 2008; Megremi, 2009, 2010; Moraki, 2010; Atsarou and Economou-Eliopoulos, 2012; Megremi et al., 2013). Detection limits, quality control samples and the precision of the analyses is in agreement with international standards (<10%) (Supplementary table).

All the data were imported into two separate spatial geodatabases (one for soil and a second for water samples), and were processed in a GIS platform (ESRI's ArcGIS v.10.3). Several layers of geographic information were combined in order to visualize the physiographical and geological properties of the studied areas in relation to the sampling sites. Geostatistical analysis using a variety of spatial tools was carried out in order to interpolate the point data measurements and create continuous information data layers covering the studied areas with the calculated values as much as close to the reality. The location of the sampling sites led us to use the ‘Nearest Neighborhood’ geostatistical method that proved to yield the most realistic results for both soil and groundwater data. The main concept of this method is to find the closest subset of the samples to a query point and interpolate a new value, after applying proportional weights to the measured values (Sibson, 1981). The Nearest Neighbor method (as used in ESRI's ArcGIS v.10.3) handles large numbers of sample points efficiently and is the most acceptable method for spatial prediction when sample data points are distributed with uneven density (Ver Hoef and Temesgen, 2013). On the other hand, geostatistical methods e.g. ‘Kriging’ (Cressie, 1990), in cases of irregular spatial sampling locations causes interpolated values to be different (either higher or lower) than the real measured values, as the predicted locations do not coincide with any of the real sampling locations during the resampling procedure (Corona et al., 2014). The geostatistical processing between mainland Greece and Evia point locations had been run independently since the sea water body of the Evia Gulf lies in between. Furthermore, a Hot Spot Analysis was applied in order to spatially identify any clustering between the sampling locations and highlight the areas of geostatistical significance. The spatial resolution of the output raster layer was set to 100 m taking under consideration the spatial arrangement and the average distances between the sampling sites.

Multivariate statistics were applied to the water dataset in order to explain the observed variability in elemental concentrations in groundwater. The computer program MINITAB_ 15 for Windows was used for multivariate (Factor) analysis (Howarth and Govett, 1983). The input has focused on seven elements, namely Na, B, As, K, Li, Mg, Ca, and Cr. Data were processed by means of R-mode factor analysis, applying the varimax-raw rotational technique. This technique can simplify a complex data set by identifying one or more underlying ‘factors’ that might explain the dimensions associated with data variability. The ‘loading’ of each factor, i.e. the degree of association between each variable and each factor, allows the recognition of clusters. A varimax rotation was applied to the initial factor loadings in order to maximize the variance of the squared loadings. The correlation matrix was computed for 204 groundwater samples (47 from central Evia and 157 from Assopos-Thiva Basin), after normalization of their concentrations by transforming the arithmetic values to their normal scores. This transformation was necessary to ensure the normal distribution for all the elements and reduce the influence of high values on the output results. Principal Component Factor Analysis with a Varimax rotation was subsequently applied to the data in order to create factors, each representing a cluster of interrelated variables within the data set.