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# Distribution and bioavailability of Cr in central Euboea, Greece

**Research Article**

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**Abstract:** Plants and soils from central Euboea, were analyzed for $Cr_{(total)}$, Cr(VI), Ni, Mn, Fe and Zn. The range of metal concentrations in soils is typical to those developed on Fe-Ni laterites and ultramafic rocks. Their bioavailability was expressed in terms of concentrations extractable with EDTA and 1 M $HNO_3$, with EDTA having a limited effect on metal recovery. Cr(VI) concentrations in soils evaluated by alkaline digestion solution were lower than phytotoxic levels.

Chromium and Ni – and occasionally Zn – in the majority of plants were near or above toxicity levels. Cr(VI) concentrations in plants were extremely low compared to total chromium concentrations.

$Cr_{(total)}$ in ground waters ranged from <1 µg.L$^{-1}$ to 130 µg.L$^{-1}$, with almost all chromium present as Cr(VI). With the exception of $Cr_{(total)}$ and in some cases Zn, all elements were below regulatory limits for drinking water. On the basis of Ca, Mg, $Cr_{(total)}$ and Si ground waters were classified into three groups: Group(I) with Cr concentrations less than 1 µg.L$^{-1}$ from a karstic aquifer; Group(II) with average concentrations of 24 µg.L$^{-1}$ of Cr and relatively high Si associated with ophiolites; and Group(III) with Cr concentrations of up to 130 µg.L$^{-1}$, likely due to anthropogenic activity. Group(III) is comparable to ground waters from Assopos basin, characterized by high Cr(VI) concentrations, probably due to industrial actrivities.

**Keywords:** soils • plants • bioavailability • water pollution • hexavalent chromium • central Euboea

## 1. Introduction

Among metals associated with Ni-laterite deposits and ophiolitic rocks, chromium is of great concern, particularly when present as Cr(VI). It has been shown that most of the Cr in soil occurs in its trivalent oxidation state (Cr(III)), within the mineral stuctures or forms of Cr(III) and Fe(III) oxides. Since Cr(III) is slightly mobile only in very acid media and at pH 5.5 is almost completly precipitated, its compounds are considered to be very stable in soils. On the other hand Cr(VI), the most toxic form of chromium, (as $CrO_4^{2-}$ and $HCrO_4^{2-}$), is very unstable in soils and is easily mobilized in both acid and alkaline soils [1]. However a potential mechanism for the oxidation of Cr(III) to Cr(VI) in soils may be via the reduction of manganese oxides [2–5]. Moreover, the impact of Cr contamination on plant physiology depends on metal speciation, which is responsible for its mobilization, subsequent uptake, translocation, accumulation and resultant toxicity in the plant system [6]. However, the form that is most unstable under normal soil conditions, and is consequently the most available to plants, is considered to be Cr(VI). Furthermore,

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phytotoxicity of Cr has been reported in plants growing on soils derived from ultrabasic rocks [1].

Numerous studies have been carried out throughout the world on the geology, geochemistry and genesis of iron-nickel deposits [7, 8], the specific vegetation linked to ultramafic or serpentine soils and the potential heavy metals availability in these soils [9–13].

Total concentrations of metals are useful, as they provide an indication of the toxicity potential of the soils although they commonly cannot be translated into bioavailable metals [13, 14]. Although lateritic soils are widespread around the Ni-laterite deposits of Greece, data concerning the investigation of heavy metal content and distribution in soils, waters and plants associated with ultrabasic rocks and nickeliferous mineralization are limited [15–17].

Several extraction agents including acids (HCl, $HNO_3$), chelating agents (EDTA, DTPA, NTA, EDDS), buffered or unbuffered salt solutions ($NH_4OAc$, $CaC1_2$, $NH_4NO_3$), and a variety of procedures have so far been used to determine the bioavailable fractions of metals in soils [14, 18–20]. However, until present there has been no consensus about a unique method that always gives the best estimate for the bioavailable fraction, as the availability of metal to plants depends on a large number of properties concerning the soil, plant and climate [21].

The availability and mobility of heavy metals in soils may be also modified by the presence of organic matter. High concentration of humified organic matter can decrease the bioavailability of heavy metals in soils [22]. As far as chromium is concerned the dominant effect of organic matter is the stimulation of the reduction of Cr(VI) to the relatively immobile Cr(III) [23].

In aqueous environments, the more toxic and mobile Cr(VI) predominates in oxidizing and alkaline conditions, while the less toxic and immobile Cr(III) is restricted to reducing ones. The European Union, including Greece, has currently regulated the limit of 50 $\mu g.L^{-1}$ for total chromium in drinking water [24], while Italy has regulated a maximum permissible level of Cr(VI) in drinking water at 5 $\mu g.L^{-1}$, [25, 26]. Cr(VI) and its compounds can originate in the aqueous environment from both anthropogenic (industry wastes and emissions, combustion processes, etc.) and natural sources (weathering of chromium bearing minerals). Numerous studies of naturally occurring aqueous Cr(VI) at concentrations up to 73 $\mu g.L^{-1}$ have been reported in ground and surface waters from New Caledonia, California, Italy and Mexico, associated mainly with serpentine soils and ultramafic rocks [27].

In the present study, soil, plants and ground waters from central Euboea were analyzed for Cr(VI) and several trace elements in an attempt to define the origin of chromium species and provide information for both total Cr and Cr(VI) bioavailability in soils associated with ophiolites and Ni-laterite deposits.

## 2. Geology - Hydrogeology

The region of central Euboea covers part of the Pelagonian zone and apart from the Quaternary alluvial deposits, which cover the lowland areas, consists of a lower sequence of Triassic-Jurassic limestones which pass upwards into silicified limestones and radiolarian mudstones of the schist-chert formation, dated by radiolarian fauna as latest Jurassic to earliest Cretaceous [8, 28]. The members of this schist-chert formation are mainly schists, sandstones, red cherts and, in its uppermost parts, olistholiths of ophiolitic rocks. These ophiolitic rocks are mainly composed of serpentines, diabases (dolerites) and peridotites and are considered the parent rocks of the laterites. During the lower Cretaceous they were deeply eroded, subsequently lateritized and transgressively overlain by shallow-water limestones of upper Cretaceous age. The Fe-Ni laterite deposits of central Euboea are resting as in-situ deposits on ophiolites or as mechanical reworked laterite detritus, either on serpentinites or karstified Triassic-Jurassic carbonates and are overlain by Upper Cretaceous limestones [8].

Sampling wells within the study area (with a depth between 5-180 m) are sited in Quaternary alluvial deposits, the upper Cretaceous karstified limestones or in the ophiolitic rocks, which are highly fractured and exhibit significant permeability. The sampled springs are located at the contact of the upper Cretaceous limestones and the underlying upper Jurassic to earliest Cretaceous schist-chert formation. Most of the sampling took place during the wet and dry seasons of one hydrologic year.

## 3. Sampling location

Sixteen soil samples and 27 plant samples were collected from the wider area of Psachna town in central Euboea. The sampling sites were located in the vicinity of the Ni-laterite deposits, the mining excavations and the ore beneficiation unit. The soil samples were collected from the rhizospheres of the plants, but in some cases more than one plant species growing on a single site with common soil were collected in order to estimate the role of the plant physiology and metabolism to metal bioavailability.

A total of 34 ground water samples representative of the main aquifer systems were collected from central Euboea (areas of N.Artaki – Kastella – Psachna – Makrymalli – Kondodespoti – Dafni) (Figure 1).

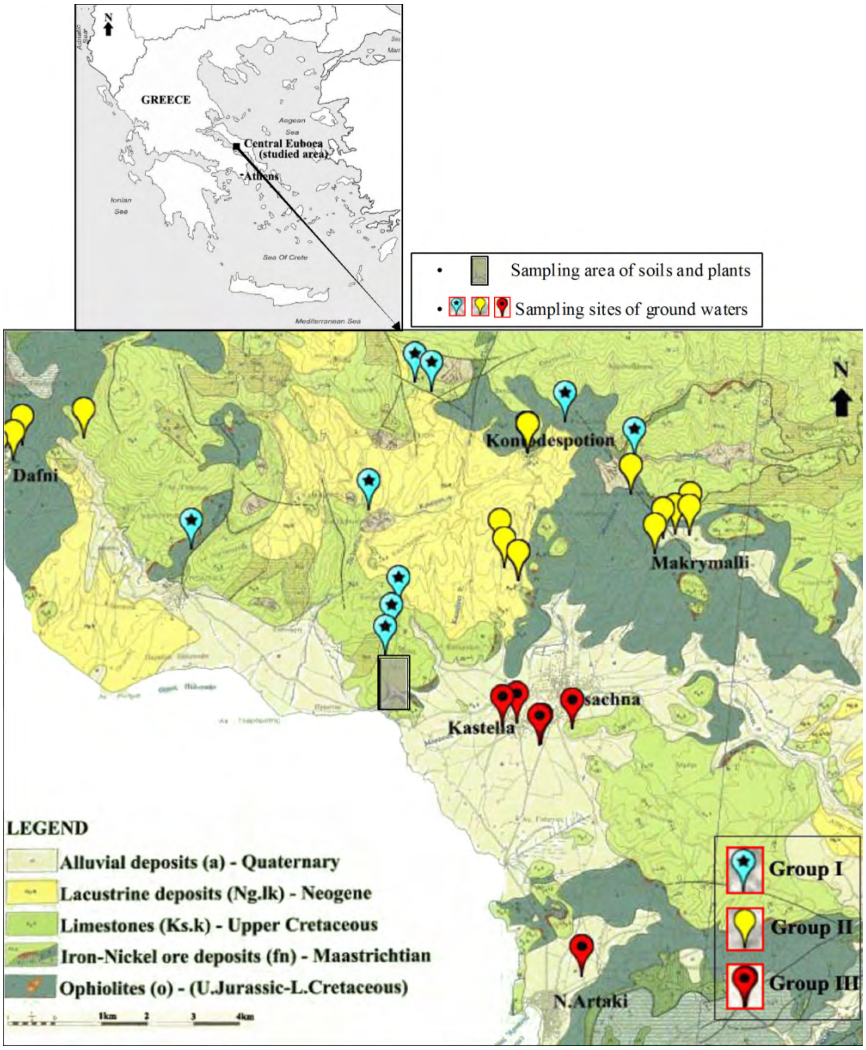

**Figure 1.** Sketch map showing the location of the studied area, central Euboea, along with simplified geological map showing the sampling sites of ground waters and the sampling area of soils and plants.

# 4. Methods and materials

## 4.1. Soils

Soil samples came mainly from the rhizosphere of each plant sample and from a maximum depth of approximately 20 cm. The collected samples were dried overnight at 70°C, passed through a 1.8 mm nylon sieve and the finer fraction (<1.8 mm) was homogenized and finally pulverized in an agate mill. A subsample of each soil weighing 0.5 grams was digested with Aqua Regia (1:3 mixture of $HNO_3$ and HCl) and analyzed mainly for five metals, Cr, Ni, Mn, Fe and Zn, using a flame atomic absorption spectrophotometer (FAAS) (Perkin Elmer 1100B) at the Laboratory of Economic Geology and Geoenvironment of the University of Athens. Other elements (Mo, Cu, Pb, Co, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Mg, Ba, Ti, Al, Na, K, W, Hg, Sc and Ga) were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at the ACME Analytical Laboratories in Canada.

The organic matter content of the soil samples was determined by measuring organic carbon, using the classical Walkley and Black (1934) [29] titration method.

A slurry was made by shaking 8 g of soil with 20 ml of deionized water for fifteen minutes and allowed to settle for thirty minutes. pH measurements were taken on this mixture using a portable Consort 561 Multiparameter Analyzer.

In order to determine the bioavailable fraction of metals in soils 0.05 M ethylenediaminetetraacetic acid (EDTA) digestion solution was used as an extraction agent [30]. 5 g of soil sample were transferred to a 125 ml Erlenmeyer flask, to which 25 ml of 0.05 M EDTA digestion solution was added. The obtained mixture was shaken on a shaking table at 120 cycles per minute for 1 hour and then filtered through Whatman No. 42 filter paper.

Metals complexed by organic matter and sorbed by or co-precipitated with hydrous oxides, carbonates and sulfides were released by the 1M nitric acid ($HNO_3$) digestion solution [30]. Thirty ml of this solution were shaken with 3 g of soil sample for 2 hours at a speed of 120 cycles per minute and then filtered through Whatman No. 42 filter paper.

Hexavalent chromium in the soil samples was measured after extraction by a concentrated alkaline extracting solution prepared by HACH Hexavalent Chromium Soil Extractant Powder Pillows, (HACH Cat. No. 24497-99 reagent, for the Method 10051, for DR/4000 procedures). This method is analogue to the United States EPA 3060A method.

The solutions extracted after the digestions of soil samples with EDTA, 1M $HNO_3$ and the alkaline extracting reagent were analyzed by a flame atomic absorption spectrophotometer (FAAS), (Perkin Elmer 1100B) for the Ni, Cr, Mn, Fe and Zn at the Laboratory of Economic Geology and Geochemistry of the University of Athens.

Data quality was assured by analyzing duplicates of selected soil and plant samples. The precision was checked by means of these duplicate samples and was found to be within international standards. In order to validate the accuracy of the extracted Cr, Ni, Mn, Fe and Zn by Aqua Regia, NIST 2709 standard reference material was analyzed as well.

## 4.2. Plants

The species of the plant samples collected were representative of the indigenous and cultivated vegetation in the area studied. They were mainly food plants and their number was determined by their availability and presence in the areas of interest (Table 1). All plant samples were carefully washed with deionized water and were oven-dried at 70°C overnight. Each plant sample was subdivided, if possible, into roots and shoots and each part was pulverized in an agate mortar. A homogenized subsample (0.5 g) of the above-ground parts of the plants and/or their edible parts, like the tubers of carrots and potatoes, were digested using a nitric acid/hydrogen peroxide mixture ($HNO_3/H_2O_2$) in conjunction with microwave heating in closed Teflon vessels (microwave oven: Ethos 1600, Advanced Microwave Labstation Milestone). The leachates were analyzed for Cr, Ni, Mn, Fe and Zn using a flame atomic absorption spectrophotometer (FAAS), Perkin Elmer (1100B) at the Laboratory of Economic Geology and Geoenvironment of the University of Athens. Mo, Cu, Pb, Ag, Co, Au, Sr, Cd, Ca, P, Mg, Ba, Ti, B, Na, K, S, Se were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at the ACME Analytical Laboratories in Canada. The same method of alkaline digestion for the determination of Cr(VI) in soils was tested on a number of plant samples and the leachates were also analyzed using a flame atomic absorption spectrophotometer (FAAS), Perkin Elmer(1100B) at the Laboratory of Economic Geology and Geoenvironment of the University of Athens.

**Table 1.** Common name, scientific name and amily of the collected plant samples.

| Common name | Scientific name | Family | No of samples |
|---|---|---|---|
| Carrot | Daucus carota | Apiaceae | 4 |
| Olea | Olea europaea | Oleaceae | 3 |
| Garlic | Allium sativum | Lilliaceae | 3 |
| Potato | Solanum tuberosum | Solanaceae | 3 |
| Sonchus | Sonchus oleraceus | Asteraceae | 5 |
| Chicory | Cichorium intybus | Asteraceae | 2 |
| Black mustard | Sinapis arvensis | Brassicaceae | 1 |
| Salsify | Tragopogon spp. | Asteraceae | 1 |
| Verbascum | Verbascum spp. | Scrophulariaceae | 1 |
| Cabbage | Brassica oleracea var. capitata | Brassicaceae | 1 |
| Pigweed | Amaranthus spp | Amaranthaceae | 1 |
| Vegetable marrow | Cucurbita Pero | Cucurbitaceae | 1 |
| Black nightshade | Solanum nigrum | Solanaceae | 1 |

## 4.3. Waters

Groundwater samples were collected from springs as well as shallow and deep wells used for urban water supply or for agricultural activities (Figure 1). The ground water samples were stored in polyethylene bottles at 4°C. Critical physical and chemical parameters were measured in the field using a portable Consort 561 Multiparameter Analyzer.

The determination of Cr(VI) in water samples was performed within 24 hours after sampling, by the 1,5-Diphenylcarbohydrazide method using a single dry powder formulation obtained from HACH (ChromaVer 3 Chromium Reagent, Cat. No.12710-99 for the Method 8023, for DR/4000 spectrophotometer). That reagent contains an acidic buffer combined with 1,5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present. The estimated detection limit of the method was determined at 4 μg.L$^{-1}$. The analyses of total chromium were performed by GFAAS (HGA 400 with a Perkin Elmer 1100B spectrophotometer) at the Laboratory of Economic Geology and Geochemistry of the University of Athens. The estimated detection limit of the method was determined at 1 μg.L$^{-1}$. Other elements (Ca, Mg, Ni, Mn, Zn, Si, Na, K, B, Li As, Cd, Co, Cu, P, Pb, S, Se, V) were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) at the ACME Analytical Laboratories in Canada.

# 5. Results

## 5.1. Soils

Mean, standard deviation, min and max values of pH, Eh, organic carbon and total concentrations of Cr, Ni, Mn, Fe and Zn are presented in Table 2.

Data on elemental concentrations resulting from selective extractions (EDTA, $HNO_3$ 1M and alkaline digestion) are reported in Table 3.

Chromium, nickel, manganese and total iron concentrations were high in the majority of soil samples. A few unusually high values of Zn (up to 900 mg.L$^{-1}$) were detected in the rhizospheres of plants which were germinated in the vicinity of an ore transporting conveyor.

Concentrations of hexavalent chromium were found to be low, ranging from 0.2 to 1.04 mg kg$^{-1}$, which is below the plant toxicity threshold value of 5 mg kg$^{-1}$ [31]. Those concentrations exhibit no correlation with $Mn_{(total)}$ concentrations in soils and faintly negative correlations with $Fe_{(total)}$ soil content and measured organic carbon.

On the other hand, total chromium soil content displays very good positive correlations with $Ni_{(total)}$, $Fe_{(total)}$ ($r = 0.98$ and $r = 0.96$, respectively) and manganese concentrations ($r = 0.75$) (Figure 2).

The bioavailable concentrations of metals (Cr, Ni, Mn, Fe, Zn) extracted with EDTA and metal contents extracted with 1M $HNO_3$ as a percentage of their total metal concentrations (Table 4) were generally low.

According to the diagrams in Figure 3, the percentage of chromium and nickel total concentrations extracted with EDTA and 1M $HNO_3$, seem to be rather constant, with a small, meaningless decrease with increasing total concentrations. On the other hand, the percentages of Mn and Fe total concentrations extracted with EDTA and 1M $HNO_3$ are rather variable. Moreover, although the percentage of total Zn extracted with EDTA seems to be very constant regardless of total concentrations, the percentage of total Zn extracted with 1M $HNO_3$ begins as rather variable and becomes constant as total concentrations increase.

**Table 2.** Soil analysis data for the rhizospheres (Number of samples = 16) in comparison with concentrations (mg kg$^{-1}$) of some metals (Cr, Ni, Mn, Fe, Zn) for surface soils worldwide [1].

| | Mean | Standard deviation | Min | Max | Means or ranges of Cr,Ni,Mn,Fe and Zn (mg kg$^{-1}$) for worldwide soils |
|---|---|---|---|---|---|
| $Cr_{(total)}$ | 1 300 | 1 100 | 540 | 3 800 | 54 |
| $Ni_{(total)}$ | 2 800 | 2 200 | 1 200 | 8 900 | 0.2-450 |
| $Mn_{(total)}$ | 1 300 | 390 | 600 | 2 200 | 450 |
| $Fe_{(total)}$ | 79 500 | 46 200 | 42 300 | 187 000 | 0.5-5% |
| $Zn_{(total)}$ | 50 | 30 | 16 | 900 | 64 |
| Mo | 1 | 1 | 0.2 | 5 | |
| Cu | 28 | 8 | 15 | 44 | |
| Pb | 35 | 90 | 3 | 370 | |
| Co | 150 | 100 | 60 | 460 | |
| As | 4 | 2 | 1 | 7 | |
| U | 0.5 | 0.2 | 0.3 | 1 | |
| Au | 15 | 19 | 1 | 74 | |
| Th | 1 | 0.4 | 1 | 2 | |
| Sr | 50 | 33 | 28 | 140 | |
| Cd | 0.3 | 0.1 | 0.1 | 1 | |
| Sb | 0.2 | 0.4 | 0.1 | 2 | |
| Bi | 0.1 | 0.03 | 0.1 | 0.2 | |
| V | 49 | 12 | 25 | 70 | |
| Ca | 71 800 | 48 300 | 8 400 | 213 000 | |
| P | 550 | 430 | 50 | 1 500 | |
| La | 7 | 3 | 2 | 10 | |
| Mg | 41 000 | 24 300 | 8 300 | 113 000 | |
| Ba | 50 | 17 | 19 | 87 | |
| Ti | 360 | 130 | 120 | 530 | |
| Al | 13 300 | 4 800 | 4 900 | 19 000 | |
| Na | 110 | 82 | 40 | 320 | |
| K | 1 800 | 920 | 500 | 3 200 | |
| W | 6 | 5 | 2 | 18 | |
| Hg | 0.02 | 0.01 | 0.01 | 0.04 | |
| Sc | 12 | 6 | 5 | 26 | |
| Ga | 4 | 1 | 1 | 5 | |
| %Organic Carbon | 0.92 | 0.76 | 0.22 | 3.51 | |
| pH | 7.97 | 0.30 | 7.12 | 8.35 | |
| Eh (mV) | -67 | 17 | -89 | -19 | |

The relations between total metal content in soil and the amounts of metals extracted with EDTA and 1M $HNO_3$ were are rather variable (Figure 4). With the exception of Zn no correlations were observed for Cr, Ni, Mn and

**Table 3.** Concentrations of metals extracted with EDTA, $HNO_3$ 1M and alkaline digestion in mg kg$^{-1}$ (N$^o$ of samples = 16).

| | Mean | Standard deviation | Min | Max |
|---|---|---|---|---|
| $Cr_{(EDTA)}$ | 1.2 | 0.7 | 0.6 | 3 |
| $Ni_{(EDTA)}$ | 27 | 20 | 8 | 90 |
| $Mn_{(EDTA)}$ | 57 | 45 | 20 | 180 |
| $Fe_{(EDTA)}$ | 110 | 71 | 30 | 250 |
| $Zn_{(EDTA)}$ | 16 | 44 | 0.5 | 180 |
| $Cr_{(1MHNO_3)}$ | 48 | 22 | 4.5 | 90 |
| $Ni_{(1MHNO_3)}$ | 310 | 180 | 74 | 830 |
| $Mn_{(1MHNO_3)}$ | 560 | 210 | 170 | 1 100 |
| $Fe_{(1MHNO_3)}$ | 2 500 | 1 800 | 42 | 6 600 |
| $Zn_{(1MHNO_3)}$ | 67 | 210 | 0.6 | 850 |
| Cr(VI) | 0.42 | 0.20 | 0.22 | 1.04 |

Fe between their total contents in soil samples and the amounts extracted by EDTA. However good positive correlations were found between total concentrations and metal contents extracted with 1M $HNO_3$.

According to the mean value of the contained organic carbon (0.92%), the soil samples studied could be characterized as medium-low in organic matter [32], with pH values ranging from neutral to alkaline.

Negative correlation was observed between organic carbon and total chromium (r = -0.57) and no correlation was found between organic carbon and hexavalent chromium. With the exception of Cr, bioavailable fractions of Ni, Mn, Fe and especially Zn extracted with EDTA showed linear positive correlations with the measured organic carbon in the studied soil samples (Figure 5). The significant relationships of Zn extracted with EDTA and $HNO_3$ 1M versus organic carbon and total metal concentrations were also observed by D. McGrath [33] in agricultural soils.

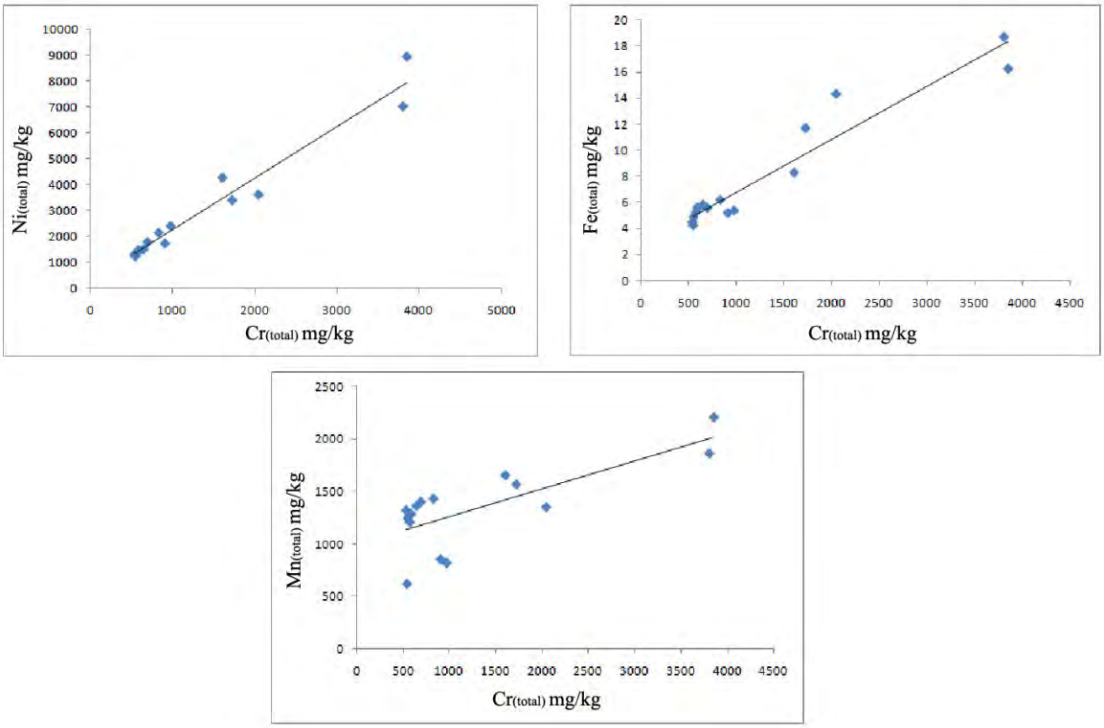

**Figure 2.** Relationships between Cr (total) concentrations and Ni, Fe and Mn total contents in soils.

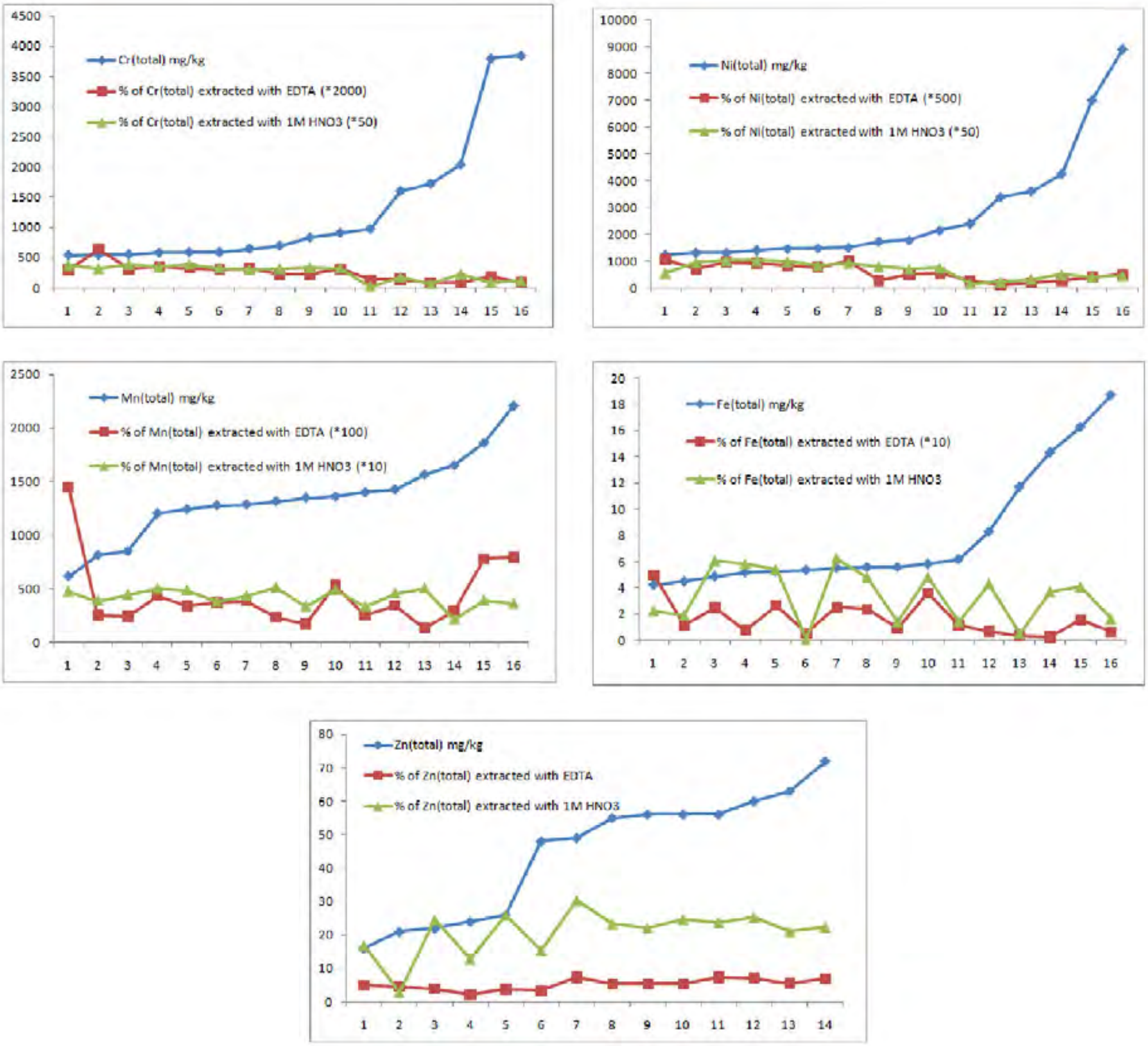

**Figure 3.** Diagrams representative of the regression of the percentages of total metal contents extracted with selective extractions (EDTA, $HNO_3$ 1M), with increasing total metal concentrations in soils.

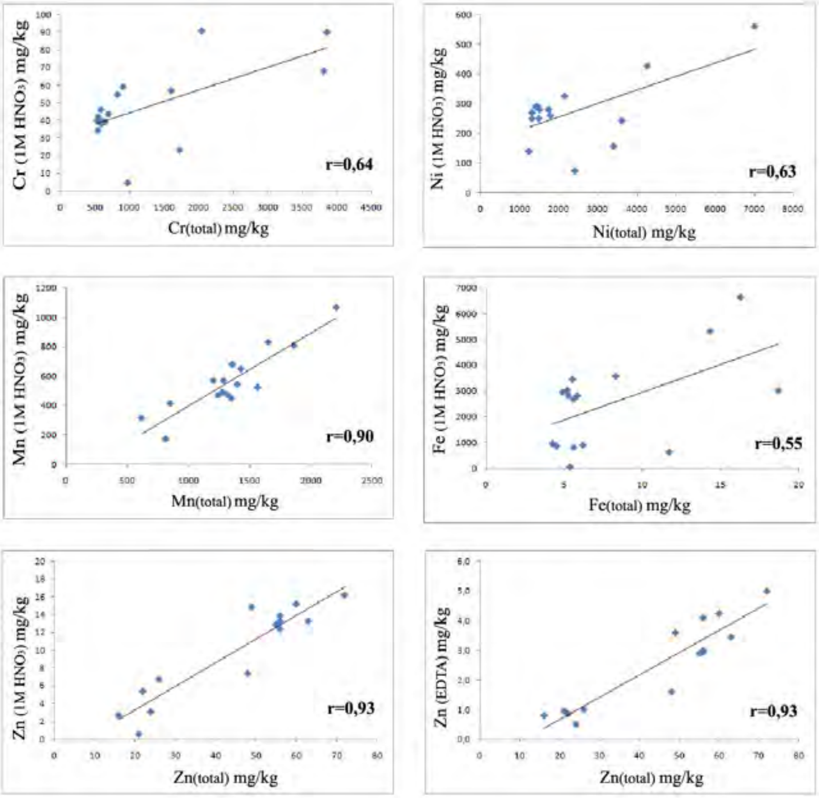

**Figure 4.** Relationships between Cr, Ni, Mn, Fe and Zn total soil concentrations and concentrations of Cr, Ni, Mn, Fe and Zn extracted with $HNO_3$ 1M and Zn extracted with EDTA.

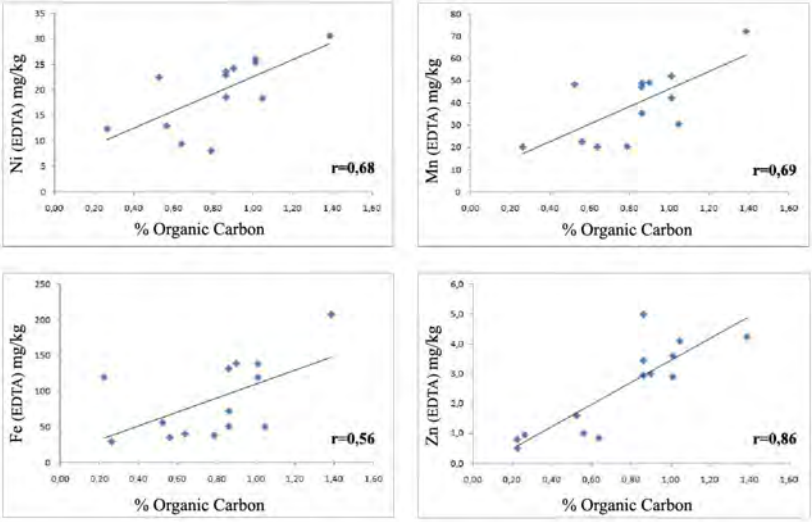

**Figure 5.** Significant linear positive correlations between the measured organic carbon in the studied soil samples and metal (Ni, Mn, Fe, Zn) concentrations extracted with EDTA.

**Table 4.** Cr, Ni, Fe, Mn and Zn concentrations from selective extractions as a ratio and percentage of extractable metal versus total metal concentration.

| | Mean | Standard deviation | Min | Max | Count |
|---|---|---|---|---|---|
| $Cr_{(EDTA)}/Cr_{(total)}$ | 0.001 | 0.001 | 0.0004 | 0.003 | 16 |
| % of $Cr_{(total)}$ extracted with EDTA | 0.1 | 0.07 | 0.04 | 0.3 | 16 |
| $Cr_{(1M\ HNO_3)}/\ Cr_{(total)}$ | 0.05 | 0.02 | 0.005 | 0.08 | 16 |
| % of $Cr_{(total)}$ extracted with 1M $HNO_3$ | 5.1 | 2.4 | 0.5 | 8 | 16 |
| $Ni_{(EDTA)}/Ni_{(total)}$ | 0.01 | 0.01 | 0.002 | 0.02 | 16 |
| % of $Ni_{(total)}$ extracted with EDTA | 1.2 | 0.6 | 0,2 | 2 | 16 |
| $Ni_{(1M\ HNO_3)}/\ Ni_{(total)}$ | 0.1 | 0.1 | 0.03 | 0.2 | 16 |
| % of $Ni_{(total)}$ extracted with 1M $HNO_3$ | 13 | 5.9 | 3.1 | 21 | 16 |
| $Mn_{(EDTA)}/Mn_{(total)}$ | 0.04 | 0.03 | 0.01 | 0.1 | 16 |
| % of $Mn_{(total)}$ extracted with EDTA | 4.4 | 3.3 | 1.3 | 14 | 16 |
| $Mn_{(1M\ HNO_3)}/\ Mn_{(total)}$ | 0.4 | 0.1 | 0.2 | 0.5 | 16 |
| % of $Mn_{(total)}$ extracted with 1M $HNO_3$ | 42 | 8.2 | 21 | 51 | 16 |
| $Fe_{(EDTA)}/Fe_{(total)}$ | 0.002 | 0.001 | 0.0002 | 0.005 | 16 |
| % of $Fe_{(total)}$ extracted with EDTA | 0.17 | 0.1 | 0.02 | 0.5 | 16 |
| $Fe_{(1M\ HNO_3)}/\ Fe_{(total)}$ | 0.03 | 0.02 | 0.001 | 0.06 | 16 |
| % of $Fe_{(total)}$ extracted with 1M $HNO_3$ | 3.4 | 2.1 | 0.1 | 6 | 16 |
| $Zn_{(EDTA)}/Zn_{(total)}$ | 0.05 | 0.02 | 0.02 | 0.07 | 16 |
| % of $Zn_{(total)}$ extracted with EDTA | 5.2 | 1.6 | 2 | 7 | 16 |
| $Zn_{(1M\ HNO_3)}/\ Zn_{(total)}$ | 0.2 | 0.1 | 0.03 | 0.3 | 16 |
| % of $Zn_{(total)}$ extracted with 1M $HNO_3$ | 21 | 6.9 | 3 | 30 | 16 |

## 5.2. Plants

Composite samples of plants were collected from cultivated and non-cultivated areas in the vicinity of Fe-Ni laterite deposits. Mean, standard deviation, minimum and maximum values of Cr, Ni, Mn, Fe and Zn in plant samples and mean values of the metal contents in rhizosphere soils are presented in Table 5. Concentrations of other chemical elements measured in certain plant samples are shown in Table 6.

The majority of plant samples exhibit concentrations of chromium and nickel within the toxicity range, according to their mean values [1] (Table 7). Zn concentrations in a few plants (black mustard, salsify, verbascum, chicory, black nightshade) sampled from close to the ore conveyor, likewise the case of their rhizospheres as earlier mentioned, were also found near or within the toxicity range. Moreover high iron concentrations were detected in the majority of plant samples.

Strong positive correlations were observed between chromium total concentrations in plant tissues and Ni, Mn, Fe and Zn total contents in plant samples as well, regardless of the species sampled (Figure 6). With the exception of Zn these relations were proportional to those between Cr and Ni and between Mn and Fe total concentrations in their rhizospheres. However, faint but positive correlations were found between total concentrations of Cr, Ni, Mn and Fe in plants and total metal concentrations in their rhizospheres. In addition, all metal concentrations in the studied plant samples, regardless of species, displayed negative correlations with metal amounts extracted by EDTA and 1M $HNO_3$.

Concentrations of hexavalent chromium were measured in a few plant samples that exhibited significant total chromium concentrations (Table 8) and were found to be extremely low compared to the total chromium concentrations. Only 3.9% of total chromium in plant samples, regardless of the species sampled, is present as Cr(VI). Moreover, hexavalent chromium concentrations were very well correlated with $Cr_{(total)}$, Fe and Mn contents measured in these plants (Figure 7). Conversely, these concentrations displayed faint or no correlation with Cr extracted with EDTA and $HNO_3$ 1M or with $Cr_{(total)}$ (r = 0.51), Cr(VI), $Fe_{(total)}$ and $Mn_{(total)}$ in soils.

**Table 5.** Cr, Ni, Mn, Fe and Zn concentrations (in mg kg$^{-1}$) in various parts of plant samples and in their rhizospheres.

| Plant | No of samples | Plant tissue | Element | Mean | Min | Max | Soil [a] | Plant | No of samples | Plant tissue | Element | Total concentrations | Soil [a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carrot | 4 | Leaves | Cr | 3.5 | 2.7 | 4 | 720 | Black mustard | 1 | Leaves | Cr | 79 | 1 700 |
| | | | Ni | 17 | 14 | 19 | 1 700 | | | | Ni | 72 | 3 400 |
| | | | Mn | 52 | 45 | 59 | 1 200 | | | | Mn | 82 | 1 600 |
| | | | Fe | 140 | 45 | 200 | 46 600 | | | | Fe | 1 690 | 117 000 |
| | | | Zn | 9 | 8 | 10 | 58 | | | | Zn | 92 | 920 |
| Carrot | 4 | Tubers | Cr | 1 | 0.4 | 3 | 720 | Salsify | 1 | Leaves | Cr | 11 | 1 700 |
| | | | Ni | 8 | 6 | 13 | 1 700 | | | | Ni | 26 | 3 400 |
| | | | Mn | 11 | 9 | 15 | 1 200 | | | | Mn | 49 | 1 600 |
| | | | Fe | 110 | 32 | 250 | 46 600 | | | | Fe | 395 | 117 000 |
| | | | Zn | 8 | 7 | 11 | 58 | | | | Zn | 380 | 920 |
| Olea | 3 | Leaves | Cr | 2.6 | 0.7 | 6.0 | 730 | Verbascum | 1 | Leaves | Cr | 82 | 1 700 |
| | | | Ni | 9 | 1.6 | 18 | 1 500 | | | | Ni | 210 | 3 400 |
| | | | Mn | 26 | 14 | 34 | 1 160 | | | | Mn | 73 | 1 600 |
| | | | Fe | 130 | 30 | 280 | 47 300 | | | | Fe | 2 620 | 117 000 |
| | | | Zn | 17 | 9 | 27 | 54 | | | | Zn | 86 | 920 |
| Garlic | 3 | Leaves | Cr | 6 | 1.8 | 13 | 1 100 | Pigweed | 1 | Leaves | Cr | 6 | 910 |
| | | | Ni | 17 | 4.0 | 34 | 2 500 | | | | Ni | 9 | 1 730 |
| | | | Mn | 32 | 28 | 34 | 1 400 | | | | Mn | 22 | 850 |
| | | | Fe | 235 | 107 | 450 | 63 760 | | | | Fe | 160 | 51 700 |
| | | | Zn | 15 | 13 | 18 | 55 | | | | Zn | 24 | 22 |
| Potatoe | 3 | Tubers | Cr | 1.3 | 0.4 | 1.9 | 2 000 | Vegetable marrow | 1 | Leaves | Cr | 20 | 540 |
| | | | Ni | 8 | 7 | 9 | 3 600 | | | | Ni | 32 | 1 240 |
| | | | Mn | 9 | 8 | 11 | 1 300 | | | | Mn | 73 | 620 |
| | | | Fe | 63 | 28 | 100 | 143 100 | | | | Fe | 560 | 42 300 |
| | | | Zn | 12 | 8 | 16 | 26 | | | | Zn | 39 | 138 |
| Sonchus | 5 | Leaves | Cr | 54 | 34 | 90 | 2 200 | Black nightshade | 1 | Leaves | Cr | 120 | |
| | | | Ni | 93 | 43 | 150 | 4 300 | | | | Ni | 140 | |
| | | | Mn | 100 | 59 | 190 | 1 400 | | | | Mn | 94 | |
| | | | Fe | 1 700 | 880 | 3 000 | 119 000 | | | | Fe | 2 460 | |
| | | | Zn | 37 | 16 | 270 | 320 | | | | Zn | 42 | |
| Chicory | 2 | Leaves | Cr | 48 | 33 | 63 | 1 700 | Cabbage | 1 | Leaves | Cr | 0.3 | |
| | | | Ni | 88 | 86 | 90 | 3 400 | | | | Ni | 13 | |
| | | | Mn | 89 | 60 | 118 | 1 600 | | | | Mn | 16 | |
| | | | Fe | 1 200 | 1 000 | 1 400 | 117 000 | | | | Fe | 40 | |
| | | | Zn | 78 | 64 | 91 | 920 | | | | Zn | 12 | |

[a] mean values of metals (mg kg$^{-1}$) in the rhizospheres

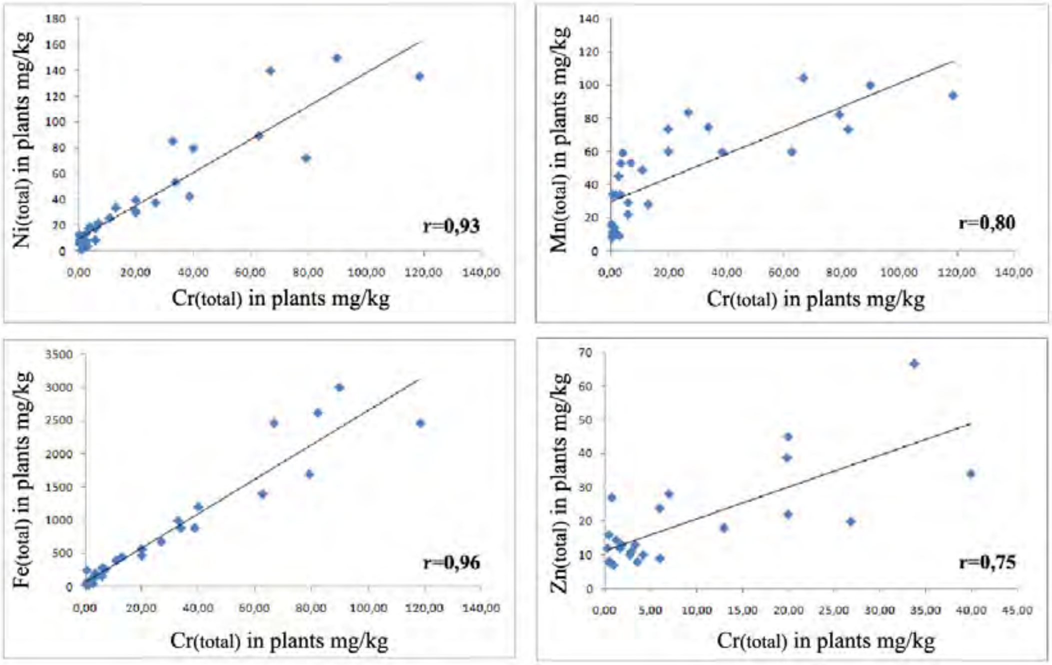

**Figure 6.** Relations of $Cr_{(total)}$ versus Ni, Mn, Fe and Zn total concentrations in plant samples.

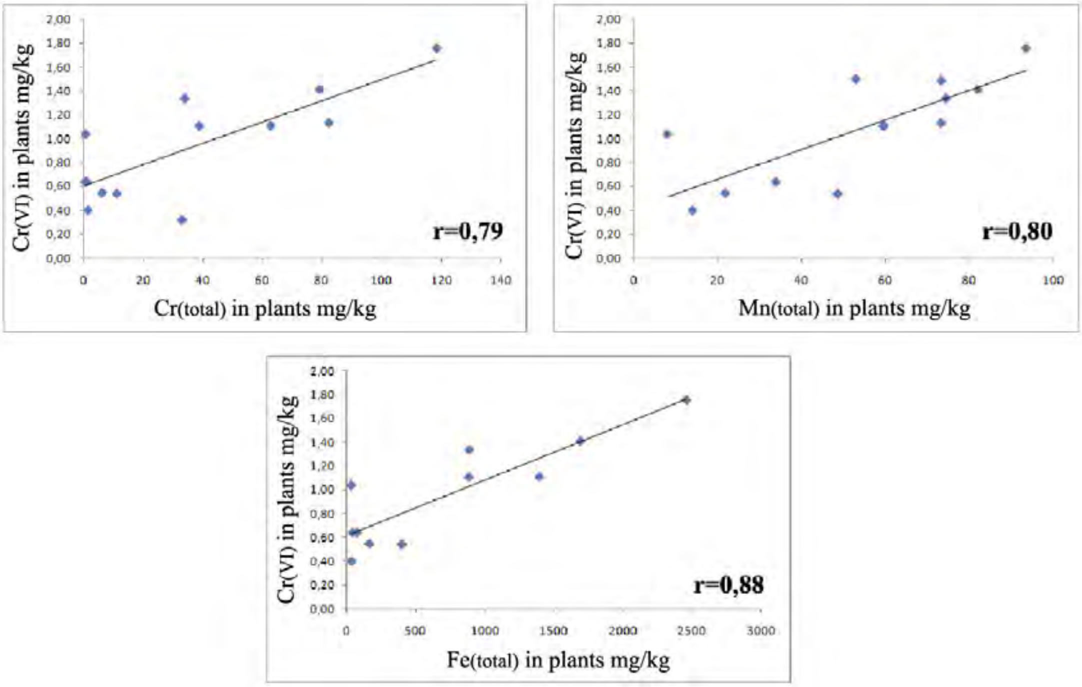

**Figure 7.** Relationships between Cr(VI) concentrations in plant samples and their total content in Cr, Mn and Fe.

**Table 6.** Average concentrations (in mg kg$^{-1}$ or weight percent) of other chemical elements measured in selected plant samples.

| Element | Ca% | Mg% | Na% | K% | Pb | Cd | Sc | Mo | Cu | Ag | Co | Au | P% | S% | Se | Hg | As | Sr | Ba | Ti | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Olea (n=3)[a] | 14 | 0.1 | 0.01 | 0.7 | 0.7 | 0.01 | 0.2 | 0.09 | 6.2 | 13 | 4.7 | 320 | 0.1 | 0.08 | 0.2 | 33 | 0.3 | 13 | 7 | 5 | 11 |
| Potatoe (n=3)[a] | 0.06 | 0.09 | 0.007 | 1.3 | 0.3 | 0.03 | 0.1 | 0.2 | 3.5 | 5 | 1.2 | 55 | 0.2 | 0.08 | 0.4 | 2.7 | 0.1 | 1.4 | 1.3 | 7 | 5 |
| Sonchus (n=5)[a] | 1.6 | 0.3 | 0.9 | 3.6 | 1.5 | 0.09 | 0.2 | 0.5 | 7 | 12 | 5 | 130 | 0.3 | 0.5 | 0.6 | 10 | 0.3 | 25 | 7 | 13 | 28 |
| Chicory (n=2)[a] | 1.7 | 0.4 | 0.6 | 3.7 | 0.9 | 0.09 | 0.3 | 0.3 | 19 | 11 | 9.7 | 74 | 0.3 | 0.3 | 0.7 | 18 | 0.4 | 39 | 8 | 16 | 32 |
| Black mustard (n=1) | 4.0 | 0.4 | 0.2 | 2.9 | 4.5 | 0.2 | 0.4 | 1.8 | 6.1 | 12 | 7 | 7 | 0.3 | 1.1 | 0.6 | 20 | 0.2 | 83 | 15 | 18 | 35 |
| Salsify (n=1) | 1.24 | 0.2 | 1.4 | 3.3 | 1.1 | 0.05 | 0.2 | 0.6 | 10 | 41 | 6 | 1 150 | 0.2 | 0.5 | 0.6 | 32 | 0.2 | 15 | 6 | 9 | 21 |
| Verbascum (n=1) | 1.3 | 0.2 | 0.03 | 2.1 | 1.3 | 0.03 | 0.4 | 0.7 | 10 | 51 | 15 | 1 690 | 0.2 | 0.1 | 0.3 | 40 | 0.3 | 23 | 8 | 13 | 15 |
| Pigweed (n=1) | 1.86 | 0.7 | 0.009 | 6.6 | 0.2 | 0.5 | 0.1 | 3.05 | 5 | 6 | 2 | 1.1 | 0.3 | 0.2 | 0.2 | 6 | 0.2 | 31 | 39 | 12 | 27 |
| Vegetable marrow (n=1) | 2.39 | 0.7 | 0.005 | 3.5 | 1.0 | 0.07 | 0.2 | 13 | 13 | 13 | 4 | 1.5 | 0.6 | 0.4 | 0.3 | 16 | 0.3 | 33 | 15 | 23 | 97 |
| Black nightshade (n=1) | 1.55 | 0.4 | 0.03 | 3.7 | 0.7 | 0.2 | 0.3 | 0.6 | 9 | 22 | 14 | 150 | 0.4 | 0.5 | 0.3 | 13 | 0.5 | 19 | 8 | 18 | 23 |

[a] mean values of metals in plants samples

n = number of samples

**Table 7.** Metal (Cr, Ni Mn Fe and Zn) ranges and means (in mg kg$^{-1}$) in the studied plant samples, in comparison with normal, excessive and deficient values (in mg kg$^{-1}$) (from [1]).

| Metals | Metal ranges in the studied plant samples | Mean values of the studied plant samples | Normal values | Deficient values | Excessive values |
|---|---|---|---|---|---|
| Cr | 0.3-119 | 27 | 0.1-0.5 | – | 5-30 |
| Ni | 4-210 | 49 | 0.1-5 | – | 10-100 |
| Mn | 8-190 | 63 | 30-300 | 10-30 | 400-1 000 |
| Fe | 28-3 000 | 775 | – | – | – |
| Zn | 8-380 | 53 | 27-150 | 0-20 | 100-400 |

**Table 8.** Concentrations of Cr(VI) in plant samples (mg kg$^{-1}$) as a percentage of their total chromium content.

| Element | $Cr_{(total)}$ | Cr(VI) in plants | % of $Cr_{(total)}$ in plants extracted with alkaline digestion |
|---|---|---|---|
| Black mustard | 79 | 1.4 | 1.8 |
| Salsify | 11 | 0.5 | 4.9 |
| Verbascum | 82 | 1.1 | 1.4 |
| Chicory | 48 | 0.7 | 1.5 |
| Sonchus | 37 | 1.2 | 3.2 |
| Pigweed | 6 | 0.5 | 9.1 |
| Vegetable marrow | 20 | 1.5 | 7.5 |
| Black nightshade | 119 | 1.8 | 1.5 |

**Table 9.** Concentrations of chemical constituents (in μg.L$^{-1}$) and other physical and chemical parameters of water samples from central Euboea.

| Sample | | Cr$_{(tot.)}$ | Cr(VI) | Ca | Mg | Ni | Mn | Zn | Si | Na | K | B | Li | As | Cd | Co | Cu | P | Pb | S (mg L$^{-1}$) | Se | V | pH | Eh (mV) | CND (mS cm$^{-1}$) | TDS (g L$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EV1 | Drilling well | <1 | <4 | 98000 | 5170 | 2 | 0.2 | 32 | 4090 | 12000 | 450 | 10 | 1.4 | <0.5 | <0.05 | 0.03 | 7 | 34 | 0.2 | 5 | 0.5 | 0.4 | 7.35 | -27 | 0.52 | 0.26 |
| EV2 | Drilling well | 15 | 15 | 68200 | 55800 | 7 | 0.8 | 6090 | 23700 | 15500 | 460 | 26 | 2.1 | <0.5 | 0.07 | 0.04 | 3 | 34 | 2 | 7 | 1.5 | 2 | 7.68 | -47 | 0.72 | 0.36 |
| EV3 | Drilling well | 16 | 16 | 15300 | 59000 | 9 | <0.05 | 1.9 | 24100 | 15800 | 600 | 25 | 2.4 | 0.5 | <0.05 | 0.04 | 0.4 | <20 | <0.1 | 7 | 0.7 | 3 | 7.43 | -36 | 0.72 | 0.39 |
| EV4 | Drilling well | 18 | 18 | 35300 | 28400 | 0.3 | <0.05 | <0.5 | 10000 | 12400 | 450 | 10 | 0.2 | <0.5 | <0.05 | 0.04 | 0.3 | <20 | <0.1 | 3 | 0.5 | 1 | 7.88 | -62 | 0.41 | 0.22 |
| EV5 | Drilling well | 37 | 36 | 7440 | 66800 | 0.8 | <0.05 | <0.5 | 33000 | 21000 | 320 | 19 | 4.3 | 0.5 | <0.05 | <0.02 | 0.3 | <20 | <0.1 | 1 | 0.8 | 8 | 7.72 | -53 | 0.70 | 0.37 |
| EV6 | Drilling well | 25 | 25 | 19900 | 52300 | 2 | <0.05 | <0.5 | 24300 | 19600 | 540 | 21 | 3.8 | 0.7 | <0.05 | 0.02 | 0.3 | <20 | <0.1 | 6 | <0.5 | 6 | 7.73 | -55 | 0.67 | 0.36 |
| EV7 | Drilling well | 3 | <4 | 86300 | 19700 | <0.2 | 9 | 2400 | 6170 | 91400 | 3300 | 43 | 3.6 | 0.7 | <0.05 | 0.04 | 2 | 40 | 0.1 | 11 | 4 | 2 | 7.30 | -33 | 0.96 | 0.47 |
| EV8 | Drilling well | 2 | <4 | 84600 | 55700 | <0.2 | 5 | 5.2 | 6700 | 438000 | 13780 | 150 | 7.8 | 2.8 | <0.05 | 0.04 | 7 | 38 | 0.1 | 50 | 19 | 4 | 7.43 | -37 | 2.77 | 1.39 |
| EV9 | Drilling well | 5 | <4 | 118150 | 47150 | 0.6 | 12 | 1540 | 8730 | 266900 | 7960 | 110 | 6.9 | 2.1 | <0.05 | 0.1 | 5 | 41 | 9 | 31 | 10 | 3 | 7.13 | -20 | 2.10 | 1.05 |
| EV10 | Drilling well | 33 | 32 | 94000 | 44900 | 5 | 1 | 55 | 19800 | 19400 | 670 | 19 | 2 | <0.5 | <0.05 | 0.1 | 25 | 30 | 1.5 | 19 | 1 | 1 | 7.47 | -35 | 0.82 | 0.41 |
| EV11 | Drilling well | 32 | 32 | 95200 | 45400 | 6 | 0.8 | 48 | 18800 | 19300 | 650 | 19 | 2 | <0.5 | <0.05 | 0.1 | 3 | 32 | 0.6 | 17 | 1 | 1 | 7.42 | -34 | 0.80 | 0.40 |
| EV12 | Drilling well | 16 | 12 | 98600 | 51600 | 11 | 2 | 2640 | 23200 | 22300 | 460 | 25 | 2.7 | <0.5 | 0.08 | 0.2 | 6 | 37 | 11 | 29 | 2 | 2 | 7.30 | -27 | 0.89 | 0.44 |
| EV13 | Drilling well | 13 | 12 | 121700 | 28600 | 33 | 0.5 | 48 | 14300 | 18800 | 480 | 22 | 2.1 | <0.5 | <0.05 | 0.1 | 1 | 35 | 0.2 | 13 | 1 | 0.7 | 7.11 | -16 | 0.78 | 0.38 |
| EV14 | Drilling well | 52 | 51 | 77800 | 83100 | 4 | 1 | 2 | 27900 | 29900 | 320 | 29 | 3.5 | <0.5 | <0.05 | 0.3 | 1 | 43 | <0.1 | 35 | 3 | 2 | 7.49 | -38 | 1.04 | 0.52 |
| EV15 | Drilling well | 130 | 128 | 17700 | 81200 | 4 | <0.05 | 2 | 19800 | 72700 | 12400 | 150 | 6.8 | 0.7 | <0.05 | 0.2 | 1 | <20 | <0.1 | 41 | 2 | 3 | 7.18 | -23 | 1.32 | 0.70 |
| EV16 | Drilling well | 53 | 51 | 32000 | 76300 | 5 | 0.11 | 110 | 16900 | 37600 | 1670 | 38 | 4.1 | 0.8 | <0.05 | 0.1 | 0.5 | <20 | <0.1 | 29 | 1 | 3 | 7.32 | -29 | 1.06 | 0.56 |
| EV17 | Drilling well | 60 | 59 | 33100 | 74500 | 4 | 0.11 | 10 | 16300 | 38000 | 1600 | 35 | 4 | 0.8 | <0.05 | 0.09 | 1 | <20 | <0.1 | 28 | 1 | 3 | 7.43 | -37 | 0.97 | 0.51 |
| EV18 | Drilling well | 114 | 110 | 63700 | 103100 | 4 | <0.05 | 0.5 | 17400 | 40200 | 4800 | 61 | 5.8 | 0.9 | <0.05 | 0.2 | 0.6 | <20 | <0.1 | 68 | 2 | 3 | 7.26 | -26 | 1.41 | 0.75 |
| EV19 | Drilling well | 15 | 15 | 9500 | 79600 | 1 | 0.5 | 0.6 | 34100 | 14700 | 380 | 15 | 1.6 | 2.6 | <0.05 | 0.03 | 0.3 | <20 | <0.1 | 8 | 0.8 | 3 | 7.68 | -50 | 0.69 | 0.37 |
| EV20 | Drilling well | 14 | 14 | 17800 | 81500 | 5 | <0.05 | <0.5 | 34100 | 35100 | 1220 | 16 | 2.3 | 1.5 | <0.05 | 0.02 | 0.5 | <20 | <0.1 | 13 | 1 | 7 | 7.52 | -41 | 0.84 | 0.44 |
| EV21 | Drilling well | 2.4 | <4 | 53400 | 11100 | <0.2 | <0.05 | <0.5 | 6760 | 15400 | 680 | 11 | 2.2 | 0.7 | <0.05 | 0.02 | 0.2 | <20 | <0.1 | 5 | 0.7 | 1 | 7.31 | -29 | 0.57 | 0.30 |
| EV22 | Drilling well | 3.4 | <4 | 43600 | 9740 | 0.7 | <0.05 | 1 | 6360 | 14000 | 470 | 11 | 0.9 | <0.5 | <0.05 | 0.06 | 0.3 | <20 | <0.1 | 5 | 0.7 | 0.5 | 7.17 | -21 | 0.62 | 0.33 |
| EV23 | Drilling well | <1 | <4 | 51100 | 4390 | <0.2 | <0.05 | <0.5 | 3900 | 11900 | 410 | 8 | 1 | 0.5 | <0.05 | 0.02 | 0.3 | <20 | <0.1 | 4 | 0.5 | 0.7 | 7.10 | -17 | 0.59 | 0.31 |
| EV24 | Drilling well | 37 | 36 | 8940 | 67500 | 0.9 | <0.05 | <0.5 | 32100 | 21600 | 350 | 21 | 4.5 | 0.5 | <0.05 | <0.02 | 0.3 | <20 | <0.1 | 1 | 1 | 9 | 7.52 | -41 | 0.70 | 0.37 |
| EV25 | Drilling well | 33 | 32 | 30200 | 50200 | 2 | <0.05 | <0.5 | 12800 | 22300 | 1230 | 30 | 2.7 | 0.9 | <0.05 | 0.11 | 0.4 | <20 | <0.1 | 15 | 0.9 | 2 | 7.34 | -31 | 0.75 | 0.40 |
| EV26 | Drilling well | 70 | 68 | 16500 | 113600 | 2 | 0.13 | 0.9 | 24500 | 52700 | 3880 | 68 | 6.8 | 1.4 | <0.05 | 0.2 | 0.8 | <20 | <0.1 | 27 | 4 | 4 | 7.76 | -55 | 1.30 | 0.69 |
| EV27 | Spring | 31 | 30 | 48600 | 74100 | 2 | 0.08 | 0.9 | 30700 | 21700 | 350 | 23 | 3.7 | <0.5 | <0.05 | 0.03 | 0.5 | 35 | <0.1 | 5 | 1 | 6 | 7.60 | -44 | 0.75 | 0.37 |
| EV28 | Spring | 33 | 32 | 47600 | 74200 | 2 | 0.13 | 0.7 | 29900 | 21600 | 350 | 23 | 3.4 | <0.5 | <0.05 | 0.05 | 0.6 | 33 | <0.1 | 4 | 1 | 6 | 7.45 | -33 | 0.79 | 0.39 |
| EV29 | Spring | 27 | 26 | 94400 | 43400 | 4 | <0.05 | <0.5 | 20700 | 19100 | 670 | 17 | 1.9 | <0.5 | <0.05 | 0.1 | 0.4 | 34 | <0.1 | 19 | 1 | 1 | 7.44 | -32 | 0.79 | 0.39 |
| EV30 | Spring | 26 | 25 | 65400 | 69900 | 2 | 0.43 | 0.6 | 26500 | 22600 | 580 | 17 | 2.7 | <0.5 | <0.05 | 0.06 | 0.4 | 33 | <0.1 | 5 | 1 | 0.8 | 7.69 | -47 | 0.81 | 0.40 |
| EV31 | Spring | 17 | 12 | 113200 | 26400 | 11 | 0.06 | <0.5 | 14100 | 16000 | 1770 | 24 | 1.6 | <0.5 | <0.05 | 0.08 | 0.4 | 75 | <0.1 | 5 | 0.8 | 0.7 | 7.15 | -15 | 0.73 | 0.36 |
| EV32 | Spring | 5 | <4 | 117900 | 12900 | 2 | 0.23 | 0.8 | 6890 | 10800 | 360 | 10 | 0.7 | <0.5 | <0.05 | 0.03 | 1 | 34 | <0.1 | 4 | 0.5 | 0.4 | 7.07 | -11 | 0.63 | 0.31 |
| EV33 | Spring | <1 | <4 | 46200 | 7730 | 1 | <0.05 | <0.5 | 5590 | 14200 | 1070 | 13 | 0.7 | 0.6 | <0.05 | 0.07 | 0.2 | <20 | <0.1 | 6 | 0.5 | 1 | 7.34 | -31 | 0.53 | 0.28 |
| EV34 | Spring | 18 | 18 | 36600 | 26900 | 7 | <0.05 | <0.5 | 15400 | 15300 | 2300 | 19 | 1.6 | 0.5 | <0.05 | 0.06 | 0.2 | <20 | <0.1 | 6 | <0.5 | 1 | 7.06 | -16 | 0.73 | 0.39 |

### 5.3. Waters

Analytical results showing concentrations of chemical constituents (in µg.L$^{-1}$) and other physical and chemical parameters of ground waters are given in Table 9.

Significant Cr(VI) concentrations were detected in the majority of the studied groundwater samples.

Total chromium concentrations range from below detection limit (BDL) to 130 µg.L$^{-1}$, with a mean value of 28 µg.L$^{-1}$. Cr(VI) concentrations range from BDL to 128 µg.L$^{-1}$. There is a very good correlation ($r = 0.99$) between $Cr_{(total)}$ and Cr(VI) indicating that chromium (VI) is the predominant form of dissolved Cr in the area studied. Concentrations over the maximum acceptable level for $Cr_{(total)}$ in drinking water (50 µg.L$^{-1}$, according to the EU Directive), [24], were detected in six groundwater samples. With the exception of $Cr_{(total)}$ and Cr(VI) – and in some cases Zn – all elements in ground water samples were found to be below the maximum permissible limits for human usage [24]. A few ground water samples derived from drilling wells exhibited extremely high values of Zn.

According to the differences in the chemical composition, the groundwater samples from central Euboea could be classified into 3 groups (Group I, Group II and Group III). The minimum, mean and maximum concentrations of chemical elements for each group are presented in Table 6.

Based on Ca, Mg, $Cr_{(total)}$ and Si contents, ground water samples can be categorized into three groups, with Group I exhibiting high values of Ca/Mg ratio (up to 19), low values of Si and Mg and mean values of $Cr_{(total)}$ below the detection limit. The rest of the water samples can be classified into the remaining two groups (Group II and Group III) according to their Cr and Si content. Group II includes mainly water samples with a mean value of 24 µg.L$^{-1}$ for Cr(VI) and relatively high concentrations of Si compared to those of Group III. Group III consists of ground water samples with high $Cr_{(total)}$ and Cr(VI) concentrations, up to 130 and 128 µg.L$^{-1}$, respectively.

## 6. Discussion

The soil Cr, Ni, Mn and Fe abundances detected are associated mainly with ultramafic rocks and iron-nickel laterite deposits. This conclusion is supported by a very good correlation of Cr to Ni due to nickeliferous mineralization and of Cr to Mn and Fe due to the underlying ultramafic rocks. The unusually high concentrations of Zn detected in plant samples and rhizospheres collected close to the ore conveyor are probably due to the alteration of the old galvanized metallic parts of the conveyor itself [34].

Among the selective extractions used, the $HNO_3$ 1M extractant removed larger amounts of Cr, Ni, Mn, Fe and Zn than the EDTA, as each extractant, as has already been reported, removes different forms of these metals from the soils.

On the basis of metal species extractable with EDTA and $HNO_3$ 1M expressed as a percentage of their total concentrations, the relative availability of the studied metals followed this order: Zn>M*n* >Ni>Fe>Cr and Mn>Zn>Ni>Cr>Fe for each digestion method, respectively. Although soil samples exhibited enrichment in total metal concentration – in the order Fe>Ni>Mn>Cr>Zn – other metal concentration sequences were presented as available to plants. The latter assumption could be enhanced by the very good positive correlation between total amount of Zn in soils and the amount extracted by EDTA and 1M $HNO_3$, which suggests that although soil solutions are enriched in the elements typical of lateritic soils (Cr, Ni, Mn and Fe), other elements like Zn can be more available for plant uptake [10]. Moreover it should be noted that the order of the elements most easily leached by either EDTA or $HNO_3$ 1M (Fe>Mn>Ni>Zn>Cr), according to their concentrations in the selective solutions, did not coincide with the order of the relative availability of these elements.

The very low ratio of $Cr_{(EDTA)}/Cr_{(total)}$ (equal to 0.001 in soil samples, meaning that only 0.1% of total chromium is extracted by EDTA and becomes available) confirms the low mobility of Cr in surface environments and its limited availability to plants, perhaps because of its retention in resistant phases such as chromite. On the other hand the constancy of the ratio suggests that regardless of the extent of soil enrichment in Cr, the amount of Cr extracted by EDTA remains constant.

The good positive correlations between total soil content and metal amount extracted with $HNO_3$ 1M suggests that with increasing total soil content, the mobile or easily $HNO_3$ 1M – extractible – and perhaps bioavailable fraction of Zn>Mn>Cr>Ni>Fe, according to the value of correlation coefficient – increases as well. However the negative correlations of metal contents extracted with $HNO_3$ 1M and EDTA versus metal amounts in plant samples suggest that either these methods of available metal extraction are unsatisfactory or that the amount of metal uptake might be independent of the amount of available metal, and instead depends on the metabolism of each plant sample [9, 10]. Perhaps the concentrations of metals measured in plant tissues should be considered to give the best measure of availability [9].

The order of bioavailable elements (Zn>Mn>Ni>Fe>Cr), most strongly correlated with total organic carbon, coincide with the order of the relative availability of metals extracted with EDTA, perhaps due to the formation of soluble or insoluble forms of organic matter with the metals studied.

The mean metal concentration values in plants and their rhizospheres and the weak positive correlations between the total content of Cr, Ni, Mn and Fe in plants and their total amount in soils suggests that plant uptake of Cr increased with increased soluble Cr in the soil of the rhizosphere.

The fact that plant samples exhibited significant Cr-Ni, Cr-Mn, Cr-Fe and Cr-Zn correlations implies that perhaps the mechanisms of absorption and translocation of Cr in plants seem to be similar to those of Ni, Mn, Fe and Zn [1, 9]. Moreover the fact that proportional relations were observed in their rhizospheres suggests that perhaps ultramafic rocks and Fe-Ni mineralization, which are responsible for these good correlations, seem to have an impact on element distributions not only in soils but in plant samples growing on them too.

**Table 10.** Mean, standard deviation, min and max values (in μg.L$^{-1}$) of the chemical elements and the physical and chemical parameters for each group of the water samples.

| | Mean | Standard deviation | Min | Max | No of samples |
|---|---|---|---|---|---|
| | | Group I | | | |
| Cr$_{(total)}$ | BDL | 1.5 | BDL | 5.0 | 9 |
| Cr(VI) | BDL | 1.1 | BDL | BDL | 9 |
| Ca | 70 900 | 29 500 | 43 600 | 117 900 | 9 |
| Mg | 10 100 | 5 200 | 4 380 | 19 700 | 9 |
| Ni | 0.8 | 0.8 | BDL | 1.9 | 9 |
| Mn | 1.4 | 3.4 | BDL | 9 | 9 |
| Zn | 350 | 910 | BDL | 2420 | 9 |
| Si | 5 680 | 1 230 | 3 900 | 6 890 | 9 |
| Na | 24 200 | 29 600 | 10 800 | 91 400 | 9 |
| K | 960 | 1 060 | 360 | 3 300 | 9 |
| B | 15 | 12 | 8 | 43 | 9 |
| Li | 1.5 | 1.1 | 0.7 | 3.6 | 9 |
| As | 0.5 | 0.2 | BDL | 0.7 | 9 |
| Cd | 0.03 | 0.00 | BDL | 0.03 | 9 |
| Co | 0.04 | 0.02 | 0.02 | 0.07 | 9 |
| Cu | 1.7 | 2.5 | 0.20 | 7 | 9 |
| P | 21 | 14 | BDL | 40 | 9 |
| Pb | 0.08 | 0.06 | BDL | 0.20 | 9 |
| S | 6 | 2.4 | 4.0 | 11 | 9 |
| Se | 1.1 | 1.3 | 0.5 | 4.0 | 9 |
| V | 0.9 | 0.46 | 0.4 | 1.5 | 9 |
| Ph | 7.23 | 0.12 | 7.07 | 7.35 | 9 |
| Eh(mV) | -24 | 8 | -33 | -11 | 9 |
| CND (ms cm$^{-1}$) | 0.63 | 0.15 | 0.52 | 0.96 | 9 |
| TDS (g L$^{-1}$) | 0.32 | 0.07 | 0.26 | 0.47 | 9 |
| | | Group II | | | |
| Cr$_{(total)}$ | 25 | 11 | 13 | 52 | 19 |
| Cr(VI) | 24 | 11 | 12 | 51 | 19 |
| Ca | 56 600 | 38 500 | 74 40 | 121 700 | 19 |
| Mg | 55 800 | 19 300 | 26 400 | 83 100 | 19 |
| Ni | 6 | 7 | 0.3 | 33 | 19 |
| Mn | 0.4 | 0.5 | BDL | 1.6 | 19 |
| Zn | 470 | 1 490 | BDL | 6 090 | 19 |
| Si | 24 000 | 7 330 | 10 000 | 34 100 | 19 |
| Na | 20 100 | 5 330 | 12 400 | 35 100 | 19 |
| K | 680 | 530 | 320 | 2 300 | 19 |
| B | 21 | 5 | 10 | 29 | 19 |
| Li | 2.5 | 1.1 | 0.20 | 5 | 19 |
| As | 0.5 | 0.6 | BDL | 2.6 | 19 |
| Cd | BDL | 0.02 | BDL | 0.08 | 19 |
| Co | 0.08 | 0.07 | BDL | 0.25 | 19 |
| Cu | 2.3 | 6 | 0.2 | 25 | 19 |
| P | 26 | 17 | BDL | 75 | 19 |
| Pb | 0.8 | 2.4 | 0.1 | 11 | 19 |
| S | 11 | 9 | 1.0 | 35 | 19 |
| Se | 1.1 | 0.5 | BDL | 2.5 | 19 |
| V | 3.3 | 2.9 | 0.7 | 9 | 19 |
| Ph | 7.49 | 0.2 | 7.06 | 7.88 | 19 |
| Eh(mV) | -36 | 17 | -62 | 16 | 19 |
| CND (ms cm$^{-1}$) | 0.76 | 0.12 | 0.41 | 1.04 | 19 |
| TDS (g L$^{-1}$) | 0.39 | 0.06 | 0.22 | 0.52 | 19 |
| | | Group III | | | |
| Cr$_{(total)}$ | 77 | 38 | 33 | 130 | 6 |
| Cr(VI) | 75 | 37 | 32 | 128 | 6 |
| Ca | 32 200 | 17 000 | 16 500 | 63 700 | 6 |
| Mg | 83 200 | 22 500 | 50 200 | 113 600 | 6 |
| Ni | 3.5 | 1.4 | 1.6 | 5 | 6 |
| Mn | 0.07 | 0.05 | BDL | 0.13 | 6 |
| Zn | 21 | 44 | BDL | 110 | 6 |
| Si | 17 900 | 3 940 | 12 800 | 24 500 | 6 |
| Na | 43 900 | 17 100 | 22 300 | 72 700 | 6 |
| K | 4 270 | 4 250 | 1 230 | 12 400 | 6 |
| B | 63 | 43 | 30 | 150 | 6 |
| Li | 5 | 1.7 | 2.7 | 7 | 6 |
| As | 0.9 | 0.2 | 0.7 | 1.4 | 6 |
| Cd | BDL | BDL | BDL | BDL | 6 |
| Co | 0.15 | 0.05 | 0.09 | 0.22 | 6 |
| Cu | 0.7 | 0.3 | 0.4 | 1.1 | 6 |
| P | BDL | BDL | BDL | BDL | 6 |
| Pb | BDL | BDL | BDL | BDL | 6 |
| S | 35 | 18 | 15 | 68 | 6 |
| Se | 1.7 | 1.0 | 0.9 | 3.5 | 6 |
| V | 2.8 | 0.7 | 1.9 | 4.0 | 6 |
| Ph | 7.38 | 0.2 | 7.18 | 7.76 | 6 |
| Eh(mV) | -34 | 12 | -55 | -23 | 6 |
| CND (ms cm$^{-1}$) | 1.13 | 0.25 | 0.75 | 1.41 | 6 |
| TDS (g L$^{-1}$) | 0.60 | 0.13 | 0.40 | 0.75 | 6 |

The variations of metal concentrations in plant samples of four species (chicory, black mustard, salsify, verbascum) growing on a single site with a common soil rhizosphere, suggests that metal concentrations were species-specific.

The very good correlations between Cr(VI) and Cr(total), and Fe and Mn in plants, in conjunction with the lack of correlation between Cr(VI) in plants and $Cr_{(EDTA)}$, $Cr_{(1M\ HNO3)}$, $Cr_{(total)}$, Cr(VI), $Fe_{(total)}$ and $Mn_{(total)}$ in soils could suggest the redox processes in soils. This correlations also rules Cr behavior and its transfer in the soil-plant system [1]. Cr(VI) presence in plants could be correlated with oxidation and reduction mechanisms taking place in the inner parts of the plants after metal uptake by plant tissues.

If we compare total chromium and nickel concentrations in plants with concentrations of these metals extracted with EDTA and $HNO_3$ 1M and with their total concentrations in soils and the local ground waters in a log-log plot of Cr vs Ni (Figure 8) it can be seen that Cr concentrations in soils are two orders of magnitude higher than in EDTA and $HNO_3$ 1M extracting solutions and in plants and at least four orders of magnitude higher than in local ground waters. This could suggest that chromium plant concentrations could be more strongly related to soils than to local ground waters.

Mg, Ca, $Cr_{(total)}$ and Si concentration differences in ground water samples resulted in the classification of the water samples into three groups (Group I, Group II, Group III). The discrimination of Group I, which may be associated with the karstic aquifer of the upper Cretaceous limestones, and the further discrimination of the rest of the ground waters samples derived from different types of aquifers, are presented in the triangular plots of Mg-$Cr_{(total)}$-Ca, $Cr_{(total)}$-Mg-Si and Mg-Si-Ca (Figure 9).

The significant concentrations of hexavalent chromium in ground waters of Group II may have originated from the ophiolites of the studied area. Ophiolitic rocks partially consist of Cr-bearing minerals such as chromite ($FeCr_2O_4$), serpentine ($(Mg, Fe)_3Si_2O_5(OH)_4$), chlorite [$(Mg, Al, Fe)_{12}(Si, Al)_8O_{20}(OH)_{16}$] and magnetite ($Fe^{2+}Fe_2^{3+}O_4$), in which chromium is present in the oxidation state of Cr(III). Serpentine and magnetite in the study area contain significant amounts of chromium reaching values of 0.80 and 0.39 wt% $Cr_2O_3$, respectively. Ophiolitic rocks may cause natural pollution of waters, not only in Cr(III), the oxidation state of Cr present in these rocks, but also in Cr(VI) [25]. Cr(VI) presence may be attributed to chromium extraction and oxidation from Cr-bearing serpentine, Cr-bearing chlorite, Cr-bearing magnetite formed at the edges of chromite, or Cr-bearing goethite (FeO(OH)) – a very common mineral in Fe-Ni laterite deposits – or, to a lesser extent, chromite, a mineral of very low solubility. Chromium in Fe-Ni-laterites is mainly hosted in chromite grains or fragments as a residual component inherited from ophiolitic parent rocks. Fine-grained silicate minerals such as chlorite and Fe-hydroxides such as goethite from the study area laterite matrix were found to contain a significant portion of chromium reaching values over to 0.97 and 1.69 wt% $Cr_2O_3$ respectively.

The above assumption concerning Cr(VI) origin from the ophiolitic rocks may be supported by the good positive correlation between $Cr_{(total)}$ and Cr(VI) versus Mg ($r = 0.74$ and 0.75 respectively) and between Mg versus Si ($r = 0.98$) (Table 11). The absence of correlation between $Cr_{(total)}$ and Cr(VI) versus Ni implies a faint connection between Cr(VI) presence and Fe-Ni mineralization.

Water samples with the high concentrations of chromium, which comprise Group III, are linked to shallow wells (with a depth ranging from 10-35 m), which are sited on the alluvial deposits within the populated places (towns? Cities?) of Psachna and Nea Artaki and as a consequence are more easily exposed to contamination due to anthropogenic impacts.

High values of Zn detected in a few ground water samples are due perhaps to the corrosion of old galvanized zinc pipes that constitute the plumbing system of those drilling wells [35]. Ground water flowing through old galvanized pipes contain significant amounts of zinc along with cadmium, copper and lead [36]. Indeed, we observed that those water samples which had high concentrations of Zn also contained elevated concentrations of Cd, Cu and Pb.

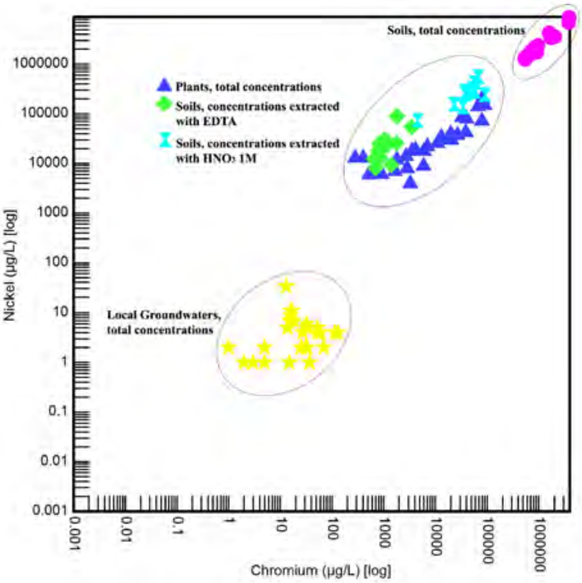

**Figure 8.** Log plot of Cr vs. Ni showing their total concentrations in soils, their concentrations in EDTA and $HNO_3$ 1M solutions after selective extraction from soils and their measured concentrations in ground waters of the studied area.

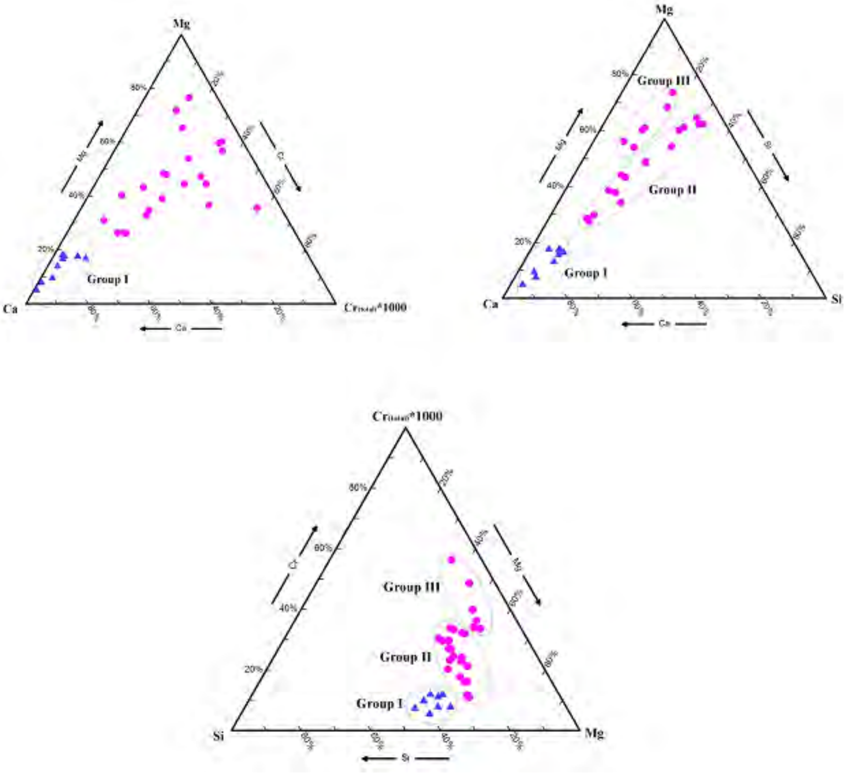

**Figure 9.** Discrimination diagrams for the water samples on the basis of their different contents in Ca, Mg, Cr and Si.

**Table 11.** Correlation coefficients of the measured chemical and physical parameters of the ground water samples from central Euboea.

| | $Cr_{(total)}$ | Cr(VI) | Ca | Mg | Ni | Mn | Si | Na | K | B | Li | As | Cd | Co | Cu | P | Pb | S | Se | V | Ph | Eh | CND | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cr_{(total)}$ | 1.00 | | | | | | | | | | | | | | | | | | | | | | | |
| Cr(VI) | 0.99 | 1.00 | | | | | | | | | | | | | | | | | | | | | | |
| Ca | -0.12 | -0.18 | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| Mg | 0.74 | 0.75 | -0.40 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| Ni | -0.05 | -0.07 | 0.51 | -0.05 | 1.00 | | | | | | | | | | | | | | | | | | | |
| Mn | 0.29 | 0.28 | 0.41 | 0.29 | 0.28 | 1.00 | | | | | | | | | | | | | | | | | | |
| Si | 0.71 | 0.72 | -0.44 | 0.98 | -0.03 | 0.21 | 1.00 | | | | | | | | | | | | | | | | | |
| Na | 0.62 | 0.61 | -0.17 | 0.74 | 0.07 | 0.25 | 0.70 | 1.00 | | | | | | | | | | | | | | | | |
| K | -0.16 | -0.20 | 0.14 | -0.26 | 0.21 | -0.27 | -0.20 | -0.03 | 1.00 | | | | | | | | | | | | | | | |
| B | 0.60 | 0.57 | 0.12 | 0.61 | 0.45 | 0.45 | 0.60 | 0.45 | 0.09 | 1.00 | | | | | | | | | | | | | | |
| Li | 0.72 | 0.72 | -0.34 | 0.72 | -0.03 | 0.11 | 0.76 | 0.63 | -0.28 | 0.59 | 1.00 | | | | | | | | | | | | | |
| As | -0.15 | -0.11 | -0.53 | 0.32 | -0.20 | -0.12 | 0.36 | 0.13 | 0.02 | -0.21 | -0.02 | 1.00 | | | | | | | | | | | | |
| Cd | -0.11 | -0.12 | 0.18 | 0.14 | 0.19 | 0.63 | 0.14 | -0.01 | -0.16 | 0.42 | 0.05 | -0.16 | 1.00 | | | | | | | | | | | |
| Co | 0.37 | 0.32 | 0.52 | 0.13 | 0.35 | 0.75 | 0.04 | 0.35 | 0.01 | 0.45 | 0.05 | -0.29 | 0.29 | 1.00 | | | | | | | | | | |
| Cu | 0.14 | 0.14 | 0.32 | -0.04 | 0.06 | 0.56 | -0.05 | 0.02 | -0.08 | 0.04 | -0.05 | -0.17 | 0.13 | 0.29 | 1.00 | | | | | | | | | |
| P | 0.17 | 0.08 | 0.78 | -0.02 | 0.41 | 0.28 | -0.05 | 0.04 | 0.29 | 0.48 | -0.03 | -0.42 | 0.17 | 0.42 | 0.12 | 1.00 | | | | | | | | |
| Pb | -0.04 | -0.08 | 0.25 | 0.09 | 0.20 | 0.70 | 0.10 | 0.12 | -0.13 | 0.30 | 0.08 | -0.14 | 0.80 | 0.56 | 0.29 | 0.15 | 1.00 | | | | | | | |
| S | 0.39 | 0.38 | 0.38 | 0.28 | 0.26 | 0.75 | 0.19 | 0.51 | -0.10 | 0.40 | 0.12 | -0.08 | 0.27 | 0.91 | 0.35 | 0.24 | 0.50 | 1.00 | | | | | | |
| Se | 0.58 | 0.56 | 0.26 | 0.60 | 0.19 | 0.71 | 0.51 | 0.66 | -0.28 | 0.61 | 0.39 | -0.15 | 0.41 | 0.67 | 0.23 | 0.36 | 0.38 | 0.76 | 1.00 | | | | | |
| V | 0.50 | 0.52 | -0.67 | 0.66 | -0.26 | -0.24 | 0.74 | 0.53 | -0.25 | 0.26 | 0.79 | 0.29 | -0.10 | -0.34 | -0.20 | -0.34 | -0.11 | -0.21 | 0.09 | 1.00 | | | | |
| Ph | 0.44 | 0.49 | -0.51 | 0.64 | -0.36 | 0.11 | 0.60 | 0.28 | -0.45 | 0.17 | 0.40 | 0.23 | 0.17 | -0.19 | 0.01 | -0.28 | -0.02 | -0.05 | 0.23 | 0.48 | 1.00 | | | |
| Eh | -0.40 | -0.44 | 0.62 | -0.57 | 0.63 | -0.02 | -0.54 | -0.23 | 0.34 | -0.07 | -0.34 | -0.26 | -0.13 | 0.23 | 0.01 | 0.36 | 0.01 | 0.08 | -0.13 | -0.48 | -0.93 | 1.00 | | |
| CND | 0.66 | 0.62 | 0.22 | 0.66 | 0.33 | 0.58 | 0.62 | 0.75 | 0.03 | 0.72 | 0.53 | -0.05 | 0.20 | 0.66 | 0.18 | 0.38 | 0.30 | 0.72 | 0.80 | 0.17 | -0.01 | 0.07 | 1.00 | |
| TDS | 0.66 | 0.64 | 0.06 | 0.69 | 0.26 | 0.52 | 0.67 | 0.78 | 0.05 | 0.69 | 0.57 | 0.06 | 0.16 | 0.60 | 0.14 | 0.24 | 0.26 | 0.69 | 0.75 | 0.26 | 0.02 | 0.01 | 0.98 | 1.00 |

## 7. A comparison of the ground water composition in Euboea and the Thiva – Tanagra – Malakasa basin (Eastern Greece)

The case of central Euboea can be compared with that of the Thiva – Tanagra – Malakasa basin (Eastern Greece), where the impact of anthropogenic activities on ground water quality is more intense [37]. For this purpose ground water chemistry data from the Thiva – Tanagra – Malakasa basin has been projected in the ternary diagrams made for the Euboea study (Figure 10). Ground water samples which are linked to the karstic aquifer of Mavrosouvala [37] have been distinguished from the others samples from the Thiva – Tanagra – Malakasa basin and plot in the Euboea Group I field. This comparison of the karstic aquifer of the Thiva – Tanagra – Malakasa basin with the karstic aquifer of Euboea (Group I) can be seen in the ternary plots of Mg-$Cr_{(total)}$-Ca and Mg-Si-Ca. However, when Si is involved in the statistical analysis, the karstic aquifer of the Thiva – Tanagra – Malakasa basin closely corresponds with the karstic aquifer of Euboea (Group I), as seen in the $Cr_{(total)}$-Mg-Si ternary plot. This differentiation may be due to the presence of ophiolitic rocks in central Euboea and the impact that these lithotypes have even on a karstic aquifer. Also, ground water samples from the Thiva – Tanagra – Malakasa basin that are characterized by high values of $Cr_{(total)}$ and Cr(VI), which are linked mainly to the industrial activities in the area, plot alongside the Euboea Group. This correlation supports the assumption that the high Cr(VI) values in central Euboea may be attributed not only to natural pollution but to anthropogenic impact also.

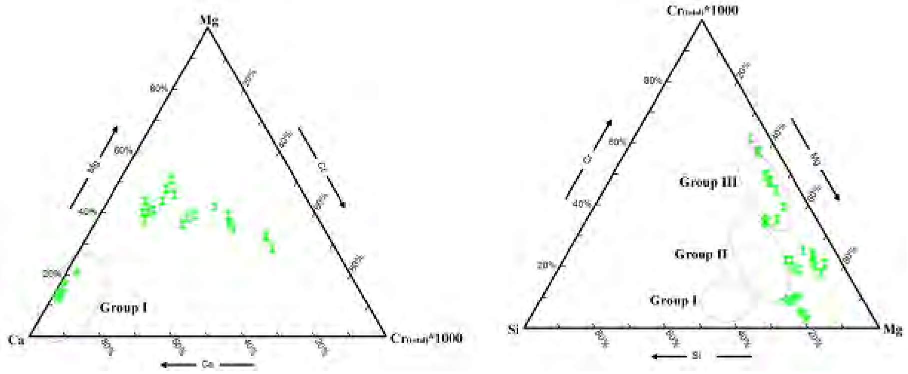

**Figure 10.** Triangular diagrams made for the case of Euboea used as background for the projection of the data from the Thiva – Tanagra – Malakasa basin.

## 8. Conclusions

Analytical data on plants and soils derived from Fe-Ni laterite deposits of central Euboea lead to the following conclusions:

- Selective extractions, although useful in the definition of metal behavior and relative metal availability in soil, do not seem proportional to in situ extraction performed by plants.
- Chromium in plants seem to be better related to chromium distribution in soils.
- Organic carbon seems to play a significant role in the order of availability and mobility of metals extracted with EDTA.
- Cr(VI) concentrations measured in soils were below the phytotoxic levels, while Cr(VI) content in plants was extremely low compared to the $Cr_{(total)}$ concentration.
- Chromium in all ground water samples was present in its hexavalent oxidation state.
- On the basis of the Ca, Mg, $Cr_{(total)}$ and Si contents, ground water samples of the study area can be classified into three groups: Group I, linked to

a karstic aquifer; Group II, which is associated with ophiolites; and Group III, which is considered to be linked to anthropogenic activity.

- The connection of Cr in ground waters with the presence of ophiolitic rocks in the study area was supported by the good positive correlation between $Cr_{(total)}$ and Cr(VI) versus Mg and between Mg versus Si.

- The group of ground waters from central Euboea connected with anthropogenic impacts exhibit similar composition with that of ground water from the Thiva – Tanagra – Malakasa basin.

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