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Article

Spatial Evolution of the Chromium Contamination in Soils from the Assopos to Thiva Basin and C. Evia (Greece) and Potential Source(s): Anthropogenic *versus* Natural Processes

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Abstract: The investigation of the contamination in soil, plants and groundwater revealed a spatial evolution, with an increasing trend in the Cr, Fe, Ni, Mn and Co contents in soils from the Assopos to Thiva basin, followed by C. Evia and Ni-laterite deposits, suggesting that the latter and their parent ophiolites are a potential source for these metals. In contrast, the contamination in groundwater by Cr(VI), ranging from 2 to 360 μg/L Cr, and a varying degree of salinization is probably due to both human activities and natural processes. A diverse source for the contamination of soil and groundwater in the Assopos-Thiva basins is consistent with the increasing trend of the Mg/Si ratio and Cr(VI) concentration in water. The use of deep karst-type aquifer instead of the shallow-Neogene one may provide a solution to the crucial environmental problem. The selective extraction by EDTA and alkaline solution showed that Cr and Fe are less available than Mn. The Cr contents in plants range from <1 to tens of mg/kg, due probably to the high resistance of chromite. However, the average Cr_{total} contents in plants/crops are higher than normal or sufficient values, whilst Cr_{total} accumulation [(% metals in plants × 100)/metal in soil] and Cr(VI) accumulation are relatively low. There is a very good positive correlation between accumulation factors for Cr and Fe ($R^2 = 0.92$), suggesting a similarity concerning their uptake.

Keywords: contamination; Cr(VI); soil; water; plant; Greece

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1. Introduction

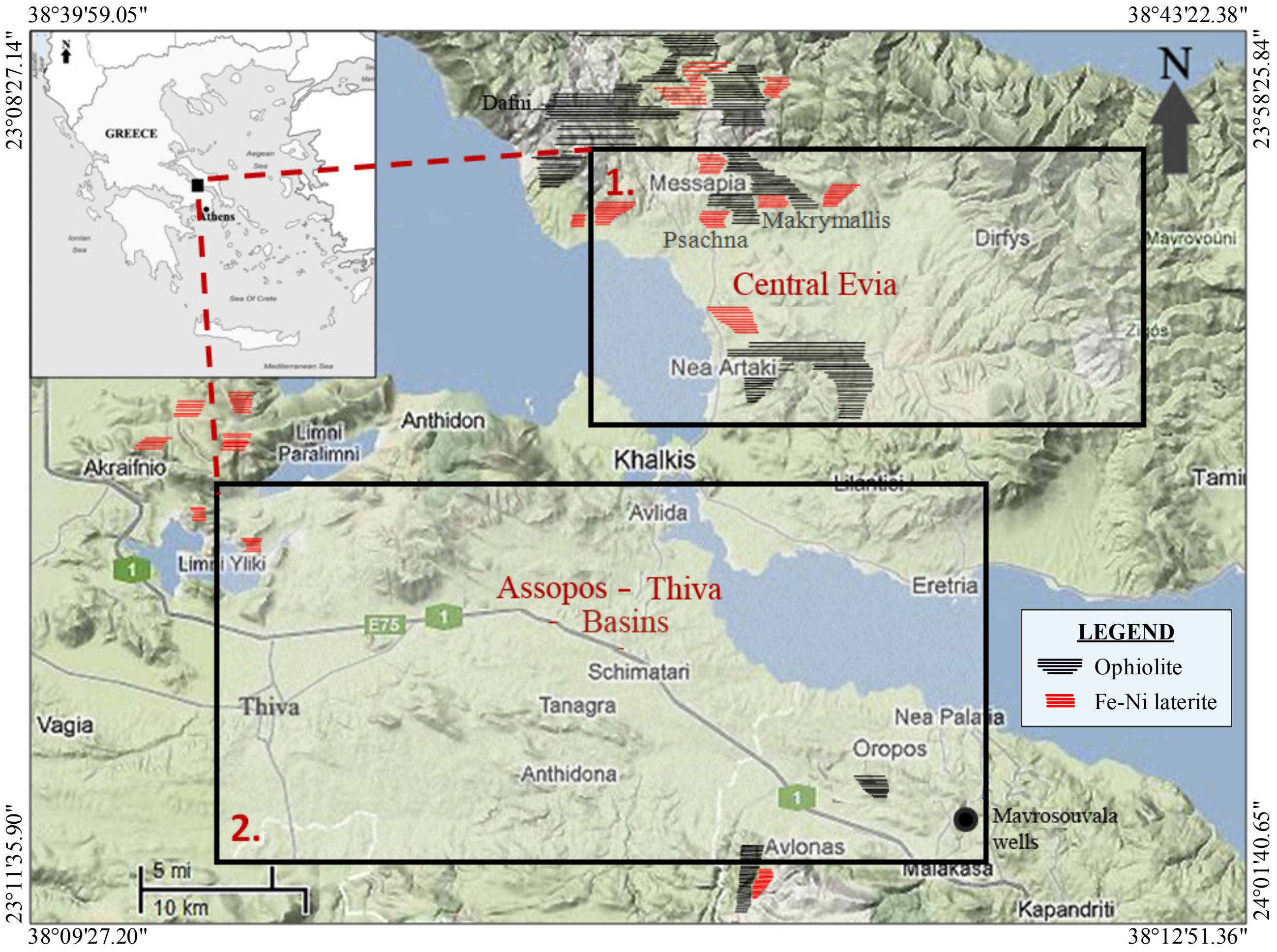
Chromium has long been used in many industrial processes, since Cr(VI) is an excellent corrosion inhibitor, and it is present in significant contents in ultramafic rocks and Ni-laterites, which are their weathering products. Cr(III) is an essential element in humans at small doses, but Cr(VI) is toxic and carcinogen [1]. Regulations from the European Union, Japan, South Africa, and the U.S. have established permissible exposure limits for air, dust, wastewater, drinking water, soil and waste. Directive 98/83/EC has established a maximum permissible limit of Cr_{total} in drinking water, 50 μg/L or ppb [2–4].

Since the source of contamination by heavy metals, including Cr(VI), in water soil and biota, is a subject of debate [5–10] the Assopos (Oropos, Avlona, Avlida)—Thiva basins, and central Evia (Messapia) were selected to investigate the effective influence of industry *versus* natural processes, such as ophiolites and/or Ni-laterites, to the soil, plant and groundwater contamination. The geochemical uptake of trace elements in host minerals of Cr and other associated metals (Ni, Co, Mn, Fe) is important in terms of control of the concentration and migration of metals in soil, water, and their availability [11]. Present integrated approach is a compilation of analytical data from several analyses of soil, plant-crops (cultivated and non cultivated) and groundwater samples and preliminary leaching data aiming to the evaluation of the extent and intensity of the contamination, the metal bio-availability, the percentage of Cr(VI) transferred into plants/crops (bio-accumulation) and the potential sources of the contamination. This paper is arising from the 3rd International Conference on Industrial and Hazardous Waste Management, held in Chania, Crete, in September 2012.

2. Geological and Hydrogeologic Outline

The formation of the Assopos and Thiva basins is the result of several normal faults, during Pliocene to present time. They are composed by alternations of marls and marl limestones at the lowest parts, and continental sediments consisting of conglomerates (pebbles derived from carbonates, basic and ultramafic rocks) with small intercalations of marl, marly limestone, metaclastic schist, sandstone, clays and flysch, at the uppermost horizons [12]. Due to the intense neotectonic deformation, those basins are characterized by a complicate tectonic structure as is exemplified by several sharp tectonic contacts between sediment types [13]. Central Evia apart from Quaternary alluvial formations, covering lowland areas, is characterized by widespread masses of ophiolites and Ni-laterite deposits. The Psachna Ni-laterite deposits in Evia and those in Larymna, north to the Yliki Lake (Figure 1), are well known from a production level corresponding to some 2%–3% of the world total nickel output, and are located in proximity to the studied areas. The Assopos-Thiva basins and C. Evia covering by quaternary sediments are characterized by the presence of two types of aquifer, although the change of the direction of the groundwater flow is common: (a) Neogene aquifers in conglomerates, sandstones and marly limestone, to a depth 200 m and (b) a deeper karst type aquifer, associated with Jurassic-Cretaceous limestones [14].

Figure 1. Location map showing the localities of sampling.



3. Analytical Methods

More than 150 soil samples were collected from cultivated and non-cultivated sites of the Assopos-Thiva basins and C. Evia, along with representative crops/plants, from 2008 to 2011 (Tables 1–3). Representative soil samples were collected from the rhizosphere of plants from a maximum depth of approximately 20 cm (horizon B) in order to investigate probable relationship between element contents in plants and soil chemistry. Special attention has paid on carrots, potatoes and onions from the Thiva basin. Soils were air dried, crumbled mechanically and then passed through a sieve with a 2 mm mesh. Samples containing large stones or clods were first sieved on a 10 mm mesh and then a 5 mm mesh. Then they passed through a 2 mm mesh, and grains finer than 2 mm were pulverized and used for analysis. The elements Al, B, Ba, Cu, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, V and Zn, were analyzed by Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) after Aqua Regia Digestion, at the ACME Analytical Laboratories in Canada. The results of standard (STD) and blank (BLK) analysis are given at the end of the Table 1.

In addition, plant samples were analyzed after cleaning and drying at 70 °C. They were powdered in an agate mortar and analyzed by ICP/MS, after Aqua Regia Digestion, at the ACME Analytical Laboratories in Canada. Reference material results are given at the end of the Table 3. Microsoft Office

XP professional was used for statistics. Cr(VI) in the soil and plant samples was determined after extraction by a concentrated alkaline extracting solution (HACK Cat. No. 24497-99-reagent).

The mineralogical composition of soil was investigated by optical microscopy and an X-ray diffractometer Siemens D5005 (Munich, Germany) power diffract meter, at the National and Kapodistrian University of Athens, Department of Geology and Geoenvironmemt, (NKUA), Greece, Cu Ka radiation at 40 kV, 40 nA, 0.020° step size and 1.0 s step time. The XRD patterns were evaluated using the EVA 2.2 program of the Siemens DIFFRAC and the D5005 software package.

Polished sections prepared from soil, after carbon coating were examined by reflected light microscopy and scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDS) analysis, NKUA, Greece. Microprobe analyses and SEM images using a JEOL JSM 5600 (Tokyo, Japan). Scanning electron microscope, equipped with automated energy dispersive analysis system ISIS 300 OXFORD (Oxford Instruments, Ltd., Buckinghamshire, UK) with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 s and beam diameter 1–2 μm.

Groundwater samples were collected from over 120 domestic and irrigation wells covering the area studied (2007 to 2011) and were analyzed. Cr(VI) was determined within 24 h following the 1,5-diphenylcarbohydrazide method, using a HACH DR/4000 spectrophotometer (Loveland, CO, USA) [15]. The physical and chemical parameters of the water samples [pH, Eh, conductivity (CND), total dissolved solids (TDS)] were measured using a portable Consort 561 Multiparameter Analyzer (Turnhout, Belgium). The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B, Waltham, MA, USA). Other elements were analyzed by ICP/MS at the ACME Analytical Laboratories in Canada.

Quantity of 2 g from the soil samples weighed and placed in porcelain crucibles in the oven at 350 °C for 3 h. The organic matter content was calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights (in duplicate) were corrected for moisture content prior to organic matter content calculation [16].

4. Results

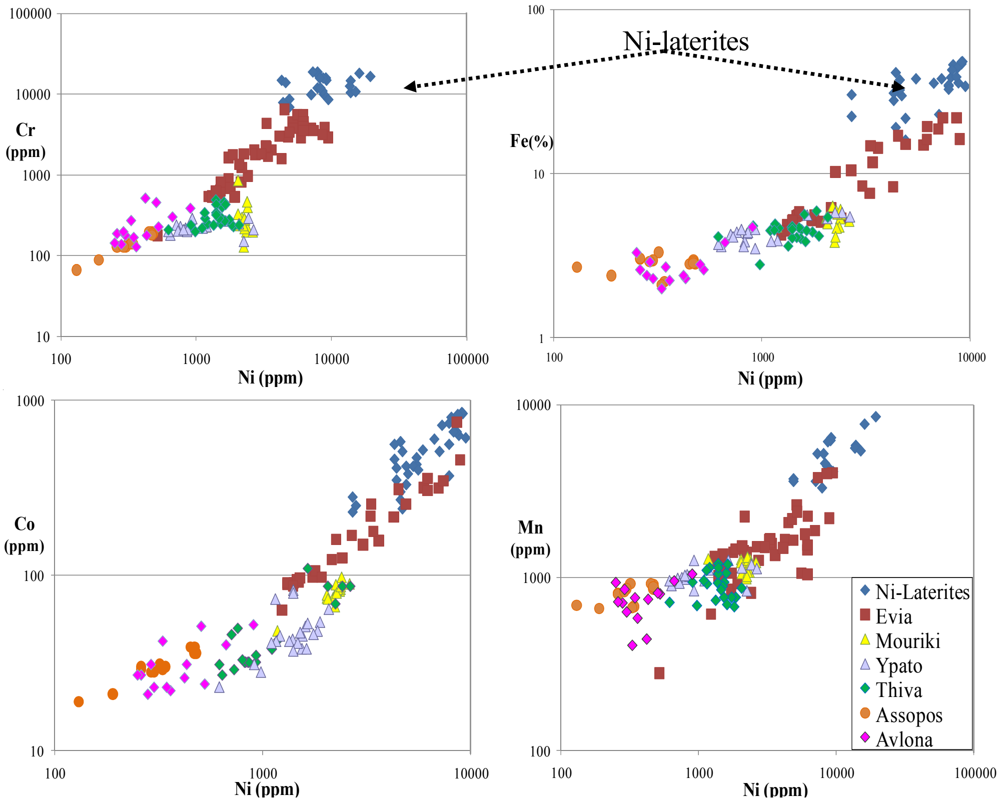
4.1. Soil Contamination and Its Spatial Evolution

Average metal values in soils range from 50 to 190 ppm Cr in the Oropos area, from 130 to 520 ppm at the Avlona area (Assopos basin), 230 to 310 ppm Cr (occasionally 800 ppm) in the Thiva basin, with an increasing trend from the southern part towards north (Mouriki), which is in a close proximity with Ni-laterite deposits (like Akrefnio) and ophiolites (Table 1; Figure 2), and a wide range of Cr in Evia (Figure 2) [17–22]. Similarly increasing trends from the Assopos basin towards north of Thiva basin, and furthermore to Evia soils are apparent for the Fe, Co and Mn *versus* Ni plots (Figure 2). Since Ni-laterite ores and their parent ophiolites have significant Cr, Fe, Ni, Mn and Co contents representative analyses of those ores are plotted as well (Figure 2) suggesting that the latter may be a major source for these metals. The enrichment of the above metals seems to be consistent with the dominated minerals in soil.

Table 1. Range and median of major and trace element contents in soils from the Assopos-Thiva basins and central Evia. Data from [18–22].

Location	Range	Cr (ppm)	Ni (ppm)	Mn (ppm)	Fe (wt %)
Evia	min	540	1200	600	4.2
	max	3800	8900	2200	19
	median	830	1800	1300	5.6
	n = 16				
Avlona	min	130	250	405	2
	max	520	900	1040	4.7
	median	200	350	750	2.6
	n = 14				
Oropos	min	50	90	260	1.1
	max	160	420	550	2.1
	median	60	120	330	1.3
	n = 12				
Thiva	min	230	710	990	4.2
	max	340	1650	1260	5.6
	median	220	1100	960	4.10
	n = 6				
	Detection limits	1	0.1	1	0.01
	STD DS7	194	50	618	2.4

Figure 2. Variation of Cr, Fe, Co and Mn *versus* Ni contents in soils from the Assopos and Thiva basins, C. Evia and Ni-laterite deposits. There is an increasing trend from the Assopos basin to Evia, which is in a close proximity with Ni-laterite deposits. Data from [18–22].



4.2. Mineralogical Composition of Soils and Mineral-Hosts of Heavy Metals

Major components in all soil samples from the studied area are quartz and calcite, chromite, ferrian-chromite, serpentine, olivine, goethite (Cr-free and Cr-bearing), hematite, magnetite, ilmenite and rutile. Montmorillonite, chlorite, apatite, Fe-Mn-hydr(oxides) zircon and REE-minerals are present in lesser amounts. The presence of rounded fragments of goethite containing fragments of chromite, chlorite, serpentine (Figure 3g,h) of a wide compositional variation is common (Table 2), reflecting a contribution from laterites and multistage weathering and transportation. There is a wide variation in the composition of chromite, the Cr# [Cr/(Cr + Al)] ratio ranging from 0.28 to 0.73 (Table 2) throughout the studied area, which is comparable to that of the chromite in both ophiolite complexes and Ni-laterite deposits of Lokris and Evia [18]. Such a variation may be related either with the contribution of various ophiolitic rocks and with alteration processes, by Al and Mg loss and Fe gained from surrounding silicates, results an increase of the Cr# and decrease of the Mg# ratios. Fragments of ultramafic rocks are mostly composed by serpentine appearing a difference in the color (Figure 3e).

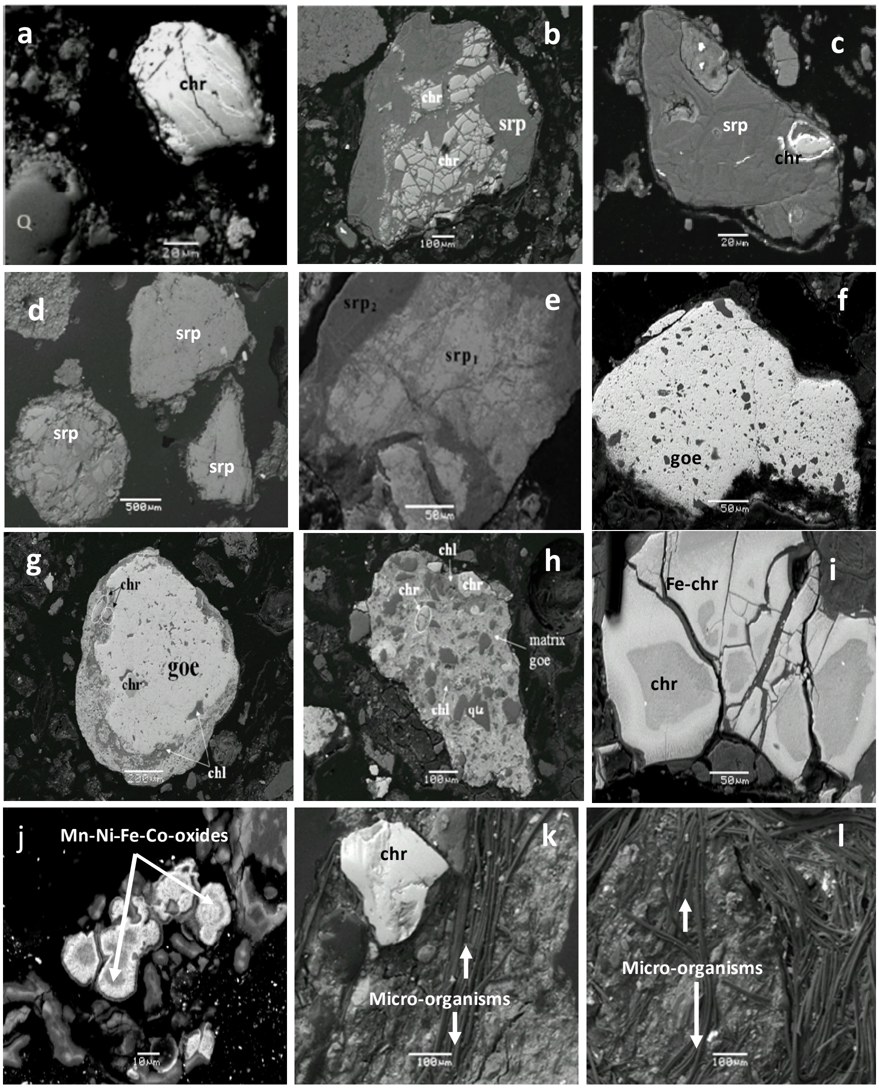
Table 2. Representative microprobe analyses of oxides and silicates from soils. Symbols: Cr# = Cr/(Cr + Al); Mg# = Mg/(Mg + Fe^{2+}).

(wt %)	Chromite					Goethite				
SiO_2	0.5	0.3	0.3	1.1	0.4	0.8	1.4	1.7	2.1	2.2
Al_2O_3	12.9	6.6	18.6	37.7	43.1	1.4	1.6	1.6	0.8	2.5
Cr_2O_3	53.4	58.2	51.6	30.9	24.8	1.6	0.8	1.0	1.7	1.6
Fe_2O_3	2.1	3.3	0.3	0.2	2.0	82.2	80.5	80.8	82.5	75.6
FeO	25.6	8.4	14.5	14.2	13.4	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	5.4	3.5	11.0	15.4	16.5	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	n.d.	13.0	1.3	n.d.	n.d.	n.d.	1.18	1.21	0.3	2.3
ZnO	n.d.	2.1	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CoO	n.d.	4.1	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
NiO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	n.d.	0.5	1.5
Total	99.9	99.6	100.7	99.5	100.2	86.03	88.2	86.3	87.9	85.7
Cr#	0.73	0.86	0.65	0.36	0.28					
Mg#	0.27	0.19	0.53	0.66	0.68					
(Mn-Co-Ni)-asbolane and silicates										
SiO_2	1.4	0.8	5.2	9.4	10.7	14.5	6.4	21.6	11.9	
Al_2O_3	4.7	2.7	n.d.	n.d.	11.3	0.7	n.d.	0.5	16.2	
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
FeOt	2.1	0.6	0.5	n.d.	4.3	1.3	n.d.	2.1	n.d.	
MgO	0.5	n.d.	2.2	4.7	0.4	5.9	3.8	11.1	n.d.	
MnO	33.1	32.7	34.7	28.3	18.7	24.4	34.6	15.5	13.7	
CaO	1.2	1.5	1.6	1.1	0.7	0.8	1.8	0.7	0.4	
CoO	8.2	14.6	8.8	12.5	10.5	10.8	8.6	7.1	5.4	
NiO	20.2	17.8	17.2	15.6	18.1	19.6	15.9	21.5	23.9	
Total	71.4	70.7	70.2	71.6	74.7	78	80.1	71.1	71.5	

Table 2. *Cont.*

(wt %)	**Chlorite within goethite**				**Serpentine**				
SiO_2	21.23	31.38	31.92	31.45	41.52	34.3	38.51	33.98	38.9
Al_2O_3	10.55	14.21	15.94	15.41	n.d.	11.6	0.73	2.22	1.2
Cr_2O_3	0.31	1.25	0.81	0.3	n.d.	n.d.	n.d.	n.d.	0.3
FeOt	32.42	14.12	17.82	13.2	6.72	11.6	3.48	14.5	8.6
MgO	14.04	19.58	14.74	14.7	38.4	29.3	1.51	3.25	37.1
MnO	0.49	0.32	0.28	n.d.	n.d.	n.d.	0.53	n.d.	n.d.
CaO	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.1	n.d.
CoO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.52	n.d.	n.d.
NiO	6.64	5.08	3.51	9.9	n.d.	0.7	39.31	26.8	0.3
Total	85.68	85.94	85.02	84.96	86.64	87.5	84.59	81.85	86.4

Figure 3. Selected backscattered images from the Assopos-Thiva basins and central Evia soils, showing rounded and angular fragments of chromite (**a**–**c**, **g**–**i**, **k**), goethite (**f**–**h**), Mn-Ni-Fe-Co-oxide and silicate intergrowths (**j**), serpentine (**b**–**e**), quartz (**a**) and filament-type microorganisms (**k**,**j**). Mineral compositions are given in Table 3. Abbreviations chr = chromite; goe = goethite; serpentine = srp; Q = quartz.



Thus, a portion of chromium in soils from the Assopos—Thiva basins and C. Evia is hosted in chromite grains or fragments, goethite and silicates (Table 2) transported as residual component inherited from Ni-laterite deposits and their parent rocks (ophiolites) as well as secondary minerals formed by epigenetic processes.

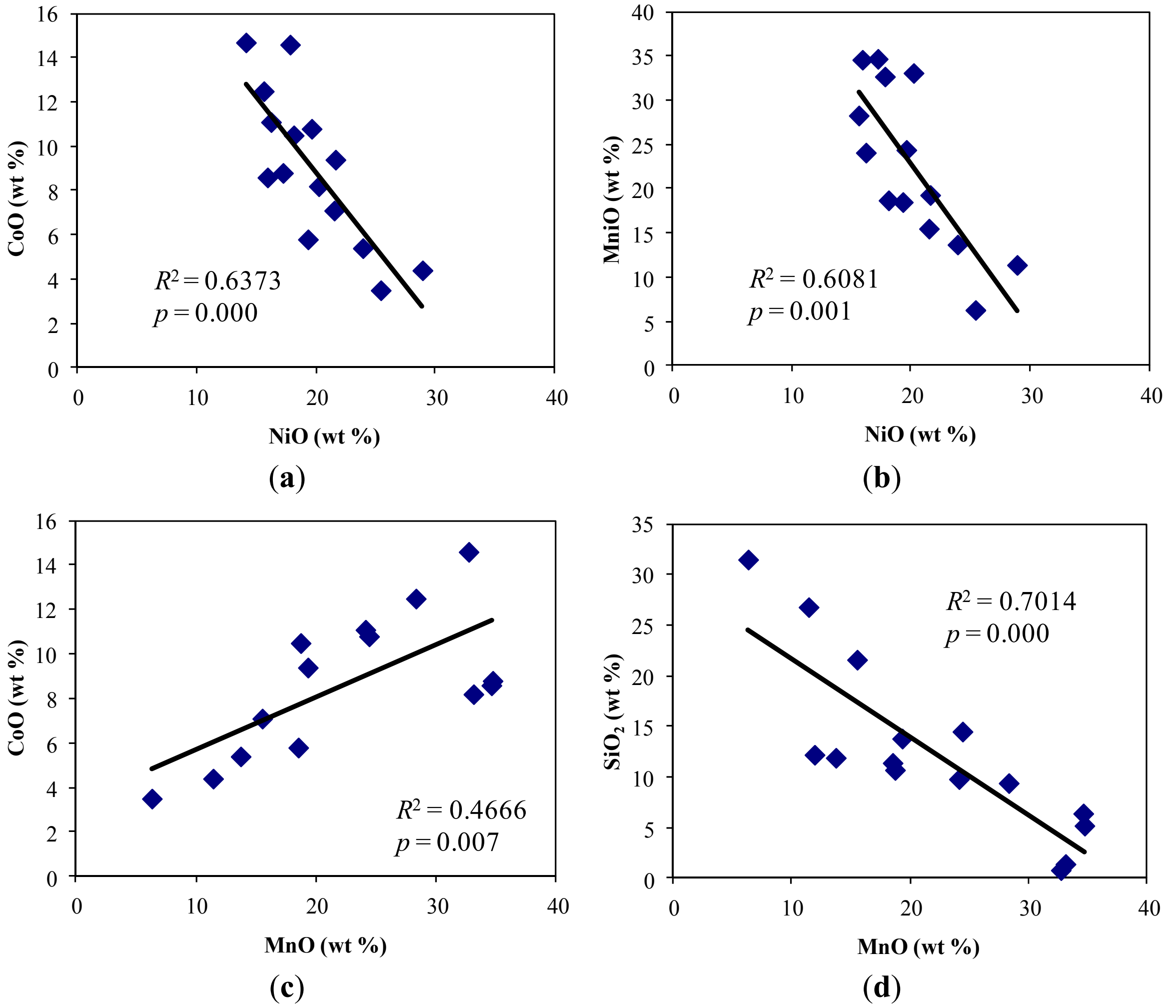
Nickel occurs mainly in goethite, chlorite and serpentine (Table 3). Goethite has variable Cr, Mn, and Ni contents. Manganese, cobalt ± nickel, form small concentric and botryoidal textures occasionally occur (Figure 3j; Table 2). A negative correlation between Co-Ni and Mn-Ni (Table 2; Figure 4), in contrast to those presented bulk analyses (Figure 2) suggest that Mn-hydr(oxides) are not main collectors of nickel. However, a positive correlation between Co and Mn reflects an association of Co mainly with Mn-hydr(oxides). Micro-organisms, with various morphological forms, mostly as filament-like (Figure 3k,l) are common and represent a portion of the organic matter ranging between 0.7 and 5 wt % (average 1.1 wt %).

On the basis of metal portion extractable using EDTA, expressed as a percentage of their total concentrations, the relative availability of the studied metals followed the order: Zn > Mn > Ni > Cr > Fe [17–22]. This order is consistent with that in previous studies [17,23,24]. Also, preliminary results on long time (one week) water extraction (leaching test) using natural Cr-free water and samples of soil and peridotites of varying degree of alteration revealed the following order of leaching: soils > highly serpentinized peridotites > less serpentinized peridotites, and an increasing trend between Cr concentrations in leachates and Cr, Mn, Fe, Co, Ni contents in soil samples.

Table 3. Range and median of trace element contents in plants from the Assopos-Thiva basins and C. Evia. Data from [18–22].

Location	Range	Cr (ppm)	Cr(VI) (ppm)	Ni (ppm)	Mn (ppm)	Fe (ppm)
Central Evia	min	0.2	0.5	2	9	20
	max	69	1.8	315	300	6090
	median	16	0.7	36	44	550
	n	95	8	95	95	95
Avlona	min	0.23	0.1	0.2	3	25
	max	11	1.8	52	105	1170
	median	2.3	0.5	5.2	20	180
	n	69	5	69	69	69
Oropos	min	0.4	0.2	0.3	9	78
	max	4.5	0.4	9.2	115	1170
	median	0.9	0.2	1.5	56	144
	n	21	5	21	21	21
Ypato	carrot	2	0.14	3.3	8	40
Ypato-	potatoes	2.1	0.23	6.2	9	90
Thiva *Eleonas*	potatoes	2.1	0.22	5.7	6	50
Charaidini	carrot	2.4	0.28	5.2	7	40
	potatoes	2.3	0.22	6.3	7.5	40
	Detection Limits	0.1		0.1	1	10
	STD DS8	114		36.4	594	2.35
	Normal values	0.1–0.5		0.1–5	30–300	
	Excessive values	5–30		10–100	400–1000	

Figure 4. Variation of MnO, CoO, NiO and SiO_2, which are components of Mn-Co-Ni-hydr(oxides), with concentric and botryoidal textures (Figure 3j). Representative analyses are given in Table 3. If possible, please redraw these figures and it will be more beautiful than adding lines in Word.



(**a**) (**b**)

(**c**) (**d**)

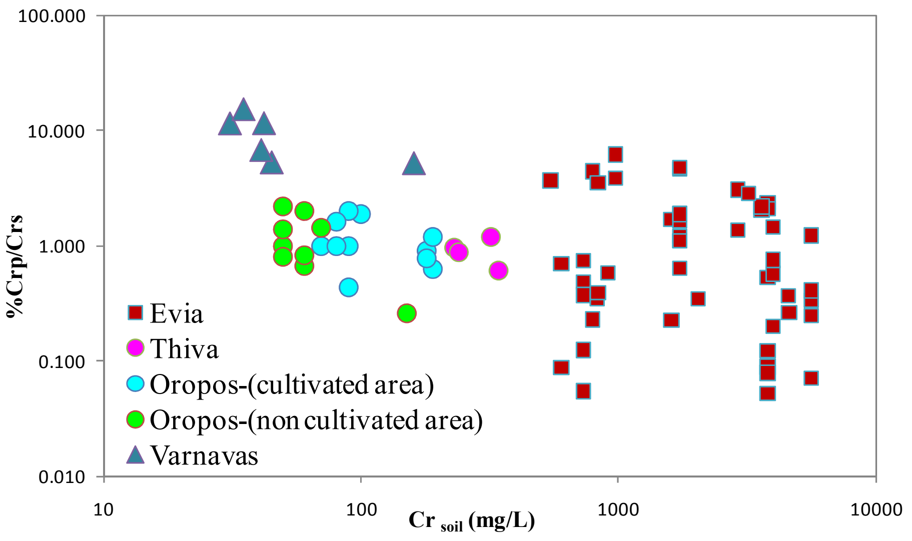
4.3. Heavy Metal Contents in Plants-Crops

Low Cr contents in plants (Table 3), suggest that chromium is poorly transported to the shoots [24]. The percentage of soil Cr, Ni, Mn and Fe in plants is relatively small (less than 4%), whilst it is much higher (more than 30%) for Zn, Cu and Mg. Any positive correlation between Cr content in plants and corresponding soil is not obvious [9–14]. The accumulation factor [(% metals in plants × 100)/metal in soil] for Cr and Fe is low (Table 4). Although any correlation between the bio-accumulation of Cr and Cr content in soil from their rizosphere, is lacking, there is a very good positive correlation between accumulation factor [(% metals in plants × 100)/metal in soil] for Cr and Fe (Figure 5a,b). On the basis of metal portion extractable using EDTA, expressed as a percentage of their total concentrations, the relative availability of the studied metals followed the order: Mn > Ni > Cr > Fe [18–22]. Available data on the metal bio-accumulation in the Assopos-Thiva basins and C. Evia are consistent with those on the metal bio-availability.

Table 4. Percentage of soil metal in plants. Data from present study and [18–22].

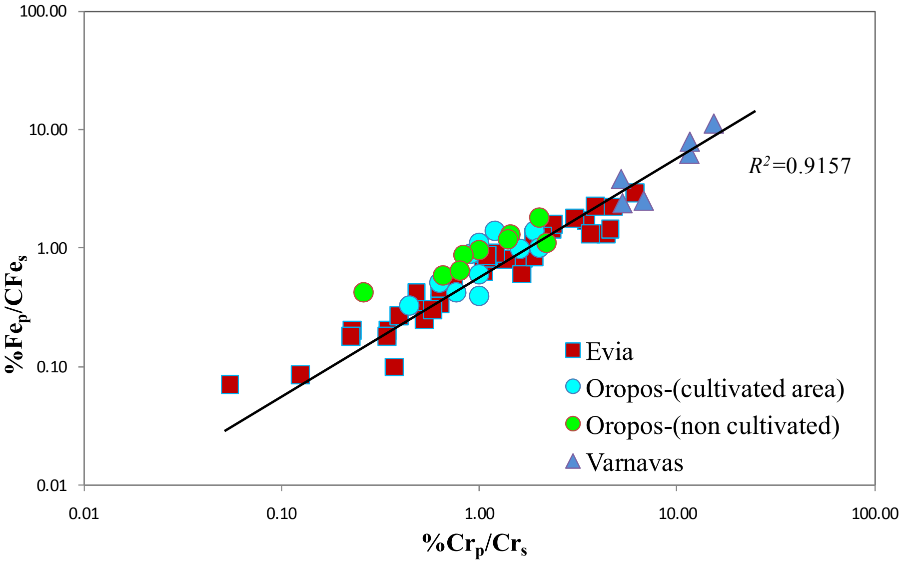
Description	Cr$_{total}$ (ppm)	Ni (ppm)	Mn (ppm)	Fe (wt %)
C. Evia				
soil	1300	2800	1300	7.9
plant	10	31	63	0.07
% mp/ms	0.8	1.1	4.8	8.6
Avlona				
soil	250	460	830	3.4
plant	3	7	30	0.023
% mp/ms	1.2	1.5	3.6	0.7
Oropos				
soil	73	157	363	1.4
plant	1.7	2.8	51	0.03
% mp/ms	2.3	1.8	14	2.1
Thiva				
soil	230	760	1000	4.39
carrot	2.2	3.5	8.8	0.004
% mp/ms	0.96	0.5	0.9	0.09
Thiva				
soil	290	930	1000	4.4
potatoe	2.2	5.8	7.5	0.006
% mp/ms	0.88	0.8	0.8	0.14
Thiva				
soil	320	1400	1140	4.58
onion	3.8	9.6	15	0.014
% mp/ms	1.2	0.7	1.3	0.31

Figure 5. Variation of the accumulation factor [(% metals in plants × 100)/metal in soil] for Cr *versus* that for Fe (**a**); and *versus* Cr content in corresponding soil (**b**). Data from Table 3 [17–22,25].



(**a**)

Figure 5. *Cont.*



(b)

4.4. Distribution of Heavy Metals in Groundwater

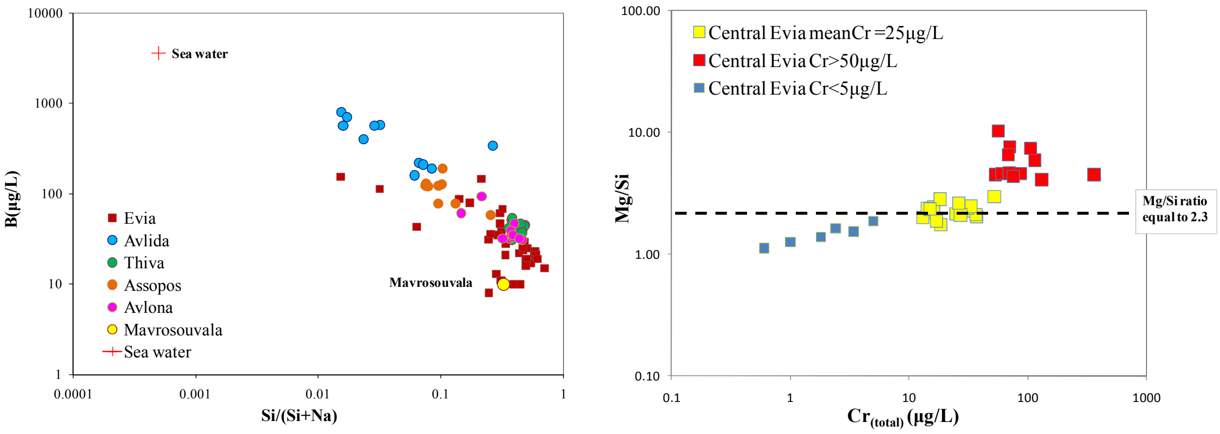
Groundwater from domestic and irrigation wells throughout the Assopos and Thiva basins, and central Evia (Messapia) are mostly hosted in the shallow (11–100 m) Neogene aquifer of the Assopos basin and C. Evia, karst-type aquifer was sampled as well. The samples from the Neogene aquifers exhibit concentrations over the maximum acceptable level for Cr_{total} in drinking water (50 μg L^{-1}) [3,11–22]. In general, there is a wide variation in the Assopos basin (<2 to 160 μg/L) and Central Evia (<2 to 360 μg/L) and relatively low (<2 to 37 μg/L) Cr(VI) concentrations in the Thiva basin (Table 5). Certain groundwater samples have been analyzed several times during the 2007–2010 period in order to define the spatial and temporal variability of chromium contamination [19]. There is a difference in the Cr concentration between wet and dry period, during a year time. The maximum Cr concentrations in groundwater wells throughout the Oropos area were observed during September–October (dry period) whilst during February (wet period) the lowest values in the Cr concentration were recorded. Any significant variation in the Cr_{max} concentration of groundwater wells at the area of Thiva, during same period (2007–2010) was not recorded [19,20].

Since Ca, Mg, Na, Si and B are major components of water, rocks and sea-water the plots of B *versus* Si/(Si + Na) ratio (Figure 6a), Mg/Si *versus* Cr (Figure 6b), Mg/Si *versus* Ca/Si ratios (Figure 6c) provide evidence for the degree of the sea-water contribution into the groundwater aquifer and the role of the water-rock interaction. The highest values of the salinization were recorded at the Avlida wells (Figure 6a).

Table 5. Trace element concentrations (μg/L) and other parameters in groundwater from the Assopos-Thiva basins and C. Evia, and sea water (data sources in text).

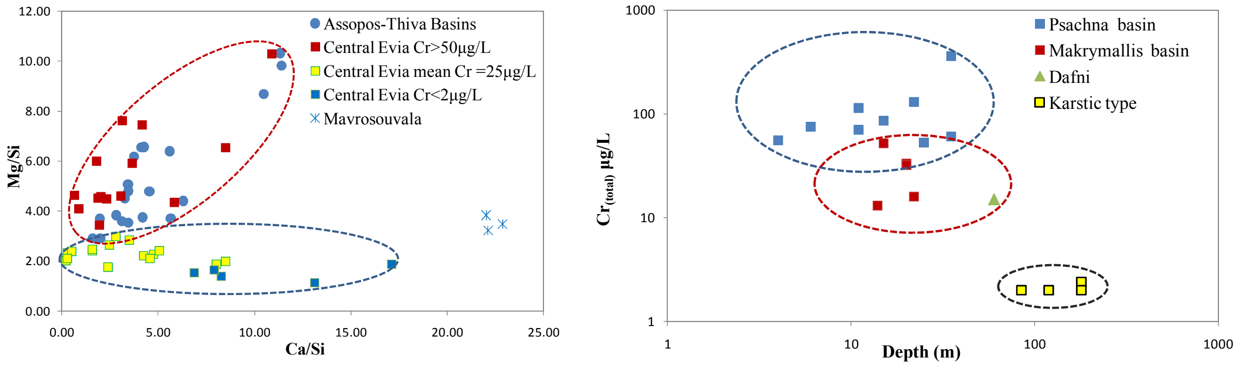
Location	Range	$Cr_{(total)}$ (ppm)	Cr(VI) (ppm)	Ca (ppm)	Mg (ppm)	Si (ppm)	Na (ppm)	B (ppm)	pH	Eh (mV)
C. Evia	min	2	4	7,400	4,400	3,900	10,800	8	7.06	−62
	max	360	360	141.500	420,000	34,000	98,000	146	7.88	16
	median	27	26	63,700	59,000	17,400	21,700	23	7.43	−34
	n = 41									
Avlona	min	2	4	25,000	11,000	5,000	7,000	9	7.10	−36
	max	90	85	62,000	132,000	23,000	104,000	420	7.54	−11
	median	50	48	40,000	61,000	19,000	32,500	30	7.3	−19
	n = 12									
Oropos	min	10	4	32,400	46,600	8,900	55,000	58	7.31	−39
	max	140	120	202,600	185,500	19,300	168,700	200	7.66	−14
	median	53	46	60,250	84,575	12,400	114,950	120	7.5	−25
	n =16									
Avlida	min	13	9	12,000	8,000	7,100	10,000	160	7.2	−47
	max	120	110	75,000	190,000	12,000	700,000	800	7.7	−12
	median	53	44	36,000	91,000	10,500	200,500	455	7.4	−24
	n = 11									
Thiva	min	8	6	13,000	44,000	6,700	9,000	31	7.12	−78
	max	37	33	42,000	88,000	15,000	16,000	54	8.09	−25
	median	27	24	25,000	58,500	9,250	12,500	43	7.6	−49
	n = 13									
Mavrosouvala		2	<4	90,000	15,000	4,200	8,700	10	7.38	−18
Sea water Evia gulf		<10		370,000	1,300,000	3,100	6,200,000	3,600		
Detection Limits		<2	<4	50	50	1	50	5		
Parameter values		50 μg/L					200 mg/L	1.0 mg/L	6.5–9.5	

Figure 6. Variation of (**a**) B *versus* Si/(Si + Na); (**b**) Mg/Si *versus* Cr; (**c**) Mg/Si *versus* Ca/Si, and a plot of well depth *versus* Cr concentration, from the Assopos-Thiva basins and Central Evia. Data from [17–22,26,27].



(**a**) (**b**)

Figure 6. *Cont.*



(c) **(d)**

The investigation of the chromium concentration in groundwater in relationship with the type of aquifer demonstrated that the highest Cr(VI) concentrations, reaching values up to 360 μg/L, were recorded in those wells that are hosted in Neogene formations, composed by intercalations of marbles, sands, clays and limestones in contrast to those hosted within deeper karst type aquifers in Triassic-Jurassic limestones (Figure 6d). The most salient feature are the Cr(VI) values of wells hosted within peridotites (ophiolitic rocks) at central Evia (Figure 6b). This group of wells, located exclusively within peridotites, is characterized by low variation, average 2 for the Mg/Si ratio, and 25 μg L^{-1} Cr. However, groundwater from the Assopos basin and C. Evia with high Cr concentrations is characterized by a wide variation of the Mg/Si ratio and any systematic relationship between Cr and Mg/Si is lacking (Figure 6c).

5. Discussion

The use of water and compost, which have been contaminated by Cr(VI) to agricultural land may input contaminants into the soil. However, the elevated Cr, Ni, Mn, Co and Fe contents in soils from the Assopos-Thiva and C. Evia, as compared to the range of world mean values in surface soils [24] coupled with the increasing trend from the Assopos basin (Avlona and Oropos) towards Thiva basin and furthermore to Evia in areas in close proximity to Ni-laterites (Figure 2) suggest that the latter may be a major source for these heavy metals in soils.

5.1. Contamination of Soils by Cr, Ni, Co, Mn and Fe and Their Bioaccumulation

Leached Fe, Mn, Zn and Co during chemical weathering of ophiolitic rocks and processes of re-working of laterites can change phase during deposition, diagenesis and meta-diagenesis stages and hence their stability and release into the associated soils. Chromium that is mainly hosted in chromite $[(Mg, Fe^{2+})(Cr, Al, Fe^{3+})_2O_4]$, is relatively immobile at near-neutral pH values [28]. The relatively low %Cr accumulated in plants (Table 4; Figure 5), although it is abundant in soil (Figure 3), and %Cr-leached from ultramafic rocks and Ni-laterite rocks by natural water, are consistent with the available thermodynamic data calculated on the basis of stability of chromite [29]. Ferrian chromite enriched in Mn, Co and/or Zn has been occasionally recorded in soil samples (Table 2). The presence of similar Fe-chromites in certain Ni-laterite deposits has been attributed to substitution for Mg^{2+} and

Fe^{2+} by Mn, Zn and Co in the chromite lattice, under favorable Eh, pH conditions, probably during diagenesis and metadiagenesis stages of the laterite ore [30].

The application of basic kinetic and thermodynamic parameters may contribute to a better understanding of the formation and stability of mineral-phases. Based on experimental data it has been concluded [31,32] that the lattice parameter of Mn-chromite spinel increases with increasing Mn content, whilst the activation energy (the minimum energy that is required for a reaction) decreases almost linearly with increasing Mn content. It has been suggested [31,32] that the relatively low values of the activation energy are thermodynamically favorable processes and hence if Mn^{2+} and Co^{2+} are available in solution a significant mutual substitution of those ions are facilitated in the chromite lattice. Although the activation energy that reactants need to give the products differs (as far as ΔH) compared to the energy required for the opposite chemical reaction [33] the low values of the activation energy may suggest that the metal release from Mn-chromite is easier than from typical chromite. However, the resistance of Cr is higher in the chromite lattice than that of the absorbed Cr on goethite [29]. Nevertheless, chromium even in small amounts, can be mobilized as stable Cr(VI) oxyanion species under oxidizing conditions, and be bio-accumulated in plants from the Assopos-Thiva basins and central Evia in contents higher than normal or sufficient values.

The abundance of organic matter (<1 to 5 wt %) and filament like microorganisms in soils may play a significant role in several oxidation-reduction reactions, including the reduction of Cr(VI) to Cr(III). Although any significant correlation between Cr and other elements is not obvious, there is a negative trend between Cr and organic matter that is better pronounced in the investigated uptake of Cr by crop plants after the addition of compost in corresponding soil system [17,21,22,34]. Since microorganisms by their enzymes catalyze electron transfer reactions (oxidation-reduction reactions) and obtain the gained energy from chemical constituents of a system that is not in equilibrium [35], the reduction of Cr(VI) to Cr(III) is probably the result of various biochemical reactions [36].

Nickel and cobalt in laterites, derived from the breakdown of olivine and serpentine minerals, are preferentially immobilized in iron oxides and can be concentrated by several times that of the parent rock. Goethite is a common mineral in soil samples from the Assopos-Thiva basins and central Evia, containing a number of chromite grains, chlorite, serpentine and quartz (Figure 2), as well as significant contents of Mn and Ni. The crystal chemistry of Cr, Mn, Co and Ni in natural goethite from an earthy saprolite formation in West-Africa has been investigated [37] by fluorescence-yield extended X-ray absorption fine structure (EXAFS). They indicated [37] that manganese is present as a phyllomanganate impurity, Co is trivalent and it is located in the phyllomanganate layer. In addition, they concluded that more than ~20% of the amounts of Mn and Co in natural goethite substitute for Fe in the structure, while 75% of total Ni is substituted for Fe and ~25% is associated with the phyllomanganate.

Cobalt and nickel are also associated with manganese oxides such as asbolane, containing Ni and Co $(Co,Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y+2x}.nH_2O$. Although the exact nature of the Co-bearing manganese species remains unknown, a good positive correlation between Mn and Co (Table 2; Figure 4) seem to be consistent with the affinity of Co for Mn oxides [37]. Dissociation at pH 7 is extensive, and the surface for most natural colloidal Mn-hydroxides has a strong negative charge, whilst under very acid conditions an excess of H^+ is adsorbed to the surface, and it has a positive charge. In addition, adsorption of Co^{2+} onto Mn-hydroxides takes place by a one-to-one exchange of ions [38]. The amount of adsorbed Co is dependent on the activity of Co^{2+} ions and the pH in the surrounding solution, the energy of bonding (as it is expressed by the equilibrium constant) and the number or density of adsorption sites [38].

Secondary silicate minerals are commonly Ni-enriched compared to primary ones, in particular those that exhibit a high crystal field stabilization energy (CFSE) as it is exemplified by the preferable distribution of Ni in garnierite [37]. It is well known that the surface charge of hydroxides and other types of colloids with constant surface potential results from ionization of surface atoms, or from chemical adsorption of dissolved ions onto the surface, depending on the pH [39]. Nickel sorption on the clay mineral and oxide surfaces exhibit typical metal-sorption behavior. The sequence of the phase formation depends on the thermodynamics of the system, oxygen and the concentration of the reacting species at the growth interface [40].

The factors governing the metal transfer from soil to corresponding plants/crops include physico/chemical parameters (pH, Eh), concentrations of completing ions, moisture, penetrability, presence of oxyhydroxides of Fe, Mn and Al, carbonate minerals organic matter content and microbial activity [1,39,41]. With respect to the bioaccumulation of heavy metals in the Assopos-Thiva basins and C. Evia the lack of any correlation between Cr bioaccumulation and Cr content in corresponding soil and a very good positive correlation ($R^2 = 0.92$) between accumulation factor for Cr and Fe (Figure 5a,b) is the most salient feature. Although Cr(III) and Fe(III) have similar chemical properties, plants usually contain much more Fe than Cr (Table 3), due probably to the lower chromium immobility in soil–plant systems compared to that of Fe [42]. A key factor that affects the rate and the extent of Cr(VI) reduction in soils is pH. More specifically, Cr(VI) may be effectively reduced in acidic soils, whilst acidic conditions enhance the rate of release of mobile Fe(II) species. Also, it has been suggested that Fe(II) species from soil minerals increases the rate of Cr(VI) reduction by organic matter [42]. Although the interaction between Cr(III) and Fe, P and Mn has been extensively studied in Fe-sufficient and Fe-deficient plants [43] the Cr uptake is still unclear. It has been suggested that Cr(III) uptake is a passive process, whilst Cr(VI) uptake is performed by carriers of essential elements such as sulfate [36]. The presence of mostly Cr(III) and less Cr(VI) in the studied plants (Table 3), coupled with the excellent positive correlation between Cr and Fe accumulation factors (Figure 5) may suggest the existence of both forms, Fe(III) and Fe(II) as well, due probably to the interaction between plants and microorganisms results in complex relations, which control the soil physico-chemical properties and metal uptake mechanisms by plants [44].

5.2. Trace Element Concentrations in Groundwater

The investigation on groundwater compositional variation (Table 5; Figure 6) provide evidence for the progressive leaching of Cr from Cr-bearing components of soils and peridotites hosting the shallow aquifer of the Assopos basin and C. Evia, as well as the karst-type aquifer, and validate the water-rocks interaction. The low Cr concentration in wells in a proximity to the neighboring Ni-laterites deposits (Figure 3) [45] may be related with the dominance of Fe(III) iron (goethite) in those ores, indicating that laterites are not a favorable environment for the oxidation of chromium. The prevalence of $Mg\text{-}HCO_3$ over $Ca\text{-}HCO_3$ compositions in the Assopos basin and C. Evia suggests that groundwater interacts chiefly with peridotites. In this case, the Mg/Si ratio in groundwater is approximately 3, as it is exemplified by the results of long water leaching of serpentinized peridotites (Figure 6b) [18]. In addition, plotting the Mg/Si ratios *versus* sea water elements (B, Na, Mg, *etc.*) a major contribution of sea water into the groundwater aquifer is obvious (Figure 6a). However, the increasing Mg/Si ratio is not always accompanied by an increase in Cr or B (Figure 6b,c), although there is a spatial association between Cr-free and Cr-contaminated irrigation well. In addition, the spatial association of Cr-free with highly contaminated by Cr irrigation wells may be related with their depth (Figure 6d). Although the determination of chromium isotopes (^{53}Cr/^{52}Cr) is required to be used as an indicator of the source of the Cr(VI) in groundwater (study in progress), the negligible Cr(VI) concentrations in deep karst-type aquifer, in contrast to the shallow-Neogene ones (Figure 6d) may suggest that the latter have been probably affected by both anthropogenic activities and natural process.

6. Conclusions

The compilation of soil, plant and groundwater analytical data from the Assopos-Thiva basins and C. Evia lead to the following conclusions:

An increasing trend in the Cr, Fe, Ni, Mn and Co contents in soils from the Assopos to the Thiva basin (Mouriki area) and furthermore to C. Evia and Ni-laterite deposits and ophiolites indicates a spatial evolution of the soil contamination, suggesting that the latter may be a major source for these metals.

The average Cr_{total} contents (dry weight) in plants/crops are higher than normal or sufficient values, whist Cr_{total} and Cr(VI) accumulation are relatively low.

Any correlation between accumulation factor [(% metals in plants × 100)/metal in soil] for Cr and the Cr content in soil is not obvious, suggesting the involvement of other controlling factors to the Cr uptake.

There is a very good positive correlation between the accumulation of Cr and Fe (R^2 = 0.92), suggesting similarity in their uptake.

The variation of the Cr concentrations in groundwater is wide in the Assopos basin (<2 to 160 μg/L) and C. Evia (<2 to 360 μg/L), relatively low (<2 to 37 μg/L) in the Thiva basin, and very low (average 5 μg/L) in wells located in a close proximity to Ni-laterite deposits.

A plot of B *versus* ratios Si/(Si + Na) reflects a varying degree of salinization, with the highest recorded values at the Avlida area (Assopos).

A group of wells located exclusively within peridotites are characterized by low variation, for the Mg/Si ratio (average 2), and Cr(VI) concentrations around 25 μg L^{-1} Cr, which are attributed to natural processes.

The negligible Cr concentrations in deep (>200 m) karst-type wells, in contrast to shallow wells in the C. Evia provide evidence for a solution of a crucial environmental problem in Evia and Assopos basin by using the deep karst-type aquifer instead the shallow-Neogene one.

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