

Review

Contamination of the Soil–Groundwater–Crop System: Environmental Risk and Opportunities

Maria Economou-Eliopoulos *  and Ifigeneia Megremi

Department of Geology and Geoenvironment, National University of Athens, GR-15784 Athens, Greece; megremi@geol.uoa.gr

* Correspondence: econom@geol.uoa.gr

Abstract: The increasing development of industries, resulting in a large volume of mining, smelting, and combustion wastes, and intense agricultural activities, due to demand for food and energy, have caused environmental hazards for food quality and ecosystems. This is a review on the contamination of the soil–groundwater–crop system and a potential reduction of the contamination by a gradual shift towards green economy within the European Union and on a worldwide scale. Available mineralogical and geochemical features from contaminated Neogene basins have shown a diversity in the contamination sources for soil and groundwater, and highlighted the need to define the contamination sources, hot spots, degree/extent of contamination, and provide ways to restrict the transfer of heavy metals/metalloids into the food chain, without the reduction of the agricultural and industrial production. Among harmful elements for human health and ecosystems, the contamination of groundwater (thousands of $\mu\text{g/L}$ Cr(VI)) by industrial activities in many European countries is of particular attention. Although Cr(VI) can be reduced to Cr(III) and be completely attenuated in nature under appropriate pH and Eh conditions, the contamination by Cr(VI) of coastal groundwater affected by the intrusion of seawater often remains at the hundreds $\mu\text{g/L}$ level. A positive trend between B and Cr(VI) may provide insights on the role of the borate $[\text{B}(\text{OH})_4]^-$ ions, a potential buffer, on the stability of Cr(VI) in coastal groundwater. Efforts are needed towards reducing toxic metal(loids) from the industrial wastewaters prior to their discharge into receptors, as well as the transformation of hazardous mining/industrial wastes to new products and applications to the optimization of agricultural management strategies.



Citation: Economou-Eliopoulos, M.; Megremi, I. Contamination of the Soil–Groundwater–Crop System: Environmental Risk and Opportunities. *Minerals* **2021**, *11*, 775. <https://doi.org/10.3390/min11070775>

Academic Editor:
Kyoung-Woong Kim

Received: 8 June 2021
Accepted: 12 July 2021
Published: 16 July 2021

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Keywords: soil; groundwater; mining; smelting; contamination; environmental risk

1. Introduction

During past decades, the increasing development of industries, intense use of chemicals, the large volume of mining/smelting residues, industrial wastes, and traffic in many urban areas have resulted in environmental hazards for terrestrial and aquatic ecosystems, and food quality and socioeconomic problems [1–4]. Soils provide plants with certain trace elements that, in small amounts, are considered to be critical for the healthy growth of humans, plants, and animals [5,6]. Potential sources of the soil/groundwater contamination, such as natural processes (weathering/alteration of rocks and raw materials) and human activities (mining, smelting, industrial, and agricultural activities), often result in elevated contents of harmful elements (Cr, Cu, Hg, Pb, Zn, Sb, Co, Ni, Cd, and As) [1,7–11]. The salinization at contaminated coastal areas, where groundwater is mixed with seawater, such as the Mediterranean, threatens plant growth [10]. Changes in agricultural production due to population growth, including expansion of agricultural land and irrigated areas and greater use of agricultural inputs (mostly fertilizers and pesticides), are used more intensively than ever before [9,12–14]. The increasing food demand, coupled with the intensive use of cultivated lands, have resulted in vital problems for the agricultural economy, societies, and increasing healthcare cost [8,15]. Recently, there has been significant

progress on environmental protection, in particular, waste prevention and management. In this frame, the European community is focused on the transition to a circular economy (green economy) in order to make it more sustainable [16–18]. The investigation of raw materials in the frame of research projects, including the ProMine databases, provides information on the mineral resources for mineral deposits, mines, mining wastes, potential products, and their importance for the EU economy [19–22]. The present review study is focused on the current status and challenges on the contamination by metal(loid)s, either by natural processes (weathering of rocks, raw material deposits, salinization) and/or human activities, (mining and smelting, energy production, agricultural), with emphasis to the soil–groundwater–plants/crops system in Greece, aiming to contribute to potential ways forward to protect and better manage soil and groundwater for human health and ecosystems.

2. Methodology of Investigation

Study Area and Sampling Procedure

The Neogene Assopos and Thiva basins, with an extension of approximately 700 km² in the former and 150 km² in the latter, located north of the Assopos, are composed of alternations of alluvial, marls, marl limestones, and continental sediments consisting of conglomerates derived from carbonates, mafic/ultramafic rocks, and Fe-Ni laterites [23,24].

Polished sections from ultramafic rocks, Fe-Ni-laterite deposits from C. Greece and Kastoria, and bauxite processing residue or red mud were carbon coated and examined with a scanning electron microscope (SEM) using energy-dispersive spectroscopy (EDS). SEM images and EDS analyses were carried out at the University of Athens, National and Kapodistrian University of Athens (NKUA) (Department of Geology and Geoenvironment) using a JEOL JSM 5600 scanning electron microscope (JEOL, Tokyo, Japan), equipped with the ISIS 300 OXFORD automated energy-dispersive X-ray analysis system. Analytical conditions were 20 kV accelerating voltage and 0.5 nA beam current.

Representative surface (up to 20 cm) soil samples from cultivated and uncultivated areas were collected during the year 2009 and spring of 2014, covering some sites of the basin from the rhizosphere of plants. They were air-dried, crumbled mechanically, and then passed through a sieve with a 2-mm mesh. The elements Se, Cu, Pb, Fe, Mn, Zn, K, Na, Ni, Ca, Mg, P, and S were analyzed by inductively coupled plasma mass spectroscopy (ICP/MS) after aqua regia digestion at ACME Laboratories Ltd., Vancouver, BC, Canada. Platinum-group element (PGE) analyses were carried out using Ni sulfide fire-assay preconcentration technique, with the nickel fire-assay technique from large (30 g) samples at Genalysis Laboratory, Perth Services, Australia. This method allows for complete dissolution of samples. Detection limits were 1 ppb for Pd, 10 ppb for Pt, and 5 ppb Au. CDN-PGMS-23 was used as standard.

Plant samples were analyzed after cleaning and drying at 70 °C. They were powdered in an agate mortar and analyzed by inductively coupled plasma mass spectroscopy (ICP/MS), after aqua regia digestion, at the ACME Analytical Laboratories, Vancouver, BC, Canada.

Average values were calculated for groundwater samples collected from domestic and irrigation wells, and municipality of the Assopos–Thiva and Evia basins (during both wet and dry seasons), which were analyzed for many elements (Al, As, B, Ba, Cu, Zn, Fe, K, Li, Mn, Na, Ni, P, S, Se, Si, and V), hexavalent chromium, Cr(VI), and physical and chemical parameters of the water samples, including total dissolved solids (TDS). Although the analytical methods applied for the determination of the groundwater composition, including chromium stable isotopes, are provided in previous publications, a brief outline is given here. Over 200 coastal groundwater samples from domestic and irrigation wells of C. Evia and Assopos-Thiva basins, collected during the period from 2007 to 2017, were analyzed for major and trace elements by inductively coupled plasma mass spectroscopy (ICP/MS) [25–30]. Detection limits, quality control samples, and the precision of the analyses are in agreement with international standards (~10%). Physical and

chemical parameters (pH and total dissolved solids) of the water samples were measured in the field using a portable Consort 561 Multiparameter Analyzer. The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B system), with an estimated detection limit of ~ 1 $\mu\text{g/L}$. The chemical analyses for Cr(VI) were performed by the 1,5-diphenylcarbohydrazide colorimetric method, using a HACH DR/4000 spectrophotometer. The estimated detection limit of the method was determined at ~ 4 $\mu\text{g/L}$.

Leaching experiments for soils, rocks, and ores were carried out in order to study the one week leaching responses of Cr under atmospheric conditions. Water and water leachates in an appropriate amount to have approximately 1 μg of Cr_{total} were used for the determination of the Cr-isotope composition following the method described by [31]. Both Cr concentrations and isotope ratios were analyzed using an IsotopX/GV IsoProbe T thermal ionization mass spectrometer (TIMS) equipped with eight Faraday cups at the University of Copenhagen, Denmark. Four Cr beams ($^{50}\text{Cr}+$, $^{52}\text{Cr}+$, $^{53}\text{Cr}+$, and $^{54}\text{Cr}+$) were analyzed simultaneously with $^{49}\text{Ti}+$, $^{51}\text{V}+$, and $^{56}\text{Fe}+$ beams, which were used to monitor interfering ions. The final isotope composition of a sample was determined as the average of the repeated analyses and reported relative to the certified SRM 979 standard as: $\delta^{53}\text{Cr}(\text{‰}) = [(^{53}\text{Cr}/^{52}\text{Cr}_{\text{sample}}/^{53}\text{Cr}/^{52}\text{Cr}_{\text{SRM979}}) - 1] \times 1000$.

The raw data were corrected for naturally and instrumentally induced isotope fractionation using the double spike routine. To assess the precision of the analyses, a double-spike-treated, certified standard reference material (NIST SRM 979) was used.

3. Potential Sources of Soil and Groundwater Contamination

3.1. Weathering of Rocks and Raw Materials

Arsenic (As) contamination by weathering of volcanic rocks, thermal springs, or deposits has been well described in Greece [32–35]. Recently, elevated As contents (61–210 mg/kg As) were found in a limestone quarry in Attica (Greece) that is exploited for a popular multicolor building material, and in the associated soil (33 to 430 mg/kg As) [36]. Applying a geographical information system (GIS), geostatistical techniques, and mapping software, a digitized geological–geomorphological map and an assessment of the extent and intensity of the As and other harmful elements in those lacustrine and fluvial sediments revealed a significant contamination in the uppermost travertine limestone, which may give rise to a significant risk to human health and ecosystems [36,37].

The exploitation of primary raw materials worldwide, as well as their metallurgical residues, is a potential source of soil and groundwater contamination by metal(loid)s [1,10]. Substantial volumes of groundwater, used for mining operations, may result in the oxidation and acid mine drainage in the case of sulfide ores [38,39]. The weathering of rocks and raw material deposits is a source of the transfer of potentially harmful elements into soil and shallow aquifer groundwater (chemical degradation), related to the type of the ore deposit, for example, mixed polymetallic sulfide deposits, which are related to calc-alkaline intrusions and are enriched in Pb, Zn, Fe, Cu, As, Sb, Ag, Bi, and Au, like the mines at the famous ancient Lavrion and Chalkidiki Peninsula (Greece) [40,41] and the Olympias-Stratoni mines at Chalkidiki [42,43]. That type of sulfide, with a long exploitation history (mining of Ag-bearing galena at Lavrion began before 3000 BC), is characterized by the production of large volumes of metallurgical wastes transferred into alluvial soil, which has caused contamination by Pb, Cd, and As of cultivated areas and groundwater [32,44,45]. In particular, at Lavrion, contaminants like Pb are still verified in blood and deciduous teeth, and As in urine of children [46].

The major type of sulfide mineralization associated with ophiolite complexes is a massive Cyprus-type, composed mainly by pyrite and Cu-pyrite, and lesser amounts of sphalerite, characterized by an increasing content of Au, Ag, As, Se, Sb, Mo, and Hg [47–49]. The Cyprus-type massive sulfide ores are associated with a volcanic/subvolcanic sequence composed mainly of basalts and basaltic andesite pillow lavas, such as the Othrys, Ermioni (Peloponnesos) to Pindos, and Mirdita (Albania) ophiolites [49,50]. In general, ophiolite complexes are a type of mafic–ultramafic complex covering more than 1% of orogenic

zones, including several European countries which are strongly enriched in heavy metals, such as Cr, Fe, Mn, Co, and Mg [51,52]. Besides the sulfide mineralization, the major types of raw minerals are chromites and Fe-Ni laterites derived by weathering/alteration processes of ultramafic/mafic rocks [53–55]. Recently, an Ultramafic Index of Alteration (UMIA) was used, applying the equation $UMIA = (Al_2O_3 + Fe_2O_3) / (Al_2O_3 + Fe_2O_3 + MgO + SiO_2) \times 100$, based on major components in ultramafic rocks and their behavior during the weathering process; the Mg and Si are mobile and they are depleted, while Fe and Al are less mobile and enriched during the weathering process [56–58]. Using analytical data provided in previous publications [50,59], the calculated values (Table 1) showed a wide variation, ranging between 1.4 and 20 in saprolite and highly weathered peridotites, 18 to 24 in soils, and from 40 to 98 in laterites of Greece, throughout the contaminated C. Evia and Assopos–Thiva basins (Greece).

Table 1. Calculated Ultramafic Index of Alteration (UMIA) for representative samples of weathered peridotites Fe–Ni-laterites, bauxite laterites, and contaminated soils from Greece. Data from [50,59].

Location	Index	wt%		mg/kg			Location	Index	wt%		mg/kg		
	UMIA	MnO	Cr	Ni	Co	UMIA		MnO	Cr	Ni	Co		
Kastoria						C. Greece, Lokris							
<i>Weathered peridotites</i>						<i>Laterites of karst type</i>							
Ka-2	1.4	0.05	120	17,000	50		52	0.18	3350	13,300	280		
Ka-3	6.9	0.08	1500	23,000	180		69.4	0.12	26,960	4790	220		
<i>Fe-Ni-Laterites</i>							77.4	0.27	40,570	5400	280		
Ka-4	54.7	0.95	16,000	8500	1600		70.2	0.13	20,190	58,900	280		
Ka-4b	69.3	0.88	23,000	10,500	1200		83.6	0.33	20,190	2360	280		
Ka-5	98.4	0.25	20,000	8000	330		85.1	1.57	20,340	6120	283		
Ka-6	93.4	1.7	15,000	9100	820		87.8	0.58	26,960	5180	219		
Ka-7	93.0	0.79	23,000	7100	420		95.1	0.17	38,800	4320	280		
Ka-8	94.6	0.3	17,000	4400	330		77.4	0.5	32,300	13,500	281		
W. Vermion							67.8	0.24	19,840	8280	286		
<i>Weathered peridotites</i>							77.1	0.31	14,650	3690	280		
PR-1	20	0.24	5800	5500	300		83.2	0.27	27,800	3700	280		
PR-2	12	0.11	2500	2200	200		59.6	0.07	19,000	4630	278		
PR-3	18	0.23	3500	4100	200		76.2	0.13	23,100	13,400	280		
PR-4	18	0.18	3300	4700	200		C. Evia (Psachna)						
P-p	14	0.1	3800	3100	240		<i>Soils</i>						
<i>Laterites</i>							19.7	0.11	1080	650	41		
PR-5	87	0.97	21,900	15,000	1300		18.7	0.09	1180	670	40		
PR-6	79	0.61	12,900	6900	700		18.8	0.11	2090	1120	62		
WV4	51	0.41	11,500	10,200	500		20.2	0.12	1500	810	52		
WV5	36	0.33	11,400	9500	400		13.6	0.1	1850	1300	66		
WV6	78	0.62	11,000	7800	820		23.9	0.15	2200	1280	76		
<i>Bauxite laterites</i>							24.1	0.16	1760	1630	88		
P-1	47	0.37	5500	5200	400		20.9	0.12	1530	700	45		
P-2	80	0.41	4400	5200	320		22.2	0.13	1230	820	52		
P-3	81	0.24	3800	6400	400		18.1	0.1	1640	730	45		
P-4	81	0.36	4100	4200	400		21.1	0.13	1650	780	52		
P-5	82	0.26	3600	4200	400		17.9	0.11	1650	650	41		
P-6	17	0.31	1900	2000	200		21.6	0.12	1460	730	48		
							18.4	0.11	1640	860	50		
							23.7	0.13	1330	720	52		
							16.7	0.09	1720	600	38		

The best pronounced relationship between the UIMA index and Fe, Cr, Mn, and Co, which are characteristic components of ophiolites, is that with Cr (Figure 1a) and MnO (Figure 1b), especially for weathered peridotites and saprolite zones.

The positive correlation between UIMA and Cr is of particular importance for human health and ecosystems because, during weathering of ultramafic rocks, the availability of Cr increases and may be transported in soil, groundwater (drinking and irrigation), and plants/crops (food chain).

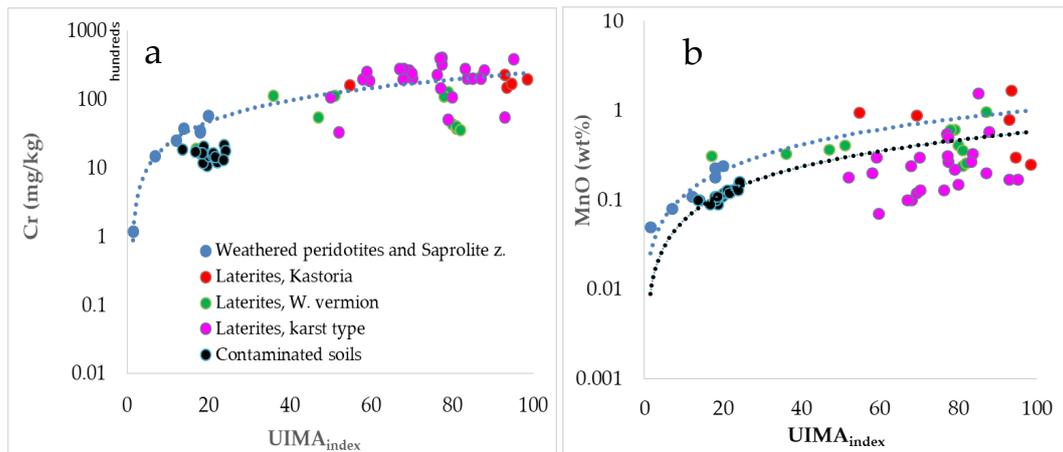


Figure 1. Plots of the UMIA (calculated ultramafic index of alteration) versus Cr contents in weathered peridotites and saprolite zone, laterites from Kastoria and W. Vermion lying on peridotites, laterites of karst type from Lokris, and contaminated soils from Evia. Data from Table 1 and [50].

Plots of Cr, Fe, Co, and Mn versus Ni contents in contaminated soils affected by the transfer of weathered ophiolite rocks, in addition to a good positive correlation, showed an increasing trend from the Assopos basin (southern part) towards north Thiva basin to C. Evia, where ultramafic rocks are dominant, while the highest contents of these heavy metals were found in laterites (Figure 2).

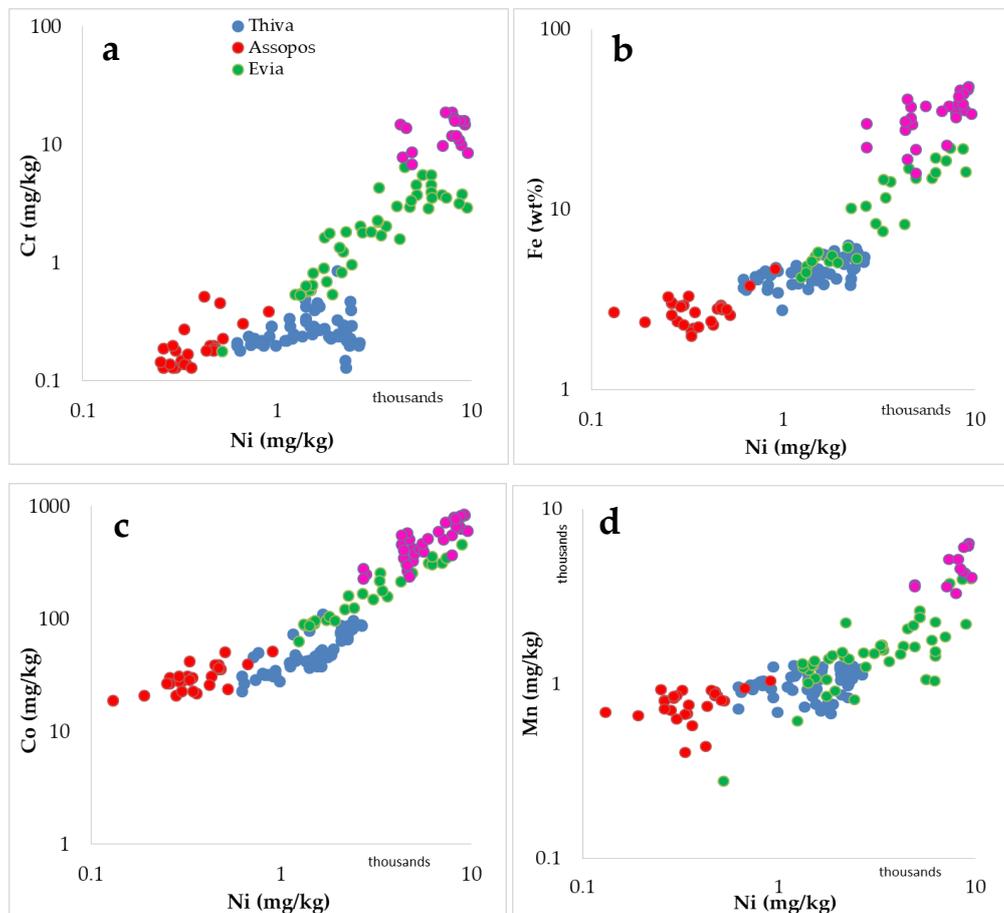


Figure 2. Variation of (a) Cr, (b) Fe, (c) Co, and (d) Mn versus Ni contents in soils from the Assopos–Thiva basins, C. Evia., and, in laterite deposits. Data from [50,60–63].

In addition, elevated contents of these elements have been determined in plants/crops grown in such soils (Table 2).

Table 2. Chromium, Ni, Mn, Co, Zn, and Fe range and mean in plants/crops from the C. Evia and Assopos–Thiva basins.

Metals	Range	mg/kg			
		Mean	Normal	Deficient	Excessive
Cr	0.3–200	27	0.1–0.5	–	5–210
Ni	4–210	50	0.1–5	–	10–100
Mn	8–190	65	30–300	0–30	400–1000
Co	0.5–15	7	10	–	50–69
Zn	28–380	50	27–150	0–20	100–400
Fe	28–3000	780	–	–	2000

The groundwater from Neogene shallow aquifers (10–100 m) throughout central Evia (Messapia), characterized by the extensive presence of ultramafic rocks and Fe-Ni-laterite deposits, contains more than 10 µg/L (up to 360 µg/L) Cr(VI) into irrigation water from Evia. Moreover, at the Assopos basin, deposits as high as 950 µg/L Cr(VI) exceed the acceptable limit for Cr_{total} in drinking water (50 µg/L), while up to 8000 µg/L Cr(VI) have been recorded at the area of Oinofyta, with intense industrial activity in that basin [29,60,64,65]. Although there is a wide variation in Cr concentrations throughout Evia and Assopos–Thiva basins, the Cr(VI) variations in groundwater wells during the dry and wet seasons have been recorded as relatively small [30,60]. Thus, in contrast to the lowest Cr content in the soil samples from the Assopos basin, the highest Cr concentrations in groundwater were recorded at the area of Oinofyta, Assopos basin, with an intense industrial activity [64]. Such a spatial diversity between the Cr distribution in soil and groundwater throughout the C. Evia and Assopos–Thiva basins (Figure 3) is a salient feature, suggesting their major sources of contamination.

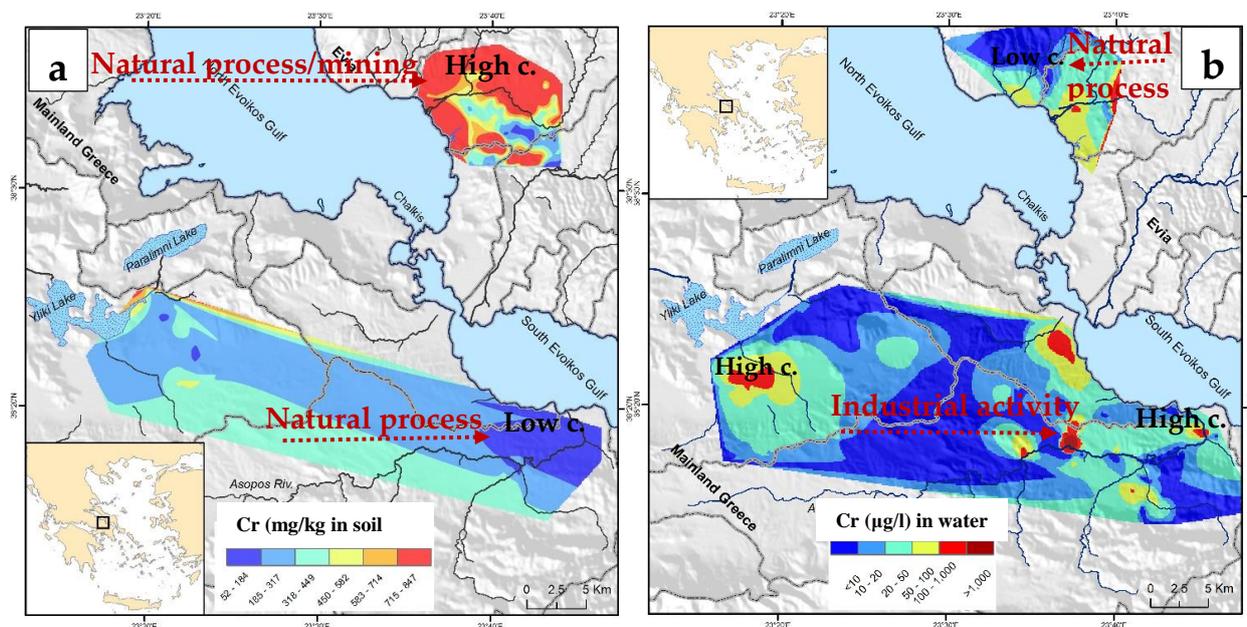


Figure 3. Maps showing spatial distribution of Cr in soils due to natural processes and mining of Fe-Ni laterites (a), and in groundwater from the Evia and Assopos–Thiva basins due to natural processes, mining, and industrial activity (b) [30].

3.2. Influence of the Groundwater Salinity

A major difference between freshwater and seawater is their salinity, expressed by the total dissolved solids (TDS), being a characteristic feature of sea and geothermal water that can be deduced from measurements of the electrical conductivity of groundwater [66]. Groundwater flowing along the land–sea margin shows that subsurface salinity distribution can extend tens to hundreds of kilometers offshore beneath continental shelves, and is often accompanied by relatively high Cr(VI) concentrations, reaching hundreds $\mu\text{g/L}$ in many countries of Europe [28–30,59,66–70]. An overview of literature data on the composition of coastal groundwater and seawater has shown a positive trend between Cr(VI) concentrations with TDS (Figure 4a) and B (Figure 4b), suggesting that seawater components significantly inhibit Cr(VI) reduction into Cr(III). In addition, in faulted regions, circulated meteoric water underground can be heated by magma or hot rocks, and geothermal water ascends back to the surface, as it is known in Greece along the Hellenic Volcanic Arc, in the Chalkidiki Peninsula, in Serres, Thrace, C. Greece, other countries in Europe (Czech Republic, Hungary, and France), and worldwide [71–77]. Contaminated groundwater in geothermal systems is commonly characterized by relatively high TDS (up to 10,000 mg/L TDS), pH ranging from 8.5 to 5.5, and As (up to 2000 $\mu\text{g/L}$ As) [78–81].

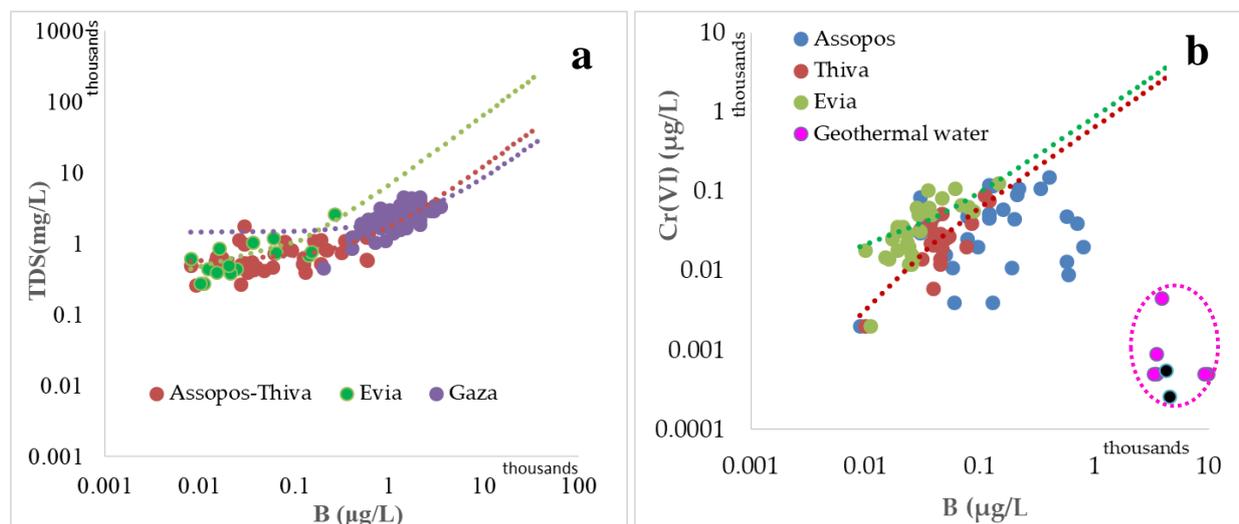


Figure 4. Plots of the Cr(VI) and total dissolved solids (TDS) versus B concentrations (a,b) for coastal groundwater from C. Evia, Assopos, and Thiva basins, seawater, and geothermal water. Data from [25,64,65,82–84].

Coastal groundwater and geothermal water are similar in terms of the high salinity, while they differ in the wide pH range (5 to 7.5), much higher As concentrations, and much lower Cr concentrations in saline deep geothermal water compared to coastal and sea water [83–85].

3.3. Smelting/Combustion of Raw Materials

3.3.1. Bauxites and Fe-Ni-Laterites

Currently, applying the Bayer process, aluminum is extracted from bauxite ore by the production of high-grade metallurgical alumina and, subsequently, the electrolytic reduction of alumina to aluminum [86]. Residues of the metallurgical process of bauxite or red mud are relatively toxic due to its high alkalinity (pH 10–12.5) and the presence of heavy and radioactive metals (V, Cr, Cd, Ni, Zn, Pb, Ba, Sr, Hf, Nd, U, Th) [2,65,86]. The bauxite deposit at the Parnassos–Ghiona mountains of Greece is the 11th largest bauxite producer in the world [87]. Alumina (Al_2O_3) has been produced for more than 100 years, and up to 120 million tons of bauxite processing residue or red mud are produced annually during Al extraction via the Bayer process, causing critical environmental problems [88,89]. Unexpectedly high (2100 $\mu\text{g/L}$) Cr(VI) concentrations have been measured in water leachates

from a representative red mud sample from the Aspra spitia plant, Greece (May 2008, mining company S & B Industrial Minerals) [65].

The Fe-Ni laterite deposits are a major source of Ni in Greece (Lokris, C. Evia, and Kastoria), mined by Larco, and produce some 2–3% of the world's total, in Serbia, Turkey, Albania (Bitinca), and elsewhere [90]. Although elevated levels of Cr have been identified in Ni laterites, Cr(VI) derived from that source, and its availability and contribution to natural waters remain poorly understood. Specifically, it is well known that the Fe-Ni-laterite ores from Kastoria are characterized by higher Cr, Co, and Mn, and lower Al₂O₃ and TiO₂ contents compared to those from the Lokris and Evia [50,91]. Water leaching (one week), using Cr-free natural water, has shown that leachates for the Kastoria laterite samples from the lower goethite zone, containing considerable amounts of Mn from Kastoria (Figure 1b), reached levels up to 1300 µg/L Cr(VI), in contrast to those from the Lokris and Evia Fe-Ni laterites with less than 10 µg/L [65].

3.3.2. Chromite Deposits and Ferrochromium (FeCr)

Ferrochromium (FeCr), which is a critical alloy in the production of stainless steel, is produced in several European countries (mainly in Finland, France, Italy, Norway, Sweden and former Yugoslavia, Germany, Italy, Switzerland, and the U.K.) and is a potential source of soil and groundwater aquifer contamination by Cr(VI). Specifically, chromite ore processing residue (COPR), a waste byproduct during the chromate production that is generated in the U.S. and European countries, is highly alkaline (pH > 12) and contains high levels of Cr(VI) under the form of water-soluble sodium chromate (Na₂CrO₄) [92–94].

3.3.3. Coal Mining/Combustion (Fly Ash)

Two main lignite-mining districts, at the Ptolemais–Amynteon (N. Greece) and Megalopolis in the Peloponnese (S. Greece), are in production, currently [95,96]. Mineralogical and geochemical data on fly and bottom ash from the lignite combustion have shown that many trace elements, including Cr, Cu, Pb, Zn, Cd, Mo, Ag, As, Au, Se, Te, U, and W, are associated with minerals in the peat and the organic matter [97–99]. In the Sarigkiol basin, a sub-basin of the Ptolemais basin, in addition to the influence from the open pit of the nearby lignite mines and fly ash produced by a power station, there is a contribution of heavy metals due to the presence of weathered ultramafic rocks and agricultural activities [100,101].

4. Discussion

Global climate changes (air quality, sea level), the increasing population, and demand for food and energy have resulted in intense agricultural activities and exploitation of raw material deposits to supply and use metals in high-tech applications and have caused environmental problems [12,102]. In general, the contamination of soil and groundwater by metal/metalloids related to either natural processes (weathering of rocks and ore deposits, salinization) and/or human activities (industrial, mining, smelting, extensive use of fertilizers and pesticides in the agricultural activities, urban pollution) are critical problems for the water quality and food chain [12,14,103]. The consequence of plant/crop irrigation with contaminated water and bioaccumulation of toxic elements by plants (transfer into food chain) are potential threats for human health and ecosystems [1,6,9,15,104].

4.1. Implications of the Green Economy

Recently, there has been significant progress on industrial waste prevention and management at a worldwide scale, including the European community, on the transition to a circular economy (green economy) in order to make it more sustainable [16–18]. The investigation of raw materials in the frame of research projects, including the ProMine databases, provides valuable information in a geographic information system (GIS) for the distribution of the major raw material deposits, mining wastes, potential products, and their importance for the economy in all European countries, as well as the creation of national

and European cultivation strategies for the optimization of agricultural management strategies [19,21,22,105].

4.1.1. Smelting Residues (Red Mud and Slag)

With respect to the hundreds of million tons of bauxite processing toxic red mud, produced during Al extraction via the Bayer process, several applications have been proposed, such as a source for the recovery of critical metals and ceramics [106–108]. A new application proposed the use of the red mud as a component in cements, in building materials, or synthesis of inorganic polymers with excellent properties [17]. Thus, the Bayer process, causing critical environmental problems, can be effectively transformed into a zero-waste process [17]. On the basis of Cr K-edge XANES and TEM analysis of the speciation of chromium in red mud samples, it has been suggested that Cr in red mud is mostly present as Cr(III), substituted into hematite and goethite [2,109]. However, unexpectedly high Cr(VI) concentrations (2100 µg/L) have been measured in water leachates of red mud [65], suggesting that the reduction of the oxidation stage of the Cr(VI) is required before the applications of red mud. Similarly, the reduction of Cr(VI) in the Cr(V)-bearing wastes during the production of FeCr from chromite [92–94] is necessary.

The reductive smelting plant for the production of ferronickel (FeNi) from Fe-Ni laterites of Central Greece (Lokris and Evia) and Kastoria at Larymna (Greece) allows the formation of one metallic phase containing all of the nickel and part of the iron and one slag residue [110]. The residue of the metallurgical process (slag) contains a glassy phase with inclusions of spherical Fe-Ni alloy of varying size [65]. Water leaching experiments on Fe-Ni laterite ores from Lokris and Kastoria deposits and metallurgical residues (slag) have shown that the Cr(VI) concentrations in leachates for the slag and the Lokris Fe-Ni laterites are very low (2 to <1 µg/L), but those from the Kastoria laterites reach as high as 1200 µg/L Cr(VI) concentrations [65]. Therefore, the release of Cr(VI) from the use of that type of slag is not facilitated under ambient conditions, but examination of potential Cr(VI) leaching during mining is required.

4.1.2. Bioaccumulation of Harmful Metal(loids)

Special attention has been paid to the soil–groundwater–plant/crop system, especially to the accumulation or transfer factor, which is the ratio of the element content in plants relative to the total element content in the relative soil, showing a wide variation as a function of the oxidation state of metals/metalloids in soil and irrigation water, the content of organic matter, and the pH and Eh parameters [111,112]. Review of the available database/literature highlights the importance of water quality on human health/ecosystems and the need to differentiate between Cr(III) and Cr(VI) discharge limits to soil and/or drinking/irrigation water for all European countries [113]. Mineralogical and geochemical data on fly and bottom ash from the lignite combustion in northern Greece, coupled with leaching experiments, suggested that applying these materials on agricultural land via the addition of a small proportion of 5 wt% fly ash in acid soil can increase the pH to 7.3–7.8, and the Ca, Mg, K, and Na content of the soil [98,99]. Although these elements can be classified as essential nutrients, the coexisting trace elements, such as As, Cr, Cu, Ni, Zn, and Hg, are considered to have some environmental or public health impacts, including potential groundwater contamination, and should be used with caution for agricultural applications [114]. In addition, organic carbon may play a key role in the mobility of added Cr(VI) to soil via irrigation water [115]. The use of leonardite, which is an oxidized form of lignite, due to its high content of humic acid, is considered to be a useful organic fertilizer that provides possibilities for combining food production with soil [116,117]. Since Europe (Germany, Greece, Poland, and the Czech Republic) accounts for roughly 40% of global lignite reserves [118], the application of the natural organic material, leonardite, as a land management technique seems to be a cost-effective method consistent to related protocols for the protection of the soil quality. In addition, several land uses in the exploited lignite quarries have been proposed in the frame of the circu-

lar economy, such as agriculture activities, greenhouses, livestock farming, forests, and photovoltaic parks, which can contribute to the energy economy cycle [96].

It is well known that selenium (Se) is an essential micronutrient for humans and animals, but both Se excess and deficiency can cause various health risks. The potential presence of selenates (SeO_4^{2-}), due to industrial activities, mines, or smelting plants, and the Se level in coastal groundwater affected by the intrusion of seawater in coastal groundwater, occasionally exceeding the guidelines [103] for Se ($10\mu\text{g/L}$) in drinking water [27,28], may cause contamination problems in cultivated plants/crops [119,120]. However, soils commonly exhibit Se deficiency, and people have insufficient levels of Se-serum [121,122]. More research on the Se distribution in crops/plants and relative soil coming from their rhizosphere is required to define potential Se source(s), factors controlling Se bioaccumulation, and ways for its enrichment in food.

4.2. Application of the Stable Chromium Isotopes to the Groundwater Contamination by Cr(VI)

Oxidative weathering and the presence of Mn oxides as a catalyst on the surface of Cr-bearing ultramafic rocks facilitate the oxidation of Cr(III) into water-soluble Cr(VI) [123], eventually being deposited in the seabed sediments [124–128]. Subsequently, during the reduction of the Cr(VI) to Cr(III), the lighter chromium isotopes (^{52}Cr) are preferentially reduced, resulting in an enrichment of ^{53}Cr relative to ^{52}Cr values ($\delta^{53}\text{Cr}$ values in units per mil (‰) relative to a standard) [31] and redox processes produce significant Cr isotope fractionation [129]. Moreover, Cr(III) forms in igneous rocks with an average $\delta^{53}\text{Cr}$ value of $-0.124 \pm 0.101\text{‰}$ [130] can be oxidized to Cr(VI) in the presence of Mn oxides (in oxidation stage +4) [51,131]. Contaminated groundwater ($4500\mu\text{g/L}$) by industrial activities (1997) at the area of Friuli Venezia Giulia (northern Italy) was completely attenuated, subsequently (2003), under pH conditions of 7.5–8.2 and Eh 0.36–0.41V [132]. However, the contamination by Cr(VI) of coastal groundwater in the Assopos basin remains at the hundreds $\mu\text{g/L}$ level [65,82]. Given the lack of seawater effect in groundwater in the case of Friuli Venezia Giulia Region, northern Italy, as is exemplified by the relatively low TDS and Na concentrations in those aquifers [133], it seems likely that the reduction of Cr(VI) to Cr(III) is not inhibited in that case. In contrast, in the coastal groundwater from C. Evia and Assopos basins, the presence of borate $[\text{B}(\text{OH})_4]^-$ ions (Figure 4a,b) [134,135], a potential buffer, may indicate that the reduction of Cr(VI) to Cr(III) is inhibited [136]. In addition, there is a difference between the Kastoria Fe-Ni laterites leaching $1300\mu\text{g/L}$ Cr(VI) and showing $\delta^{53}\text{Cr}$ values ranging between $+0.03 \pm 0.06\text{‰}$ and $-0.21 \pm 0.08\text{‰}$, and the laterite from Lokris leaching $<2\mu\text{g/L}$ Cr(VI) and showing $\delta^{53}\text{Cr}$ values of $+1.01 \pm 0.05\text{‰}$ (Figure 5). The Cr stable isotope data of soil profiles developed on serpentinized, chromite-bearing ultramafic rocks at La Cabana have shown negative $\delta^{53}\text{Cr}$ values (-0.089 to -0.320‰ , average of -0.178‰) [137]. According to these authors, the degree of weathering of the La Cabana soils corresponds to an early to intermediate stage of weathering compared to the traditional tropical laterite deposits.

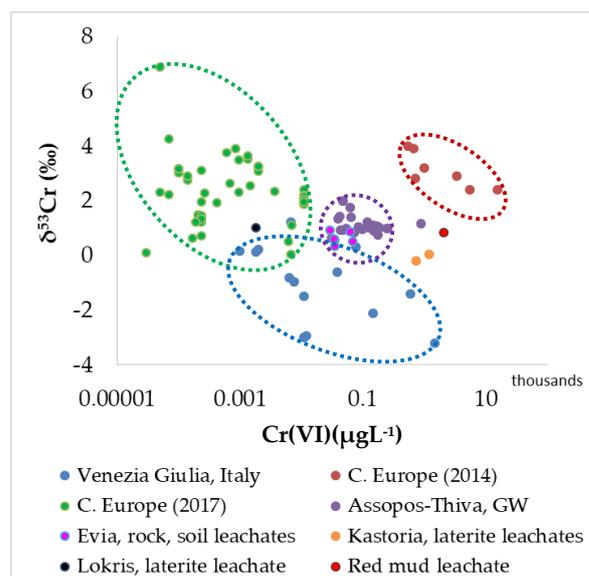


Figure 5. Plot of the $\delta^{53}\text{Cr}$ values *versus* Cr(VI) in contaminated by Cr(VI) groundwater by industrial activities in the Friuli Venezia Giulia (Italy), the Czech Republic (Central Europe), the Assopos, Thiva basin affected by both industrial activities and natural processes, and Central Evia of geogenic origin. Data from [82,132,138–140].

Thus, available analytical data on groundwater contamination by Cr(VI) (either by natural processes and/or industrial activities) show a well-pronounced negative trend between chromium isotopes ($\delta^{53}\text{Cr}$ values) *versus* Cr(VI) concentrations, suggesting that the dominant cause of Cr isotope fractionation is post-mobilization reduction of Cr(VI) [82,132,138,141,142]. However, the abundance of Cr(VI) in coastal groundwater may be related to the presence of $[\text{B}](\text{OH})_4^-$ ions, which significantly inhibit Cr(VI) reduction to Cr(III).

4.3. Knowledge Gaps

The consequences of the cultivation of plants/crops in contaminated soil and their irrigation with contaminated water, resulting in the bioaccumulation of toxic elements (transfer into food chain), are important threats for human health and ecosystems [1,6,9,15,104]. A review of the available database/literature highlights the need for the protection of soil and water quality. Although many cities in Europe have been geochemically mapped [143], application of GIS (geographical information system) and risk analysis (mapping) for groundwater and soil geochemistry for every city in Europe is required in order to define contamination/pollution sources, the presence of hotspots, and the degree and extent of groundwater contamination. Efforts need to assess heavy metal and/or metalloid contamination, and the creation of national and European cultivation strategies are needed in the cultivated land. Free or low-cost access for everybody to the information obtained could facilitate optimization of agricultural management strategies.

According to recent legislation [113], Cr discharge to the aquatic environment is regulated by EU member states at maximum discharge limits of 1 mg/L Cr(VI) and 5 mg/L Cr_{total} for EU member states [144]. Efforts need to differentiate between Cr(III) and Cr(VI) discharge limits to soil and/or aquatic environments, as well as in the drinking water for all European countries.

Recently, there has been significant progress on industrial waste prevention and management on a worldwide scale, including the European community on the transition to a circular economy (green economy), making it more sustainable [16–18]. However, further research on the transformation of mining, smelting, and combustion wastes to new products and the creation of cultivation strategies for the optimization of agricultural management strategies [19,21,22] are required.

5. Conclusions

Natural processes (weathering of rocks and ore), the intense exploitation of raw material deposits to supply metals in high-tech applications, and agricultural activities have caused soil and groundwater contamination by heavy metals and metalloids, which, in turn, are transferred into the food chain. The present review of literature data suggests that, despite the environmental risk, potential opportunities can contribute towards the development of new products and new ways for groundwater management and land use:

Efforts need to provide ways to restrict the transfer of heavy metals/metalloids from soil to plants/crops and groundwater, without the reduction of agricultural and industrial production.

Mining wastes from the mining of coal/lignite (leonardite), and combustion byproducts (fly ash) may be used to optimize agricultural production.

Efforts are needed towards reducing Cr(VI) from industrial wastewaters, prior to their discharge into receptors.

Soil and groundwater contamination, due to mining, smelting, or combustion, can be reduced by applying transformations of harmful wastes into new products with potential applications towards a circular economy.

At the abandoned mines, quarries, and surroundings, changes in land use may allow the development of a new land management and the production of green energy.

Author Contributions: Both authors, M.E.-E. and I.M., contribute to the conceptualization, methodology, software and validation of data, writing—original draft preparation. All authors have read and agreed to the published version of the manuscript.

Funding: The Municipality of Oropos, Greece (Grand No AK 70/3/9997) and the University of Athens (Grant No KE 11078).

Acknowledgments: Many thanks are expressed once again to the University of Athens, the Municipalities of Oropos and of Dirfys-Messapia (Greece) for the financial support of the assessment of soil and groundwater contamination in Greece, and to the anonymous reviewers for their criticism and suggestions on an earlier draft of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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