The Cr(VI) Stability in Contaminated Coastal Groundwater: Salinity as a Driving Force

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Abstract: Chromium concentrations in seawater are less than 0.5 µg/L, but the Cr(VI) in contaminated coastal groundwater affected by Cr-bearing rocks/ores and/or human activities, coupled with the intrusion of seawater may reach values of hundreds of µg/L. A potential explanation for the stability of the harmful Cr(VI) in contaminated coastal aquifers is still unexplored. The present study is an overview of new and literature data on the composition of coastal groundwater and seawater, aiming to provide potential relationships between Cr(VI) with major components in seawater and explain the elevated Cr(VI) concentrations. It is known that the oxidation of Cr(III) to Cr(VI) and the subsequent back-reduction of Cr(VI) processes, during the transport of the mobilized Cr(VI) in various aquifers, facilitate the natural attenuation process of Cr(VI). Moreover, the presented positive trend between B and Cr(VI) and negative trend between δ53Cr values and B concentration may suggest that seawater components significantly inhibit the Cr(VI) reduction into Cr(III), and provide insights on the role of the borate, [B(OH)4]− ions, a potential buffer, on the stability of Cr(VI) in coastal groundwater. Therefore, efforts are needed toward the prevention and/or minimization of the contamination by Cr(VI) of in coastal aquifers, which are influenced by the intrusion of seawater and are threatened by changes in sea level, due to climate change. The knowledge of the contamination sources, hotspots and monitoring of water salinization processes (geochemical mapping) for every coastal country may contribute to the optimization of agricultural management strategies.

Keywords: groundwater; contamination; chromium(VI); salinization; borate; chromium isotopes

1. Introduction

The scientific interest on the sustainable management of water resources and the effect on groundwater aquifers by either nature processes and/or extensive application in industry, is an attractive and fundamental subject to global food security. Among heavy metals, chromium (Cr) has become widespread in the environment. It appears in several oxidation states, the trivalent Cr(III) and hexavalent forms [Cr(VI)] being the most thermodynamically stable Cr forms in nature [1,2]. Cr(III) is necessary for lipid and sugar metabolism, and it is an essential trace element for human and animal health, whereas Cr(VI) in the food chain (groundwater, soil and plants), has created an alarming situation for human life and ecosystems [3–5]. Potential sources for the relatively high Cr contents in soil and groundwater may be the widespread Cr-bearing peridotites, which are parts of ophiolite complexes, covering more than 1% of the earth, along orogenetic zones [6], intense ore mining/smelting, industrial and agriculture activities (fertilizers and pesticides) [7,8]. The weathering processes of ultramafic rocks, depending mainly on the climate conditions and morphology, may result in the formation of laterites, both releasing elevated Cr(VI) concentrations. It is known that the oxidation of Cr(III) to Cr(VI) and the subsequent back-reduction of Cr(VI) processes, during the transport of the mobilized Cr(VI) in various aquifers, facilitate the natural attenuation process of Cr(VI). Moreover, the presented positive trend between B and Cr(VI) and negative trend between δ53Cr values and B concentration may suggest that seawater components significantly inhibit the Cr(VI) reduction into Cr(III), and provide insights on the role of the borate, [B(OH)4]− ions, a potential buffer, on the stability of Cr(VI) in coastal groundwater. Therefore, efforts are needed toward the prevention and/or minimization of the contamination by Cr(VI) of in coastal aquifers, which are influenced by the intrusion of seawater and are threatened by changes in sea level, due to climate change. The knowledge of the contamination sources, hotspots and monitoring of water salinization processes (geochemical mapping) for every coastal country may contribute to the optimization of agricultural management strategies.
groundwater by Cr may be derived from industrial activities, such as in the Czech Republic (a highly industrialized country in Central Europe) [17], at the area of Friuli Venezia Giulia (northern Italy) [18], the Assopos Basin (Oinofyta or Inofyta, near the Assopos river) in Greece, exhibiting as high as 8000 μg/L Cr(VI) in shallow groundwater [19]. Additionally, ferrochromium (FeCr), which is a critical alloy in the production of stainless steel, is produced in several European countries (Finland, France, Italy, Norway, Sweden, the nations formerly comprising Yugoslavia, Germany, Italy, Switzerland, and the U.K.) generating Cr-bearing wastes [7,20].

In coastal groundwater that is contaminated by either Cr-bearing rocks/ores or industrial wastes, Cr(VI) often exceeds the maximum acceptable level for Cr_{total} in drinking water (50 μg/L) [21]. Such groundwater, at the interface zone between land and sea, is continually influenced by both marine and terrestrial processes, and it often contains elevated concentrations of Na, Cl, B, Li, Se, As, S, Ca, and Mg, which is characteristic of the seawater composition [22,23]. Although about one quarter of the global population lives in the vicinity of the world’s coastlines [24], the potential role of the presence of seawater components, which may significantly facilitate the Cr(VI) stability, inhibiting the Cr(VI) reduction to Cr(III), is unexplored in groundwater. Additionally, because high technology metals such as the rare earth elements (REEs) have become contaminants in the environment [25,26], this study presents new data on the composition of coastal water, including REEs, from the industrial zone of the Assopos and other Neogene Basins. They are combined with available data from previous studies, and the delineated relationships are presented. A major aim was the interpretation of the Cr(VI) stability, as a function of the salinity in groundwater resulting from the intrusion of seawater, the prevention of groundwater from further degradation, and protection of the valuable water resources.

2. Chromium Background
Structure of Cr(III) and Cr(VI) and Soluble Products

Assuming that Cr(III) forms hexa-coordinate complexes with the octahedral arrangement of ligands, [Cr(H_2O)_6^{3+}] is the main Cr species in solutions of inorganic Cr(III) salts under strongly acidic pH, while at pH ≥ 4, Cr(III)-bound H_2O molecules undergo hydrolysis, resulting in the formation of soluble oligomeric products, whilst polymeric products are insoluble (Figure 1) [27].

Surface waters commonly contain a mixture of soluble monomeric and oligomeric Cr-products [28]. Additionally, in the presence of organic matter, the formation of stable Cr(III) complexes with small organic molecules can increase their mobility at the source of contamination sites and maintain the solubility of Cr(III) even at neutral pH [27].

Chromate and dichromate have tetrahedral arrangements of coordinated oxygen (Figure 2). The chromate anion (CrO_4^{2−}) is the predominant form of Cr(VI) in dilute solutions at neutral pH, co-existing in equilibrium with its protonated form [HCrO_4]^{−} in an approximately 3:1 ratio at these conditions [29].
Figure 2. Structures of tetrahedral chromate, and dichromate (modified from ref [27]).

3. Geological and Hydrological Outline

Detailed studies in Greece have shown that the main aquifers in the Mesogeia Basin in Attica, which is part of the Attica–Cyclades zone, are constituted by Triassic–Jurassic limestones, Upper Cretaceous limestones, marly limestones, and travertine limestones (permeable rocks) [34–38]. The main part of the Mesogeia Basin, including the Koropi area (Figure 2), is occupied by Quaternary formations (gravels, sand, and clays) which characterize a low productive phreatic aquifer [35]. The alluvial deposits form a phreatic aquifer displaying limited permeability and poor hydraulic characteristics, due to fine grain compositions; they feed a large number of wells and boreholes, with depths ranging from 10 to 20 m [35–37].

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Figure 3. Sketch map showing locations of contaminated groundwater by Cr(VI) coasts (a) examples such as in California, Pakistan, India, Northern China, the Mediterranean Sea, etc. [23]; (b) Karstic-type aquifer developed in Neogene lacustrine formations of the Mesogeia Basin in Attica [34,35,37]; (c) simplified geological map presenting the sites of the groundwater well and soil samples at the C. Evia and Assopos–Thiva Basins [11,36].

4. Materials and Methods

Although the details of the analytical methods applied for the determination of the groundwater composition, including chromium stable isotopes, are provided in relative references, a brief outline is given here. More than two hundred coastal groundwater samples from domestic and irrigation wells from the C. Evia, Assopos–Thiva, and Attica Neogene Basins, and seawater samples from the Mediterranean Sea (Evoic gulf), collected during the period from 2007 to 2017, have been analyzed for major and trace elements by inductively coupled plasma mass spectroscopy (ICP/MS) [11,12,31–38]. In addition, representatives of those groundwater samples were analyzed in the present study for major and trace elements, including rare earth elements (REEs) and platinum-group elements (PGEs) by inductively coupled plasma mass spectroscopy (ICP/MS) (Table 1). Detection limits, quality control samples and the precision of the analyses were 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 (Turnhout, Belgium). The analyses of total chromium were performed by GFAAS (Perkin Elmer 1100B system, Waltham, MA, USA), with an estimated detection limit of ~1 µg/L. The chemical analyses for Cr(VI) were performed by the 1.5-diphenylcarbohydrazide colorimetric method, using an HACH DR/4000 spectrophotometer (Loveland, CO, USA). The estimated detection limit of the method was determined at ~4 µg/L.
Table 1. Major and trace element concentrations in groundwater and water leachates for peridotites from C. Evia, Assopos–Thiva, and Attica Basins.

| µg/L | U.C. | K.2 | V.3 | V.4 | KA.5 | KP6 | Ass. A1 | Ass. A2 | Ass. AK3 | EV.1 | EV.2 | EV.3 | EV.4 | EV.5 | R2BA | R2BB | R3 | Limit |
|------|------|-----|-----|-----|------|-----|--------|--------|----------|------|------|------|------|------|------|------|-----|-------|
| As   | 2.5  | 6.4 | 1.3 | 1.2 | 2.3  | 2.2 | 1.0    | 3.5    | 4.8      | 1.5  | 0.9  | <0.5 | 0.7  | 0.7  | 1.7  | 0.5  | 0.8  | 0.5   |
| B    | 62   | 31  | 105 | 89  | 17   | 18  | 35     | 37     | 130      | 54   | 35   | 87   | 57   | 136  | 124  | 98   | 78    |
| Li   | 7.8  | 9.8 | 2.4 | 3.0 | 2.3  | 5.8 | 12     | 32     | 84       | 33   | 7.5  | 8.9  | 5.1  | 3.2  | 1.7  | 0.3  | 1.5   | 0.1   |
| Se   | 1.8  | 1.4 | 1.3 | 0.7 | 0.9  | 1.2 | 0.9    | 2.2    | 3.5      | 1.7  | 0.6  | 1.8  | 2.2  | 0.6  | <0.5 | <0.5 | <0.5  | 0.5   |
| Ba   | 35   | 50  | 42  | 41  | 35   | 40  | 37     | 64     | 42       | 4    | 16   | 74   | 27   | 21   | 3.30 | 2.36 | 5.08  | 0.05  |
| Br   | 230  | 210 | 190 | 200 | 130  | 210 | 150    | 296    | 1400     | 237  | 132  | 210  | 290  | 143  | 13   | <5   | <5    | 5     |
| Cu   | 0.9  | 2.3 | 2.0 | 2.2 | 1.2  | 1.1 | 1.1    | 0.6    | 2.1      | 2.6  | 0.9  | 2.7  | 2.6  | 1.8  | 1.5  | 0.3  | 0.6   | 0.1   |
| Cr   | 8.3  | 19.0| 6.0 | 6.2 | 6.9  | 6.1 | 59     | 114    | 900      | 105  | 52   | 128  | 320  | 91   | 35   | 64   | 32    | 0.5   |
| Mn   | 0.05 | 0.29 | 0.08 | 0.09 | 0.77 | 0.06 | 0.73   | 0.05   | <0.05    | 0.26 | <0.05 | 0.21 | 1.21 | 0.36 | 0.13 | 0.15 | 0.48  | 0.05  |
| Mo   | 0.7  | 0.2  | 0.2  | 0.3  | 0.2  | 0.2  | <0.1   | 0.1    | 0.2      | 0.2  | 0.1  | 0.4  | 0.1  | 0.5  | 1.7  | 0.3  | 0.1   | 0.2   |
| Nb   | 0.02 | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | <0.01  | <0.01    | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | 0.01  |
| Dy   | <0.01| 0.01 | 0.01 | 0.01 | <0.01| <0.01| <0.01  | <0.01  | <0.01    | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | 0.01  |
| Cu   | 0.9  | 2.3 | 2.0 | 2.2 | 1.2  | 1.1 | 1.1    | 0.6    | 2.1      | 2.6  | 0.9  | 2.7  | 2.6  | 1.8  | 1.5  | 0.3  | 0.6   | 0.1   |
| Cr   | 8.3  | 19.0| 6.0 | 6.2 | 6.9  | 6.1 | 59     | 114    | 900      | 105  | 52   | 128  | 320  | 91   | 35   | 64   | 32    | 0.5   |
| Mn   | 0.05 | 0.29 | 0.08 | 0.09 | 0.77 | 0.06 | 0.73   | 0.05   | <0.05    | 0.26 | <0.05 | 0.21 | 1.21 | 0.36 | 0.13 | 0.15 | 0.48  | 0.05  |
| Mo   | 0.7  | 0.2  | 0.2  | 0.3  | 0.2  | 0.2  | <0.1   | 0.1    | 0.2      | 0.2  | 0.1  | 0.4  | 0.1  | 0.5  | 1.7  | 0.3  | 0.1   | 0.2   |
| Nb   | 0.02 | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | <0.01  | <0.01    | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | 0.01  |
| Dy   | <0.01| 0.01 | 0.01 | 0.01 | <0.01| <0.01| <0.01  | <0.01  | <0.01    | <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01| <0.01  | 0.01  |
| Cu   | 0.9  | 2.3 | 2.0 | 2.2 | 1.2  | 1.1 | 1.1    | 0.6    | 2.1      | 2.6  | 0.9  | 2.7  | 2.6  | 1.8  | 1.5  | 0.3  | 0.6   | 0.1   |
| Cr   | 8.3  | 19.0| 6.0 | 6.2 | 6.9  | 6.1 | 59     | 114    | 900      | 105  | 52   | 128  | 320  | 91   | 35   | 64   | 32    | 0.5   |
| Mn   | 0.05 | 0.29 | 0.08 | 0.09 | 0.77 | 0.06 | 0.73   | 0.05   | <0.05    | 0.26 | <0.05 | 0.21 | 1.21 | 0.36 | 0.13 | 0.15 | 0.48  | 0.05  |
A series of batch water-leaching experiments for serpentinized peridotites were carried out in order to study the long-term (one week) leaching responses of Cr under atmospheric conditions [38]. Water and water leachate samples in an amount which would yield about 1 µg of total chromium were used for the Cr isotope composition, and the solutions were prepared following the method from ref [39]. Both Cr concentrations and isotope ratios were analyzed using an IsotopX “Phoenix”multicollector thermal ionization mass spectrometer (TIMS) equipped with eight Faraday cups at the University of Copenhagen, Denmark. Four Cr beams (\(^{50}\)Cr\(^{+}\), \(^{52}\)Cr\(^{+}\), \(^{53}\)Cr\(^{+}\), and \(^{54}\)Cr\(^{+}\)) were analyzed simultaneously with \(^{49}\)Ti\(^{+}\), \(^{51}\)V\(^{+}\), and \(^{56}\)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:

\[
\delta^{53}\text{Cr}(\text{‰}) = \left[ \frac{^{53}\text{Cr/}^{52}\text{Cr}_{\text{sample}}}{^{53}\text{Cr/}^{52}\text{Cr}_{\text{SRM}}_{979}} - 1 \right] \times 1000. \tag{1}
\]

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.

5. Global Distribution of Coastal Groundwater

Climate change, due to increasing concentrations of greenhouse gases, may affect the saltwater intrusion through changes in precipitation and temperature [40]. Coastal aquifers within the zones of influence are threatened by rising sea levels worldwide (Figure 3). The phenomenon of seawater intrusion has been recorded in many coastal areas, such as in Texas, Florida, Indonesia, Syria, in South Asia (Bangkok) in Africa (Nigeria, Egypt and Tunisia), China, Australia, and Europe (Cyprus, Turkey, Estonia, Italy, and Greece) [10,12,23,25,31–38]. Global review publications provide an extensive array of field, laboratory, and computer-based techniques for the investigation of the seawater intrusion, its composition, and prediction of freshwater–saltwater interfaces over regional scales [25,41–46].

6. Geochemical Characteristics and Salinization of Coastal Groundwater

A common feature of the groundwater from the Neogene lacustrine formations of the Attica Basin, which has been affected by occasionally enclosed (tectonically) serpentinized peridotites, and the C. Evia, Assopos–Thiva Basins and the Loutraki area (Figure 3b,c) is the effect of the seawater intrusion [11–14,31–38,41], although they have been classified in various water types: the water samples from Attica as a Ca–HCO\(_3\) water type [37], while those from C. Evia and Assopos–Thiva Basins and the Loutraki area are of Mg–HCO\(_3\) type, due to the CO\(_2\)-driven dissolution of dominant minerals, such as serpentine and Mg-carbonates/hydroxides [11,14,31]. In order to better understanding the hydrochemistry of the above aquifers and the driving force of the Cr(VI) stability in contaminated coastal water, representative groundwater samples from the Attica, Assopos–Thiva, and C. Evia Neogene Basins were analyzed in the present study for major and trace elements, including rare earth elements (REEs) and platinum group elements (PGEs) (Table 1), which were combined with the relative literature data.

Major and trace elements (Table 1) are in a good agreement with those in previous studies, often exhibiting Cr(VI) concentrations over the maximum acceptable level for Cr\(_{\text{total}}\) in drinking water (50 µg/L), although the water contaminated by industrial activities in the area of Oinofita (or Inofyta), near the Assopos river (Assopos Basin) has shown concentrations higher than 8000 µg/L [19]. Besides the elevated B, Br, Se, Li, As, V, U, S, Na, K, Ca and Mg concentrations, the concentrations for the majority of REEs are lower than the detection limit of the method (<0.01 µg/L), except values of 0.02 µg/L La and 0.01 to 0.02 µg/L Nd measured in the Assopos and C. Evia aquifers, and 0.02 µg/L Gd and 0.02 µg/L Dy measured in the Attica aquifers. The measured range for Sc of lanthanides was 2–3 µg/L in the Attica aquifers and 4–14 µg/L Sc in the C. Evia and Assopos Basins (Table 1). With respect to platinum-group elements, Pd was lower than the detection limit.
of the method (0.2 µg/L). The Pt was lower than detection limit (0.01 µg/L) in the Attica aquifers, while 0.01 values were measured in the C. Evia and Assopos aquifers. The Ru concentrations ranged from 0.06 to 0.3 µg/L in Attica, and from 0.06 to 0.19 µg/L in the C. Evia and Assopos Basins (Table 1). Additionally, these water samples were analyzed for the elements Au, Ag, Al, Ti, W, Ti, Te, Ta, Sn, In, Hf, Ge, Pb, Cs, Hg, Be, Bi, Cd, Ga and Y, but their concentrations were lower than the detection limit of the method. The measured concentrations for REEs and PGEs in water leachates for altered peridotites were also too low (Table 1). The available data on groundwater from previous studies exhibiting the lowest B and Cr(VI) concentrations have been recorded in the Mavrosouvala wells of karst type (Table 2), which are used for the municipal water supply of Athens city.

Table 2. Average composition of groundwater from the Assopos, Thiva, Attica Basins and C. Evia and seawater. Data from refs [19,32–38,46–49].

| Location                  | µg/L  | mg/L | g/L | %  |
|---------------------------|-------|------|-----|----|
| Groundwater               |       |      |     |    |
| Karst type                |       |      |     |    |
| Mavrosouvala              | 3     | <1   | 18  | 2.5|
| Attica, Athens            | 19    | 9.7  | 43  | 6.4|
| Attica, Koropi            | 31    | 12   | 130 | 8  |
| Assopos basin             |       |      |     |    |
| Avlida                    | 10    | 70   | 64  | 16 |
| Oropos                    | 3     | 61   | 57  | 120| 23 |
| Avlona                    | 2     | 72   | 66  | 36 |
| C. Evia                   | 7     | 63   | 70  | 3.3|
| Geothermal water          |       |      |     |    |
| Aedipsos, Evia            | 9     | n.d. | 9500| 1400| 68 |
| K. Vourla, C. Greece      | 5     | n.d. | 3400| 380 | 29 |
| Vendenheim, France        | 2     | 2.7  | 155,000 | 960 | 145 | 350 | 200 | 45,800 | 110 | 6.1 | 9.0 |

Present analytical data (Table 1) combining those from previous studies (Table 2) indicated that the best pronounced positive trend between B and Cr(VI) was recorded in C. Evia and Attica (Figure 4a). Limited data from the neighboring Mediterranean seawater (Assopos river estuary and Evoic Gulf) were plotted in a separate field characterized by much higher B and lower Cr(VI), comparable to those for geothermal water (Figure 4a). In addition, a good positive correlation between total dissolved solids (TDS) and B concentrations is a common feature of those water types (Figure 4b). A negative trend between the mass ratio Ca/Mg and the Cr(VI) concentrations recorded in groundwater from the studied Neogene Basins was followed by geothermal water (Figure 4c). In addition, a negative trend was clear between total organic carbon and Cr(VI) concentrations, for both lower and higher Cr(VI) concentrations of 50 µg/L in groundwater from the Assopos Basin (Figure 4d).
The plots of available stable chromium isotopes \([38,46]\) expressed as \(\delta^{53}\text{Cr}\) values versus \(B\) and \(\text{Cr(VI)}\) concentrations for coastal groundwater from the C. Evia, Assopos Basin and water leachates for peridotites showed a negative trend (Figure 5a). Moreover, plots of \(\delta^{53}\text{Cr}\) values versus \(\text{Cr(VI)}\) concentrations for seawater from the Pacific and Atlantic oceans, and Mediterranean and Baltic seas \([43]\), showed a negative trend as well (Figure 5b).

7. Discussion

7.1. REE and PGE as Potential Contaminants in Groundwater

Given that REEs have become contaminants in the environment, due to industrial activities \([25,26]\), and hundreds of industrial plants are still active at the Assopos Basin, analyses of groundwater including REE are presented (Table 1) in order to evaluate the level of REEs and potential environmental impact. Although the REE concentrations were lower
that the detection limit, using inductively coupled plasma–mass spectrometry, even the very low measured concentrations of La, Nd, Gd and Dy suggest that analysis using a more sensitive analytical method [51] is required to provide evidence for the REE behavior in that type of groundwater. With respect to PGE concentrations in groundwater, only Ru values (ranging from 0.06 to 0.30 µg/L) are often higher than the detection limit of the method (0.05 µg/L) (Table 1), suggesting that Ru is relatively mobile in the Neogene unconfined aquifers. It has been shown that humic and fulvic acids are capable of taking the PGE into solution from sulphides and Platinum Group Minerals (PGM). The complete sequence of alteration of the PGM from the fresh rocks to the weathered rocks has been proposed [52]. However, the available thermodynamic data for aqueous organic or hydroxide complexes involving the PGE are limited, and their impact on natural hydrological processes, water quality, and ecosystem processes are still unexplored [53].

7.2. Interaction between Cr(III) with Major Seawater Ions in Coastal Groundwater

Among potential redox couples in natural aquatic environments are \( \text{H}_2\text{O}/\text{O}_2 \), \( \text{Mn(II)}/\text{Mn(IV)} \), \( \text{N}_2/\text{NO}_3^- \), \( \text{NH}_4^+)/\text{NO}_3^- \), \( \text{Fe(II)}/\text{Fe(III)} \), \( \text{HS}^-/\text{SO}_4^{2-} \) and \( \text{CH}_4/\text{CO}_2 \) [54,55]. In particular, \( \text{H}_2\text{O}_2 \), high-valent Mn-oxides, and \( \text{MnO}_4^- \) may act as oxidants of Cr(III) [6,56,57] because their higher standard potentials favor that reaction [58]. Experimental data have shown that chromate adsorption by goethite is thermodynamically favorable through both inner- and outer-sphere surface complexation reactions [2]. These authors indicated that chromate adsorption decreases with increasing pH towards the zero-point-of-surface-charge (pHPZC 9.1) of the adsorbent surface, and ionic strength and temperature both affected outer-sphere surface complex.

Experimental results have indicated that \( \text{H}_2\text{O}_2 \) becomes a reductant at low pH [55,59]:

\[
2\text{HCrO}_4^- + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 8\text{H}_2\text{O} + 3\text{O}_2
\]

However, under alkaline conditions, hydrogen peroxide is an efficient oxidizing agent which can oxidize Cr(III) [59,60]:

\[
2\text{Cr(OH)}_3^- + 3\text{H}_2\text{O}_2 + 4\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O}
\]

7.3. Salinity as a Common Feature of Geothermal and Coastal Groundwater

The salinity, which is expressed by the total dissolved solids (TDS) and deduced from measurements of the electrical conductivity of groundwater, is a characteristic feature of sea and the geothermal water as well (Table 2 [23,48,49]). Geothermal water has been described in Greece, along the Hellenic Volcanic Arc, the Chalkidiki Peninsula, in Serres, many places in Thrace [61], in hot springs in the NW part of Evia (or Euboea) island, and in Central Greece [48], as well as in Hungary, Germany, France and many other countries [49,62]. In faulted regions, meteoric water can be circulated underground where it is heated by magma or hot rocks, and geothermal water ascends back to the surface; Na–Cl brines, with TDS values ranging from 99 to 107 g/L, pH values close to 5 and a reservoir rocks temperature value close to 225 ± 25 °C are well known in Germany [49,62]. According to these authors, their high Na, B, Li, Cl, and As concentrations may be related to processes of mixing between primary brines formed by advanced evaporation of seawater and meteoric freshwaters. Relatively low Cr concentrations (4.5 µg/L) and/or no detected concentrations in geothermal water [48,49,62] seems to be consistent with the assumption that hot brines have penetrated the granite basement below the sedimentary cover and the low pH from about 5, before cooling and degassing [49].

7.4. Decreasing Cr(III) Precipitation in the Presence of [B(OH)4]⁻ Ions, a Potential Buffer

It has been suggested that adsorption–desorption reactions may be the only significant mechanism influencing the fate of B in water, depending on the pH of the water and the B concentration in the solution, with the greatest adsorption being recorded at pH 7.5–9.0 [63]. Additionally, the dependence of the Cr sorption extent on the solution composition, which decreases from pure water to seawater, with no evidence for Cr(VI) sorption in seawater,
is probably due to the competition between Cr(VI) and other anions for sorption sites [64].

In addition, the B(OH)$_3$ is acidic because of its reaction with OH$^-$ from water, forming the complex [B(OH)$_4$]$^-$ and releasing the corresponding proton left by the water auto-protolysis:

$$\text{B(OH)}_3 + 2 \text{H}_2\text{O} \rightleftharpoons [\text{B(OH)}_4^-] + [\text{H}_3\text{O}]^+ \quad (2)$$

The p$\text{K}_a$ value (=$-\log(\text{$K_a$})$) of boric acid has been determined to be $p\text{K}_a = 8.98$ [59]. Due to a relatively high $p\text{K}_a$, boric acid has limited dissociation at neutral or low pH values. Additionally, it has been emphasized [65] that borate may be the only ion which inhibits the Cr(VI) reduction to Cr(III) [66]. The Cr(VI) reduction/removal under alkaline conditions was investigated experimentally, applying the efficient reduction of Cr(VI) by UV/sulfite process, and it was indicated that after the addition of borate buffer ($p\text{H} = 9.2$) the precipitation of Cr(III) was inhibited, due to the formation of a Cr(III)–borate complex [66]. Thus, the formation of the Cr(III)–borate complex tends to inhibit the precipitation of Cr(III) and facilitate the stability of Cr(VI), although under acidic conditions the Cr(VI) is effectively reduced into Cr(III) and is precipitated [67]. The negative relationship between the Ca/Mg mass ratio and Cr(VI) concentrations (Figure 4d) may suggest that the reduction of the Cr(VI) to Cr(III) precipitation is facilitated by the presence of Ca ions [66].

7.5. The Cr Isotopes ($\delta^{53}\text{Cr}$ Values) as an Evidence of the Cr Redox Processes

The oxidation of Cr(III) to Cr(VI), and subsequent back-reduction of Cr(VI) processes, have been shown to produce significant Cr isotope fractionation [68]. During reduction, the lighter isotopes are preferentially reduced, resulting in an enrichment of $^{53}\text{Cr}$ relative to $^{52}\text{Cr}$ values in the remaining Cr(VI) pools. This enrichment is measured as the change in the ratio of $^{53}\text{Cr}/^{52}\text{Cr}$, and is expressed as $\delta^{53}\text{Cr}$ values in units per mil ($\permil$) relative to a standard [39,60]. Thus, during the transport of the mobilized Cr(VI) in various aquifers, low Cr(VI) concentrations and elevated positive $\delta^{53}\text{Cr}$ values imply reductive processes, probably due to the presence of Fe(II) and/or organic matter [18,38,46,69]. The Cr isotope data for groundwater from the C. Evia and Assopos–Thiva Basins [38,46,70] imply oxidative mobilization of Cr(VI) from the ultramafic host rocks, and successive back-reduction of the Cr(VI), as is exemplified by the recorded range of the $\delta^{53}\text{Cr}$ values between 0.8 and 1.99$\permil$. In addition, a series of leaching experiments carried out for ultramafic rock (natural outcrops) from C. Evia, have shown $\delta^{53}\text{Cr}$ values ranging between 0.56 and 0.96$\permil$ for the rock leachates (Table 2). Applying the available literature data concerning the redox reaction between Cr(III) and Cr(VI) and the Cr isotope fractionation during Cr redox reactions, the stability of Cr(VI) in contaminated coastal groundwater seems to be consistent with the oxidizing role of H$_2$O$_2$ in the presence of high B concentration in seawater (around 4.5 mg/L) [59]. Specifically, the potential Cr(III) oxidation by H$_2$O$_2$ in the presence of abundant tetra-hydroxyborate [(B(OH)$_4$)$^-$] complex at pH > 7.5 in contaminated coastal groundwater may be reflected in the preferential reaction of heavier Cr isotopes, leaving the reactant enriched in isotopically light Cr (Figure 4 [60,71,72]). Thus, the positive trend between B and Cr(VI) recorded in coastal groundwater from C. Evia (Figure 4a), and the negative $\delta^{53}\text{Cr}$–Cr(VI) and $\delta^{53}\text{Cr}$–B trends for coastal groundwater from C. Evia and Assopos Basin seawater (Figure 5a), may point to the role of borate in seawater on the stability of Cr(VI) in coastal groundwater from the cultivated C. Evia and Assopos–Thiva Basin. Therefore: (i) the low $\delta^{53}\text{Cr}$ values, high Cr(VI) concentrations and the dominance of [B(OH)$_4$]$^-$ ions, as a buffer, potentially imply oxidative and alkaline pH ($p\text{H} > 7$) conditions, and decreasing precipitation kinetics of Cr(III) [59,60]; and (ii) elevated $\delta^{53}\text{Cr}$ values potentially imply reductive processes, probably due to the presence of organic matter (Figure 4d), which serves various functional groups as electron donors for Cr(VI) reduction. In general, during the transport of the mobilized Cr(VI) in various aquifers, natural attenuation processes may be facilitated.

7.6. Implications of the Salinity Effect in Coastal Groundwater Contaminated by Cr(VI)

According to the structural data on the Cr(III) and Cr(VI) forms and their soluble products [27], Cr(III) at $p\text{H} \geq 4$ may form insoluble polymeric products (Figure 1), while
in the presence of organic matter, the formation of stable Cr(III) complexes with small organic molecules can increase their mobility and maintain the solubility of Cr(III) even at neutral pH [27]. Additionally, the chromate anion (CrO$_4^{2-}$) is the predominant form of Cr(VI) in dilute solutions at neutral pH [27]. Under pH conditions 7.5–8.2 and Eh 0.36–0.41 V, reduction of the Cr(VI) to Cr(III) recorded at an aquifer past-contaminated by Cr(VI) (up to 4500 g/L), due to industrial activities in 1997, in the Friuli Venezia Giulia Region (N. Italy). Subsequently, it was naturally attenuated, and the contamination completely disappeared in 2003 [18]. However, the abundance of Cr(VI) in coastal groundwater (Table 2), contaminated by Cr(VI) by either human activities and/or natural processes, is a potential risk, causing serious constraints to food production. The lack of the seawater effects in groundwater in the case of Friuli Venezia Giulia Region, northern Italy, as exemplified by the relatively low TDS and Na concentrations in those aquifers [73] and in turn in borate ions, may indicate that the reduction of Cr(VI) to Cr(III) is not inhibited, due to the absence of borate ions.

Assuming that, in coastal groundwater, the Cr(VI) concentrations reaching values of hundreds µg/L Cr(VI) (Table 2) may be facilitated by the presence of the [B(OH)$_4^{-}$] ions, a potential buffer [66], efforts are needed toward the: (i) prevention and/or minimization of the contamination of aquifers by Cr(VI), which are influenced by the intrusion of seawater; (ii) prevention of coastal aquifers within the zone threatened by changes in sea level, due to climate change. The knowledge of the contamination sources, the presence of hotspots, the degree and extent of the groundwater and soil contamination, monitoring of water salinization processes, expressed by GIS (geographical information system) and risk analysis (mapping) for every coastal country would facilitate optimization of agricultural management strategies; (iii) protection from the consequence of the plant/crops irrigation with contaminated water and the bio-accumulation of toxic elements by plants, which in turn are transferred into food chain, an important threat for human health and ecosystems [74]. Efforts need to apply ways to decrease the seawater intrusion and/or the Cr(VI) concentration, such as the use of organic matter during its cultivation [75]. For example, the application of the natural organic material leonardite, which is an oxidized form of lignite, as a land management technique, seems to be a cost-effective method consistent to related protocols for the protection of the soil quality [75]. Europe accounts for roughly 40% of global lignite reserves; the top European producers include Germany, Greece, Poland, and the Czech Republic [76].

8. Conclusions

The compilation of the present and available databases/literature on the composition of coastal groundwater, and the Cr mobility as a function of the salinity led us to the following conclusions:

- Although the Cr concentrations in seawater are less than 0.5 µg/L, the Cr(VI) concentrations in coastal groundwater affected by the intrusion of seawater reached values of hundreds of µg/L;
- There is a pronounced positive trend between B and Cr(VI) and a negative trend between $\delta^{53}$Cr values and B concentrations for coastal groundwater and seawater;
- The negative relationship between the Ca/Mg mass ratio and Cr(VI) may suggest that Ca facilitates the Cr(VI) reduction and Cr(III) precipitation;
- Despite the precipitation of Cr(III) under alkaline conditions, the potential formation of a Cr(III)–borate complex in contaminated coastal groundwater tends to inhibit the precipitation of Cr(III) and facilitate the stability of Cr(VI);
- The abundance of Cr(VI) in coastal groundwater may be related to the presence of [B(OH)$_4^{-}$] ions, a potential buffer, which significantly inhibit Cr(VI) reduction to Cr(III).
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