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Review

Salinity-Induced Changes in Heavy Metal Behavior and Mobility in Semi-Arid Coastal Aquifers: A Comprehensive Review

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Abstract: Semi-arid coastal aquifers face critical challenges characterized by lower rainfall, higher evaporation rates, and looming risk of over-exploitation. These conditions, coupled with climate change, are conducive to seawater intrusion and promote mechanisms associated with it. The understanding of metal behavior in such environments is limited, and hence, an attempt is made through this review to bridge the knowledge gap. A study on the behavior of trace metals within a specific context of semi-arid coastal aquifers was carried out, and 11 aquifers from 6 different countries were included. The review observed that trace metals within semi-arid coastal aquifers exhibit distinctive behaviors influenced by their surrounding environment. The prevalence of evaporation and continuous seawater intrusion played a pivotal role in shaping trace metal dynamics by curtailing groundwater flux. The findings suggest that the formation of stable Cl and organic ligands under increased alkaline conditions (pH > 8) has higher control over Zn, Pb, and Cd toxicity in a highly ionic reactive condition. In addition, dominant control of Fe/Mn-hydroxide association with Pb and high organic affinity of Zn played a pivotal role in controlling its bioavailability in aquifers such as WFB, Saudi Arabia NW-C and India. On the contrary, under prevailing acidic conditions (pH < 6), carbonate and SO_4-ligands become more dominant, controlling the bioavailability/desorption of Cu irrespective of its origin. The behavior of Ni is found to be controlled by stable organic ligands increasing salinity. An increase in salinity in the considered aquifers shows an increase in bioavailability of Ni, except UmC, South Africa, where organic ligands act as a sink for the metal, even at low pH conditions (pH < 5.5). This study indicates that factors such as mineral saturation, carbonate complexes, pH variations (pH > 8), and chloride complexes govern the distribution of trace metals further enhanced by prolonged water residence time. Nonetheless, specific conditions, such as a reducing and acidic environment, could potentially elevate the solubility of highly toxic Cr (VI) released from anthropogenic sources.

Keywords: groundwater; salinization; semi-arid region; coastal aquifer; contamination; toxicity

1. Introduction

Groundwater is a crucial natural resource, and its importance cannot be overstated due to its indispensable need for all life on earth. About 16 out of 32 megacities around the world with a population of more than 10 million are highly reliant on groundwater for water supply [1]. Approximately 70% of global groundwater withdrawals are attributed to agriculture, followed by the domestic sector accounting slightly over 20%, and industries consume for just under 10% [2]. Increases in global temperature coupled with evaporation and overexploitation actively reduce groundwater levels in various regions, as confirmed by satellite gravity measurements from the Gravity Recovery and Climate Experiment [3,4]. Such depletion was noticed in the southern aquifers of Australia, Northwestern India, the Central Valley of the USA, the Middle East, and the North China Plain [4]; however, contrary increases in the water level in various aquifers were denoted towards excessive irrigation return flow [5]. Such observation confirms the detrimental effect of overexploitation and degrading quality control in recent decades, which has contributed to a rapid increase

in human interference with aquatic systems [6]. Being the primary and only source of drinking water in many dry and semi-arid regions, groundwater plays a crucial role in meeting the freshwater needs of both people and the environment [7]. The impact on the quality and quantity of available groundwater in semi-arid/arid regions poses a bigger threat to the intertwined ecological balance of human and vegetation ecosystems. The vegetations in arid or semi-arid regions are partially and completely dependent on groundwater fluctuation levels. Contamination is considered to have detrimental effects, including reduced growth rate, plant density, high mortality [8], increased land erosion and desertification [5,9]. Globally, semi-arid regions characterized by low/erratic precipitation sustain about 15.2%, approximately 1.1 billion of the total population, from which the majority are poor [10]. Due to the high failure rate of rain-fed agriculture in these areas, livestock farming, such as cattle, sheep, goats, and camels, prevails as the major activity [11].
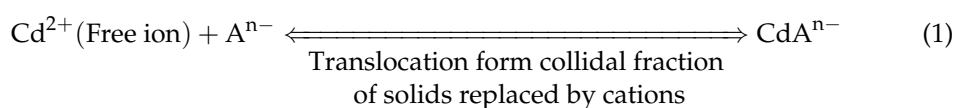
However, opportunistic dryland prevails, primarily in certain areas with relatively high moisture and supporting environments. Thus, adaptation to natural and temporal variability is a major concern in such regions, as is extensive land degradation due to intensive agricultural practices during abundant rainfall; this further formulates catastrophic collapses during subsequent drought periods [10,12,13]. A few such instances might include the Dust Bowl in the southern USA [14], China's Loess Plateau [15], the Mallee Lands in southeast Australia [16], and South Africa's Little Karoo [17]. The influence of such factors has proven to be a major contributor to groundwater pollution in semi-arid regions around the world [18,19], which might also include toxic detrimental elements like trace metals even at very low concentrations [20]. Some of such similar potentially toxic elements may include Cd, Cr, Pb, Zn, Cu, and Ni, known for their ecotoxicity, biomagnification, and carcinogenicity when exposed to biota [21]. Excessive use of agrochemicals, untreated wastewater, landfill leaching, inadequate waste disposal, and industrial or chemical spills are some of the major processes that contribute to the concentration of these metals in groundwater [22–24]. To ensure groundwater sustainability in water-stressed semi-arid regions, a systematic study on factors contributing to trace metal concentration in groundwater and its impact on groundwater quality is necessary.

Coastal groundwater serves billions of populations worldwide while facilitating fresh and saline water discharge into the marine environment [25,26]. The interaction between terrestrial freshwater and saline water triggers biochemical reactions, effectively altering the composition of various solutes such as metals and their associated discharge towards the sea or ocean [5]. As the coastal groundwater serves as a subsurface interface of saline and freshwater, climate change and the over-extraction of freshwater in coastal areas increase the threat of salinization, making it increasingly susceptible to rising sea levels [27,28]. Some areas, such as the northern Morocco aquifers, would be vulnerable to significant salinization by 2040 [29], while another study indicates that seawater intrusion has increased by tens of kilometers away from the coast in Pakistan [30]. The extraction of groundwater, especially for agricultural usage and drinking water supply, has led to the issue of seawater intrusion in numerous coastal aquifers across the Mediterranean region [31,32]. On the other hand, overexploitation of groundwater due to rapid growth in population, extensive agriculture, and industrialization has influenced the flow of anthropogenic contaminants into semi-arid [33–35]. Contamination flow, saline water intrusion evaporation due to low precipitation, over-exploitation, oxidation-reduction processes [36–39], dissolution and precipitation of minerals and salts due to higher residence time [40–42], and evaporite dissolution [43] causes salinization in the aquifers. Concurrently, factors affecting salinization mainly depend on aquifer lithology, hydraulic gradient, groundwater recharge rate and coastal topography [44,45]. An interplay between evaporation, tides, waves, and precipitation could potentially cause highly intricate driving mechanisms, which significantly influence the subsurface flow patterns and transport of solutes or contaminants [37,46]. Numerous studies have concluded that seawater intrusion has major control over the concentration of contaminants in aquifers [47–50].

2. Heavy Metal Dynamics in Seawater-Induced Aquatic System

Metals are eminent toxicants of the environment and are considered tenacious and incremental in nature [51,52]. In this era of enhanced technology and rapid urbanization, hazardous amounts of heavy metals entering groundwater systems are highly concern among scientific communities as they cause both deleterious and devasting impacts on human and coastal environment [53]. Generally, natural metals occur in groundwater in minor amounts and fulfill the essential needs of humans and aquatic organisms [54]. However, numerous studies observed that elevated concentrations of heavy metals, even in minor quantities, precede the natural accumulation of heavy metals in plant tissues, affecting their metabolism and functional means [55]. Elevated concentration of Pb can cause abrupt brain development [56], Cd could cause acute and chronic diseases [57], and Cu is used in the treatment of anemia, bone weakness, and cardiovascular issues [47] at elevated concentrations.

The recent trend of weathering of bedrock, volcanic emissions, flushing watersheds, seawater intrusions [58,59], and influential factors like rapid urbanization, increasing population, mining, and agricultural activities along the coastal areas have contributed toward higher concentrations of heavy metals in coastal aquifers [60]. Various researchers have suggested that saline water intrusion into coastal aquifers has greater control over metal solutes through chemical processes like dissolution, oxidation and reduction, acidification, absorption and desorption and Fe/Mn/Al-hydroxide coprecipitation depending upon the residence time, groundwater flow, and the depth of water [54,59,61–63]. Studies by [61] further confirmed that freshwater–seawater transition zone increased the concentration of metals such as Fe, As, Mn, and Ba compared to terrestrial freshwater discharge in the aquifers. The interface of seawater into the freshwater system affects the stability and solubility of metals by the formation of metal chloro-complexes and ion exchange [64]. In such scenarios, the formation of soluble $CdCl_2$ complexes is very common and enhances its concentration and toxicity due to low absorption during solid phases. The mobility of Cu and Ni chloro-complexes is observed to be less mobile under the same conditions [65]. Additionally, the release of Cd and Zn-S complexes is a common phenomenon under increasing salinity associated with reduction reaction and ion exchange mechanism [66]. Contrarily, seawater intrusion enhances the absorption of ions at metal absorption sites, making them more mobile. The formation of Ca-salts was found to be more effective in releasing metals from their absorption sites compared to Na-salts [67] and follows a similar pattern in soluble Cd complex formation in Equation (1) [68].

$$Cd^{2+}(\text{Free ion}) + A^{n-} \xrightleftharpoons[\substack{\text{Translocation form collidal fraction} \\ \text{of solids replaced by cations}}]{} CdA^{n-} \qquad (1)$$

In such conditions, the alkaline nature of seawater coupled with increasing chloride concentration also plays a vital role in altering metal concentration in coastal aquifers. A study by [69] shows that hydrolysis of metal ions such as Pb (II), Cd (II) and Zn (II) are predominantly observed with pH values above 5, 7 and 8, respectively. In an increasing alkaline condition, soluble MCl^+ (where M: Pb, Cd or Zn) starts appearing at 35 ppm Cl^- whereas highly soluble MCl^2 complexes start occurring at 350 ppm Cl^-. At a pH of 8.5, the chloride concentration could range from 350–60,000 ppm and would dominantly form soluble Cd complexes, whereas Zn (II) and Pb (II) would be limited to hydroxy complexes under such conditions. Under similar pH and increased salinity conditions, humic substances play a vital role in metal speciation between solid and liquid mediums. With the exception of Cu, the majority of the metals (e.g., Ni, Cd, Zn, Mn, etc.) usually desorb into soluble media with the introduction of high salinity [64]. A study by [70] suggested that stable humic complexes of Cu sustain up to 35% salinity is introduced and start desorbing due to Ca, Mg-humic ligand formation, and increased pH (>8) influencing the formation of carbonate and hydroxy species in groundwater.

The freshwater–seawater transition zone in coastal aquifers is a phenomenon controlled by intruding seawater and submarine groundwater discharge [71]. This zone is distinguished by the stratification of the saltwater–freshwater interface and creates a redox-sensitive environment while exhibiting a prominent ORP gradient [72]. The trace metals' behavior in such conditions depends on the balance shift towards oxidizing and reducing environmental conditions. During groundwater submarine discharge and freshwater dominance moves, the zone to oxidizing conditions results in the precipitation of Fe/Mn/Al hydroxides with higher absorptions of metals due to their scavenging nature [73,74]. On the other hand, redox-sensitive Fe/Mn hydroxides dissolve in reducing conditions created by a higher seawater intruding environment coupled with alkaline pH, giving rise to higher concentrations of metals in the water table [75,76]. As previously discussed, semi-arid coastal aquifers face the challenge of low rainfall coupled with high evaporation rates, exacerbated by the increased risk of over-exploitation. These conditions create a conducive environment for seawater intrusion and the associated controlling mechanisms. While numerous studies have addressed and elucidated the phenomenon of seawater intrusion and its mechanisms in coastal aquifers, research pertaining to the behavior of trace metals in semi-arid coastal aquifers subject to continuous influence from the sea or ocean has been notably scarce. This review aims to address this critical gap in our understanding by focusing on the behavior of trace metals within such semi-arid coastal aquifers. By investigating the transport, distribution, and transformation of trace metals in these specific conditions, this research endeavors to shed light on the intricate dynamics that may have significant implications for water quality, environmental management, and human health.

Recent studies conducted in diverse regions worldwide were examined to assess the impact of seawater intrusion on metal behavior in semi-arid coastal aquifers. These studies encompassed aquifers located in regions such as China (JA—Jiangsu Aquifer and LB—Laizhou Bay), Egypt (EM—East Matrouh and NE-ND—NE-Nile Delta), India (NW-C—Northwestern Coastal Aquifers, PR—Pondicherry Region, and TCA—Toothukudi Coastal Area), Saudi Arabia (H AL-S—Hada Al-Sham and WFB—Wadi Fatimah Basin), South Africa (MA—Maputaland Aquifer, UmC—Umhlathuze Catchment), and Tunisia (MA—Monastir Aquifer). Collectively, these investigations explored the behavior and average concentrations of various metals, including chromium (Cr), cadmium (Cd), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), and lead (Pb), with a specific focus on their responses to the introduction of salinity caused by seawater intrusion. For the review, more than 150 articles, reports, and books were utilized, and publications from the last 5–7 years were prioritized. The scientometric analysis is represented in Figure 1. The comprehensive findings from these studies contribute significantly to our broader understanding of how the presence of saline water influences the mobility and distribution of these metals in semi-arid coastal aquifers across diverse geographic regions, highlighting the intricate interplay between salinity and metal dynamics in these critical groundwater systems.
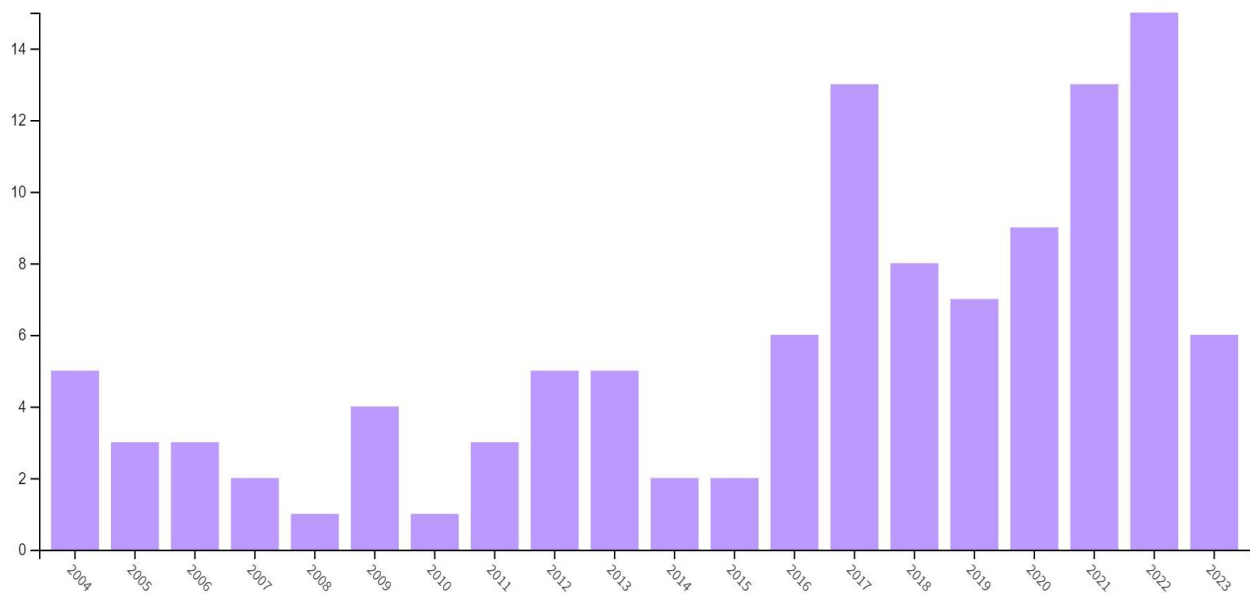
Figure 1. Scientometric analysis of the publications utilized in the study.

3. Metal Concentrations in Considered Coastal Aquifers

In order to provide information regarding the impact of metals on drinking water quality in considered coastal aquifers, a comparison of their range and average values with WHO was conducted and is presented in Table 1. The Umhlathuze Catchment (UmC) was heavily contaminated with all the metals except Zn. On the other hand, Zn contamination was found to be dominant in MA, South Africa, and NW-C, India. The highest average of Cr above permissible limits was noticed in UmC, South Africa, WFB, Saudi Arabia, and NW-C, India. Similarly, Cd was found to be above permissible limits in EM, Egypt, along with UmC, South Africa. Pb concentration was found to be above permissible limits in all the considered aquifers, except the coastal aquifers of China and MA, which have a lower number of stations falling within the permissible limits.

Table 1. Range and average values of metals in considered coastal aquifers.

	Metals	Cr		Cd		Ni		Cu		Zn		Pb		References
		Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	
China	Jiangsu Aquifer (JA)	BDL-1.01	0.133	BDL-77	1.31	BDL-7.93	0.726	BDL-110	4.8	BDL-20	1.53	BDL-10	0.3	[60]
	Laizhou Bay (LB)	BDL-7.63	6.27	BDL-0.26	0.03	2.05–32.12	8.03	0.22–6.04	1.15	0.35–195.30	17.16	0.06–14.52	0.65	[56]
Egypt	East Matrouh (EM)	10–37.1	15.1	0.6–9493	486.764	2–132.8	28.4	6–3369	200.8	11.3–256.7	72.1	8–117.1	49.4	[61]
	NE-Nile Delta (NE-ND)	BDL-2	0.5	2–3	2	8–31	19	8–85	41	NC	NC	BDL-7	0.1	[62]
India	NW Coastal Aquifers (NW-C)	8.67–292.88	102.94	1.23–63.23	12.94	6.36–237.95	40.6	3.1–297.8	56.3	11.15–29503	800	0.56–209.82	29.75	[63]
	Pondicherry Region (PR)	NC	NC	NC	NC	NC	NC	BDL-46	13	BDL-2290	133	BDL-290	14	[77]
	Toothukudi Coastal Area (TCA)	1.5–80	13.086	0.012–2.1	0.296	0.082–11	5.192	2.7–236.5	31.661	0.94–870	203.49	0.45–18	4.376	[78]
Saudi Arabia	Hada Al-Sham (H AL-S)	5–119	38	NC	NC	4–138	42	24–2320	643	1–366	53	7–673	169	[55]
	Wadi Fatimah Basin (WFB)	17–501	101	NC	NC	17–623	122	BDL-2440	276	19–335	79	6–196	39	[79]
South Africa	Maputaland Aquifer (MA)	BDL-8.4	3.4	BDL-4.6	1.7	BDL-9.3	2.1	BDL-279.5	61.2	1.9–19964.5	499.9	BDL-26	6.6	[50]
	Umhlathuze Catchment (UmC)	24–110	103	23–59	26	91–107	94	11–107	23	83–221	104	91–117	109	[53]
Tunisia	Monastir Aquifer (MA)	2–73	28	7–20	3	BDL-80	31	1–90	3	BDL-720	50	NC	NC	[80]
	Permissible Limits	50		3		70		2000		5000		10		[81]

3.1. Metal Sources and Salinity-Induced Alteration in Coastal Aquifers

3.1.1. Zinc

Zinc is an uncommon metal in terms of natural availability in aquatic systems. Naturally, this occurs in small amounts in all kinds of igneous rocks and varies from 1–300 mg/kg in soils [82,83]. However, Zn dissolution by water is relatively low, implicating its existence in high-concentration groundwater sources is mainly from anthropogenic sources such as its utilization in construction, which goes back to Middle Ages (e.g., roof surface, chimneys, and gutters) [60], corrosion-resistant coating and extraction from ore for the purpose of utilization in industries through smelting of ZnS [56], byproducts of steel production, coal-fired power stations, burning of waste materials, and agricultural fertilizers [84].

A considered coastal aquifer review suggested that the average Zn concentration exceeded standard limits [66] in Northwestern aquifers (NW-C), India [63], and the Maputoland coastal aquifer (MA), South Africa [50] (Figure 2). These studies concluded that industrial inputs such as steel-producing industry, fossil fuel consumption, mining, and agriculture are results of leaching and land weathering. However, in NW-C, Zn was found to be 10 times higher than coastal sediment, indicating an active desorption and seawater ingress and intrusion bringing in more Zn concentration into coastal aquifers in addition to the industrial inputs [63,85], whereas Zn concentration in MA, South Africa was mainly controlled by pH changes in the aquifer [50]. Reducing conditions prevailed in NW-C, indicating transition zone shifting towards reducing environments while releasing absorbed Zn from precipitated Fe/Mn hydroxides and ferrihydrites, which is a common phenomenon under seawater-intruding conditions [85]. Increases in concentration and toxicity of Zn in coastal aquifers also depend upon the presence of transient, labile, or reactive substances in groundwater [85]. One such substance is organic matter content in water and underlying or adjacent coastal sediments, towards which Zn possesses a higher affinity [86]. Additionally, under increasing seawater intrusion, increased ionic strength and alkalinity [87], organic affinitive metals form ligands and hydroxides act as a sink, e.g., [88,89]. Such metal-absorbing groups also include oxygen-containing functional groups such as –COOH, phenolic and enolic –OH, and sulfur-containing functional groups [90]. In evaporation-dominating regions such as semi-arid aquifers, continuous intrusion and reduced kinetic flux of groundwater provide an ideal opportunity and conditions for stable organic–metallic matter transformation, where Zn progressively incorporates and retains itself in organo-mineral associations [86,87]. Similarly, halide dissolution in this aquifer helps in forming Zn-Cl and SO_4-Cl stable metal ligands under alkaline conditions, reducing the reactive species in water and controlling the toxicity in such scenarios [91,92].
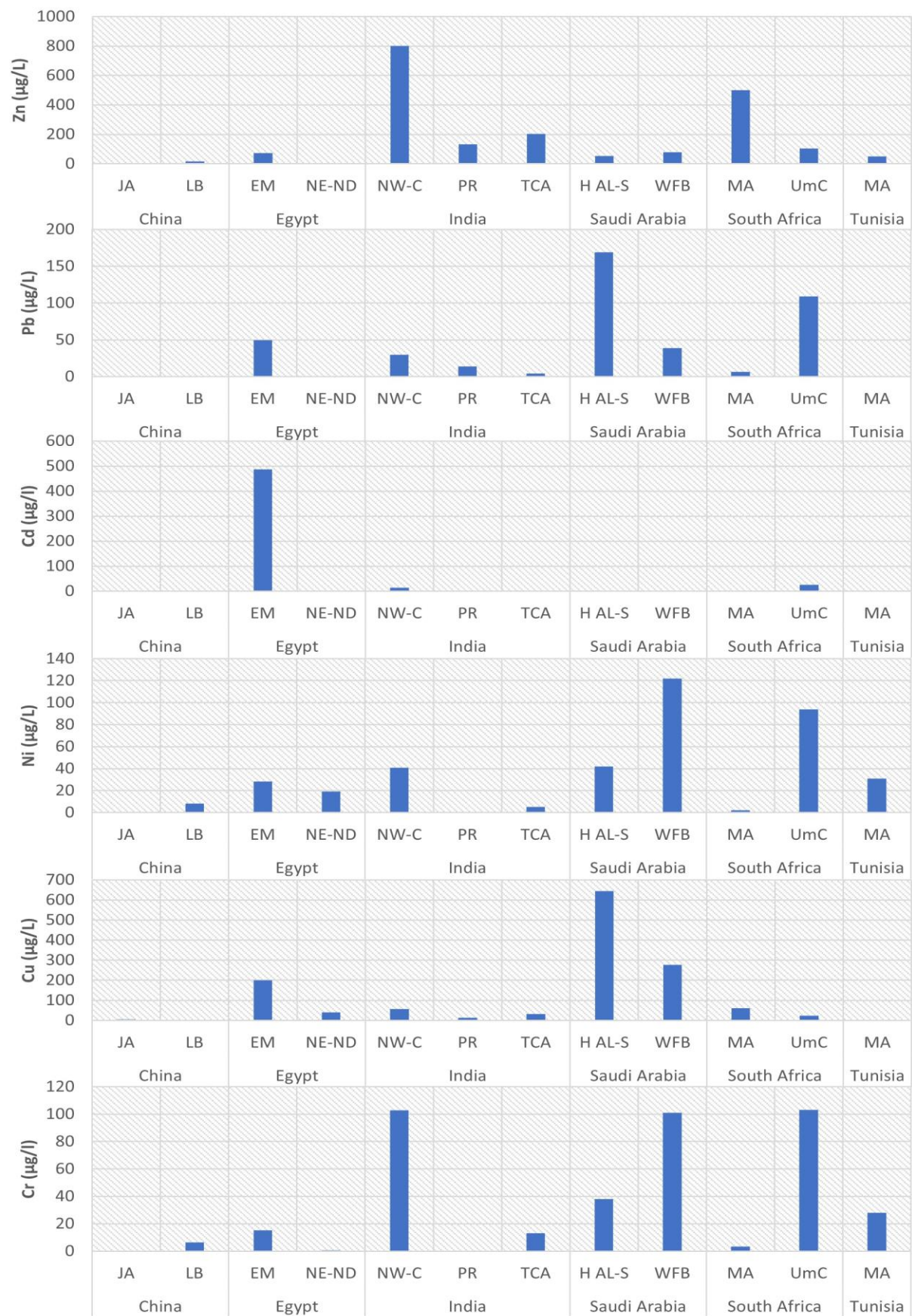
Figure 2. Comparison of average metal concentrations in considered coastal aquifers.

3.1.2. Lead (Pb)

Lead is one of the most commonly occurring metals, amounting to 13 mg/kg in the earth's crust [80], with a specific density of more than 5 g/cm^3 [93]. Pb is a highly toxic metal [94] with no vital role in the human body, and its availability in groundwater systems represents numerous non-carcinogenic along with carcinogenic risks [95]. The presence of this metal in water amounting to more than 10 µg/L is considered unsafe for drinking purposes [80]. Its toxicity is very well documented in numerous studies, such as [96–98]. It has the potential to cause various neurological diseases, especially in children and women, which include developmental delays, lowered IQ, and behavioral problems [96,99]. It has the potential to cause cardiovascular diseases [93], kidney damage, fertility issues and cognitive impacts linked with behavioral issues even at the part per billion level [97].

In considered coastal aquifers, concentrations above [81] have been noted in SW-C, India [64], Umhlathuze catchment, South Africa [50], and H AL-S [55], WFB [79], Saudi Arabia (Figure 2). The primary sources were found to be both anthropogenic and geogenic in all the coastal aquifers, which might be due to their availability in the earth's crust [100], as previously mentioned. The nature of anthropogenic influences was mainly found to be dependent on the land utilization of each aquifer, which might include the petrochemical industry, antifouling paint from ships and salt production industry in SW-C, India [54], agrochemicals input from the upper strata in South Africa [50], alloy production in Laizhou Bay, China [56], and the Jianshu coastal zone, China [60]. On the other hand, Pb Hada Al-Sham (H AL-S) and Wadi Fatimah Basin (WFB) were found to come mainly from geogenic sources that include volcanic and basaltic rocks associated and transported Al, Fe hydroxides, and carbonates [49,60]. The dissolution of such hydroxides and carbonates (e.g., [55,79]) and undersaturation minerals, such as dolomite and calcite [63], could contribute towards elevated Pb concentration depending upon pH conditions, which might be a direct influence on saline water intrusion. To explain it further, the saturation factor and dissolution of minerals (e.g., carbonates) and Fe or Al hydroxides are highly dependent on the acidic/alkaline state of water [101]. Higher concentrations of CO_2 in seawater and its mixing in freshwater aquifers increases the formation of carbonic acid, whilst higher dissolution of carbonates with the help of changing pH conditions gave rise to high concentration of Pb in groundwater with increased seawater intrusion.

On the other hand, Fe/Al hydroxide dissolution is highly dependent on redox conditions and pH [102]. Still, seawater intrusion increases the ionic reactiveness of these resistance bonds, which further enhances the potential of absorption of metals such as Pb [103] in groundwater. Such a process is dependent on the residence time of seawater in the aquifer [101], which in the case of semi-arid regions is more due to limited freshwater recharge coupled with higher evaporation [104]. With that being said, the higher residence of seawater in aquifers also allows for stable ligand formations where Cl-ligands are dominant and less reactive than SO_4-ligands, irrespective of the source of metals [63]. Such scenarios have a bigger role in the assessment of toxicity and bioavailability of Pb high/low concentration coastal aquifers. This comparison in this study suggests that the association of carbonates and increased anthropogenic influence are prominent processes in the case of making Pb (e.g., [50]) available in water. On the contrary, longer residence time due to semi-arid climate coupled with seawater influence in these coastal aquifers allows Pb to form stable bonds of ligands with Cl and Fe/Al hydroxides, which seems to control the toxicity despite being in higher concentration (e.g., [54,63,79]).

3.1.3. Cadmium (Cd)

Cd is a non-essential carcinogen widely available in environments with a crustal mean of 0.2 mg/kg. One study [81] suggests that a concentration above 3 µg/L in water is unsuitable for direct consumption, whereas elevated concentrations with direct and indirect exposure could severely affect human health with diseases like cancer [105,106] and aquatic biota due to its proven toxic and mobile nature [107]. The worldwide mean concentration of Cd in soil is around 0.36 mg/kg; however, the mean groundwater concentration stands

at 1 µg/L [108]. In groundwater or other aqueous environments with concentrations of 55 to 90%, Cd occurs as divalent Cd^{2+} and remains in the form of water inorganic soluble complexes such as $CdCl_2$, $CdSO_4$, $CdNO_3$ [109,110], and organic matter [108]. It has a tendency to replace Ca^{2+} due to a similar ionic radius, charge, and chemical behavior, making it highly mobile and toxic in nature [89].

In considered coastal aquifers, the highest mean concentration was noted in the East Matrouh Aquifer (EM), Egypt, whereas the mean concentrations above permissible limits were observed in the NW Coastal Aquifers (NW-C), India, Umhlathuze Catchment (UmC), South Africa, and the Monastir Aquifer (MA), Tunisia (Figure 2). The source of Cd in these aquifers mainly originated from agricultural fertilizers or pesticides [53,61,82,111], except for NW-C, India, where the saturation of minerals, such as Mg-bearing minerals like aragonite, brucite, and magnesite [64]. In the case of agricultural aspects, numerous studies have linked increased Cd concentration with phosphate-based fertilizers (e.g., [112–115]) and biomass after wildfires used as fertilizers [116,117]. As per various studies, phosphate fertilizers contain 77 mg/kg Cd in kg of P_2O_5 in Mediterranean countries [118] and 36 mg/kg of P_2O_5 in Europe [119], signifying the distribution of Cd in groundwater due to agricultural leaching. Apart from these considerations, domestic waste and sewage treatment output has the potential to increase Cd concentration in groundwater drastically (e.g., [120,121]), such as in the case of the East Matrouh Aquifer, Egypt [61]. Considering salinization in the coastal aquifer as a prominent scenario, the mobility of Cd could be due to various environmental conditions such as the presence of hydrous oxides, clay minerals, and organic matter, and its mobility is further influenced by pH, the redox state, and ionic strength of the solution [107]. In the current consideration, Cd–Cl ligand formation seemed prominent in EM, Egypt [62] and NW-C, India [63], irrespective of their source, indicating the seawater carrying Cl-complex formation in the aquifers. This could be denoted by stable inorganic formation constants of Cd (e.g., $CdCl^+$, $CdCl_2$, $CdCl_3$) as determined by [122] and explained in Equation (1). On the other hand, complexes with carbonates become more stable with increasing pH and become very favorable at pH > 8 (Mean seawater pH: 8.4) in the form of $CdCO_3$ [108]. Such a mechanism is well observed in the Maputoland Aquifer (MA), South Africa, where the pH was measured to be higher than 8 at many boreholes and shared a high correlation with Cd [44]. In the case of the Monastir Aquifer (MA), Tunisia [80], contrary conditions, such as the moderate salinization and pH ranging from 7 to 7.98 and higher dissolution of halite and gypsum, gave rise to the cation exchange of Na and Ca with a Cd-controlled distribution mechanism in the aquifer. According to [104], cation exchange is the most prominent mechanism after pH, which controls the distribution of Cd in the rock/soil-water interface.
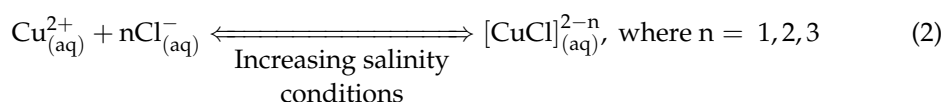
3.1.4. Nickel (Ni)

Ni is an essential metal with a wide range of benefits for biological ecosystems in aquatic environments, such as healthy plant growth and animals, photosynthesis, soil microbes, etc. It is the 24th most abundant element in Earth's crust and is constantly released into the atmosphere due to its volatile and light nature [123]. Ni has varying oxidation states ranging from −1 to +4, with the most stable being Ni^{2+}, where soluble forms with sulfides are most common in natural systems [124]. Industrial usage, such as electroplating [125], electronics, batteries [126], ceramics [127,128], nickel alloys, etc., have increased the exploitation of metals and resulted in anthropogenic inputs with elevated concentration in aquatic systems [129]. From these sources, Ni might be released from sulfides, oxides, and silicates [130]. When exposed to humans at higher concentration, Ni can cause allergies in the form of contact dermatitis; accumulation in the body leads to cardiovascular and kidney diseases, whereas its carcinogenic effects could cause lung and nasal cancer over time [130–133]. The permissible limit of Ni in water for drinking purposes is limited to 20 µg/L [134], whereas its essentiality as a plant nutrient is limited to 10 mg/kg [135]. The considered semi-arid coastal aquifers, WFB and H AL-S, Saudi Arabia [55,79]), UmC, South Africa [54], MA, Tunisia [80], and NW-C, India [63] (Figure 2), show higher concentrations of Ni than the permissible limits. Saudi Arabian aquifer

dissolution of aluminum silicates and Fe-oxide/hydroxides from basaltic and volcanic rocks are the main sources of Ni. Such a dissolution occurred with the help of higher evaporation and residence time of recharge water in the aquifer and gave rise to more than 72% and 98% higher enrichment of Ni [55,79]. The shallow nature and higher elevation of these aquifers' limits influence seawater into them, which is why metals do not show a dominant seawater influence. A similar case has been noted in UmC, South Africa [50], where evaporation dominance mainly controlled the chemistry and release of Ni into groundwater that originating from overlying industrial landfills, leachates, and dissolution of silicates along with Mn-hydroxides due to the higher residence period of groundwater [135,136]. The association of leachates in this aquifer indicates a high amount of organic Mn hydroxide association, allowing metals such as Ni to form stable ligands or complexes formed at low pH such as 5.5 [137], and the stable organic affinity of Ni is highest in 5–7 pH range [138]. Under such conditions, the organic dissolution of Mn complexes is very unlikely [139] and controls the bioavailability of Ni in the respective environment. However, in the case of MA, Tunisia [80], NW-C, India [63], and LB, China [55], the enrichment of Ni in the groundwater saw an increasing trend with increased salinization. The concentration in these aquifers saw an increase in concentration irrespective of the source of Ni, which is from mica dissolution (NW-C, India), industrial, mining wastewater in LB, China, and wastewater effluents in MA, Tunisia. Such increases are mainly due to the absorption nature of Ni clay minerals experimentally explained by [140], where desorption was found higher with increasing salinity by 30% owing to competition between the metals and cations in seawater solution by the limited cation exchange sites on clay minerals [141,142].

3.1.5. Cppper (Cu)

Cu is the third most-used heavy metal widely occurring in nature worldwide. It is an essential metal in humans as it plays a crucial role in enzyme synthesis, bone and tissue development [143], and various aquatic biota [144]. It has transitional properties, which mainly occur in 2 soluble forms in aquatic systems, such as Cu(I) (cuprous ion) and Cu (II) (copper ion), among which Cu (II) is considered the most toxic in nature [145]. Cu is considered the most hazardous part of industrial affluents due to its wide range of applications, including electroplating as $CuSO_4$ [146], petroleum refining as a catalyst [147], Cu_2O in paints [148], mining, explosives [149], fertilizers [150], and steel industries [151] around the world. Naturally, Cu is distributed in various rocks and soil in minute amounts in mg/kg levels such as granites (as high as 160 mg/kg) [152], shales (as high as 20–200 mg/kg) [153], sulfate-bearing ores (e.g., chalcopyrite and galena) along with volcanic release [154]. In considered semi-arid coastal aquifers, Cu concentration is found higher in EM, Egypt [61], H Al-F and WFB, Saudi Arabia [79] (Figure 2). In EM, Egypt, TDS, Cl, SO_4, and Na evidentially shared higher correlation, whereas in the cases of H AL-F and WFB, EC and B confirmed seawater influence on the metals. Evaporation dominance, which creates ideal situations for induced salinity [55], was prominent in these aquifers. However, toxicity Cu in these aquifers found to be limited despite anthropogenic influence indicates active absorption mechanisms in the aquifers due to higher residence time along with the formation of Cu (II) Cl-complexes in low chloride concentration and CuCl in high chloride conditions (Equation (2)) [155]. The increased seawater domination and the presence of CuCl complexes reduce the availability of Cu in water due to its insoluble nature [90].

$$Cu_{(aq)}^{2+} + nCl_{(aq)}^{-} \xrightleftharpoons[\text{Increasing salinity conditions}]{} [CuCl]_{(aq)}^{2-n}, \text{ where } n = 1,2,3 \qquad (2)$$
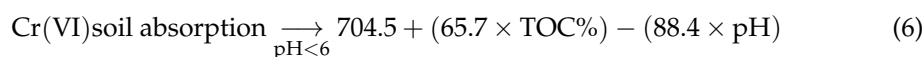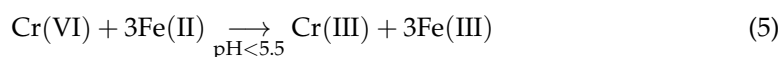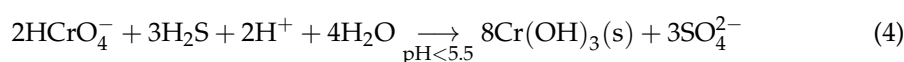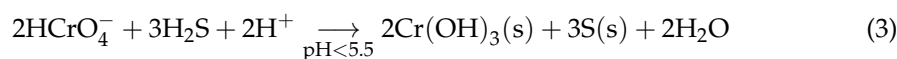
Additionally, these basins recorded alkaline natures (pH: 6–8), where Cu has the highest tendency of absorption among other chalcophile metals such as Zn and Pb on clay minerals such as montmorillonite [137], zeolite [156], and kaolinite, which are common in Cu-bearing rocks [157]. On the other hand, in terms of concentrations in aqueous solutions,

Cu-reactive species increased with seawater intrusion in NW-C, India [63] (Figure 2). This study noted the acidic nature of groundwater (pH < 6) and a higher tendency of Cu-SO_4 and Cu-CO_3 ligands with increased salinity compared to Cu–Cl ligands, which are prone to disintegration with higher evaporation and higher residence time. Sulfides are prone to disintegration under reducing conditions, whereas carbonates are prone to disintegration under oxidizing conditions [155], making them more bioavailable in nature even at combatively low concentrations.

3.1.6. Chromium (Cr)

Cr is one of the most prioritized metals existing in aqueous systems and is the first element in terms of toxicity potential when its bioavailable speciation is taken into account [158]. It exists in two oxidation states, such as Cr (III) and Cr (VI), where Cr (VI) has carcinogenic potential through inhalation exposure [112]. It can originate from both geogenic (e.g., ultramafic rocks) and anthropogenic sources, which might include industrial waste [159], coal combustion [160], and agricultural fertilizers [161]. Ultramafic rocks such as peridotites, pyroxenites, and harzburgites can contain up to 60,000 mg/kg in ophiolitic complexes and serpentinites [162,163]. The highly resistant minerals might include pyroxene and olivine, whereas secondary silicates include serpentine, amphibole, and clay minerals [164]. Cr (III) is essential for metabolism, making it very important for humans and animals. Cr (VI) in food streams is extremely dangerous [165,166], which is mainly contributed by industrial sources, and could go as high as 8000 µg/L [167]. Cr (III) forms hexa-coordinate complexes with octahedral organic salts under high acidic salinity conditions at pH > 4 and are soluble oligomeric products [168], whereas chromate anion (CrO_4^{2-}) is the predominant form in neutral pH conditions [166,169]. Highly toxic Cr (VI) is known to be the dominating form in oxidating and alkaline conditions, whereas Cr (III) dominates in acidic and reducing conditions in aquatic systems [170], which makes it a prominently available metal in the cases of saltwater-intruding environments, such as coastal aquifers. Available sulfides (Equations (3) and (4)), Fe (II) bearing minerals (Equation (5)) and organic matter (Equation (6)), such as humic acid below pH 5.5 helps to convert Cr (VI) to Cr (III) [171]. In considered aquifers like H Al-S and WFB, Saudi Arabia [55] and NW-C in India [63] (Figure 2), Cr was found to be associated with Al and Fe hydroxides and was concluded to be a part of geogenic sources. As discussed before, the geologic-resistant association of Cr with silicates might have denoted insolubility while keeping the toxicity in check, which was less in these studies. In addition, under acidic conditions, the enhanced absorption of Cr (VI) by cationic collides such as Fe/Al hydroxides (e.g., Feo (OH) and Al_2O_3) are dominating mechanisms [166,171,172] and might be responsible for controlling the toxicity in the aquifers. However, anthropogenic associations in LB, China's industrial activities [56] have tended toward higher toxicity with increasing pH conditions and Cr (VI) concentration groundwater, e.g., >90%.

$$2HCrO_4^- + 3H_2S + 2H^+ \xrightarrow[pH<5.5]{} 2Cr(OH)_3(s) + 3S(s) + 2H_2O \tag{3}$$

$$2HCrO_4^- + 3H_2S + 2H^+ + 4H_2O \xrightarrow[pH<5.5]{} 8Cr(OH)_3(s) + 3SO_4^{2-} \tag{4}$$

$$Cr(VI) + 3Fe(II) \xrightarrow[pH<5.5]{} Cr(III) + 3Fe(III) \tag{5}$$

$$Cr(VI) \text{soil absorption} \xrightarrow[pH<6]{} 704.5 + (65.7 \times TOC\%) - (88.4 \times pH) \tag{6}$$

4. Identified Controlling Mechanisms

Coastal aquifers in semi-arid climate conditions constitute unique environmental characteristics and challenges shaped by thigh evaporation rates, higher residence time, and higher rates of seawater intrusion. Apart from high salinity, the controlling mechanisms like pH fluctuations and transition zone shifts created by seawater-subsurface discharge [75,

76,87] wielded significant influence over fundamental metal-controlling processes like ion exchange, ORP, absorption, and desorption [72–74] regardless of the origin of considered metals in the aquifers. The desorption of Zn and Pb from precipitated Fe/Mn hydroxide under reducing conditions in NW-C in India and MA, South Africa, and the dissolution of Pb in H AL-S and WFB in Saudi Arabia are the prime examples of pH-controlled metal alterations in the aquifers. On the contrary, observed acidic pH conditions (pH < 5.5) allowed conversion of Cr (VI) to Cr (III) by cationic collides such as Fe/Mn hydroxides [166, 171,172] and were found to control the toxicity of Cr in H AL-S, Saudi Arabia [55], and NW-C, India [63]. The residence time of groundwater and continuous chemical variations that are being introduced in such aquifers might be the reason behind deviated controlling and alteration process of metals apart from their origin, such as Ni in H AL-S and WFB, Saudi Arabia and UmC, South Africa [50,55,79]. Additionally, the transition zones that shifted toward oxidation enhanced the formation and absorption by humic and organo-metallic complexes, leading to the absorption of metals facilitated by factors like reactivity of labile matter and MNOx, especially in the pH range of 5–7 [138], as in the case of Ni and Zn. On the other hand, the transition shift towards aquifers and the higher inflow from sea/ocean introduces redox conditions with higher concentrations of SO_4 and Cl. This allows the formation of Cl and SO_4 complexes in alkaline conditions with the coupled effect of increased ionic strength introduced by seawater [155]. Such formations in aquifers act as a dominant controller of the bioavailability of metals in coastal aquifers due to the high residence times of groundwater, allowing the formation of a stable bond, e.g., the formation of Cu-SO_4 and Cu-CO_3 formation under seawater-dominating zones in NW-C, India [63], and Cd–Cl complexes in EM, Egypt [61]. However, carbonate and sulfide complexes are sensitive to disintegration under the higher residence times of water and oxidizing conditions, giving rise to the higher bioavailability of both Cd and Cu, even at low concentrations [155].

5. Conclusions

The review highlights major processes under saline water intrusion in coastal aquifers situated in semi-arid regions. Most of the metals have shown direct and indirect influence of evaporation, reduced kinetic influx of freshwater and residence time of water in salt-freshwater interface have direct influence on metal toxicity and bioavailability in these aquifers. After conducting a thorough investigation of the behavior within the considered aquifers, the following observations were made:

- The reduced kinetic flux of groundwater into aquifers and transition zone shifts between the freshwater–seawater interface play an intricate role in changing pH conditions and controlling metal behavior in coastal aquifers.
- Ion exchange, absorption/desorption, and humic/organic ligands were found to control metal variation in aquifers.
- Reactive and labile substances exhibited a greater control over the distribution and absorption of Zn and Ni, where labile matter contributed towards higher bioavailability of Zn, and Ni-organic ligands controlled the toxicity, especially in low salinity conditions.
- Metals such as Ni, Cr and Pb associated with oxidation-sensitive Al/Fe hydroxide and carbonates mobilized metals under increasing alkaline conditions (pH > 8).
- Cu-complexes with Cl and SO_4 were found to be stable under increasing alkaline conditions in aquifers where metals like Ni, Cd and Zn tend to be bioavailable with the introduction of saline water.
- Mobility and toxicity of Cr (VI) were found to be controlled by soil and Fe/Al hydroxide absorption under acidic conditions.

Author Contributions: R.R.G.: Conceptualization, investigation, visualization, writing-draft and editing; V.E.: Conceptualization, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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