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Cobalt content and its availability in soils: A review

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Abstract

Cobalt (Co) is a trace element of significant importance in soil systems, influencing plant nutrition, microbial activity, and overall soil health. This review paper provides a comprehensive analysis of cobalt in soils, focusing on its total content, various forms, availability, factors affecting its dynamics, and interaction of cobalt with essential plant nutrients. Both natural processes and anthropogenic activities influence the total cobalt content in soils. Naturally, cobalt is derived from the weathering of cobalt-bearing minerals and atmospheric deposition. Anthropogenic sources, including mining, industrial emissions, and the application of cobalt-containing fertilizers, can significantly alter the concentration of cobalt in soils. Cobalt exists in several chemical forms in soils, including soluble, exchangeable, carbonate-bound, organic matter-bound, and oxide-bound species. The distribution of these forms affects cobalt's bioavailability and its uptake by plants. The availability of cobalt in soils is governed by a range of factors, including soil pH, organic matter content, soil texture, and the presence of competing ions. Cobalt interacts intricately with other essential plant nutrients. These interactions can influence nutrient uptake and utilization by plants. Cobalt's presence can affect the availability of phosphorus and other nutrients through competitive interactions and changes in soil chemistry. This review synthesizes current knowledge on cobalt in soils and its interactions with essential nutrients, highlighting key research findings and identifying gaps in understanding. By examining the interplay between cobalt forms, availability, influencing factors, and interactions with essential nutrients, the paper aims to provide insights into effective management practices and strategies to optimize cobalt's benefits while mitigating potential risks.

Keywords: Cobalt, total, available, interaction, soils

Introduction

Cobalt (Co) has been considered a beneficial element for plant growth (Pilon-Smits *et al.*, 2009; Lyu *et al.*, 2017) [73, 51]. However, it is regarded as an essential nutrient for prokaryotes, human beings, and other mammals (Hu *et al.*, 2021) [31]. A beneficial element is an element that can improve plant health at low concentrations but adversely affects plant growth at high concentrations (Pais, 1992) [69]. An element is to be considered essential if it fills an element's essentiality criteria (Arnon and Stout, 1939) [6]. It is essential for the processes of stem growth, elongating the coleoptiles, and expanding leaf discs in plants. It is also important for a plant to reach maturity and for healthy bud development (Minz *et al.*, 2018) [64]. Cobalt is an essential component of several enzymes and coenzymes.

Retardation of senescence of leaf, increase in drought resistance in seeds, regulation of alkaloid accumulation in medicinal plants, and inhibition of ethylene biosynthesis are some important beneficial effects of cobalt in plants (Palit and Sharma, 1994) [70]. Cobalt is an essential element for the synthesis of vitamin B12, which is required for human and animal nutrition.

Despite its importance, cobalt's availability in soils is limited and highly variable, influenced by factors such as soil type, pH, organic matter content, and redox conditions (Kabata-Pendias, 2011) [34]. Cobalt is predominantly present in soils as divalent (Co^{2+}) and trivalent (Co^{3+}) ions, with the former being more soluble and bioavailable. The primary sources of Co in soils include parent rock material, atmospheric deposition, and anthropogenic activities such as mining, industrial emissions, and the application of Co-containing fertilizers and manures (Alloway, 2013) [2].

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The bioavailability of Co in soils is governed by several key processes such as adsorption and desorption (McGrath *et al*., 2010) [57], soil pH (Nielsen *et al*., 2013) [68], redox potential (Smith and Giller, 1992) [96], organic matter (Li and Thornton, 2001) [45], and cation exchange capacity (Mengel and Kirby, 2001) [63]. Understanding the factors that influence Co availability in soils is crucial for managing soil fertility and ensuring optimal plant growth, particularly in Co-sensitive crops.

Cobalt significantly impacts the growth and health of plants and soil microorganisms. Its interaction with essential plant nutrients plays a vital role in determining its availability and efficacy in supporting plant functions. These interactions can be synergistic or antagonistic, affecting nutrient uptake, assimilation, and overall plant health (Alloway, 2013) [2]. Sightedness of these interactions is essential for managing soil fertility and ensuring the adequate supply of Co and other nutrients. This review aims to provide an in-depth examination of cobalt in soil systems, addressing its sources, distribution, bioavailability, the impact of soil properties on Co dynamics, and mechanisms of Co interaction with essential plant nutrients.

Natural sources of cobalt in soils

Cobalt (Co) is a lustrous, tough silvery metal belonging to a transition metal group. It is one of the only three ferromagnetic transition elements, along with iron and nickel. It is known to be a chalcophile, siderophile, and lithophile element (Poznanovic Spahic *et al*., 2019) [74]. In nature, it is found along with iron, nickel, silver, lead, copper, and manganese, and also found to exist as carbonates (Gradedel *et al*., 2014) [26]. It also exists in the form of minerals like cobaltite, skutterudite, erythrite, spherocobaltite, and heterogenite. It is found profusely in both sedimentary and igneous rocks. The average content of Co in Earth's crust is low (25-30 mg kg^{-1}) as compared to other heavy metals. The natural Co content in the Earth's crust is assumed not to exceed 12 mg kg^{-1} (Sheppard *et al*., 2007) [90]. Alkaline igneous rocks are the largest Co accumulators. They contain up to 200 mg kg^{-1} of this element, but acidic rocks contain no more than 15 mg kg^{-1}. Sedimentary rocks contain a small amount of Co, where its concentration is highest in mudstones (approximately 20 mg kg^{-1}) and lowest in limestones (approximately 3 mg kg^{-1}). The ultramafic rocks have a higher abundance of Co (100 mg kg^{-1}). The Co concentration in soil profiles and its distribution depends on the soil forming processes, differing from soils of different agroclimatic regions (Khalid *et al*., 2023) [36].

Total cobalt content in soils

The average total Co content in the earth's crust is 40 mg kg^{-1} (Rudnick and Gao, 2003) [86]. The mean content of Co in world soils is 8 mg kg^{-1} (Tsamo *et al*., 2022) [101]. However, its content may differ from 0.1 to 100 mg kg^{-1} in different soils (Tsamo *et al*., 2022) [101]. Usually, the total Co content in normal soils ranges from 1.0 to 40 mg kg^{-1}, and seldom from 1.0 to 100 mg kg^{-1} (Chatterjee and Chatterjee, 2002) [17]. The highest natural Co content in soil may reach up to 500 mg kg^{-1} of soil (Tappero *et al*., 2007) [100]. The total average content reported in different soils includes 5.5 mg kg^{-1} for sandy podsol soils, 4.4 mg kg^{-1} for organic soils, and 10-12 mg kg^{-1} in dark brown clay soils, limestone soils, and fen soils (Tsamo *et al*., 2022) [101]. Soils from different regions of the world have reported different ranges of Co such as 16.5-26.8 mg kg^{-1} in Egyptian soils, 116 mg kg^{-1} in the soil of Japan, 122 mg kg^{-1} in Australian ferrosols, and 12700 mg kg^{-1} in the United States (Tsamo *et al*., 2022, Rawat *et al*., 2019) [101,80], 0.44 to 14.66 mg kg^{-1} in grassland soils of New Zealand (Li *et al*., 2004) [46], 1.42 to 6.51 mg kg^{-1} in soils of the 10th of Ramadan city of Egypt (Bahnasawy *et al*., 2019) [7], and 76.0 to 147.0 mg kg^{-1} in Spain soils. The Co content of the European soil samples (FOREGS database) was in the range of 0.5-255 mg kg^{-1}, whereas in the Flemish data, Co concentrations between 0.27 and 17 mg kg^{-1} were found (Cappuyns and Mallaestrs, 2014) [16]. Soils from various states of India have reported different ranges of total Co in soils such as 4.4 to 32.5 mg kg^{-1} (Kanwar and Randhawa, 1974) [35] and 10.4 to 17.5 mg kg^{-1} (Randhawa, 1982) [77] in soils of Punjab, 4.4 to 15.0 mg kg^{-1} in surface samples and 5.9 to 17.5 mg kg^{-1} in subsurface samples of soils of Haryana (Yadav, 1978) [110], 64 to 139 mg kg^{-1} in soils of Central India (Patel *et al*., 2015) [71], 6.6 to 46.0 mg kg^{-1} in alluvial and sedentary soils of Bihar (Roy, 1985) [85], 0- 7.82 mg kg^{-1} in soils of national capital region Delhi (Rani *et al*., 2021) [78], 3.0 to 30 mg kg^{-1} in Ranga Reddy district of Andhra Pradesh (Dantu, 2009) [19]. Recently, Daulta *et al*. (2022) [20] reported that cobalt content in soils of some states of India ranged from 0.13 to 19.28 mg kg^{-1} in Punjab, 5.1 to 12.9 mg kg^{-1} in Haryana, 0.01 to 3.91 mg kg^{-1} in Rajasthan, and 0.14 to 19.28 mg kg^{-1} in Uttar Pradesh. The Co concentration in soils reported from different regions of India is shown in Table 1.

Table 1: Cobalt concentration (mg kg^{-1}) in soil reported from different regions of India

Location	Cobalt Content	Reference
North India	0.14-19.28	Daulta *et al.* (2022) [20]
Western India	7.8-11.2	Mohanty *et al.* (2021) [65]
Western India	24.4-51.3	Krishna and Govil (2007) [40]
Western India	27.1-84.0	Ladwani *et al.* (2012) [41]
Central India	30.0-40.0	Kori *et al.* (2020) [38]
Southwest India	7.6-97.5	Bhagure and Mirgane (2011) [9]
Southeast India	3.8-28.7	Dantu (2009) [19]
Southeast India	10.5-20.8	Satyanarayana *et al.* (2021) [87]
West coast of India	0.12-0.33	Singh *et al.* (2020) [93]

The Co distribution in soil depends on geogenic, anthropogenic, and climatic conditions. The highlands are generally devoid of dense vegetation, hence, the soil of these areas has less concentration of Co compared to the lowlands. Upland soils had less total Co in the upper horizons than in the lower horizons (Mcintosh *et al*., 1986) [58]. The upland soils are known to be more leached than the lowland soils (Mcintosh *et al*., 1986) [58], due to higher rainfall and probably overall moisture conditions. Rawat *et al*. (2018) [80] studied the total Co content in three agroclimatic zones of India's Jharkhand state. They reported that the mean total Co content in upland soils of zones IV, V, and VI was 94.27, 103, and 93.8 mg kg^{-1}, respectively, in midland soils of zones IV, V, and VI was 110.04, 106.4, and 102.84 mg kg^{-1}, respectively, whereas in lowland soils of zones IV, V, and VI were 122.72, 113.36, and 111.12 mg kg^{-1}, respectively.

Factors affecting total cobalt content in soils

Various factors, including parent material, pH, organic matter, clay content and mineralogy, cation exchange capacity, redox conditions, fertilizers and amendments, atmospheric deposition, land use and management practices, and soil texture can influence the total Co content in the soil. Total Co content in various Irish soils formed from a variety of parent materials is shown in Table 2 (Fleming, 1978) [23].

Table 2: Total cobalt (mg kg^{-1}) content of soils formed from different parent materials

Parent material	Range	Mean
Basic igneous	6.3-17.0	12.8
Mica schist	10.4-14.2	12.6
Shale	1.6-18.4	8.2
Limestone	1.8-17.5	6.0
Sandstone	0.5-13.8	3.6
Gneiss	0.2-4.4	2.4
Granite	0.3-17.5	2.1
Blown sand	0.2-1.0	0.4

The organic matter content in soil significantly influences the soil Co content, as this element was highest in loam soils and alluvial soils (Faucon *et al*., 2007) [22]. Studies have shown that soils with higher organic matter content tend to have higher total Co concentrations due to the increased binding capacity and reduced leaching losses. Kabata-Pendias and Pendias (2001) [33] indicated that organic-rich soils can retain more Co compared to mineral soils. The presence of organic matter enhances the adsorption capacity of soils for Co due to the large surface area and numerous functional groups of organic matter that can bind Co (Stevenson, 1994) [98]. Yadav *et al.* (1978) [110] and Roy (1985) [85] found that a significant positive relationship between organic matter and total Co.

Soil pH is crucial in determining soil's total Co content and behavior. Soil pH affects the solubility, mobility, adsorption, desorption, complex formation with organic matter, and precipitation of cobalt. The total cobalt content in soil measures all cobalt present in the soil, irrespective of its form or availability. Soil pH affects how cobalt interacts with soil components and its availability to plants. Still, the total cobalt content is more influenced by the original soil mineral composition and less directly by pH. In their study, McBridge (1994) [54] and Sims and Lue-Hing (1986) [92] observed that total Co levels in the soil might not be directly correlated with pH.

Soils with higher CEC generally have higher total Co content due to better retention and reduced leaching losses. Soils with high clay content and organic matter typically have higher CEC and are more effective at retaining Co (Kabata-Pendias and Pendias, 2001) [33]. Beckwith *et al.* (2002) [8] found that the soils with higher CEC had a greater capacity to hold onto Co ions, thereby increasing the total Co content in these soils.

Clay minerals in soils significantly impact the retention and availability of cobalt. Clays, such as montmorillonite and kaolinite, can adsorb cobalt ions, influencing their total soil content. Higher clay content generally correlates with higher total cobalt content due to increased surface area for adsorption. The mineral composition of soils affects cobalt content through several mechanisms. Soils rich in iron oxides (e.g., hematite, goethite) tend to have higher cobalt content because cobalt can substitute for iron in crystal structures. Similarly, soils containing manganese oxides (e.g., birnessite) may also have elevated cobalt levels due to analogous substitution processes. A significant and positive relationship between clay and total Co and between total iron and total Co had been reported by Roy (1985) [85]; Yadav *et al.* (1978) [110]; and Singh and Singh (1966) [95].

Under aerobic (oxidizing) conditions, cobalt tends to be less soluble and more likely to form insoluble oxides or hydroxides, potentially leading to lower soil extractable cobalt levels. In contrast, under anaerobic (reducing) conditions, cobalt can become more soluble due to the reduction of iron and manganese oxides, which bind cobalt in soils. This can lead to higher extractable cobalt levels. A study by Neal *et al.* (2000**)** [67] investigated the mobility and speciation of cobalt in soils under varying redox conditions. They found that cobalt solubility and mobility were significantly influenced by redox potential changes. Gleyzes *et al.* (2002) [25] also discussed the effects of redox conditions on metal extractability in soils, including cobalt, highlighting the importance of redox reactions in controlling cobalt speciation and availability.

The effect of fertilizers and soil amendments on total cobalt content in soils can vary depending on the specific product and its composition. Organic fertilizers and amendments can potentially increase total cobalt content in soils. Organic matter can be complex with cobalt and other trace elements, enhancing their availability to plants. Inorganic fertilizers may also contribute to cobalt content, particularly those containing micronutrients or trace elements. However, their direct impact on cobalt levels can vary depending on soil properties and application rates. Rosenfeld *et al.* (2013) [84] investigated the influence of organic and mineral fertilizers on the content of heavy metals, including cobalt, in soils. They found that organic fertilizers could increase cobalt levels due to their higher content of organic matter. Kabata-Pendias and Pendias (2001) [33] discuss the impact of fertilizers on trace element content in soils. They provide insights into how different fertilization practices can affect cobalt levels.

The effect of atmospheric deposition on total cobalt content in soils is an important consideration due to the potential for airborne pollutants to introduce trace elements into terrestrial ecosystems. Atmospheric deposition of cobalt can originate from both natural sources (e.g., volcanic eruptions, and dust storms) and anthropogenic sources (e.g., industrial emissions, and combustion of fossil fuels). Cobalt can be transported over long distances in the atmosphere before being deposited onto soils through wet (rain, snow) or dry deposition processes. Once deposited, cobalt can accumulate in soils, influencing total cobalt content. This accumulation can vary depending on factors such as deposition rates, soil properties, and land use (Reimann and de Caritat, 2017) [81]. Lovett and Lindberg (1993) [50] studied atmospheric deposition of trace metals, including cobalt, in forest ecosystems. They found that atmospheric inputs significantly contribute to trace metal content in soils and vegetation.

The total cobalt content in soils can be significantly influenced by land use and management practices. Intensive agriculture can affect cobalt levels through the use of fertilizers, irrigation practices, and crop uptake. Changes in soil pH and organic matter content due to agricultural activities can also impact cobalt availability. Urbanization and industrial activities can lead to higher cobalt concentrations in soils due to atmospheric deposition from emissions and waste disposal practices (Kabata-Pendias and Pendias, 2001) [33]. Different fertilization practices (organic vs. inorganic) can alter cobalt levels in soils. Organic amendments can increase cobalt availability due to their higher organic matter content. The use of lime, gypsum, and other soil amendments can influence cobalt mobility and availability by altering soil pH and chemical properties. Crop rotation and tillage practices can impact cobalt content by affecting soil structure and nutrient cycling processes (McBride, 1994) [54].

The effect of soil texture on total cobalt content in soils can vary due to differences in surface area, organic matter content, and cation exchange capacity. Clay soils generally have higher cation exchange capacities (CEC) and can adsorb more cobalt compared to sandy soils. The finer particles in clay soils provide more surface area for the adsorption of cobalt ions. Sandy soils, with their larger particle sizes and lower CEC, may have a lower retention capacity for cobalt. Cobalt in sandy soils may be more susceptible to leaching, depending on soil pH and organic matter content (Kabata-Pendias and Pendias, 2001; Boulyga and Becker, 2003) [33, 11].

Availability and forms of cobalt in soils

Available Co is the part of the total Co in soil that can be readily taken up by plants. Cobalt exists in the environment in four major forms (+1 to +4) (Bidast *et al*., 2022) []10. Most often, Co exits as +2, +3, and rarely as a +1-oxidation state. Cobalt often transforms from Co^{2+} to Co^{3+} oxidation state in soil, primarily due to the Mn oxides. Cobalt in soils primarily exists in several forms, each influencing its availability and behavior in the environment. The main forms of cobalt in soil include:

1. **Soluble cobalt:** This form is present in soil solution and is readily available for plant uptake. It includes free Co^{2+} ions and small Co complexes.
2. **Exchangeable cobalt:** This form is adsorbed onto soil particles and organic matter, exchangeable Co can be replaced by other cations in the soil, making it moderately available to plants.
3. **Bound to carbonates:** Cobalt can be precipitated with carbonate minerals, especially in alkaline soils, reducing its availability.
4. **Bound to organic matter:** Cobalt can form complexes with organic matter, which can either increase or decrease its availability depending on the nature of the organic matter.
5. **Bound to oxides and hydroxides:** Cobalt can adsorb or coprecipitate with iron and manganese oxides and hydroxides. This form is often less available to plants.
6. **In primary and secondary minerals:** Cobalt can be a constituent of primary minerals (such as Co-bearing minerals) and secondary minerals (formed through weathering processes). This form is typically the least available to plants due to its incorporation in the mineral matrix.

The amount of available Co varies with the soil type and the extractant used in extraction. Water-soluble cobalt is typically found in low concentrations. It represents cobalt that is immediately available to plants and is influenced by soil moisture and pH. Studies have shown that this fraction is often less than 0.1 mg kg^{-1} in most soils, which indicates limited immediate availability for plant uptake (Singh and Gilkes, 1992) [93]. Exchangeable cobalt is generally more significant than water-soluble cobalt in terms of bioavailability. The concentration of exchangeable cobalt can range from 0.1 to 1 mg kg^{-1}. This form is considered readily available to plants and is influenced by soil pH and the presence of other cations (Tandon, 1995) [99]. Acid-extractable cobalt, often measured using hydrochloric acid, typically ranges from 1 to 10 mg kg^{-1}. This form includes cobalt bound to soil minerals and organic matter that can be released under acidic conditions, reflecting its potential mobilization in acidic soils (Schwertmann and Taylor, 1989) [88]. DTPA-extractable cobalt concentrations typically range from 0.1 to 5 mg kg^{-1}. This method is widely used to estimate cobalt that is available to plants, as DTPA chelates cobalt from soil particles and organic matter (Lindsay and Norvell, 1978) [47]. EDTA-extractable cobalt typically ranges from 0.5 to 10 mg kg^{-1}. EDTA is a strong chelating agent that extracts cobalt from soil particles, providing an estimate of cobalt potentially available to plants (Viets, 1962) [103]. Oxalate-extractable cobalt concentrations can vary widely from 1 to 20 mg kg^{-1}. This fraction includes cobalt bound in organic matter and iron oxides, providing insights into cobalt associated with soil components that may be less directly available but still important for soil health (McKeague and Day, 1966) [59]. The cobalt content in soil organic matter can vary significantly, from 5 to 50 mg kg^{-1}. Extracting cobalt from organic matter using strong acids or organic solvents provides insights into cobalt complexed with organic fractions (Stevenson, 1994) [98].

A study by Bahnasawy *et al.* (2019) [7] indicated that the soluble, exchangeable, carbonate bound, Fe-Mn bound, and organic bound forms of Co ranged from 1.38 to 4.23%, 5.26 to 45.58%, 1.79 to 7.34%, 2.63 to 7.75%, and 2.29 to 9.52%, respectively. They also reported that the distribution of Co forms among the different fractions was in the sequence of residual>exchangeable>organic bound>Fe-Mn bound>carbonate bound>soluble.

Roy (1985) [85] noticed that available Co showed variation from 0.06 to 1.0 mg kg^{-1} with an average value of 0.30 mg kg^{-1} in sedentary and alluvial soils of Bihar. A study by Patti *et al.* (2010) [72] found that cobalt content in Australian soils ranged widely depending on soil type and location, with levels typically being in the range of 0.1 to 2.0 mg kg^{-1} in available forms. Li *et al.* (2004) [46] found that available Co content was 0.03 to 6.45 µg g^{-1} by EDTA extraction and 0.014 to 0.132 µg g^{-1} by $CaCl_2$ extraction in 18 grassland soils of New Zealand. The available Co content in various Spain soils extracted by different extractants was in the range of 3.29 to 25.59 mg kg^{-1} by $CaCl_2$, 0.84 to 2.49 mg kg^{-1} by EDTA, 0.17 to 1.16 mg kg^{-1} by DTPA, 0.34 to 1.17 mg kg^{-1} by low molecular weight organic acids and 0.01 to 0.07 mg kg^{-1} by distilled water (Lago-Vila *et al*., 2015) [42]. The DTPA extractable Co content ranged from 0.65 to 1.75 mg kg^{-1} in the soils of Egypt (Bahnasawy *et al*., 2019) [7] and below 0.02 mg kg^{-1} in soils of different soil series of Hisar, Haryana (Louhar *et al*., 2020) [49]. The soil profile depth also influenced the soil's available Co content. Rana and Quellette (1967) [76] reported that available Co content ranges from 0.03 to 0.83 mg kg^{-1} in the surface and from 0.03 to 0.44 mg kg^{-1} in the subsurface soils of Quebec. The available Co ranges from 0.13 to 0.55 mg kg^{-1} in the surface and from 0.03 to 0.9 mg kg^{-1} in subsurface soils of various profiles of Haryana soils (Yadav *et al*., 1978) [110].

Altitude and agroclimatic conditions have a major impact on the distribution and availability of Co in soils. Rawat *et al.* (2018) [80] studied the distribution of available Co in different locations and topo-sequences of three agroclimatic zones of Jharkhand, India. They found that DTPA extractable Co in the upland soils of areas of zones IV, V, and VI range from below detection limit to 2.08 mg kg^{-1}, below detection limit to 0.76 mg $kg^{-1,}$ and 0.1 to 2.86 mg kg^{-1}, respectively. Midland soils of areas of zones IV, V, and VI range from 0.32 to 1.94 mg kg^{-1}, 0.12 to 1.08 mg $kg^{-1,}$ and below the detection limit to 3.72 mg kg^{-1}, respectively. Whereas lowland soils ranged from 0.3 to 0.9 mg kg^{-1}, 0.28 to 1.3 mg kg^{-1}, and 0.32 to 3.04 mg kg^{-1}, respectively.

Factors affecting the availability of cobalt in soils

The distribution and availability of Co forms depend on various soil properties, including pH, redox conditions, organic matter content, and the presence of other competing ions. Plant roots absorb Co in the form of Co^{2+} ions. The availability of cobalt to plants is influenced by soil pH, with slightly acidic to neutral soils (pH 5.5-7.5) generally favouring better availability (McLean, 1982) [61]. A study by Xie *et al*. (2016) [108] investigated the effects of soil pH on cobalt availability in agricultural soils. They found that cobalt availability peaked in soils with a pH around 6.5 and decreased significantly in both acidic and alkaline soils. McGrath and Smith (1990) [55] found that soil pH significantly affects the distribution of Co between solid and solution phases. They also observed higher concentrations of Co in the soil solution at lower pH levels, which supports the notion that acidic conditions enhance Co solubility. Kabata-Pendias and Pendias (2001) [33] indicated that Co tends to be more mobile and available in acidic soils due to increased solubility. Conversely, Co is more likely to be adsorbed onto soil particles or precipitated as insoluble compounds in alkaline soils, reducing its availability. Available Co exhibited a highly significant negative correlation with soil pH (Roy, 1985) [85]. McLaughlin *et al*. (2005) [60] investigated the relationship between soil pH and Co availability and found that cobalt availability decreased significantly in acidic soils (< pH 5.5) and slightly alkaline soils (> pH 7.5).

Soil redox conditions, particularly the presence of reducing or oxidizing environments, play a significant role in cobalt availability. In reducing conditions (anaerobic environments), cobalt tends to be more soluble and hence more available for plant uptake. This is because under reducing conditions, cobalt may form soluble complexes and remain in a mobile phase. Conversely, under oxidizing conditions (aerobic environments), cobalt can precipitate as less soluble forms or become bound to iron and manganese oxides, reducing its availability for plants. Chlopecka and Adriano (1996) [18] found that reducing conditions enhanced cobalt solubility and availability.

The organic matter content of soils significantly influences the availability of cobalt (Co), primarily through its role in complexation, chelation, and ion exchange processes. Organic matter in soils acts as a reservoir and a source of functional groups (such as carboxyl, hydroxyl, and phenolic groups) that can be complex with cobalt ions. High organic matter content generally increases cobalt availability by enhancing its solubility and mobility in soil solutions. Organic matter can stabilize cobalt in forms that are readily accessible to plants. Additionally, organic matter influences soil pH and redox conditions, which indirectly affect cobalt availability. Martínez *et al*. (2013) [53] investigated the influence of organic matter on cobalt bioavailability in soils from mining areas. They found that soils with higher organic matter content tended to have higher cobalt availability due to increased complexation and solubilization. Higher organic matter content was associated with increased cobalt availability due to enhanced solubility and bio accessibility (Qin *et al*., 2018; Gao *et al*., 2019) [75, 24].

The availability of cobalt (Co) in soils can be influenced by the presence of other competing ions, which can affect cobalt speciation, solubility, and ultimately its bioavailability. Other ions in soil solution, such as iron (Fe), manganese (Mn), calcium (Ca), and aluminium (Al), can compete with cobalt for binding sites on soil particles and organic matter. This competition can reduce cobalt's availability by limiting its desorption and mobility in soil. Some ions can form complexes with cobalt, altering its speciation and reducing its concentration in bioavailable forms. Phosphate ions (PO_4^{3-}) can form insoluble complexes with cobalt, reducing its availability for plant uptake. The presence of certain ions can influence soil pH and redox conditions, indirectly affecting cobalt availability. Sulphate ions (SO_4^{2-}) can acidify the soil and promote the precipitation of cobalt as less soluble forms under acidic conditions. A study by Guo *et al*. (2017) [28] investigated the interactions between cobalt and other competing ions in contaminated soils. They found that the presence of competing ions, such as iron and manganese, significantly influenced cobalt sorption and availability. Similarly, Larsson *et al*. (2009) [43] explored the influence of phosphate ions on cobalt availability in soils and reported that phosphate ions formed insoluble cobalt-phosphate complexes and reduced their bioavailability.

Interaction of cobalt with essential plant nutrients

Cobalt can affect nitrogen fixation and microbial activity in soils. Research by Xie *et al*. (2017) [109] demonstrated that Co supplementation enhanced nitrogen fixation by rhizobia in legume nodules, thereby influencing soil nitrogen dynamics. Cobalt influences nitrogen uptake and assimilation in plants. Li *et al*. (2019) [44] found that Co supplementation increased nitrogen use efficiency (NUE) in maize plants by modulating root physiological traits and nitrogen assimilation processes. Excessive cobalt levels can disrupt soil nitrogen cycling and affect plant growth. A study by Starns *et al*. (2020) [97] highlighted the negative impacts of Co contamination on soil microbial communities and nitrogen mineralization processes.

The interaction between cobalt (Co) and phosphorus (P) in soils involves their chemical dynamics, competitive adsorption processes, and their influence on plant nutrition. Phosphorus, typically present in soils as phosphate ions (PO_4^{3-}), competes with cobalt for binding sites on soil particles and organic matter (Mortvedt *et al*., 1991) [66]. High concentrations of phosphorus in soil solutions can reduce the availability of cobalt to plants. This competition for adsorption sites can affect cobalt mobility and its uptake by plants, depending on soil pH and phosphorus levels (Gupta *et al*., 1993) [29]. Changes in soil phosphorus levels can influence cobalt uptake by plants, affecting their growth, metabolism, and overall nutrient status (Marschner, 2012) [52].

Cobalt and potassium can interact in soils through competitive adsorption processes on soil particles. Potassium, being a monovalent cation, competes with cobalt for binding sites on clay minerals and organic matter in soil

(Lindsay, 1979) [48]. High concentrations of potassium in soil solutions can reduce the availability of cobalt to plants. This competition for adsorption sites can affect cobalt mobility and its subsequent uptake by plants (Shorrocks, 1997) [91]. Changes in soil potassium levels can influence cobalt uptake by plants, impacting their growth and overall nutrient balance (Marschner, 2012) [52].

Cobalt and sulphur can interact in soils through various chemical processes, including complexation and precipitation. Sulphur can form complexes with cobalt, affecting its mobility and availability in soil solutions (McBride, 1994) [54]. Cobalt sulphide (CoS) is a relatively insoluble compound that can reduce the availability of Co to plants in certain soil conditions (Brady and Weil, 2008) [12]. The presence of sulphur compounds in soils, such as sulphates, can influence the adsorption and retention of cobalt. Sulphur competes with cobalt for binding sites on soil particles and organic matter, impacting cobalt availability for plant uptake (McGrath and Zhao, 1996) [56]. Changes in soil sulphur levels can affect cobalt uptake by plants, thereby influencing their growth and metabolic processes (White and Brown, 2010) [107].

Cobalt and calcium interact primarily through competitive adsorption on soil particles. As a divalent cation, calcium competes with cobalt for binding sites on clay minerals and organic matter in soil (Hinsinger *et al*., 2003) [30]. High concentrations of calcium in soil solution can reduce the availability of cobalt to plants, as calcium competes for adsorption sites on soil particles (Ammar *et al*., 2010) [4]. Excessive calcium levels can indirectly affect cobalt uptake by plants due to competitive adsorption and soil solution dynamics (Broadley *et al*., 2012) [13].

Cobalt and magnesium can interact in soils through competitive adsorption processes on soil particles. Magnesium is a divalent cation like calcium, that competes with cobalt for binding sites on clay minerals and organic matter in soil (Kabata-Pendias and Mukherjee, 2007) [32]. High magnesium concentrations in soil solution can reduce the availability of cobalt to plants, similar to the competitive effect observed with calcium. This competition for adsorption sites can affect the mobility and bioavailability of cobalt in soils (Mench, 2008) [61]. Changes in soil magnesium levels can influence cobalt uptake by plants, impacting their growth and nutrient status (Alloway, 2008) [3].

Both cobalt and zinc can compete for uptake mechanisms due to their similar physicochemical properties. High levels of cobalt can inhibit the uptake of zinc in plants, possibly due to competitive inhibition at uptake sites or interference in transport processes within the plant (Wang *et al*., 2018) [105]. Cobalt and zinc can interact in soils through adsorption processes, where they may compete for binding sites on soil particles. Soil pH and redox conditions influence the availability and mobility of both elements, thereby affecting their uptake by plants (Alloway, 2013) [2]. While cobalt and zinc can compete for uptake, in some cases, they may also exhibit synergistic effects where their combined presence enhances certain metabolic processes or growth parameters in plants. Elevated levels of cobalt might lead to antagonistic impacts on zinc uptake and utilization in plants, affecting overall nutrient balance and physiological functions (Khan *et al*., 2019) [37].

Cobalt and iron share similar uptake mechanisms in plants, and their interactions can lead to competition for uptake sites. Cobalt can interfere with iron uptake and utilization in plants, potentially leading to iron deficiency symptoms. (Rellan-Alvarez *et al*., 2010) [82]. Cobalt and iron can interact through adsorption processes, influencing their availability to plants in soils. Soil pH and redox conditions play an important role in determining the availability and mobility of cobalt and iron in soils (Kabata-Pendias, 2011) [34]. Cobalt and iron can exhibit synergistic effects under certain conditions, enhancing metabolic processes or growth parameters in plants. High cobalt levels may antagonize iron uptake and utilization in plants, impacting overall nutrient balance (Guerinot and Yi, 2018) [27].

Research suggests that cobalt can interfere with manganese uptake and utilization in plants, potentially leading to manganese deficiency symptoms even if manganese is present in sufficient quantities. A study by Ying *et al*. (2019) [111] suggested that elevated cobalt levels reduced manganese uptake and affected plant growth. Cobalt and manganese can interact through adsorption processes, where they may compete for binding sites on soil particles. Soil pH and redox conditions influence the availability and mobility of both elements, thereby affecting their uptake by plants (Alloway, 2013) [2]. Cobalt and manganese can also exhibit synergistic effects under certain conditions, where their combined presence might enhance metabolic processes or growth parameters in plants. Elevated cobalt levels may antagonize manganese uptake and utilization in plants, impacting overall nutrient balance (Andreini *et al*., 2018) [5].

A study by Vazquez *et al*. (2018) [102] investigated the competition between Co and Cu in maize plants. They found that elevated cobalt levels reduced copper uptake and affected plant growth and nutrient balance. Soil pH and redox conditions influence the availability and mobility of both elements, thereby affecting their uptake by plants (Alloway, 2013) [2]. Cobalt and copper can also exhibit synergistic effects under certain conditions, where their combined presence might enhance metabolic processes or growth parameters in plants. High cobalt levels may antagonize copper uptake and utilization in plants, impacting overall nutrient balance and physiological functions (Kovacs *et al*., 2019) [39]. Copper and cobalt interactions in the soil can be antagonistic. High copper levels can reduce Co availability and uptake, while adequate Co can enhance Cu utilization in plants.

Cobalt and molybdenum (Mo) can compete for uptake by plants due to their similar chemical characteristics and transport mechanisms. This competition can influence the bioavailability of these elements in plants (Kabata-Pendias and Mukherjee, 2007) [32]. Soil pH and redox conditions affect the availability of both Co and Mo. Higher pH generally enhances Mo availability, while lower pH can affect Co availability (Alloway, 2013) [2]. High levels of cobalt can interfere with molybdenum uptake due to competitive binding sites or toxicity effects. Adequate levels of both micronutrients can enhance nitrogen fixation and overall plant growth (Vose *et al*., 1984) [104].

There are limited studies specifically focusing on the interaction between cobalt and boron. High levels of cobalt might potentially interfere with boron uptake due to competitive binding or toxicity effects. Synergistic effects could occur when both micronutrients are present in balanced amounts, possibly enhancing overall plant growth and development (Marschner, 2012) [52].

There is limited specific research on the interaction between cobalt and chlorine in plants. Higher salinity levels can affect Co uptake by plants and alter soil chemistry dynamics (White and Brown, 2010) [107]. High levels of chlorine can potentially inhibit cobalt uptake by plants, affecting Co-dependent processes such as nitrogen fixation in legumes (Epstein and Bloom, 2005) [21]. Adequate levels of both micronutrients may support overall plant health and growth, as they contribute to essential metabolic processes (White and Broadley, 2001) [106].

Cobalt is generally less mobile in soils compared to nickel (Ni). Acidic soils tend to increase Co availability, whereas Ni is more mobile in soils, especially under acidic conditions (Adriano, 2001) [1]. Cobalt and Ni can compete for binding sites on soil particles and organic matter. High concentrations of one can reduce the availability of the other due to competitive adsorption (Kabata-Pendias, 2011) [34]. Both Co and Ni are taken up by plants through the roots. They utilize similar transporters, leading to competitive uptake. Excessive Ni can inhibit Co uptake and vice versa (Broadley and White, 2010) [14]. Elevated levels of cobalt and nickel in soils can adversely affect plant growth, leading to symptoms of toxicity such as chlorosis, reduced biomass, and altered nutrient uptake. The specific physiological responses vary among plant species and depend on the concentrations of Co and Ni present in the soil (Rascio and Navari-Izzo, 2011) [79].

Conclusion

In conclusion, this review underscores the intricate dynamics of cobalt (Co) in soils, highlighting the significance of its total concentration, bioavailability, and various forms, as well as its interaction with essential plant nutrients. The distribution and forms of cobalt in the soil matrix, including its soluble, exchangeable, and organically bound fractions, play a pivotal role in determining its availability to plants and its subsequent impact on plant nutrition.

Cobalt's interaction with essential macro and micronutrients is particularly noteworthy, as it can either enhance or inhibit their uptake and utilization, thereby affecting overall plant health and productivity. The balance between cobalt's beneficial and potentially detrimental effects is influenced by soil properties, pH, and nutrient status.

Future research should focus on refining our understanding of cobalt's speciation and bioavailability in diverse soil types, as well as developing management strategies to optimize cobalt levels and mitigate any negative interactions with essential nutrients. Such insights will be crucial for improving soil fertility management practices and ensuring sustainable agricultural systems. By integrating this knowledge, we can better manage cobalt's role in soil ecosystems and its impact on plant nutrition, ultimately supporting both agricultural productivity and environmental health.

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