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RESEARCH ARTICLE

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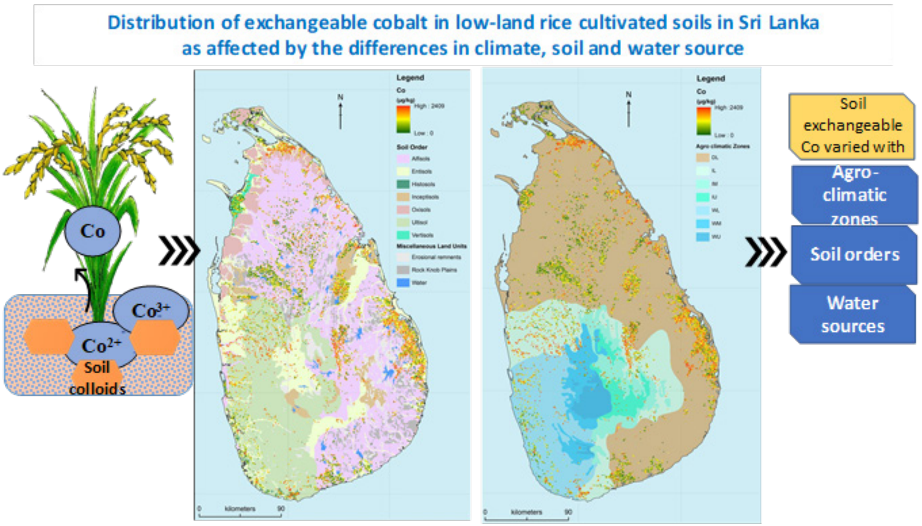
T. Weerasooriya, D.M.S.B. Dissanayake, M. Ariyaratne, U.K. Rathnayake, H.K. Kadupitiya, R. Chandrajith and L.D.B. Suriyagoda*



Highlights

- Cobalt (Co) is considered a beneficial element for plants
- Exchangeable Co concentration, [Ex-Co], in Sri Lankan paddy soils is not known
- 77.5% of the soil samples tested were Co deficient, i.e. <250 µg Co kg^{-1} soil
- Ex-Co varied among agro-climatic zones and soil orders
- Ex-Co had negative correlations with soil pH and rice crop productivity

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DISTRIBUTION OF EXCHANGEABLE COBALT IN LOW-LAND RICE CULTIVATED SOILS IN SRI LANKA AS AFFECTED BY THE DIFFERENCES IN CLIMATE, SOIL AND WATER SOURCE

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Abstract: Cobalt (Co) is considered a beneficial element for plants. However, when soils contain excessive amounts of Co, it could cause phytotoxicity. Despite this, the current status of Co in Sri Lankan rice-cultivated soils is not known. Therefore, this study was conducted to (i) determine the distribution of exchangeable Co concentration, and (ii) examine the interactive effects of climatic zone (CZ), agro-climatic zone (ACZ), soil order, water source, and their interactions in determining exchangeable Co concentration in lowland rice fields in Sri Lanka. A total of 8,292 soil samples representing six ACZs, six soil orders, and three water sources were collected using a stratified random sampling approach. Cobalt was extracted in 0.01 M $CaCl_2$ and measured using Inductively Coupled Plasma Mass Spectrophotometry. Exchangeable Co concentration ranged between 0.03-2,409 μg kg^{-1} with a mean value of 185.9 μg kg^{-1}. Over 77.5% of the soil samples tested were Co deficient, i.e. <250 μg kg^{-1}. Samples collected from the Intermediate zone, particularly Intermediate zone Mid country, had higher Co concentration than that reported in other ACZs ($p<0.05$). Among the soil orders, Histosols had higher (232 μg kg^{-1}) and Vertisols had lower (91 μg kg^{-1}) Co concentrations ($p<0.05$). Moreover, Co concentration was negatively correlated with soil pH ($r=-0.3391$, $p<0.0001$) and rice crop productivity ($r=-0.1512$, $p<0.0001$). Although exchangeable Co concentration in rice cultivated soils was low, it is important to implement strategies such as proper waste management, treatment of industrial effluents, and the use of safer and more sustainable practices in the chemical and mining industries to minimize further accumulation of Co exceeding the critical limit (i.e. 30 - 40 mg Co kg^{-1} rice grain), and to ensure the safety of rice production in situations where geological and anthropogenic activities can increase soil exchangeable Co concentration.

***Keywords*:** bioavailable; irrigation; paddy; soil orders; toxicity

INTRODUCTION

Cobalt (Co) is naturally found in a variety of substances, including water, plants, animals, and soils (Smith, 2001). The normal states of cobalt are cobaltous (Co^{2+}) and cobaltic (Co^{3+}). However, due to thermo-dynamical instability, Co^{3+} only exists in certain complexes under typical redox potential and pH levels (Ziwa et al., 2020). The majority of the world's Co-production often results from the extraction of other metals, such as Ni and Cu. Mostly Cu-Co deposits are hosted by sediments, but there are also Ni-Co laterites, Ni-Cu-Co sulfides, or hydrothermal and volcanic deposits. Those differ substantially depending on the ore's characteristics (Dehaine et al., 2021). Anthropogenic inputs such as pesticides and fertilizers may also add Co to soil (Bhattacharyya et al., 2008). Therefore, the topsoil has reported high levels of Co than the sub-soil layers (Paputri et al., 2021).

The transfer of Co in soil is controlled by sorption and co-precipitation interactions with the minerals containing iron (Fe) and manganese (Mn) oxides. The majority of Co in soil is associated with Fe and Mn oxides, demonstrating that these two oxides are key determinants of Co movement. The adsorption of Co by Fe and Mn oxides is a result of the strong affinity of these metals for the metal-binding sites on the surfaces of the oxides. This association can significantly reduce the mobility of Co in soil and limit its availability to plants and other organisms. However, the mobility of Co in soil can also be influenced by other factors such as pH, organic matter content, and the presence of other minerals. With rising pH, Co sorption is increased. As a result, soils with high $CaCO_3$ have high Co sorption and low Co desorption capacities (Jalali & Majeri, 2016). Therefore, poor mobility and leaching potential of sorbed Co in calcareous soils are expected (King, 1988). In addition, certain microorganisms are capable of solubilizing or precipitating Co, which can affect its availability and distribution in soil.

In many species, several systems regulate the uptake of Co. Despite being regarded as a beneficial element for higher plants, Co has not yet been included in the list of essential nutrient elements. An element that can improve plant health status at low concentrations but can be toxic at high concentrations is known as a beneficial element (Pais, 1992). Numerous researchers have noted the contribution of Co to higher plant output. The addition of Co resulted in a large boost in the yield of several species (Gad & Kandil,

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2010). The growth of the plants in the family Fabaceae and marine algae species like diatoms, chrysophytes, and dinoflagellates depends on Co (Gad et al., 2014; Hu et al., 2021). Its involvement in nitrogen (N) fixation by symbiotic bacteria is thought to be vital to leguminous plants. Certain bacteria in the roots of plants use Co in the soil to produce traces of the macronutrients required for strong plant growth. The vitamin B12 or cobalamin, which is needed by several enzymes involved in N_2 fixation, contains Co as an essential component (Hu et al., 2021). In addition, Co application has been found to increase the yield of other crops such as maize, wheat, and rice by enhancing their photosynthetic efficiency and stress tolerance. Cobalt is an element of numerous enzymes and proteins that are involved in plant metabolism. Additionally, Co promotes the growth of wheat and rice in salinity-prone environments (Attia et al., 2014). If the availability of Co is severely constrained, plants may display Co shortage (Hu et al., 2021).

The average worldwide soil total Co concentration in surface soils is estimated to be 10 mg kg^{-1} (Kabata-Pendias and Pendias, 2001), and the mean total soil Co concentration reported in Sri Lankan rice soils is 7.75 mg kg^{-1} which is lower than the global average (Balasooriya et al., 2022). High levels of Co, however, interfere with many metabolic processes and poison the plants, as seen by diminished root growth and phytomass, chlorosis, photosynthetic impairment, stunting, and oxidative stress. Eventually, this can result in phytotoxicity for plants and plant death. Nevertheless, Co shortage has frequently been documented in soils with less than 0.5 to 5 mg kg^{-1} of total Co. Moreover, exchangeable Co concentration less than 0.25 mg kg^{-1} is considered Co deficient. For rice grain, the tolerable limit of Co absorption is set at 30 to 40 mg kg^{-1} (Kabata-Pendias, 1992).

The biological role of Co is, it includes in vitamin B12 (cobalamin), a coenzyme in numerous enzymatic reactions that is linked to hematopoiesis, growth, and healthy neural function (Martens et al., 2002). Additionally, non-ruminant animals must consume Co together with a physiologically active form of vitamin B12 through their food to meet nutritional demands. Cobalt requirements for the body are very low which is sufficient from daily food intake without taking supplements. More than half of the world's population, mostly in Asia, consumes mostly rice (*Oryza sativa* L.), making it the most significant food crop in the world (Fageria, 2013). Waterlogged and reduced conditions in soil ecosystems that exist mostly in rice cultivating systems improve the solubility and mobility of trace metals such as Co, initially by dissolving Mn and Fe oxides (Bhattacharyya et al., 2008). The dissolved metals can then accumulate in the rice plants, potentially leading to health risks for human consumption (Hasan et al., 2022). Therefore, it is important to monitor and manage the trace metal concentrations in soil and water resources in rice-growing regions to ensure food safety and environmental sustainability.

In Sri Lanka, rice is widely cultivated in the lowlands, mostly under alternate wetting and drying soil conditions. Based on the rainfall, Sri Lanka is divided into three climatic zones (CZs). Areas receiving mean annual rainfall less than 1750 mm with a relatively dry season from March to August (*i.e. Yala* season) are identified as Dry zone. The Wet zone receives a mean annual rainfall greater than 2500 mm and is distributed throughout the year without a distinct dry season while the Intermediate zone has in-between characteristics with respect to the amount and distribution of annual rainfall. When considering elevation, areas located below 300 m, between 300-900 m, and above 900 m of sea level are called as Low, Mid, and Up Country regions, respectively. Based on the mean annual rainfall and elevation, Sri Lanka is divided into seven ACZs. Therefore, the seven ACZs are Dry zone Low country (DL), Intermediate zone Low country (IL), Intermediate zone Mid country (IM), Intermediate zone Up country (IU), Wet zone Low country (WL), Wet zone Mid country (WM) and Wet zone Up country (WU). Out of those, rice is widely cultivated in all the ACZs except WU due to topographical limitations.

Rice cultivation in DL and IL of Sri Lanka largely depends on the well-distributed cascade irrigation network developed due to the uneven annual rainfall distribution. However, rice cultivation in other regions largely depends on rainfall. Depending on the size of the command area, irrigation schemes are categorized as major (more than 80 ha command area) or minor (less than 80 ha command area) (Imbulana et al., 2006). Moreover, DL and IL in Sri Lanka are warmer and receive higher solar radiation indicating higher yield potential than other ACZs (DOA, 2020). Soils used to cultivate rice in Sri Lanka have different geological origins such as Alfisols, Entisols, Histosols, Inceptisols, Ultisols and Vertisols (Panabokke, 1978). It has also been found that the rice crop productivity in Sri Lanka varies among ACZs, soils and water availability (Kekulandara et al., 2019; DOA, 2020; Kadupitiya et al., 2022; Suriyagoda et al., 2022). The existing variability of climate, soil and water availability in different regions of Sri Lanka may have interactively influenced the exchangeable Co concentration in lowland rice fields and this had not been explored. Therefore, the objectives of this study were to (i) determine the distribution of exchangeable Co concentration, and (ii) examine the interactive effects of ACZ, soil order and water source on determining the concentration of exchangeable Co in lowland paddy fields in Sri Lanka.

MATERIALS AND METHODS

Soil sample collection

A total of 8,292 soil samples representing six agro-climatic zones and six soil orders were collected using a stratified random sampling approach (Tables 1 and 2; Fig. 1). Selection of sampling locations and collection of soil samples were completed following the approach described by Kadupitiya et al. (2021). In brief, Sri Lanka was divided into 1 km^2 grids using vector operations in QGIS free software (version 3.16.0-Hannover, https://qgis.org). A unique identification number was assigned for each grid by combining latitude and longitude km distance unit (using projected coordinate system EPSG: 5234 Kandawala / Sri Lanka Grid). The whole country was divided into 65,610 grids. After overlaying with the rice land map (1:50,000, survey department) 35,537 grids were found to be containing rice-cultivated lands. Out of 35,537 grids containing rice lands 8,292 grids with rice lands were selected for this study using a stratified random sampling approach, based on the administrative districts. The sample collection was done with a smartphone-based location tracking approach which was facilitated by Google Maps as the base map for convenient location tracking (Kadupitiya et al., 2021). Samples were collected in October-November 2019. Grid ID, ACZ, district, divisional secretariat division (DSD), and the village name of each grid were recorded for each sample during sample collection. From each village, one rice track (i.e., a geographically confined lowland area usually owned and managed by a group of farmers) was selected randomly for sample collection. One sample was taken by combining six subsamples collected at 0-15 cm depth from a paddy track to overcome the field-level heterogeneities. Soil samples were air-dried, debris were removed, homogenized, and sieved using a 2 mm sieve. The CZ, ACZ, soil order, and water source used for rice cultivation relevant to each sampling location were extracted by overlaying relevant GIS map layers in QGIS software. Rice yield realized during the immediate previous cropping season (t ha^{-1}) was also recorded from the farmer during soil sample collection.

Laboratory analysis

Cobalt was extracted using 0.01 M $CaCl_2$ solution (Houba et al., 2000; van Erp et al., 2001; Zbíral & Němec, 2005). The extraction was made with a soil/solution ratio of 1:10 (w/v) i.e. 5 g soil was dissolved in 50 mL 0.01 M $CaCl_2$ solution. Samples were shaken for 2 hours on an orbital shaker at 200 rpm, and then the solution was centrifuged at 3,600 rpm for four minutes. The supernatant was filtered through a 0.45 μm cellulose acetate syringe filter. The Co concentration in the solution was determined using an Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS) (Thermo iCapQ). Forty samples were tested at once in each round. It consisted of 36 soil samples, two laboratory standard soil samples, and two blanks with 0.01 M $CaCl_2$ solution without soil samples for quality control.

For the determination of soil pH, 10 g of soil was measured from each sample and mixed with 50 mL of distilled water. Samples were shaken for two hours in an orbital shaker

Table 1: The number of soil samples collected from each climatic zone (CZ), agro-climatic zone (ACZ) and soil order to test exchangeable cobalt (Co) concentration in soil.

CZ →	Dry Zone	Intermediate Zone			Wet Zone		Total
ACZ → / Soil orders ↓	Dry zone Low country	Intermediate zone Low country	Intermediate zone Mid country	Intermediate zone Up country	Wet zone Low country	Wet zone Mid country	
Alfisols	2735	328	12	2	3	-	3080
Entisols	1486	153	26	5	227	34	1931
Histosols	-	25	-	-	28	-	53
Inceptisols	406	13	10	-	-	-	429
Ultisols	31	356	29	3	343	8	770
Vertisols	177	-	-	-	-	-	177
Total	4835	875	77	10	601	42	6440
	4835	962			643		

Note: soil order of some samples was not known, therefore the sample size stated in this table is less than the total number of samples collected, i.e. <8,292.

Table 2. The number of soil samples collected from each climatic zone (CZ), agro-climatic zone (ACZ) and water source to test exchangeable cobalt (Co) concentration in soil.

CZ →	Dry Zone	Intermediate Zone			Wet Zone		Total
ACZ → / Water sources ↓	Dry zone Low country	Intermediate zone Low country	Intermediate zone Mid country	Intermediate zone Up country	Wet zone Low country	Wet zone Mid country	
Major	2326	389	6	-	56	-	2777
Minor	1214	265	21	-	102	-	1602
Rainfed	1295	221	50	10	443	42	2061
Total	4835	875	77	10	601	42	6440
	4835	962			643		

Note: water source of some samples was not known, therefore the sample size stated in this table is less than the total number of samples collected, i.e. <8,292.

at room temperature. After resting for 15 minutes, soil pH was measured using a pH meter (Eutech WC PC 650, Singapore). Two laboratory standard soil samples and two blanks only with distilled water were used in each batch (i.e. 36 samples) for internal quality control. Moreover, pH electrode was calibrated daily using the manufacturer standards (Eutech WC PC 650, Singapore).

Preparation of spatial maps

Since each sampling point was tagged with a unique Grid-ID, which was coded with distance (km) coordinate X-Y, the same ID was maintained from field data collection to laboratory analysis and data analysis. This procedure allowed easy spatial reference for data set development and facilitated user-friendly GIS map production.

Statistical analysis

Descriptive statistics of Co concentration were obtained. Cobalt concentration was tested for normality using the Shapiro-Wilk test, and all statistical analyses were performed based on the normal distribution after the log transformation (Fig. 1). Analysis of Variance (ANOVA) was performed as a two-step process. First, the difference in Co concentration of soil samples among ACZs, soil orders, water sources, and their interactions was determined using the General Linear Model procedure. As most of the higher order interactions of ACZ, soil order and water source were significant, in the second step, differences in Co concentration of soil samples among soil orders and water sources were tested within each ACZ using ANOVA. The means were compared using Duncan's New Multiple Range Test (DNMRT). Statistical significances were expressed at α=0.05. Statistical analyses were performed using SAS 9.1 software.

RESULTS

Exchangeable Co concentration was in the range of 0.03 - 2,409 µg kg^{-1} with the mean and median concentrations of 185.9 and 86.9 µg kg^{-1}, respectively (Fig. 1). Out of the tested soil samples, 77.5% had Co concentration less than 250 µg kg^{-1}, i.e. the critical Co concentration considered as Co deficient. The distribution was right skewed due to the presence of a large majority of soil samples with low Co concentrations while only a small fraction of soil samples with extremely high Co concentrations. As a result, natural log-transformed Co concentrations were the best approximation to reach normality.

When comparing climatic zones, exchangeable Co concentration was the highest in IZ (293 µg kg^{-1}) whereas that in DZ was the lowest (163 µg kg^{-1}) (Fig. 2). Moreover, there was a large variation of Co concentration among ACZs (Fig. 3). Paddy cultivated soils in IM had the highest (375 µg kg^{-1}) Co concentration whereas DL recorded the lowest (163 µg kg^{-1}) ($p<0.05$, Fig. 3). Concentration of Co in IL, IM, IU and WM was similar ($p>0.05$) (Fig. 3). Despite Sri Lanka is divided into seven ACZs, DL consists of approximately 2/3 of the land area (Fig. 4). There was a large variability of exchangeable Co in DL, i.e. northern and eastern coastal regions of DL contained higher soil exchangeable Co concentration while that in the central and western regions of DL was lower.

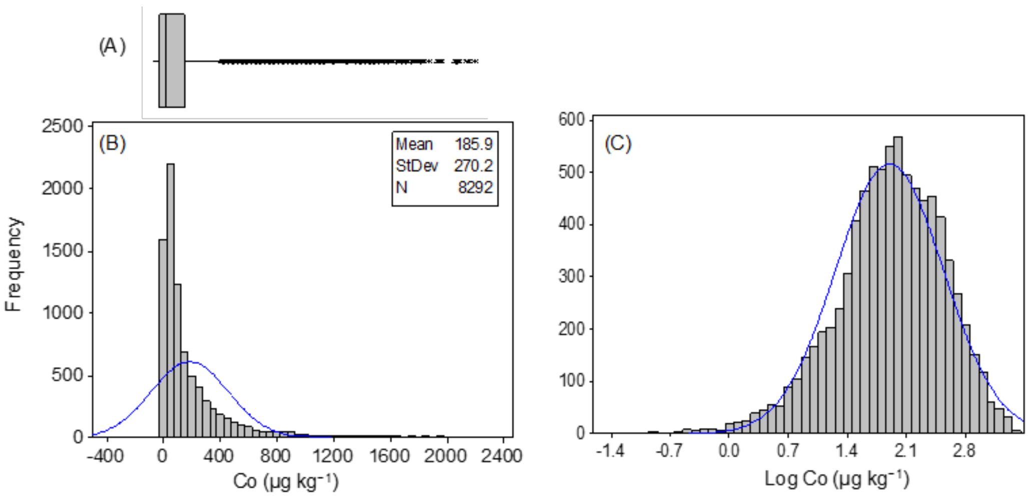

Figure 1: Box plot (A), histogram (B), and log-10 transformed values (C) of Co concentration of paddy soil samples collected from Sri Lanka.

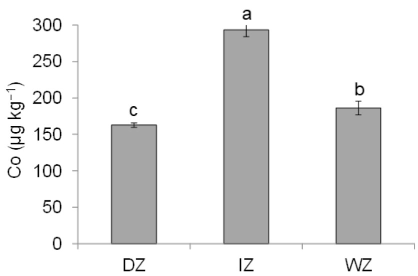

Figure 2: Concentration of cobalt (Co) in the paddy fields used to cultivate rice in different climatic zones of Sri Lanka (mean±S.E.) Note: DZ-Dry Zone, IZ-Intermediate Zone, WZ-Wet Zone

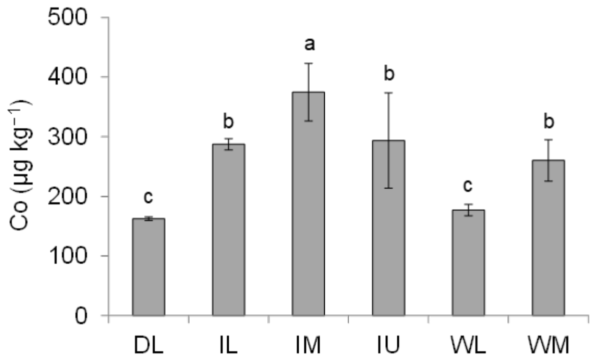

Figure 3: Concentration of cobalt (Co) in the paddy fields used to cultivate rice in different agro-climatic zones of Sri Lanka (mean±S.E.) Note: DL-Dry zone Low country, IL-Intermediate zone Low country, IM-Intermediate zone Mid country, IU-Intermediate zone Up country, WL-Wet zone Low country, WM-Wet zone Mid country, WU-Wet zone Up country.

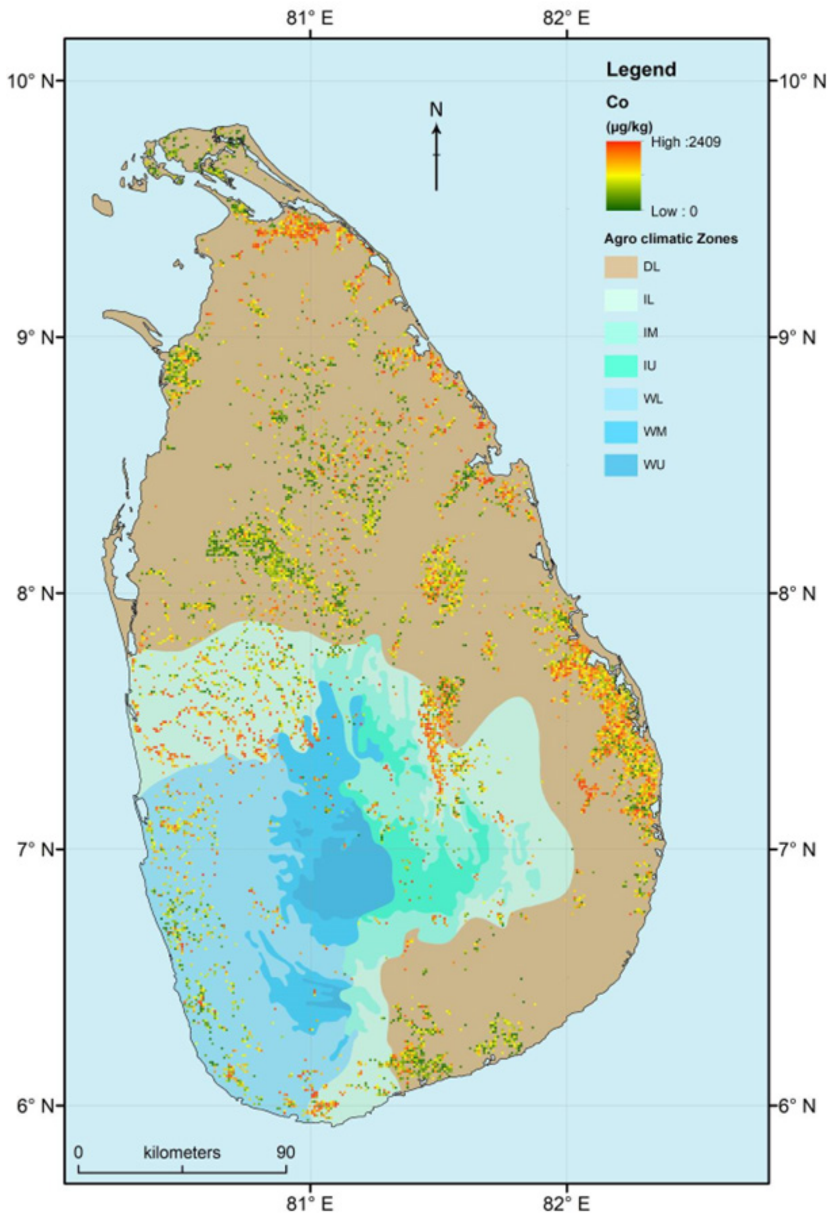

Figure 4: Spatial distribution of cobalt (Co) concentration in the paddy fields used to cultivate rice in different agro-climatic zones of Sri Lanka. Note: DL-Dry zone Low country, IL-Intermediate zone Low country, IM-Intermediate zone Mid country, IU-Intermediate zone Up country, WL-Wet zone Low country, WM-Wet zone Mid country.

When comparing different soil orders used to cultivate rice, Entisols (221 µg kg^{-1}), Histosols (232 µg kg^{-1}), Inceptisols (188 µg kg^{-1}) and Ultisols (206 µg kg^{-1}) had the highest Co concentration and was significantly higher than that in Alfisols (167 µg kg^{-1}) ($p<0.05$) (Fig. 5). Vertisols had the lowest (96 µg kg^{-1}) Co concentration (Fig. 5). Most of the paddy lands containing Alfisols in the northern peninsula, Vertisols in the north-western region and Alfisols in the north-central region had lower Co concentration. On contrary, Inceptisols contained in the eastern region and Entisols in the northern region had higher Co concentration (Fig. 6). Moreover, the dominant soil in the southern region of the country; Ultisols had lower Co concentration.

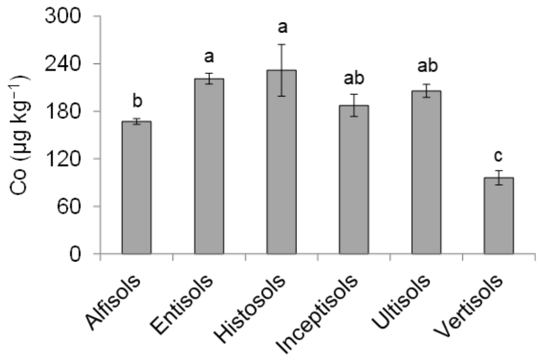

Figure 5: Concentration of cobalt (Co) in the paddy fields used to cultivate rice under different soil orders of Sri Lanka (mean±S.E.).

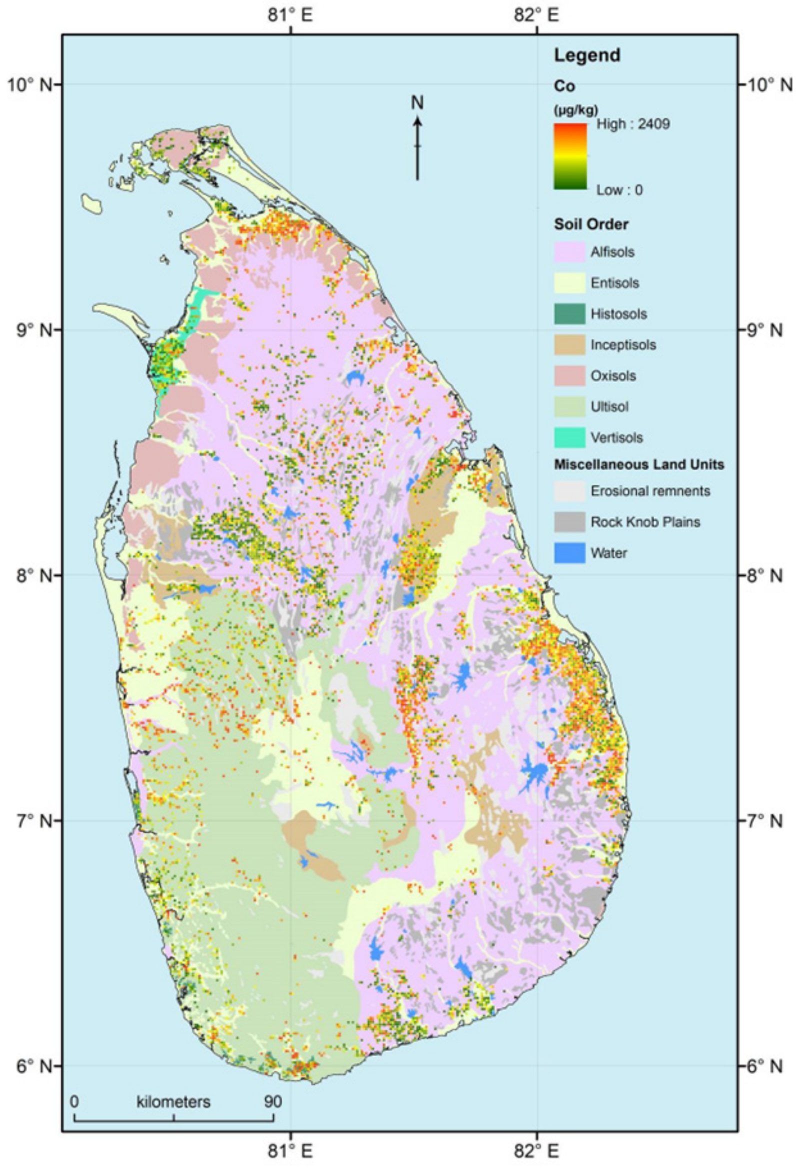

Figure 6: Spatial distribution of cobalt (Co) concentration in the paddy fields used to cultivate rice under different soil orders of Sri Lanka

There was a significant interaction between ACZ and soil orders in determining Co concentration in soil ($p<0.05$). Both DL and IL had five soil orders, IM and WL had four soil orders, and IU and WL had three and two soil orders, respectively (Fig. 7). Entisols and Ultisols were observed in all the ACZs while Vertisols was found only in a much-localized region in the DL (Figs. 4, 6, 7). Moreover, Alfisols was found in four out of five ACZs. In DL, Entisols and Inceptisols had higher Co concentration while Vertisols and Ultisols had a lower Co concentration ($p<0.05$, Fig. 7). Vertisols was found only in a restricted area located in the low-lying north-western region of Sri Lanka (Fig. 6). Entisols was largely found in the low-lying flat terrain as localized patches close to the coastal regions of the DL while Alfisols was the major soil type found in DL (Figs. 4, 6). In IL, Entisols and Histosols had higher Co than that observed in Ultisols ($p<0.05$) (Fig. 7). The two dominant soil orders found in IL were Ultisols and Alfisols (Figs. 4, 6). In IM, Inceptisols reported a very high Co concentration which was significantly higher than other soils orders found in IM ($p<0.05$) (Fig. 7). In IU, Entisols had lower soil Co concentration than Alfisols and Untisols (Fig. 7). Soil Co concentration among soil orders in WL and WM was similar ($p>0.05$) (Fig. 7).

There was a significant interaction between ACZ and water source when determining exchangeable Co concentration in soil ($p<0.05$). Major and minor irrigation schemes provided supplementary water for rice cultivation in four ACZs while rainfed paddy fields were observed in all six ACZs (Fig. 8). In DL, paddy fields receiving water only from rainfall retained more Co than those receiving supplementary irrigation water from either major or minor irrigation schemes ($p<0.05$). In IL, soil Co concentration among different water sources was similar ($p>0.05$). In IM, paddy fields receiving water from major irrigation schemes retained more Co than the paddy fields receiving water from other sources ($p<0.05$). In WL, paddy fields receiving water from minor irrigation schemes retained more Co than the paddy fields receiving water from other sources ($p<0.05$).

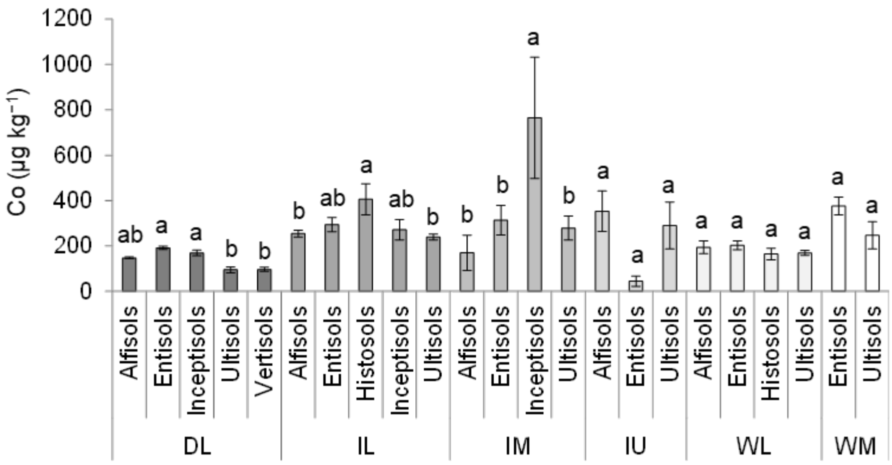

Figure 7: Concentration of cobalt (Co) in the paddy fields used to cultivate rice in different soil orders and agro-climatic zones (ACZ) of Sri Lanka (mean±S.E.) Note: DL-Dry zone Low country, IL-Intermediate zone Low country, IM-Intermediate zone Mid country, IU-Intermediate zone Up country, WL-Wet zone Low country, WM-Wet zone Mid country, Different letters over the bars, within each ACZ, indicate statistically significant difference at $p<0.05$.

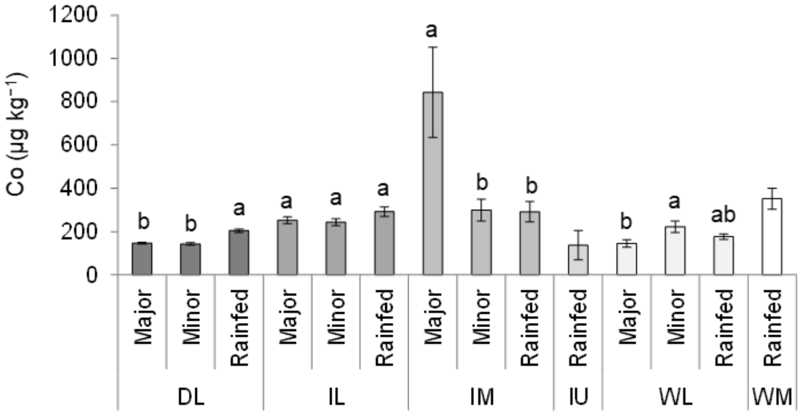

Figure 8: Concentration of cobalt (Co) in the paddy fields used to cultivate rice using different water sources and agro-climatic zones (ACZ) of Sri Lanka (mean±S.E.). Different letters over the bars, within each ACZ, indicate statistically significant difference at $p<0.05$.

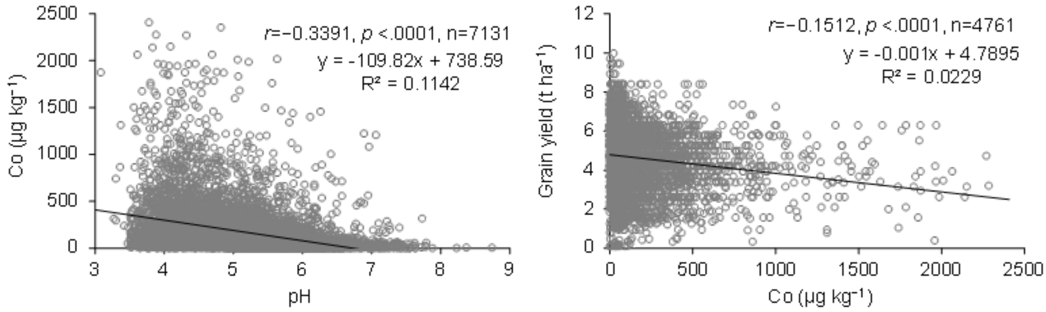

Figure 9: Relationships between cobalt (Co) concentrations with soil pH of lowland paddy cultivated soils and grain yield.

There was a significant negative correlation between soil Co concentration and pH (r=−0.3391, p<0.0001) (Fig. 9). Availability of Co was the highest in the pH range of 4-5 and then gradually decreased until pH of 8. Moreover, the correlation between the grain yield of rice and Co concentration was also significant and negative (r=−0.1512, p<0.0001).

DISCUSSION

Distribution of Co in Sri Lankan paddy soils

Cobalt has been distributed in all the CZs, ACZs, soil orders and areas receiving water from different sources for rice cultivation in Sri Lanka with varying concentrations. The range of soil exchangeable Co concentration reported in this study was 0.03-2,409 µg kg^{-1}, and 77.5% of the samples had Co concentration less than 250 µg kg^{-1}, i.e. the critical Co concentration considered as Co deficient. Therefore, most of the Sri Lankan rice fields are deficient in exchangeable Co and would not show Co toxicity.

It has been reported that several plant species grow better in low concentrations of Co whereas toxicity occurs at higher Co concentrations (Palit et al., 1994). Despite soil exchangeable Co concentration was within the safe limit to produce rice grains in the present study, there was a negative correlation between grain yield and soil exchangeable Co concentration (Fig. 9). The reason for this type of correlation is not clear and may be due to the multicollinearity with soil pH, Mn or organic matter content in soil (McLaren et al., 1986; Kirk, 2004). However, as the results of the present study contradict the general pattern at low Co concentration, this relationship needs to be explored further.

Effects of climate, water source and soil orders on determining Co concentration

Formation of Sri Lanka's soils is significantly influenced by the climate, particularly the amount and distribution of rainfall (Indraratne, 2020). When considering the stage of soil development, soils in the Dry zone are younger or less weathered compared to the soils in Wet zone. This is due to the less intercepted rainfall from Dry zone soils during a narrow window of a year (Weerasuriya et al., 1991). However, the high and well-distributed rainfall that occurs in WZ causes high leakage, percolation, and surface runoff of mineral elements than that in DZ (Kumaragamage et al., 2010). Therefore, highly weathered WZ soils also retain a lesser amount of exchangeable Co in soil. Intermediate zone, which is geographically positioned between DZ and WZ, experiences average conditions with respect to the weathering process and rainfall distribution. Apart from the receipt of an average amount of annual rainfall, IZ also has the access to irrigation water throughout the year. The possibility of maintaining favorable soil moisture condition during the year may have contributed IZ soils to retaining higher Co concentration than that observed in DZ (which receives rainfall only during one season slowing down the weathering process) and WZ (which receive a high amount of annual rainfall causing the leaching out of Co).

Usually, crop diversity is high in IZ than in other CZs. As a result, the cultivation of vegetables in rotation with rice is a prominent cropping system in IZ (Gunasena, 2001; Kadupitiya et al., 2021). Farmers use a broad range of agrochemicals, including fertilizers and fungicides for vegetable crops (Wimalawansa & Wimalawansa, 2014). It has been reported that N, P and K fertilizers act as a primary source of Co in tobacco fields in Brazil (Zoffoli et al., 2013). This is because Co is often present in these fertilizers as a contaminant, either as an impurity in the raw materials used to make the fertilizer or as a byproduct of the manufacturing process. The overuse of agrochemicals for different crops in the IZ may also be a factor contributing to the development of higher soil exchangeable Co in IZ soils compared to the other two zones.

Changes in soil moisture condition (redox potential), pH, Fe, Mn, and SO_4^{2-} affect the solubility and transport of metal ions in soil solution including Co (McLaren et al., 1986; Kirk, 2004; DeLaune & Seo, 2011). In the present study, pH and Co had a strong negative correlation. As a result, exchangeable Co concentration was high at low pH. As pH decreases, metals that may exist as free hydrated cations become more soluble. Additionally, the desorption of metal cations from organic matter or the surface of clay minerals and other sorbents at low pH could be another factor for this. It is also reported that slightly soluble or insoluble forms of metals are common in oxidized, nonacidic conditions while soluble species of many metals are widely found at low pH and reduced conditions (DeLaune & Seo, 2011). It has been reported that soil exchangeable Co is maximum in the pH range of 4.5 to 5.5 (Park et al., 2007). Moreover, the rate of Co sorption is the greatest in the pH range of 4.5-7.0, and this is likely due to a rise in negative charge at the mineral's edge sites (Hodgson, 1960). Adsorption becomes less effective when conditions get more alkaline (pH > 8) (Smith, 1999; Theis et al., 1988). Therefore, the optimum range of pH to take up Co for plants is in the neutral range.

The positive correlations between Co and Fe/Mn suggest that Co is attached to Fe and Mn oxides via co-precipitation or adsorption in an oxidizing environment (Shukla et al., 2018; Burns, 1976). As a result, when the oxides are reductively dissolved, any associated Co is eliminated; but, when the environment is oxidized, Fe and Mn oxides precipitate, and the Co is sequestered. As a result, under oxidizing conditions, Fe (hydro-)oxides may function as crucial binding agents for Co. Metals are primarily deposited as oxides and/or oxyhydroxides, which are then broken down by bacteria during the breakdown of organic matter, increasing the amount of those metals in the dissolved phase or solution (Shaheen et al., 2014). Given the ecotoxicology risk of dissolved toxic metals in flooded acidic soils, the risk of Co polluting irrigation water and contaminating crops and its effect on food security have to be carefully monitored (Shaheen et al., 2014).

The occurrence of soil influences agricultural crop selection and water use. Histosols have a high content of organic matter and water-holding capacity enabling it to bind with Co (Pereira et al., 2006; Fageria, 2013; Rawat et al., 2019). This may be the reason for the higher Co concentration observed in Histosols found in IL. Vertisols, with low organic matter content and high soil pH, retained low concentrations of exchangeable Co. Vertisols found in India, Australia, Sudan, Ethiopia, and other parts of Africa also had pH in the range of 7.5 to 8.5 (Virmani et al., 1982), making Co less available (Sanders, 1983).

Possible interventions to manage Co concentration in paddy soils

Higher plants do not necessarily require Co, however, there have been reports of the benefits of Co in plants such as retarded leaf senescence, drought tolerance in seeds, control of alkaloid buildup, and the reduction of ethylene production (Palit et al., 1994). Additionally, the creation of many coenzymes, symbiotic N fixation, root development, activation of glycolytic enzymes, and oxidation activities are mostly dependent on Co (Mahey & Thukral, 2014). Therefore, Co acts as a beneficial element for plants (Broadley et al., 2012). However, spraying or ground application of Co in high quantities can have deleterious effects on plants (Nagpal, 2004).

Most of the Sri Lankan rice soils have exchangeable Co concentration in the deficient range. Similar results have also been reported in Cambodia (Domingo & Kyuma, 1983). Therefore, regular soil testing is important for ensuring optimal plant growth and productivity, as it helps to identify any nutrient deficiencies or imbalances in the soil. This information can then be used to develop appropriate fertilization strategies that provide plants with the nutrients they need to thrive.

Studying the interactions between Co and other mineral elements such as Fe and Mn are important, as these elements can affect the uptake and utilization of Co by plants. For example, high levels of Fe or Mn in the soil can reduce the availability of Co to plants, leading to potential Co deficiencies. As stated previously, the safe threshold of Co concentration in rice grain is within the range of 30 to 40 mg Co kg^{-1} (Kabata-Pendias, 1992). Understanding how Co affects the growth and yield of rice can help to develop better fertilizer management strategies to improve rice production, which could have significant impacts on global food security.

The main anthropogenic sources of Co are chemical industries, mineral fertilizers, untreated industrial effluents, sewage, and mine wastes (Gautam et al., 2015). There is a continuous rise in the generation of these materials risking the increase in Co concentration in soil becoming phytotoxic (Kirkham, 1986). It is important to monitor and control the release of Co and other toxic elements into the environment to protect both human health and the ecosystem. This can be achieved through proper waste management, treatment of industrial effluents, and the use of safer and more sustainable practices in the chemical and mining industries. Additionally, measures such as soil testing and remediation can help to reduce the negative impact of Co and other contaminants on agricultural lands.

CONCLUSION

Exchangeable Co concentration in lowland rice cultivated soils in Sri Lanka was affected by ACZs, soil orders, water sources, and their interactions. Availability of Co was the highest at a pH range of 4-6. Moreover, as soil pH increased, exchangeable soil Co concentration decreased. There was a spatial heterogeneity of soil Co distribution, e.g. when comparing ACZs, exchangeable Co concentration was higher in IM while it was lower in DL and WL. Among the soil orders, exchangeable Co concentration was higher in Histosols while it was lower in Vertisols. The spatial maps generated in this study could be used to identify the areas with low and high Co levels in the country and make area-specific agronomic and administrative decisions/ recommendations. Despite soil exchangeable Co concentration was low in most of the rice growing soils compared to the threshold level reported in the literature, it is important to implement strategies to minimize further accumulation and/or reduce the existing higher concentrations of Co in some parts of the country to ensure the safety of rice production.

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DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest.

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