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Heavy Metals in Paddy Soils of Brunei Darussalam and Their Relationship with Selected Soil Properties

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Abstract: In Brunei Darussalam, available information of heavy metals in agricultural soils is sparse and hence a baseline study was carried out on soils in rice growing areas. In this study, trace elements as well as common soil characteristics were determined from twenty six of major rice fields such as Wasan, Limau Manis, Selapon and Lot Senkuang. Al, Fe, Mn and Cd were high in these areas however; Cu, Zn, Cr, Co, Ni and Pb were below safety limit of soil while Mn and Cd were above the permissible limit according to the WHO/CCME/European Union guidelines. The variations in metal concentrations in these samples are highly correlated to the acidic condition, organic matter and CEC of the paddy soils. The distributions of Al, Fe, Cu, Mn, Cd, Cr, Co, Pb were high at low pH. Cu, Zn, Cd, Ni and Pb showed positive correlation with organic matter while the quantities of Al, Fe, Mn, Cr and Co were negatively correlated. Correlation analyses showed that the Cd, Zn and Ni were associated with CEC while most of the metals were related to Al and Fe. The soils of the studied areas are extremely acidic with pH 3.0-4.6, and low in cations, CEC and available P, while having a high OM content. Low content of P was due to high amount of Al and Fe in these areas.

Keywords: Heavy Metals, Soil Acidity, Aifisols, Histosols, Vertisols

1. Introduction

A great deal of attention has been paid towards the monitoring of heavy metals (HMs) in recent years due to concern over their effects on human health [51]. The contamination of soils by HMs has emerged from natural origin (parent materials) and anthropogenic actions such as improper use of agrochemicals, animal manures and some activities of industrialization [56, 75]. Dissolving of metals by the oxidation of sulphidic materials has been observed to occur in acid sulphate soils (A. S) [76] which are widespread throughout Brunei Darussalam [30]. The total worldwide area of A. S soils is about 17-24 million hectares [6] and these soils release massive amounts of acid and toxically high contents of metals which disturb the surrounding environment [28]. This process can have a detrimental impact on the agriculture sector as the acidity and the increase of soluble metals result in toxicity and a decrease in nutrient availability of some nutrients, which lowers productivity [23]. In agriculture system, the amount of HMs in soils is an important factor because a high level of HMs deteriorates soil quality and threatens food security [41]. It is also harmful to human health and sustainability of agricultural land such as soil and water pollution and phytotoxicity, failure of crop growth and quality [15, 77].

Availability of HMs is influenced by pH, organic matter (OM), cation exchange capacity (CEC), calcium carbonate, Fe and Mn oxides [70]. Among them, pH was the main influence of metal solubility in soil and soil solution as well [85]. The second factor is the OMcontent in soil which is also affecting the availability of heavy metals as it retains the HMs in soil and hence enhances crop metal availability [50]. Soil contamination became hazardous due to the continuous degradation of soil OM into the environments reported by [27]. Humic acids, which are the main part of soil OM, represent the heart of the interaction process of inorganic pollutants with soil [25]. The evaluation of soil quality and status of soil HMs is an excellent step to be taken for protecting not only the environment but also sustaining the agriculture system to ensure the health and safety of the consumers [49]. Usually, the concentration of HMs in soils, resulting from parent materials, is not high enough to damage human health. However, anthropogenic sources such as industrialization, agrochemical and other man made factors cause an increase in the HMs content in soil [8]. Accumulation of HMs in soils affects the soil function, crop growth and development as well as human health [44].

However, no sufficient information on HMs in agricultural soils in Brunei Darussalam is available. Only arsenic and cadmium studies have been carried out by [30]. Currently, studies of HMs pollution in soil and crop and their special effects on the human health has happened an important topic among the world. Decreasing of crop production and quality was affected by growing in heavy metals contamination of soil and then more than acceptable limit of HMs content in crops also be risky of consumers' health. Phosphate fertilizers and irrigation water contaminated with Cd will leach into the soil and water reservoirs, and finally transfer along thefood chain, causing chronic renal failure amongst consumers [12]. Phosphatic fertilizer and other sources include farmyard manure, sewage sludges are the most common source of Cd contamination of agricultural soils [5, 57]. Cd is readily taken up by plant root which is then translocated to above ground tissues [81]. This poses a potential threat to human health as it enters the food chain [53]. Food intake and tobacco smoking is the main route where Cd enters the body [48]. So this study was carried out the following objectives: (1) to determine the concentrations of Cd, Co, Cr, Fe, Cu, Mn, Zn, Ni, Pb and Al in soils from major paddy plantation areas in Brunei Darussalam and (2) to study the correlation of HMs with soil properties.

2. Methodology

2.1. Study Site

Brunei Darussalam is located in the northern region of Borneo Island, bordering the South China Sea and the Malaysian state of Sarawak. This area is well known for its equatorial climate, characterized by uniformly high temperatures and rainfall throughout the year with average temperature of 27.5°C and average precipitation of over 2800 mm per year. Brunei has four administrative districts, namely Brunei-Muara, Tutong, Belait and Temburong. The study was carried out on four agricultural development areas (Wasan, Limau Manis (LM), Selapon and Lot Senkuang (LS)). Wasan and Limau Manis (LM) are located in the Brunei-Muara District; Selapon is in the Temburong District and Lot Senkuang (LS) is in the Belait District (Figure. 1). According to [32], the soil types of studied areas were fall into different categories as follow: Wasan- Vertisols, Limau Manis-Vertisols and Histosols, Selapon- Alfisols and Lot Senkuang-Histosols.

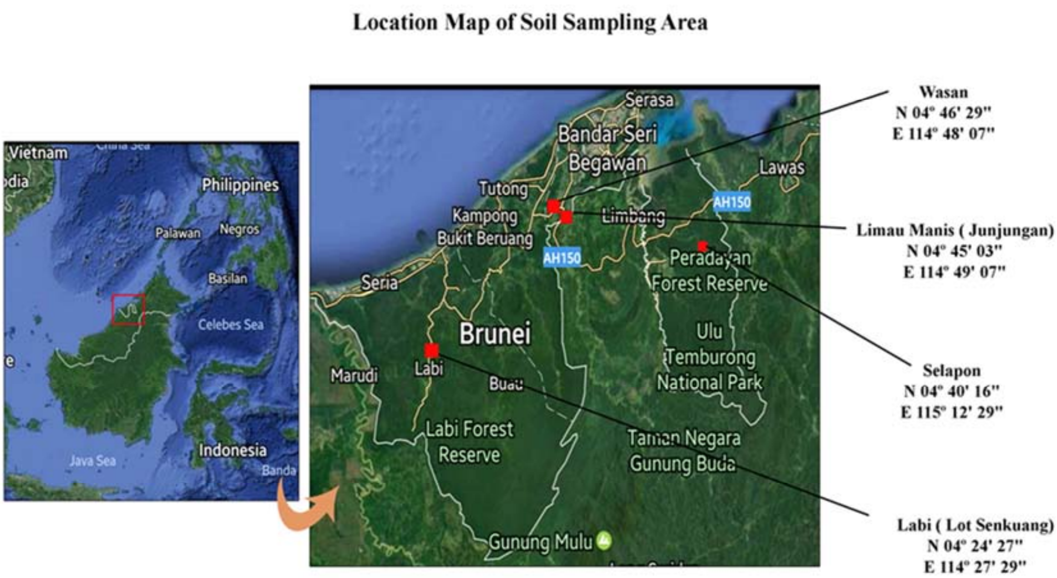

Figure 1. *Location of study areas in Brunei Darussalam.*

2.2. Sampling and Chemical Analysis

Twenty-six surface samples (to a depth of 20 cm) from Wasan (W1-W7), Limau Manis (LM1-LM7), Selapon (S1-S7) and Lot Senkuang (LS1-LS5) were collected. Prior to laboratory analysis, the samples were dried for 5 days at 40°C and passed through a 2 mm sieve. For the determination of OM, the 2 mm soils were further sieved through a 0.2 mm sieve. All analysis was done in triplicate. The measurement of soil pH and EC (1:2.5 soil-water) was performed by using a pH meter (GP 353 ATC) and a conductivity meter (DDS-307). Walkley and Black's method was used for determining the OM with 5 mL of potassium dichromate (1M), sulphuric acid (95-97%) and orthophosphoric acid (85%) [72]. CEC was determined as summation of calcium, magnesium, sodium and potassium [79]. These cations were extracted with 1 M NH_4OAc solution (1:10) and measured with an inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP6000 ICP). The available phosphorus (P) and total P was determined by Bray I and the nitric acid digestion method, respectively. For Bray 1 P, two grams of soil was extracted with NH_4F (0.03 M) and HCl (0.025 M) solution and mixtures were shaken at 180 rpm for five minutes and then filtrated through a What man No. 2 filter paper [72] and analyzed by the ascorbic acid method [52] using a UV colorimetric absorption spectrophotometry. The content of HMs was extracted by hot plate extraction according to the acid digestion of soil, Method 3050B (69). One gram of soil was mixed with 10 mL of concentrated nitric acid (65%) in a 250 mL beaker and the slurry was covered through a watch glass and heated to 95°C±5°C for ten minutes without boiling. After the sample was cooled, 5 mL of concentrated nitric acid was added and the solution was then heated to 95°C±5°C for thirty minutes until no brown fumes appeared. After cooling, 10 mL of hydrogen peroxide (30%) was added followed by warming until no change in the appearance of the sample was observed. Subsequently 10 mL of hydrochloric acid (35.4%) was added and the sample was heated to 95°C±5°C for fifteen minutes. The cooled sample was then centrifuged at 3000 rpm for ten minutes and the supernatant solution was kept at 5°C until analysis. Prior to heavy metal analysis, all glassware and polyethylene bottles were soaked in 10% nitric acid for 24 hours and rinsed with ultrapure water. For quality control, method blank and soil certified reference material (CRM, SQC-001) were analyzed and determined by ICP-OES.

2.3. Statistical Analysis

All of the parameters are expressed as mean and standard error values in tables. In graphic representations only mean values are used. The relationships between heavy metal and soil chemical properties are expressed as Pearson's linear correlation coefficients using SPSS 21 (36).

3. Results and Discussion

3.1. Chemical Properties

The performances of the USEPA extraction method 3050B as well as the ICP analytical method for metals analysis in soil samples were tested using the CRM (SQC-001) for metals in soil. The experimental results together with the certified values of the CRM and their standard deviations are summarized in Table 1. As can be seen from Table 1, the results compare favorably with the certified values and the recovery percentages were in the range of 86 to 120. Therefore, the tested method was acceptable for the analysis of heavy metals in soil.

Table 1. *Experimental parameters used and percentage recovery of heavy metals from the analysis of the CRM SQC-001 samples.*

No.	Element	Wavelength of ICP analysis (nm)	R^2 value of calibration curve	Certified value (mg/kg)	Measured value (mg/kg) (No of analysis =3)	Recovery (%)
1	Cd	214.4	0.995	123 (2)	141 (15)	114.8
2	Co	228.6	0.997	50.9 (1.1)	52.0 (8.8)	102.1
3	Pb	220.3	0.994	108 (2)	93 (12)	86.3
4	Ni	221.6	0.998	285 (4)	265 (20)	93.0
5	Fe	371.9	0.999	5230 (142)	5261 (89)	100.6
6	Cu	224.7	0.999	211 (3)	213 (18)	100.9
7	Mn	403.1	0.999	133 (5)	122 (13)	91.4
8	Zn	481.0	0.981	203 (5)	197 (14)	97.1
9	Al	308.2	0.997	8100 (954)	8048 (104)	99.4
10	Cr	283.5	0.993	63.2 (1.7)	74.8 (10.0)	118.4

* Mean values are followed by standard deviations in brackets.

Table 2. *Chemical characteristics of soil samples collected from four major rice growing areas.*

Soil parameters	Wasan (n = 21)	Limau Manis (n = 21)	Selapon (n = 21)	Lot Senkuang (n = 15)	All Locations Pooled
pH	3.6 (0.1)	3.6 (0.1)	3.9 (0.0)	4.2 (0.0)	3.8 (0.1)
EC (dS/m)	0.074 (0.000)	0.068 (0.000)	0.071 (0.000)	0.073 (0.000)	0.072 (0.000)
OM (%)	9.8 (0.7)	11.4 (1.2)	8.0 (0.3)	5.7 (0.2)	8.7 (0.6)
Available P (mg/kg)	6.3 (0.9)	9.7 (1.8)	6.2 (1.0)	2.4 (0.1)	6.2 (1.0)
Ca (cmol (c)/kg)	1.25 (0.08)	1.64 (0.21)	0.93 (0.04)	0.79 (0.02)	1.15 (0.09)
Mg (cmol (c)/kg)	1.14 (0.10)	1.16 (0.12)	0.81 (0.07)	0.20 (0.03)	0.83 (0.08)
Na (cmol (c)/kg)	0.14 (0.01)	0.14 (0.01)	0.12 (0.02)	0.14 (0.01)	0.14 (0.01)
K (cmol (c)/kg)	0.24 (0.01)	0.21 (0.01)	0.17 (0.01)	0.20 (0.00)	0.21 (0.01)
CEC (cmol (c)/kg)	2.7 (0.2)	3.1 (0.3)	2.0 (0.1)	1.4 (0.0)	2.3 (0.2)

* Mean values are followed by standard error in brackets.

The chemical properties (pH, EC, OM, available P, Ca, Mg, Na, K and CEC) of the surface soil samples are summarized in Table 2. Soil pH is of prime importance in controlling the availability of micronutrients, since it affects directly their solubility as well as mobility activity in the soil environment (21, 22). The mean pH value was extremely acidic (3.8) according to the [63]. The pH range varied from 3.6 to 4.2 among sample sites which may be due to the climate and geology of the region and studies have shown the presence of pyrites in the soil [30]. Additionally, the aciditymay be caused by the acceleration of the leaching of basic cations from the soil by rainfall [20]. A wide range of strongly acidic soils or acid sulphate soils occur in Brunei Darussalam due to the organic-rich materials, sulphidic material and sulphuric horizons reported by [31]. This pH level is critical and it has negative influence on the production potential of the crop because the acceptable pH level for most of the crops is in the range of 5.5-6.5. At low soil pH, microbial activity declines and nutrients such as phosphorus, calcium, magnesium and molybdenum become less available. Furthermore, these extremely acidic conditions favour the mobility and availability of heavy metals in the soil [17, 73]. The lower pH of the Wasan and Limau Manis (3.6) compared with that of the Selapon (3.9) and Lot Senkaung (4.2) may partially due to the leaching of coarser texture of the soils and exchangeable cations. In addition, an agricultural area of Wasan and Limau Manis are more developed and with higher usage of inorganic fertilizer which might lead to nitrification and acidification processes [46]. Moreover, sulphidic and sulphuric mineral soils in Brunei Muara district (Wasan and Limau Manis) attributes affect the soil pH.

The mean value of the EC was 0.072 dS/m which indicates non-saline conditions according to [60]. With the range of 0.068 – 0.074 dS/m among the four study areas, these findings indicate thatthere is no major difference in cumulative salt accumulation among the study areas. Non-saline conditions in Brunei Darussalam agricultural areas may be due to continuous rainfall with higher intensity than evaporation rate [43]. In this study, the average OM content was high (8.7%) according to [18]. Among the areas, the range of organic matter differs which may be depend on the soil types, texture, topographic setting and climate conditions such as rainfall, temperature and humidity affect the rate of OM decomposition. Lot Senkuang has the lowest amount of OM (5.7%) which may be the effect of sandy texture, steep slopes and erosion hazard.

Table 3. *Interpretation of the soil fertility condition.*

Test name	Unit	Very Low	Low	Moderate	High	Very High
Phosphorus (Bray P1)	mg/kg		<20	20-40	40-100	>100
CEC	Cmol (c)/kg	<6	6-12	1-25	25-40	>40
Extractable calcium	Cmol (c)/kg	-	<5	5-10	>10	-
Exchangeable magnesium	Cmol (c)/kg	<0.3	0.3-1	1-3	3-8	>8
Extractable sodium	Cmol (c)/kg	0-0.1	0.1-0.3	0.3-0.7	0.7-2	>2
Exchangeable potassium	Cmol (c)/kg	0-0.2	0.2-0.3	0.3-0.7	0.7-2	>2

Source: [62]

Table 4. *Statistical analysis of toxic metals in soil.*

Heavy metals (mg/kg)	Wasan (n = 21)	Limau Manis (n = 21)	Selapon (n = 21)	Lot Senkuang (n = 15)	All locations pooled	Agricultural soil quality guidelines [16]	[24]	[79]
Al	9906.1 (286.9)	10123.2 (558.6)	9192.3 (192.1)	12847.9 (538.7)	10338.1 (247.9)	NA	NA	NA
Fe	13447.9 (456.9)	9748.7 (855.4)	22598.7 (192.1)	14220.6 (1217.7)	15064.2 (655.6)	NA	NA	NA
Cu	3.9 (0.7)	12.4 (1.0)	3.4 (0.5)	17.1 (1.9)	9.1 (0.8)	63	140	30
Mn	32.6 (10.9)	16.7 (2.0)	406.1 (26.1)	25.3 (2.0)	127.5 (20.7)	NA	NA	80
Zn	32.2 (2.5)	50.0 (7.6)	3.8 (1.1)	54.7 (15.1)	34.4 (4.9)	200	NA	200
Cd	4.7 (0.3)	11.0 (0.9)	10.2 (0.3)	2.5 (1.6)	8.1 (0.5)	1.4	3.0	NA
Cr	ND	37.1 (2.4)	ND	45.5 (2.4)	38.4 (2.1)	64	150	100
Co	1.2 (0.5)	0.34 (0.28)	10.7 (0.3)	3.8 (0.3)	4.9 (0.5)	40	NA	NA
Ni	14.3 (5.5)	ND	13.3 (1.7)	7.5 (2.2)	11.7 (2.5)	45	75	NA
Pb	11.0 (0.3)	14.1 (0.6)	9.1 (0.2)	17.3 (1.0)	12.6 (0.4)	70	300	NA

ND = Not detected (below lowest detection limit Cr (0.1590) and Ni (0.0465) mg/kg; NA = Not available

* Mean values are followed by standard error in brackets.

The average value of exchangeable cations (Ca, Mg, Na and K) CEC and available Pwas low in these areas according to Table 3. A similar result was also observed by [43]. Here, humid weather accelerates mineral weathering process and strong leakage of cations responsible for depletion of exchangeable cations. No significant difference in soil exchangeable cations content was observed in any of the locations. The lowest CEC (1.4 cmol/kg) found in Lot Senkuang was dominated by sandy soils, poor organic matter and additionally high Al content in soils (Table 4) cause a low number of negative charges per unit of soil and high leaching problems. For study areas P fixation is likely to be a problem according to Table 3. Under extremely acid conditions, P fixation was expected because of Fe and Al ions, which combine with P to form insoluble compounds at low pH [37]. Among the areas, available P (9.7 mg/kg) contents of Limau Manis was a higher than the Wasan (6.3 mg/kg), Selapon (6.2 mg/kg) and Lot Senkaung (2.4 mg/kg); it was due to the decomposition of soil organic matter or organic P amendments. Furthermore, a lower content of Fe (9748.7 mg/kg) in Limau Manis soil compared to those in the areas of Wasan (13447.9 mg/kg), Selapon (22598.7 mg/kg) and Lot Senkaung (14220.6 mg/kg) according to Table 4 indicates a lower fixation of P in Limau Manis than the other areas.

3.2. Heavy Metals Status

The total heavy metals content of the samples of the areas are presented in Table 4. The Fe content was found to be the most predominant metal amongst all the metals in this study, followed by Al. All the trace metals have mean values below the safety limit of the [80, 16, 24] guideline except for Mn and Cd. Reasons attributed are the degradation of soil health as evidenced by the increase in acidity and concentration of Fe, Al, Mn and Cd to toxic levels. Soil metal content was mainly contributed by parent materials, topography, acidic condition and additionally iron oxides and hydroxides accumulate trace elements through the adsorption mechanism [58, 84, 54, 42]. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction [4, 71].

Large quantityof Cd was found in Limau Manis (11.0 mg/kg) and Selapon (10.2 mg/kg); it was mainly from the P content and manganese oxide of soil. According to Table 3 and 4, Limau Manis and Selapon have the highest amount of P (9.7 mg/kg) and manganese (406.1 mg/kg) among the study. The same findings were reported by [7, 13, 14] Cd is associated with manganese-oxide in soil andtriple superphosphate (TSP) fertilizer was primary supply of Cd toward soils as it has 0.1-170 mg/kg of Cd. We observed that TSP used by Brunei Darussalam carried 2.87 mg/kg of Cd. Application of fertilizer influence Cd content in soil and fertilizers affect Cd movement of plant roots and Cd uptake of plant [78]. Wasan and Selapon areas have more Ni concentration than other areas; and sources of Ni could be from the weathering of minerals which contributes to the increased mobilization of Ni [61].

According to Table 4, Brunei soils have found very high concentration of Fe (average value 15064.2 mg/kg). This was attributed to predominantly iron pyrite [29] and leaching of iron from soil at low pH conditions. Furthermore, the equatorial climatic condition of Brunei Darussalam which favors weathering process and origin of parent materials may be high level of Fe concentration in the soils. A higher content of Fe (22598.7 mg/kg) was found in the Selapon as compared to the other areas; it is the different of soil taxonomy in the study areas. Large amounts of Fe in Alfisols resulting in iron- bearing minerals [67] and it is supported to the present study which Selapon areas were fallen the Alfisols order of soil classification [32].

A higher content of Mn (406.1 mg/kg) and Co (10.7 mg/kg) in Selapon soil compared to Wasan, Limau Manis and Lot Senkaung soil and may be due to the prevalence of soil type and dependent upon mobilization and immobilization processes. Furthermore, the presence of very high values of Mn in Selapon can be attributed to the presence of Mn-oxides concentrations under anaerobic conditions such as flooding or poor drainage of soil [10]. The high amount of soil Mn in the study area was attributed to the application of various types of pesticides and mineral fertilizers for increasing plant growth and yields [42]. While the high amount of Co in Selapon may be due to the prolonged waterlooging, the poorly drained type, sulfuric and sulfidic soils [32]. It is accordance with the findings of ATSDR, 2004; Co is mainly as sulphides with Co_3S_4, $CuCo_2S_4$ being the most common Co minerals.

Most of toxic metals such as Al (12847.9 mg/kg), Cu (17.1 mg/kg), Zn (54.7 mg/kg), Cr (45.5 mg/kg) and Pb (17.3 mg/kg) were observed at highest solubility in Lot Senkuang compared to Wasan, Limau Manis and Selapon. The amount of metals in soil relied on the soil type; Lot Senkuang soils are organic or peat soils under the Histosols according to [32]. Similarly, [82] reported that peat soils accumulate heavy metals in a much higher amount. Noteworthy, Al has been classified as a contaminant of potential concern only in soils with a pH of 5.5 or less [68]. This may be the reason why no standards have been set for Al in soil (Table 5). The reason for the high Al concentration in all the study areas is because Al is very mobile due to characteristic soil acidic conditions (pH 3.6-4.2) which promote aluminosilicate weathering and Al-hydroxide dissolution and thus Al solubilisation and transport [26]. This result was shown that Al toxicity isamain constraint of plant growth in these areas.

High concentrations of metals could have a potentially negative impact on plants, microorganisms and animals [83]. The concentrations of heavy metals in soil and their impact on ecosystems can be influenced by many factors such as parent material, climate, topography, pH, OM, CEC, clay content, soil texture and anthropogenic activities [35, 55]. The correlations between HMs concentrations and soil properties are shown in Table 5. There was significantly positive correlation between the HM contents (Al, Fe, Cu, Mn, Cd, Cr, Co, Pb) and soil pH values of range from 3.0 to 4.6 except for Zn and Ni. This finding was in accordance with [38, 33]'s observation, where soil acidity influence of mobility and bioavailability HMs in the soil. When pH falls below 5, metals mobility is enhanced as a result of the increased proton concentration [59]. It is relevant with our results that extremely strong acidic conditions (pH value- 3 to 4.6) in the Brunei Soils increased metal availability (Table 5). Similar results reported by [66, 2]; nearly all the metals in higher soil acidic conditions are activated which promote metal uptake of the plant.

Table 5. *Correlation of heavy metals versus chemical properties.*

Parameter	Al	Fe	Cu	Mn	Zn	Cd	Cr	Co	Ni	Pb
pH	.231*	.296**	.304**	.274*	-.150	.067	.047	.465**	-.467**	.141
OM	-.218	-.207	.025	-.103	.278	.244*	-.232	-.061	.233	-.104
CEC	-.228*	-.264*	-.012	-.166	.282	.225	-.210	-.170	.344*	-.089
Available P	-.186	-.241*	-.165	-.041	.239	.345**	-.241	-.086	.158	-.097
Al	1	.079	.603**	-.263*	.599**	-.387**	.840**	-.322**	-.172	.704**
Fe	.079	1	-.384**	.793**	-.432**	-.063	.793**	.829**	-.149	-.418**
Cu	.603**	-.384**	1	-.474**	.684**	-.203	.562**	-.336**	-.106	.911**
Mn	-.263*	.793**	-.474**	1	-.595**	.316**	.762**	.929**	-.122	-.517**
Zn	.599**	-.432**	.684**	-.595**	1	-.297*	.325	-.630**	.395	.732**
Cd	-.387**	-.063	-.203	.316**	-.297*	1	-.733*	.591**	-.204	-.249*
Cr	.840**	.793**	.562**	.762**	.325	-.733**	1	.448	-	.791**
Co	-.322**	.829**	-.336**	.929**	-.630**	.591**	.448	1	-.209	-.412**
Ni	-.172	-.149	-.106	-.122	.395	-.204	-	-.216	1	-.017
Pb	.704**	-.418**	.911**	-.517**	.732**	-.249*	.791**	-.412**	-.017	1

**; *Correlation is significant at the 0.01 and 0.05 level (2-tailed)

High organic matter (OM) content is favorable for the sorption of HMs in soils. The significant positive correlations between Cd and OM obtained in this study (Table 5); it showed that organic matter plays a fundamental role of Cd contents in soil. According to [74, 50], OM is also involved in supply inorganic chemicals to the soil solution, which may serve as chelates and increase metal availability to plants. However, the Al, Fe, Mn, Cr, Co and Pb contents were negatively correlated with OM (Table 5). Similar results were observed by [11, 19, 47] also reported that OM-bound Mn reaches the rhizosphere, the oxidized soil conditions possibly mineralize the OM, which transforms Mn into less available forms.

The results of the correlation analysis (Table 5) indicate that Cd, Zn and Ni were positively correlated with CEC and available P. It is agreed with [40, 64] also found that the total content of micronutrients increased with an increase in CEC and phosphate fertilizers are the main sourceof Cd contaminant as well. Other metals (Al, Fe, Cu, Mn, Cr, Co and Pb) were negatively associated with CEC and available P. This is great of concern as increased levels of these metals in the environment consequently result in the decreased mineral element composition of the soil. It is expected that available P has negative correlation with Al and Fe because of fixation of Al and Fe. An increasing copper content of soils reduced the amount of plant available P in soil [3].

Significant and/or positive correlations were also found between most of the trace elements (Table 5), suggesting that they may be mainly associated with the mineral phase in soils. The significant and/or positive correlation is seen between Al vs. Fe, Cu, Zn, Cr, Pb. The significant and/or positive correlation is seen between Fe vs. Al, Mn, Co and Cr (Table 5). The content of Fe had a significant positive correlation with Mn ($r=.793$, $P < 0.01$) as Fe and Mn are the most abundant metals in the lithosphere, and they generally occur as Fe-Mn oxides and hydroxides, which play an important role in the precipitation or solubility of some heavy metals in soils [39]. The facts that trace element concentrations correlated better with Fe and Al suggests that the elements might have co-precipitated with Fe-Al oxides during the formation in soils [65]. Hernandez et al., 2003 and Li et al., 2014 reported that levels of soil HMs are controlled by concentrations of Al and Fe content [34, 45]. Similarly, the significant positive correlation between Pb and Zn in our study can be explained because Pb was found to coexist with Zn in the internal growth of a crystal lattice [1].

4. Conclusion

The findings from the study have broadened our knowledge on the heavy metals (HMs) content and their possible sources in the agricultural soils, a representative area of the Brunei Darussalam. Based on the safety limits of HMs concentrations in soil, the paddy fields showed high level of Al, Fe, Cd and Mn. This may be due to the parent material, heavy rainfall and/or poor drainage conditions, extremely acidic and high organic matter of the study areas. These factors cause crop failure and decreased production as evidenced by low rice yield (1.7 tons/ha) in Brunei Darussalam compared to other rice producing countries. The study areas have a low fertility status because of extremely acidic condition, low level of P, poor in basic cations and CEC but rich in organic matter content. Soil acidity is one of the most important constraints; when pH drops below 4.5, it is difficult to produce food crops. Soil acidification and the enrichment of toxic elements are important factors affecting ecological safety. Phosphorus is the most deficient nutrient as a result of the high P fixing capacity due to presence of Fe and Al. This may provide basic information for soil fertility management based on the soil properties in the paddy fields.

Therefore, this study suggests promoting natural and artificial methods that minimize the soil acidity and reduce Al, Fe, Cd and Mn toxicity levels. More studies are neededin order to monitor the relationship between soil properties and HMs content, especially Al, Fe, Cd and Mn.

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