Assessment of Multi-Nutrients and Heavy Metals in Inorganic Fertilizers Widely Used by Indonesian Farmers Using NAA

Sri Murniasih[1,2], Sri Juari Santosa[1*], and Roto Roto[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia*

[2]*Center for Science and Accelerator Technology, The National Nuclear Energy Agency, Jl. Babarsari No. 21, Yogyakarta 55281, Indonesia*

* ***Corresponding author:***

tel: +62-8164262984
email: sjuari@ugm.ac.id

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Abstract: *This research aims to determine the concentration of multi-nutrients and heavy metals and investigate the correlation among them in the seven inorganic fertilizers in Indonesia. Sample analysis was carried out using the NAA method. The highest concentrations of macro-nutrients were K (36.54 %) and Cl (18.09%) found in the KCl sample, while Ca (23.01%) was observed in the TSP sample. In the case of micro-nutrients, the highest concentrations of Se (0.36 mg/kg), Ti (597 mg/kg), Br (1.84%), and Ni (2.46 mg/kg) detected in the NPK sample. Meanwhile, the highest concentrations of Co (19.57 mg/kg) and Na (1.40%) were measured in the ZA sample, while Mg, with the highest concentration of 1.78%, was found in the KMgS sample. The micro-nutrients with the highest concentration detected in the TSP sample were Cr (45.96 mg/kg), Zn (342.6 mg/kg), and Mn (1331 mg/kg). Non-essential elements such as U, V, La, Sb, Sm, Th, Hf, Sr, Cs, Tb, Sc, Rb, Ta, and Eu were also detected in the fertilizer samples with the highest concentrations in the TSP sample. Statistical tests of multi-nutrient and heavy metals concentrations indicated that multi-nutrient and heavy metals in fertilizers are complex.*

Keywords: *inorganic fertilizer; multi-nutrients; heavy metals; essential elements; non-essential elements*

■ INTRODUCTION

Plants require multi-nutrients to grow and develop properly [1]. The presence of multi-nutrients is naturally available in nature, or they can be added to increase soil fertility. The use of fertilizers as one of the efforts to increase soil fertility is commonly carried out by the community [2]. Thus, natural or synthetic fertilizers are chemical compounds used to provide additional amounts of multi-nutrients to the soil to stimulate the growth of plants [3].

The multi-nutrients needed by plants are categorized into three classes, namely macro, micro and trace elements. Macro-nutrient elements include calcium, phosphorus, sulfur, and chloride, while microelements include iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium, and boron. Macro elements are needed in amounts greater than 1000 mg/kg, and microelements are needed in amounts 10 – <1000 mg/kg, and trace elements are needed in amounts less than 10 mg/kg. Some micro-nutrients can be categorized as heavy metals for plants if their presence exceeds their needs [4-6].

Several micro and trace elements occur naturally in soil. Their presence is caused by the weathering of the parent material [7]. The use of fertilizer is one of the anthropogenic processes that can affect the amount of micro and trace elements in the soil. The high concentration of micro and trace elements causes environmental risks because they are accumulated in soil, plants, animals, and water. Furthermore, they can also reduce soil fertility [8]. A study by Wang et al.

showed that long-term use of organic and inorganic fertilizers caused a significant increase in the concentration of Cu, Zn, Pb, and Cd in the soil [9]. The use of phosphate mineral fertilizers has been proven to increase the content of trace elements in agricultural soil. There was a correlation between the increasing concentration of Cd, U, V, Sb, Cr, As, and Ni with the P concentration. This correlation indicates that these trace elements come from phosphate rocks used as raw material for mineral phosphate fertilizers [10]. The continuous utilization of inorganic fertilizers for 25 years has influenced the accumulation of Pb, Cd, Ni, Co, and Cr elements in agricultural soil [11]. The use of Zn fertilizers for eight years has increased the concentration of Zn in soil and wheat plants grown in this soil [12].

Additionally, the use of phosphate fertilizers for ten years continuously has increased 83.31% of Cd concentration in agricultural soil [13]. Qian et al. reported that synthetic fertilizers affected the concentrations of Fe, Co, Ni, Se, Rh, Eu, Pr, Tl, and Pt in the soil. In contrast, the use of pesticides affected the concentrations of Al, Ni, and Co in rice plants [14]. Extensive, excessive, and continuous use of fertilizers can lead to a more significant accumulation of heavy metals in the soil. Heavy metals originating from fertilizers can stay in the soil for a certain period and can be transferred and accumulated in plants [9,12,15].

Naturally, heavy metals can be found in the earth's crust. However, most cases of environmental heavy metal contamination are caused by anthropogenic activities such as industrial and agricultural activities that use fertilizers [16-17]. The accumulation of heavy metals and metalloids produced from natural and anthropogenic sources has indirectly become a public health problem [12-13]. The heavy metals in the soil that cause this accumulation can be transported and accumulated in the plants that grow on it. This problem increases the potential health and food safety risks and threatens human health safety [18-19]. Accordingly, this study was conducted to determine the concentration of multi-nutrient elements and heavy metals and investigate the correlation and relationship in commercial fertilizers used by farmers in Indonesia.

■ EXPERIMENTAL SECTION

Sample Collection

Seven inorganic fertilizers that are commonly used and commercially available were purchased at a local shop in Brebes District, Central Java–Indonesia, in February 2020. The fertilizer samples consist of NPK 15-15-15, Urea, Kamas (KMgS 30-11-17), Ammonium sulfate (ZA), Trubus (NPK+TE 35-7-8), Potassium chloride (KCl), and Triple superphosphate (TSP). All samples were obtained in small packages (500–1000 g), except for Trubus (NPK+TE 35-7-8) sample that was purchased in 500 mL bottle packages. The collected samples were in the granule form, except for the Trubus sample, liquid form.

Sample Preparation

The granules samples were refined using a Fritsch Pulverisette 5/2 Classic Grinding Planetary ball mill with 200 rpm. Then the sample was sieved to pass 200 mesh [20]. Short and long irradiation samples were weighed to 200 mg using a Sartorius BSA 42245-CW digital scale and inserted into EP 338 polyethylene vials to be later identified [21-22]. One milliliter of the liquid fertilizer sample was taken using an Eppendorf Research 1000 µL micropipette and inserted into EP 338 polyethylene vials and identified.

Sample Analysis

Sample analysis was performed using the Neutron Activation Analysis (NAA) method. Samples were irradiated using the Kartini reactor in the Center for Science and Accelerator Technology–National Nuclear Energy Agency with a thermal neutron flux of 2×10^{11} $n.s^{-1}.cm^{-1}$. Elemental concentrations based on short-lived radionuclides, i.e., Cl, V, Mg, Ti, Al, Ca, and Mn, were determined by irradiation for three minutes in a pneumatic facility. In this process, one irradiation capsule contained one sample and was irradiated. After 5 and 15 min decays, the samples were measured for 5 min consecutively. The long-lived isotopes, namely Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zn, Sb, Cs, La, Sm, Eu, Tb, Hf, Ta, Th, and U were irradiated at the Lazy Susan facility of the Kartini reactor for 20 h. In this process, one irradiation capsule consisted of six samples, one standard, one blank vial, and one SRM. Specifically, the irradiation of the Ni element was carried out for 2 h in the Lazy Susan facility and was measured after a cooling time of 2 h. The irradiated samples were wrapped in new plastic clips to avoid contamination of equipment and the addition of other elements to the sample being analyzed. Samples were measured twice after 3 and 15 days. The samples were measured using a gamma spectrometer equipped with an HPGe detector with an efficiency of 35% and Genie 2000 software. The measurements of Na, As, Br, K, Sm, La, and U isotopes were carried out for 20 min, while Sc, Cr, Fe, Co, Se, Rb, Sr, Zn, Sb, Cs, Eu, Tb, Hf, Ta, Th, and Zn isotopes were measured for 2 h. The measurement of the Ni element was conducted for 30 min after samples were irradiated for 2 h and cooled for 2 h. The sample measurement distances from the end-cap detector for short, medium, and long half-lives were 10, 4, and 2 cm, respectively. The distance setting of the sample measurement aims to consider dead time less than 20% [23], 10%, and 5% for short, medium, and long-lived elements, respectively [22].

Analytical Method Validation

The analytical performance of the method was checked by analysis of the certified reference materials NIST SRM 695— Trace Elements in Multi-Nutrient Fertilizer. NIST SRM 695 was chosen to determine the method's precision and accuracy because the reference material contained the certificate value of all analyzed elements. The relative error, expressed as the percentage of the standard deviation of the mean of three determinations [24], was below 10% for all elements. The Relative Standard Deviation (RSD) was given as the percentage deviation from the certified value material [25]. The value of RSD varied between 1 and 10%.

Statistical Analysis

The correlations among multi-nutrients and heavy metals in the fertilizer samples analyzed using NAA were determined using correlation coefficients analysis in the SPSS version 22 for Windows 10. The correlation coefficient values (r), which measured the strength of the linear and inter-relationship between each parameter that ranged between −1 and +1, were determined. A correlation was assumed to be statistically significant at $\rho<0.05$ and $\rho< 0.01$. In this study, the values of $\rho<0.05$ and $p<0.01$ indicate a significant and very significant correlation for one to other variables, respectively. The probability of incorrectly rejecting a true null hypothesis (H_0) is almost 23% for $\rho<0.05$ and 7% for $\rho<0.01$. Because of better precision, the two-tailed test was conducted assuming that these variables were higher than average mean or lower than average mean [26-28].

■ RESULTS AND DISCUSSION

Quality control is necessary to ensure the validity of the analysis results. A certified reference material, NIST SRM 695, was employed to validate the analytical method used. The relative errors and relative standard deviations obtained from 3 repetitions of the SRM analysis are shown in Table 1. As shown from the value of the relative error, the Ca, Fe, Mn, Na, Co, and V elements were smaller than 5%, while that of Mg, K, Zn, Al, As, Cr, Cu, Hg, Ni, and Se elements was below 10%. Since the deviation from the certificate value was less than 10% for all elements, the NAA method used in this case had good precision. This finding means that the NAA method can be used for analyzing samples and providing a valid value [24-25]. Furthermore, Table 1 also showed that the experimental values for all tested elements did not significantly differ from the certified values, indicating that the NAA used in this experiment was highly accurate.

The seven inorganic fertilizers widely used by Indonesian farmers were known to contain macro, micro, and trace nutrients and heavy metals (Table 2). The macro-nutrients detected were K, Mg, Ca, and Cl. The concentration of K (36.54%) and Cl (18.09%) was the highest in the KCl sample. The highest concentration of Mg (1.78%) was detected in the KMgS sample, while that of Ca (23.01%) was detected in the TSP sample. High concentrations of macro-nutrients in fertilizers are needed to support plant growth. The average concentration of K, Ca, Mg, and Cl elements necessarily needed for plants are 1, 0.5, 0.2, and 0.01%, respectively [29].

Table 1. Analytical results of the certified reference material, NIST SRM 695 (Trace Elements in Multi-Nutrient Fertilizer) by NAA method

Elements	Certified value	Experimental value	Relative error (%)	RSD (%)
Ca	2.26±0.04%	2.201±0.069%	2.61	3.13
Fe	3.99±0.08%	4.09±0.102%	2.51	2.49
Mg	1.79±0.05%	1.89±0.064%	5.59	3.52
Mn	0.305±0.005%	0.296±0.016%	2.95	5.41
Na	0.405±0.007%	0.389±0.022%	3.95	5.66
K	11.65±0.13%	12.298±0.512%	5.56	4.34
Zn	0.325±0.005%	0.301±0.023%	7.38	7.69
Al	0.61±0.03%	0.579±0.049%	5.08	8.46
As	200±0.2 mg/kg	215±6.12 mg/kg	7.50	2.85
Cr	244±6 mg/kg	227±8.98 mg/kg	6.97	3.96
Co	65.3±2.4 mg/kg	66.4± 1.42 mg/kg	1.68	2.15
Cu	1225±9 mg/kg	1125±43.45 mg/kg	8.16	3.86
Hg	1.955±0.036 mg/kg	2.119±0.119 mg/kg	8.39	5.89
Ni	135±2 mg/kg	124±8.43 mg/kg	8.15	6.80
V	122±3 mg/kg	116±5.93 mg/kg	4.92	5.11
Se	2.1±0.1 mg/kg	2.21±0.19 mg/kg	5.24	8.60

Table 2. Multi-nutrients and heavy metal concentrations in fertilizers widely used in Indonesia

Elements	$KMgS_{30-11-17}$	KCl	Urea	$NPK_{15-15-15}$	TSP	ZA	$NPK + TE_{35-7-8}$
Macro (%)							
K	25.53±1.57	36.54±2.41	<0.002	19.126±1.11	0.45±0.03	0.75±0.04	0.39±0.02
Mg	1.78±0.12	<0.003	<0.003	0.34±0.02	0.31±0.02	<0.003	0.09±0.008
Ca	0.31±0.2	<0.0005	<0.0005	2.59±0.19	23.01±1.92	<0.0005	1.00±0.09
Cl	1.62±0.14	18.09±1.21	0.01±0.001	7.42±0.51	<0.001	<0.001	1.39±0.01
Micro-trace (mg/kg)							
Co	0.05±0.004	0.06±0.004	0.02±0.003	1.10±0.09	4.42±0.31	19.57±1.34	0.003±0.005
Ti	<0.1	<0.1	<0.1	596.86±41.37	179.64±18.78	<0.1	226.33±20.34
Br	1934.08±18.74	5050.03±45.27	<0.01	11398.73±251.32	37.21±2.54	37.88±2.27	0.25±0.01
Na	4357.91±23.98	9468.21±98.44	4.06±0.35	3891.75±198.23	1840.69±29.56	14129.73±130.84	2910.61±120.4
Cr	0.57±0.04	0.37±0.033	0.07±0.008	14.85±1.12	45.96±3.2	51.32±3.94	0.30±0.029
Al	106.76±7.92	10.67±1.85	<5	868.16±21.73	7249.74±60.85	<5	526.93±32.48
Fe	101.89±8.24	682.21±45.11	6.76±0.45	1070.41±79.38	7691.44±52.96	47521.57±214.2	136.37±7.12
Zn	1.97±0.14	3.08±0.31	2.53±0.22	257.18±17.37	342.60±38.34	90.25±7.25	4.51±0.35
Mn	<0.1	<0.1	<0.1	332.17±21.82	1331.17±27.92	<0.1	4.71±0.33
Ni	0.03±0.005	0.07±0.009	<0.01	2.46±0.28	0.06±0.009	<0.01	<0.01
Heavy metal (mg/kg)							
As	0.05±0.007	0.08±0.009	<0.01	<0.01	37.48±2.91	2.19±0.18	<0.01
Hg	0.03±0.006	0.03±0.005	0.05±0.007	<0.01	0.17±0.02	<0.01	0.004±0.001
Trace elements non-essential (mg/kg)							
Se	<0.01	<0.01	<0.01	0.36±0.042	0.27±0.03	0.20±0.015	0.02±0.004
U	1.01±0.1	6.16±0.79	<0.01	3.00±0.27	6.92±0.55	<0.01	<0.01
V	<0.01	<0.01	<0.01	16.42±1.91	26.20±2.34	<0.01	<0.01
La	0.06±0.008	0.06±0.009	<0.01	412.82±67.88	15.70±1.37	8.48±0.91	<0.01
Sb	<0.01	<0.01	<0.01	0.34±0.023	5.84±0.48	0.17±0.02	<0.01
Sm	0.01±0.002	<0.01	<0.01	31.022±5.32	3.28±0.41	<0.01	<0.01
Th	0.03±0.002	0.03±0.002	<0.01	7.97±0.68	2.30±0.19	3.78±0.32	0.03±0.004
Hf	0.01±0.002	0.02±0.003	0.01±0.002	0.21±0.019	0.37±0.033	3.02±0.27	<0.01

Table 2. Multi-nutrients and heavy metal concentrations in fertilizers widely used in Indonesia (*Continued*)

Elements	$KMgS_{30-11-17}$	KCl	Urea	$NPK_{15-15-15}$	TSP	ZA	$NPK + TE_{35-7-8}$
Sr	60.34±5.54	<0.01	<0.01	2881.01±95.02	274.56±12.43	211.44±11.37	<0.01
Cs	0.02±0.004	0.01±0.005	<0.01	0.12±0.03	<0.01	1.65±0.21	<0.01
Tb	<0.03	<0.03	<0.03	3.92±0.41	0.46±0.05	0.35±0.05	<0.03
Sc	0.03±0.004	0.02±0.003	0.002±0.001	0.07±0.009	1.52±0.11	18.68±1.15	<0.001
Rb	29.42±2.45	139.84±9.87	<0.02	13.87±1.42	15.08±1.67	19.88±2.0	1.25±0.2
Ta	<0.1	<0.1	<0.1	0.23±0.03	0.03±0.009	0.23±0.004	<0.1
Eu	0.003±0.001	0.004±0.001	0.004±0.001	10.19±0.08	0.45±0.041	3.09±0.029	<0.001

The micro-nutrients detected in nearly all fertilizers were Co, Ti, Na, and Br. The highest concentration of Co (19.57 mg/kg) and Na (1.41%) was found in the ZA sample. The highest concentration of Se (0.36 mg/kg), Ti (597 mg/kg), and Br (1.84%) was found in the NPK samples. The titanium element is still not considered an essential micronutrient for plants. The addition of the Ti element has been proven to increase the absorption of several essential elements and improve the activity of several enzymes [30]. Leaf fertilization is the most efficient Ti supply because Ti has low mobility in the soil and deficient absorption. The use of large amounts of Ti has not been proven to impact plants negatively, but plants that have high contents of Ti have been proven to be dangerous for consumption [31]. The concentration of Co and Se in all fertilizer samples was still below the limits allowed by the Canadian standard trace metal safety guidelines, i.e., 150 and 14 mg/kg, respectively [8].

The presence of heavy metals in the soil does not always have a negative impact as long as they are within a specific concentration limit. The elements of Al, Co, Se, Na, and Si were considered functional elements to plants, although plants did not need them. They can support growth and are essential for the metabolism of certain plants, but their support depends on environmental conditions, their concentration, and the type of plant species [19].

The concentration of Hg and As heavy metals and Al, Cr, Fe, Mn, Ni, and Zn varied in the seven tested inorganic fertilizers. Among others, Al and Fe were the most dominant in all examined fertilizers. The highest concentrations of Al and Fe were detected in the TSP fertilizer. There are no safety standards set for Al and Fe in fertilizers.

Iron is an essential micronutrient for plant growth because it is a vital component for photosynthesis and respiration in plants. Iron is not readily available in neutral or alkaline soils. It makes plants become Fe deficient even though Fe is abundant in nature [32]. The addition of Fe through fertilizers is still needed since the requirement of Fe is considerably high for plants [8].

Aluminum is the most abundant metal in the earth's crust, but its availability depends on soil pH. Despite its abundance, Al has not been considered an essential element for plants. In plants and other organisms, Al may be considered either beneficial or toxic depending on its concentration and chemical form and the growing condition and species of the plant. Although there are no established guidelines for Al in fertilizers, Al can be accumulated in plant tissues and become toxic to plants. In plants, the first sign of Al accumulation is the discoloration of the roots, which causes a decrease in root permeability for water and nutrient absorption. In contrast, low concentrations of Al can stimulate plant root growth [33].

The highest concentrations of As Hg, Cr, Zn, and Mn were found in the TSP fertilizer. Their concentrations were 37.47, 0.17, 45.96, 342.6, and 1331 mg/kg, respectively. The highest concentration of Ni was 2.46 mg/kg and was detected in the NPK fertilizer. Currently, no allowable limit is set as the standard safety guidelines for Mg in fertilizers. In plants, Mn is considered an essential element for growth and reproduction. The requirement of Mn in plants is only in small amounts, but it plays an important role in growth. The use of Mn fertilizers is a way to overcome the shortage of Mn availability. The availability of Mn in soil drastically decreases at high pH value because the soluble Mn

(Mn^{2+}) is rapidly converted to insoluble Mn oxide, which is not needed by plants, especially in alkaline sandy soils [29]. In addition, spraying Mn on leaves is only effective for a limited period because Mn moves very little within the plant [31]. On the other hand, Mn toxicity can occur in poor drainage and highly acidic soils [20]. Indicators of Mn toxicity in plants can be observed by decreasing growth rate, chlorosis of the leaves, and the presence of necrotic leaf spots [32].

The detected concentrations of As, Hg, Cr, Zn, and Ni heavy metals in all samples of fertilizers were still below the allowable limits set in the Canadian standard trace metal safety guidelines, which are 75, 5, 1060, 1868, and 180 mg/kg, respectively [34]. In this study, non-essential elements were also detected in the inorganic fertilizers, namely U, V, La, Sb, Sm, Th, Hf, Sr, Cs, Tb, Sc, Rb, Ta, and Eu. The highest content of V was 26.2 mg/kg and was detected in the TSP fertilizer. This value is still below the allowable limit set in the Canadian standard trace metal safety guidelines, 656 mg/kg [34]. The content of U, La, Sb, Sm, Th, Hf, Sr, Cs, Tb, Sc, Rb, Ta, and Eu elements can be closely related to the raw material content of the mineral phosphate fertilizers [7]. It was proven that the content of U, V, La, Sb, Sm, Th, Hf, Sr, Cs, Tb, Sc, Rb, Ta, and Eu elements were dominantly detected in NPK and TSP fertilizers, where both fertilizers include mineral phosphate fertilizers.

The concentration of trace elements and heavy metals in fertilizers was strongly influenced by the main raw material used to make the fertilizers. Phosphorus, nitrogen, and potassium fertilizers contain more trace elements and heavy metals. In this study, fertilizers made from phosphorus, namely TSP with 46% phosphorus composition, contained more trace elements than the NPK fertilizer (15% of P) and NPK+TE fertilizer (7% of P), as shown in Table 2. This result follows the result of Molina et al. in which the concentration of trace elements in phosphorus fertilizer > K fertilizer > N fertilizer [35]. Based on the research by Gambuś and Wieczorek, it was observed that the concentration of phosphorus provided a higher correlation coefficient ($r=0.764$) to Cd, Cr, and Zn than that of N ($r=0.564$) and K ($r=-0.135$) [36]. This was consistent with the current study, where the concentration of trace elements and heavy metals in the NPK fertilizer (N=15%, P=15% and K=15%) were higher than that in NPK+TE (N=35%, P=7% and K=8%). Nitrogen concentration in the NPK+TE fertilizer was twice higher than that in the NPK fertilizer, but phosphorus concentration in the NPK fertilizer was twice higher than that in the NPK+TE fertilizer.

Table 3 compares this study and other studies related to the concentration of multi-nutrients and heavy metals in fertilizer samples. The concentrations of Cr and Zn in the Indonesian urea fertilizers were not significantly different from those in Brunei Darussalam [8]. Still, they were much lower than those found in China [37], Iran [38], and Nigeria [39]. The concentrations of As, Hg, Cr, Al, Fe, Zn, and Ni in the Indonesian KCl fertilizer were not much different from those found in KCl fertilizers from China [40-41], Chile [35], Iran [38], and Nigeria [39]. The concentrations of Cr, Fe, and Mn elements in the Indonesian NPK fertilizer were similar to those in the Iran NPK fertilizer [38] but lower than those in Brunei Darussalam [8] and Lebanon [42]. The concentrations of Zn and Ca elements in NPK fertilizers in Indonesia were lower than in Lebanon [42]. The concentrations of As, Hg, Fe, and Mn in Indonesian TSP fertilizers were higher than those found in TSP fertilizers in Chile [35,43], Iran [43], Lebanon [42], Europe [10], and Nigeria [39]. The concentration of the Ca element in the Indonesian TSP fertilizer was much lower than that in Lebanon [42] and Europe [10]. Meanwhile, the concentrations of Ni and V elements in the Indonesian TSP fertilizer were much lower than those in Iran [38] and Europe [10]. The concentration of the Co element in the Indonesian TSP fertilizer was lower than that in Chile [35] and Europe [10] but lower than that in Iran [38]. The concentrations of U, K, and Mg in the Indonesian TSP fertilizer were much lower than those in Europe [10]. Meanwhile, the concentrations of Al, Na, and Sb in the Indonesian TSP fertilizer were higher than those in Europe [10]. The concentrations of As, Cr, Zn, and Co in the ZA fertilizer circulated in Indonesia were higher than those in ZA fertilizers found in China [37] and Iran [38]. Overall, the concentrations of Hg, Cr, Zn, and Ni elements in the

Table 3. Concentration of multi-nutrients and heavy metals in inorganic fertilizer samples used Indonesia farmers in comparison with results other studies

elements	Urea (mg/kg)					KCl (mg/kg)						$NPK_{15-15-15}$ (mg/kg)			
	This study	Nigeria [39]	Brunei Darussalam [8]	China [37]	Iran [38]	This study	China [41]	China [40]	Poland [36]	Iran [38]	Chile [35]	This study	Iran [38]	Brunei Darussalam [8]	Lebanon [42]
As	ND	0.0013	NA	0.0106	NA	0.08	NA	0.19060	NA	NA	12.1	ND	NA	NA	NA
Hg	0.05	NA	NA	9E-05	NA	0.03	NA	0.01004	0.011	NA	NA	ND	NA	NA	NA
Cr	0.07	NA	0.04	1.1677	7.6	0.37	NA	0.00	0.29	9.7	82.3	14.85	12.3	23.1	NA
Al	ND	NA	ND	0.0716	NA	10.67	3.83	NA	NA	NA	NA	868.16	NA	2916	NA
Fe	6.76	NA	ND	NA	3846	682.21	500.83	NA	NA	1265	8515	1070.41	1446	1987	1700
Zn	2.53	3.90	1.10	0.0645	51.3	3.08	0.21244	NA	45	1	63.5	257.18	387	NA	541
Mn	ND	NA	0.001	NA	119	ND	5.44	NA	NA	15	142	332.17	371	85.2	NA
Ni	ND	5.87	0.48	0.1886	12.7	0.07	0.06554	0.06554	0.55	7.9	4.9	2.46	8.5	4.5	NA
V	ND	1.53	NA	NA	NA	ND	NA	NA	NA	NA	47	16.42	NA	NA	NA
Co	0.02	NA	ND	NA	1.5	0.06	0.01312	NA	NA	7.2	2.8	1.10	5.2	7.3	NA
Mg	ND	NA	NA	NA	NA	ND	50.51	NA	NA	NA	NA	0.34	NA	NA	NA
Ca	ND	NA	NA	NA	NA	ND	1309.48	NA	NA	NA	NA	2.59	NA	NA	9200
Se	ND	NA	NA	NA	NA	ND	0.02325	NA	NA	NA	NA	0.36	NA	NA	NA
Na	9468.21	NA	NA	NA	NA	4357.91	25095.89	NA	NA	NA	NA	4.06	NA	NA	NA
Sb	ND	NA	NA	NA	NA	ND	NA	0.00297	NA	NA	NA	0.34	NA	NA	NA
Ti	ND	NA	NA	0.0054	NA	ND	NA	NA	NA	NA	NA	596.86	NA	NA	NA
K	ND	NA	NA	NA	NA	365400	NA	NA	NA	NA	NA	191260	NA	NA	NA
U	ND	NA	NA	NA	NA	6.16	NA	NA	NA	NA	NA	3	NA	NA	NA

elements	TSP (mg/kg)						ZA (mg/kg)			$KMgS_{30-11-17}$ (mg/kg)		$NPK+TE_{35-7-8}$ (mg/kg)	
	This study	Chile [35,43]	Nigeria [39]	Iran [38]	Lebanon [42]	Europe [10]	This study	China [37]	Iran [38]	This study	Poland [36]	This study	Poland [36]
As	37.48	17.9	0.0012	NA	NA	5.5	2.19	0.04254	NA	0.05	NA	ND	NA
Hg	0.17	NA	NA	NA	NA	NA	ND	0.0272	NA	0.03	0.446	0.0037	0.023
Cr	45.96	633	NA	110	NA	70	51.32	2.53927	13.4	0.57	475.4	0.30	0.35
Al	7249.74	NA	NA	NA	NA	1591	ND	1.34513	NA	106.76	NA	526.93	NA
Fe	7691.44	6003	NA	3092	1400	2321	47521.57	NA	926	101.89	NA	136.37	NA
Zn	342.60	600	15.91	178	239	251	90.25	0.27079	2.2	1.97	600	4.51	26
Mn	1331.17	67.7	NA	316	NA	227	ND	NA	13	ND	NA	4.71	NA
Ni	0.06	10.6	5.26	29.7	NA	16	ND	0.28726	7.7	0.03	460	ND	0.78
V	26.20	430	1.92	NA	NA	62	ND	NA	NA	ND	NA	ND	NA
Co	4.42	2.5	NA	7.4	NA	1.3	19.57	NA	3.1	0.05	NA	0.00	NA
Mg	0.31	NA	NA	NA	NA	7100	ND	NA	NA	1.78	NA	0.09	NA
Ca	23.01	NA	NA	NA	149300	57000	ND	NA	NA	0.31	NA	1.00	NA
Se	0.27	NA	NA	NA	NA	NA	0.20	NA	NA	ND	NA	0.02	NA
Na	6891.75	NA	NA	NA	NA	3800	1840.69	NA	NA	ND	NA	14129.73	NA
Sb	5.84	NA	NA	NA	NA	0.52	0.17	NA	NA	ND	NA	ND	NA
Ti	179.64	NA	NA	NA	NA	NA	ND	0.03512	NA	ND	NA	226.33	NA
K	4500	NA	NA	NA	NA	92000	7500	NA	NA	255300	NA	3900	NA
U	6.92	NA	NA	NA	NA	41	ND	NA	NA	1.01	NA	ND	NA

ND: no detected; NA: not available

Indonesian KMgS and NPK+TE fertilizers were much lower than those found in similar fertilizers distributed in Poland [36].

The correlation between multi-nutrients and heavy metals was tested using a correlation coefficient matrix. The correlation of two elements with a high positive or negative correlation coefficient (r close to +1 or −1) indicates that these elements were bound to each other in a fertilizer. This correlation means that the change of concentration of one element will be accompanied by the change of concentration of the second element proportionally [8].

According to Table 4, the correlation coefficient matrix for elements in the urea fertilizer sample with a confidence level value of less than 0.05 (ρ<0.05) was r=0.816 for Hg-Cl and r=0.792 for Hf-Cr. Both had a significant positive correlation, while Na-Cl had a significant negative correlation r=-0.835. In the confidence level ρ<0.01, Co-Cr and Co-Hf had a very significant positive correlation of 0.939 and 0.882, respectively, while Eu-Sc had a very significant negative correlation r=-0.979. This indication shows that Co, Cr, and Hf in urea fertilizer samples have a positive correlation, where Co affects the presence of Cr and Hf. Meanwhile, the presence of Cl was positively correlated with Hg, but it was negatively correlated to Na.

Almost all elements of multi-nutrients and heavy metals in the ZA fertilizer sample did not provide significant correlation coefficients, except Th-Hg and Sc-Na. A perfect positive correlation (r=1.000) with ρ<0.01 was found for Th-Hg, while Sc-Na had a positive correlation coefficient (r=0.755) with ρ<0.05, as shown in Table 5.

The correlation coefficients of elements in NPK 35-7-8 fertilizers are given in Table 6 in which some of them show significant value with confidence level ρ<0.05. Elements with ρ<0.05 that have positive correlation coefficients were Na-Cl (r=0.873), La-Na (r=0.763), and Co-Br (r=0.803), while those with negative correlation coefficients were Th-Mg (r=-0.779), Th-Ca (r=-0.821), Rb-Se (r=-0.761), Rb-Hg (r=-0.780), Fe-Cl (r=-0.798), Fe-Mn (r=-0.831), and Fe-Na (r=-0.765). The positive significant correlation coefficients with ρ<0.05 were found for elements in the KCl fertilizer (Table 7)

Table 4. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in urea sample

elements	Cl	Na	Hg	Cr	Hf	Sc	Fe	Zn	Co	Eu
Cl	1	**-.835***	**.816***	0.450	0.615	-0.248	0.266	0.719	0.527	0.221
Na		1	-0.713	-0.190	-0.471	0.102	-0.641	-0.619	-0.318	-0.007
Hg			1	-0.007	0.189	-0.040	0.183	0.346	0.162	0.059
Cr				1	**.792***	-0.383	-0.201	0.645	**.939****	0.316
Hf					1	-0.143	0.317	0.695	**.882****	0.113
Sc						1	0.016	0.140	-0.172	**-.979****
Fe							1	0.090	-0.060	-0.065
Zn								1	0.691	-0.229
Co									1	0.114
Eu										1

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

Table 5. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in ZA sample

elements	Na	Hg	Th	Cr	Hf	Sc	Fe	Zn	Co	Eu
Na	1	0.208	0.212	-0.474	0.168	**.755***	-0.092	0.421	-0.365	0.085
Hg		1	**1.000****	-0.570	0.457	0.083	-0.455	-0.306	0.132	0.165
Th			1	-0.570	0.460	0.081	-0.463	-0.299	0.124	0.170
Cr				1	0.060	-0.279	-0.035	0.179	-0.318	0.070
Hf					1	-0.076	0.011	0.090	0.017	0.328
Sc						1	-0.063	-0.118	-0.597	0.496
Fe							1	-0.087	0.556	-0.158
Zn								1	-0.097	-0.553
Co									1	-0.619
Eu										1

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

Table 6. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in NPK_{35-7-8} sample

elements	Ti	Mg	Cl	Al	Mn	Ca	Br	Na	K
Ti	1	-0.053	0.585	0.187	0.297	-0.517	-0.495	0.553	-0.221
Mg		1	-0.287	-0.307	0.312	0.423	0.652	-0.260	-0.443
Cl			1	0.251	0.459	0.018	-0.106	**.873***	0.200
Al				1	-0.543	-0.490	0.000	0.147	-0.420
Mn					1	0.627	0.035	0.315	0.502
Ca						1	0.612	-0.066	0.505
Br							1	-0.009	-0.228
Na								1	0.178
K									1
La									
Se									
Hg									
Th									
Rb									
Fe									
Zn									
Co									

elements	La	Se	Hg	Th	Rb	Fe	Zn	Co
Ti	0.564	-0.048	0.155	0.172	-0.193	-0.387	-0.636	-0.534
Mg	0.319	-0.064	0.356	**-.779***	0.290	-0.024	0.237	0.293
Cl	0.658	-0.225	-0.506	-0.022	0.310	**-.798***	-0.387	-0.082
Al	0.152	-0.215	-0.433	0.546	0.368	0.247	-0.673	-0.125
Mn	0.485	-0.294	-0.121	-0.674	0.221	**-.831***	0.076	0.047
Ca	0.155	-0.210	-0.270	**-.821***	0.485	-0.478	0.551	0.603
Br	0.333	0.088	-0.051	-0.701	0.522	-0.096	0.485	**.803***
Na	**.763***	0.274	-0.122	-0.080	-0.043	**-.765***	-0.076	0.194
K	-0.056	0.031	-0.244	-0.143	-0.125	-0.516	0.342	0.219
La	1	0.159	0.048	-0.488	0.189	-0.734	-0.106	0.352
Se		1	0.741	-0.033	**-.761***	0.059	0.600	0.491
Hg			1	-0.157	**-.780***	0.248	0.403	0.104
Th				1	-0.301	0.517	-0.536	-0.606
Rb					1	-0.203	-0.298	0.122
Fe						1	-0.063	-0.245
Zn							1	0.733
Co								1

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

namely Br-Al (r=0.792), La-Na (r=0.859), Cr-Th (r=0.855), Hf-Al (r=0.866), Cs-Al (r=0.812), Cs-Br (r=0.784), Rb-Br (r=0.771), and Eu-Hf (r=0.815). On the other hand, the negative significant correlation coefficients were obtained for Hg-Al (r=-0.837), Hg-Na (r=-0.776), Sc-Cr (r=-0.810), Co-Cr (r=-0.789), and Eu-Hg (r=-0.803).

There were positive correlation coefficients with $\rho<0.05$ for elements in the KMgS fertilizer as illustrated in Table 8. Those elements were Br-Sm (r=0.836), Na-As (r=0.783), K-Mg (r=0.809), Sc-Th (r=0.798), Fe-Cr (r=0.768), Zn-As (r=0.773), Zn-Hg (r=0.761), Eu-U (r=0.759), and Eu-Cs (r=0.790), while negative correlation

Table 7. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in KCl sample

elements	U	Cl	Al	Sm	Br	As	Na	K	La	Hg	Th
U	1	0.685	0.092	0.404	0.049	0.452	0.352	-0.451	0.462	0.136	0.325
Cl		1	-0.280	-0.072	-0.268	0.472	-0.218	-0.640	-0.061	0.570	0.481
Al			1	-0.293	**.792***	-0.268	0.556	-0.278	0.428	**-.837***	-0.139
Sm				1	-0.076	0.548	0.137	0.129	0.383	0.208	0.330
Br					1	0.041	0.062	-0.205	0.030	-0.441	0.233
As						1	-0.328	-0.508	-0.031	0.454	0.739
Na							1	0.027	**.859***	**-.776***	-0.501
K								1	-0.279	-0.048	-0.681
La									1	-0.560	-0.046
Hg										1	0.527
Th											1
Cr											
Hf											
Cs											
Sc											
Rb											
Fe											
Zn											
Co											
Eu											
Ni											

elements	Cr	Hf	Cs	Sc	Rb	Fe	Zn	Co	Eu	Ni
U	0.112	-0.271	-0.071	-0.051	-0.410	-0.512	-0.475	0.019	-0.376	0.039
Cl	0.414	-0.648	-0.539	-0.036	-0.736	-0.236	-0.007	0.023	-0.527	-0.457
Al	0.158	**.866***	**.812***	-0.623	0.669	-0.329	-0.294	-0.632	0.747	0.405
Sm	-0.161	-0.209	-0.100	0.154	-0.204	0.151	-0.660	0.185	-0.395	0.137
Br	0.453	0.585	**.784***	-0.683	**.771***	-0.178	-0.618	-0.680	0.576	0.568
As	0.397	-0.418	-0.489	-0.145	-0.484	0.089	-0.687	-0.099	-0.192	-0.156
Na	-0.528	0.603	0.418	0.024	0.148	-0.425	-0.054	0.024	0.308	0.231
K	-0.729	-0.026	0.129	0.702	0.378	-0.113	0.276	0.668	-0.035	0.539
La	-0.194	0.489	0.310	-0.253	-0.075	-0.041	-0.244	-0.241	0.069	-0.114
Hg	0.326	**-.948****	-0.668	0.260	-0.596	0.271	0.045	0.293	**-.803***	-0.379
Th	**.855***	-0.326	-0.172	-0.602	-0.302	0.457	-0.557	-0.563	-0.348	-0.406
Cr	1	-0.087	0.087	**-.810***	-0.016	0.389	-0.318	**-.789***	-0.083	-0.366
Hf		1	**.766***	-0.488	0.706	-0.025	-0.123	-0.527	**.815***	0.309
Cs			1	-0.506	**.879****	-0.130	-0.265	-0.523	0.469	0.549
Sc				1	-0.311	-0.346	0.389	**.997****	-0.313	0.203
Rb					1	-0.110	-0.189	-0.347	0.632	0.705
Fe						1	0.095	-0.375	-0.218	-0.620
Zn							1	0.351	-0.119	-0.406
Co								1	-0.351	0.203
Eu									1	0.418
Ni										1

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

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

Table 8. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in KMgS$_{30\text{-}11\text{-}17}$ sample

elements	U	Mg	Cl	Al	Ca	Sm	Br	As	Na	K	La	Hg
U	1	0.320	0.029	-0.534	0.468	0.690	0.375	0.384	-0.035	0.151	-0.129	-0.177
Mg		1	-0.112	-0.704	-0.183	0.423	0.719	-0.053	-0.078	**.809***	-0.002	**-.805***
Cl			1	0.437	0.709	0.116	0.022	-0.384	-0.169	-0.016	0.490	-0.034
Al				1	0.407	-0.754	**-.853***	-0.351	-0.063	-0.386	0.466	0.411
Ca					1	0.134	-0.246	-0.093	-0.236	-0.183	0.530	0.166
Sm						1	**.836***	0.295	-0.093	0.008	-0.207	-0.075
Br							1	0.039	-0.106	0.403	-0.312	-0.466
As								1	**.783***	-0.295	0.153	0.350
Na									1	-0.042	0.300	0.111
K										1	-0.107	**-.993****
La											1	0.170
Hg												1
Th												
Cr												
Hf												
Sr												
Cs												
Sc												
Rb												
Fe												
Zn												
Co												
Eu												
Ni												

elements	Th	Cr	Hf	Sr	Cs	Sc	Rb	Fe	Zn	Co	Eu
U	-0.450	0.057	0.144	0.204	0.502	-0.229	-0.089	-0.169	0.108	-0.389	**.759***
Mg	-0.405	0.644	0.193	-0.716	0.410	-0.485	-0.202	0.652	-0.668	-0.191	0.382
Cl	-0.053	-0.264	-0.454	-0.068	-0.324	0.050	0.217	-0.067	-0.150	-0.378	0.006
Al	0.733	-0.177	0.089	0.189	-0.590	0.605	-0.207	-0.018	0.227	0.138	-0.453
Ca	0.139	-0.181	0.039	0.079	-0.268	0.359	-0.112	-0.033	0.128	-0.561	0.186
Sm	**-.839***	-0.323	-0.488	-0.056	0.253	-0.418	0.571	-0.280	-0.058	-0.583	0.348
Br	**-.874***	0.012	-0.472	-0.351	0.391	-0.696	0.477	0.041	-0.454	-0.344	0.287
As	0.110	-0.196	0.187	0.256	0.005	0.354	-0.012	-0.452	**.773***	0.208	0.321
Na	0.358	0.015	0.174	0.189	-0.024	0.305	-0.185	-0.337	0.637	0.630	0.292
K	-0.183	**.878****	0.350	-0.453	0.624	-0.595	-0.523	0.650	-0.720	0.222	0.543
La	0.604	0.006	0.202	-0.455	-0.712	0.743	-0.228	0.291	0.191	-0.205	-0.204
Hg	0.282	**-.824***	-0.254	0.423	-0.655	0.675	0.440	-0.605	**.761***	-0.170	-0.549
Th	1	0.213	0.615	-0.026	-0.494	**.798***	-0.614	0.228	0.378	0.407	-0.277
Cr		1	0.737	-0.422	0.498	-0.259	**-.829***	**.768***	-0.537	0.350	0.430
Hf			1	-0.133	0.194	0.322	**-.935****	0.526	0.044	0.319	0.294
Sr				1	0.296	-0.045	0.099	**-.832***	0.622	0.356	0.286
Cs					1	**-.795***	-0.282	-0.023	-0.286	0.325	**.790***
Sc						1	-0.187	-0.016	0.614	-0.064	-0.439
Rb							1	-0.540	0.080	-0.434	-0.411
Fe								1	-0.723	-0.142	-0.107
Zn									1	0.248	0.018
Co										1	0.217
Eu											1
Ni											

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

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

Table 9. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in $NPK_{15\text{-}15\text{-}15}$ sample

elements	U	Ti	Mg	V	Cl	Al	Mn	Ca	Sm	Br	Na	K	La	Se	Th
U	1	**.839***	0.595	**-.761***	-0.516	0.463	0.035	-0.210	0.292	0.735	-0.312	-0.706	0.414	0.325	-0.221
Ti		1	0.144	**-.765***	-0.644	0.567	0.158	-0.076	0.276	0.365	-0.137	**-.888****	0.422	0.593	-0.243
Mg			1	-0.298	0.128	0.028	0.065	-0.045	0.132	0.641	-0.189	-0.020	0.098	-0.126	-0.003
V				1	**.847***	**-.876****	0.378	0.568	-0.366	-0.287	0.101	0.543	-0.626	0.056	0.104
Cl					1	**-.912****	0.442	0.523	-0.068	-0.020	-0.030	0.408	**-.768***	0.089	0.212
Al						1	-0.345	-0.487	-0.007	-0.104	0.307	-0.332	0.677	-0.187	0.059
Mn							1	**.878****	-0.473	-0.054	0.447	-0.286	-0.358	**.778***	0.165
Ca								1	-0.596	-0.281	0.361	0.075	-0.173	0.641	-0.175
Sm									1	0.443	-0.728	-0.373	-0.185	-0.056	-0.050
Br										1	-0.629	-0.448	-0.081	0.132	-0.073
Na											1	0.136	-0.030	0.017	0.543
K												1	0.013	-0.691	-0.073
La													1	-0.150	-0.639
Se														1	-0.179
Th															1
Cr															
Hf															
Sr															
Cs															
Tb															
Sc															
Rb															
Fe															
Zn															
Co															
Ta															
Eu															
Sb															
Ni															

elements	Cr	Hf	Sr	Cs	Tb	Sc	Rb	Fe	Zn	Co	Ta	Eu	Sb	Ni
U	0.541	0.085	0.701	0.226	0.427	0.354	0.475	**-.774***	-0.024	**.946****	**.831***	-0.627	-0.245	0.715
Ti	0.292	-0.047	0.670	0.167	0.151	0.357	0.151	-0.600	-0.213	**.774***	0.598	-0.716	-0.460	**.850***
Mg	0.339	0.346	0.348	0.102	0.667	0.166	0.415	-0.382	0.027	0.677	**.843***	0.013	0.196	0.068
V	-0.750	-0.057	-0.606	-0.494	0.068	-0.210	-0.649	0.662	-0.378	-0.589	-0.567	**.836***	0.107	**-.868***
Cl	-0.753	0.312	-0.284	-0.276	0.332	0.126	-0.558	0.688	-0.418	-0.307	-0.098	**.771***	0.089	**-.878****
Al	0.733	-0.061	0.168	0.227	-0.409	-0.109	0.509	-0.515	0.375	0.266	0.206	-0.724	0.186	**.885****
Mn	-0.652	0.105	-0.247	**-.756***	0.269	0.051	**-.802***	0.252	**-.977****	0.234	0.162	0.366	0.014	-0.031
Ca	**-.755***	-0.271	-0.375	**-.837***	0.401	-0.314	**-.860***	0.228	**-.912****	0.070	-0.055	0.689	-0.131	-0.270
Sm	0.130	0.405	**.840***	**.922****	0.090	**.765***	0.402	0.005	0.405	0.184	0.390	-0.504	-0.487	0.003
Br	0.375	0.307	0.611	0.327	0.525	0.546	0.498	-0.482	0.097	0.691	0.666	-0.357	-0.156	0.146
Na	-0.131	0.109	-0.728	-0.632	-0.503	-0.377	-0.421	0.331	-0.342	-0.306	-0.272	0.155	0.671	0.205
K	-0.095	-0.256	-0.613	-0.184	0.007	-0.662	0.004	0.285	0.312	-0.606	-0.493	0.735	0.377	-0.683
La	0.607	-0.689	0.164	0.015	0.140	-0.575	0.454	**-.821***	0.297	0.388	0.141	-0.249	-0.195	0.595
Se	-0.531	-0.084	0.252	-0.389	0.297	0.293	-0.637	-0.035	**-.856***	0.452	0.251	-0.043	-0.529	0.243
Th	-0.027	**.828***	-0.355	-0.011	-0.596	0.405	-0.086	0.604	-0.001	-0.357	-0.078	-0.174	0.747	-0.024
Cr	1	-0.025	0.236	0.412	-0.145	-0.078	**.927****	-0.701	0.723	0.322	0.266	-0.633	0.277	0.595
Hf		1	0.155	0.333	-0.201	**.759***	0.070	0.483	0.024	-0.009	0.370	-0.270	0.430	-0.067
Sr			1	0.707	0.413	0.636	0.402	-0.426	0.158	0.657	0.699	-0.569	-0.668	0.333
Cs				1	-0.109	0.566	0.650	-0.086	0.715	0.046	0.260	-0.581	-0.278	0.085
Tb					1	-0.016	-0.007	-0.401	-0.321	0.663	0.614	0.373	-0.437	-0.207
Sc						1	0.078	0.229	-0.037	0.251	0.461	-0.522	-0.206	0.081
Rb							1	-0.601	**.851***	0.274	0.312	-0.555	0.144	0.340
Fe								1	-0.223	-0.732	-0.446	0.405	0.262	-0.629
Zn									1	-0.242	-0.133	-0.377	0.183	0.042
Co										1	**.881****	-0.361	-0.334	0.557
Ta											1	-0.329	-0.161	0.382

Table 9. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in $NPK_{15\text{-}15\text{-}15}$ sample (*Continued*)

elements	Cr	Hf	Sr	Cs	Tb	Sc	Rb	Fe	Zn	Co	Ta	Eu	Sb	Ni
Eu												1	0.094	**-.793***
Sb													1	-0.032
Ni														1

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

coefficients were detected for Br-Al (r=-0.853), Hg-Mg (r=-0.805), Th-Sm (r=-0.839), Th-Br (r=-0.874), Cr-Hg (r=-0.824), Sc-Cs (r=-0.795), and Rb-Cr (r=-0.829). For the confidence level $\rho<0.01$, a very significant positive correlation coefficient was found for Cr-K (r=0.878), while a very significant negative correlation coefficient was found for Hg-K (r=-0.993) and Rb-Hf (r=-0.935).

According to Table 9, there were positive significant correlation coefficients with $\rho<0.05$ in the NPK 15-15-15 fertilizer. Those elements were Ti-U (r=0.839), Cl-V (r=0.847), Se-Mn (r=0.778), Hf-Th (r=0.828), Sr-Sm (r=0.840), Sc-Sm (r=0.765), Sc-Hf (r=0.759), Zn-Rb (r=0.851), Co-Ti (r=0.774), Ta-U (r=0.831), Ta-Mg (r=0.843), Eu-V (r=0.836), Eu-Cl (r=0.771), Ni-Ti (r=0.850), and Ni-Al (r=0.885), while negative significant correlation coefficients were found for V-U (r=-0.761), V-Ti (r=-0.765), La-Cl (r=-0.768), Cl-Ca (r=-0.755), Cs-Mn (r=-0.756), Cs-Ca (r=-0.837), Rb-Mn (r=-0.802), Rb-Ca (r=-0.860), Fe-U (r=-0.774), Fe-La (r=-0.821), Zn-Se (r=-0.856), Ni-V (r=-0.868), and Ni-Eu (r=-0.793). For the confidence level $\rho<0.01$, very significant positive correlation coefficients were found for Ca-Mn (r=0.847), Cs-Sm (r=0.922), Rb-Cs (r=0.927), Co-U (r=0.946), and Ni-Al (r=0.885), while very significant negative correlation coefficients were detected in Al-V (r=-0.876), Al-Cl (r=-0.912), K-Ti (r=-0.888), Zn-Mn (r=-0.977), and Ni-Cl (r=-0.878).

In the TSP sample as shown in Table 10, significant positive correlation coefficients with $\rho<0.05$ were found for V-U (r=0.805), As-Ca (r=0.784), Na-As (r=0.788), Na-Br (r=0.839), Hg-Al (r=0.825), Hg-Se (r=0.811), Th-Ti (r=0.760), Cr-Sm (r=0.861), Hf-Na (r=0.841), Co-As (r=0.865), Eu-Al (r=0.824), Eu-Sm (r=0.755), Eu-Se (r=0.759), and Eu-Hg (r=0.869), while significant negative correlation coefficients were detected for Al-Mg (r=-0.847), Mn-Al (r=-0.765), Br-U (r=-0.813), Na-U (r=-0.766), Cr-Ti (r=-0.770), Sr-Se (r=-0.871), Sr-Hg (r=-0.852), Tb-Se (r=-0.799), Sc-Al (r=-0.866), Eu-Tb (r=-0.785), Ni-Mn (r=-0.775), and Ni-Sr (r=-0.796). For the confidence level $\rho<0.01$, there were very significant

Table 10. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in TSP sample

elements	U	Ti	Mg	V	Al	Mn	Ca	Sm	Br	As	Na	K	La	Se	Hg
U	1	-0.197	0.160	**.805***	0.098	-0.439	-0.287	0.146	**-.813***	-0.014	**-.766***	0.127	0.312	-0.025	0.272
Ti		1	-0.482	-0.378	0.157	-0.158	0.537	-0.474	-0.224	0.268	0.267	0.129	-0.421	-0.710	-0.353
Mg			1	0.338	**-.847***	0.620	-0.347	-0.035	-0.007	0.271	-0.317	-0.438	-0.336	-0.149	-0.567
V				1	-0.064	0.024	-0.370	0.141	-0.540	-0.097	-0.686	0.350	0.366	-0.038	0.087
Al					1	**-.765***	0.260	0.489	-0.067	-0.222	0.153	0.345	0.435	0.487	**.825***
Mn						1	-0.316	-0.448	0.330	-0.086	0.009	-0.175	-0.432	-0.318	-0.714
Ca							1	0.295	0.380	**.784***	**.788***	0.405	0.092	-0.274	-0.170
Sm								1	0.290	0.306	0.242	0.091	0.427	0.702	0.562
Br									1	0.204	**.839***	0.122	0.143	0.304	-0.094
As										1	0.477	0.083	-0.120	-0.381	-0.465
Na											1	0.255	0.073	0.020	-0.134
K												1	0.737	-0.148	0.133
La													1	0.429	0.589
Se														1	**.811***
Hg															1
Th															
Cr															
Hf															

Table 10. Matrix of correlation coefficient among multi-nutrients and heavy metal concentrations in TSP sample (*Continued*)

elements	U	Ti	Mg	V	Al	Mn	Ca	Sm	Br	As	Na	K	La	Se	Hg
Sr															
Tb															
Sc															
Rb															
Fe															
Zn															
Co															
Ta															
Eu															
Sb															
Ni															

elements	Th	Cr	Hf	Sr	Tb	Sc	Rb	Fe	Zn	Co	Ta	Eu	Sb	Ni
U	-0.340	0.289	-0.740	-0.147	-0.338	-0.002	0.249	0.527	-0.134	-0.049	0.347	0.242	-0.292	0.215
Ti	**.760***	**-.770***	-0.062	0.533	0.733	-0.502	0.019	-0.749	-0.268	-0.115	-0.009	-0.367	-0.541	-0.109
Mg	-0.135	0.405	-0.244	0.280	0.018	0.747	0.054	0.539	0.388	0.293	0.501	-0.448	0.466	-0.690
V	-0.274	0.408	-0.588	-0.196	-0.484	0.171	0.612	0.452	-0.300	0.079	0.430	0.286	-0.248	0.033
Al	0.028	0.057	0.004	-0.635	-0.399	**-.866***	0.154	-0.158	-0.320	-0.133	-0.150	**.824***	-0.343	**.954****
Mn	0.104	-0.124	0.150	0.311	0.144	0.642	0.080	-0.203	-0.090	-0.002	0.150	-0.535	0.145	**-.775***
Ca	0.720	0.016	0.434	0.428	0.604	-0.470	0.353	-0.123	0.433	0.697	-0.052	-0.016	0.248	0.064
Sm	-0.061	**.861***	0.079	-0.556	-0.490	-0.376	0.370	0.628	0.405	0.570	0.271	**.755***	0.487	0.612
Br	0.119	0.253	**.896****	0.018	0.104	0.137	0.010	-0.021	0.465	0.466	-0.366	0.022	0.689	-0.100
As	0.615	0.287	0.130	0.602	0.617	-0.063	0.360	0.298	0.699	**.865***	0.331	-0.276	0.489	-0.303
Na	0.494	0.007	**.841***	0.253	0.455	-0.234	0.074	-0.235	0.461	0.545	-0.354	-0.035	0.484	-0.002
K	0.106	0.043	0.331	0.069	-0.004	-0.185	0.642	-0.095	-0.182	0.319	-0.353	0.301	-0.158	0.196
La	-0.490	0.444	0.338	-0.332	-0.434	-0.019	0.290	0.405	0.093	0.239	-0.495	0.570	0.174	0.479
Se	-0.584	0.611	0.169	**-.871***	**-.799***	-0.152	-0.168	0.440	0.122	-0.057	-0.132	**.759***	0.347	0.689
Hg	-0.516	0.324	-0.039	**-.852***	-0.734	-0.485	-0.102	0.229	-0.179	-0.259	-0.240	**.869***	-0.112	**.943****
Th	1	-0.298	0.016	0.479	0.647	-0.480	0.427	-0.489	-0.018	0.385	0.397	-0.237	-0.163	-0.204
Cr		1	0.018	-0.414	-0.536	0.113	0.384	**.877****	0.505	0.618	0.322	0.525	0.650	0.255
Hf			1	0.165	0.249	0.153	-0.127	-0.133	0.426	0.340	-0.711	-0.073	0.560	-0.080
Sr				1	**.927****	0.365	-0.018	-0.193	0.349	0.320	-0.066	**-.875****	0.120	**-.796***
Tb					1	0.071	-0.123	-0.386	0.330	0.267	-0.113	**-.785***	0.066	-0.605
Sc						1	-0.256	0.352	0.324	0.030	-0.174	-0.587	0.439	-0.743
Rb							1	0.115	-0.166	0.565	0.464	0.356	-0.097	0.070
Fe								1	0.619	0.492	0.232	0.248	0.636	0.077
Zn									1	0.708	-0.079	-0.234	**.910****	-0.240
Co										1	0.228	0.029	0.679	-0.159
Ta											1	0.075	-0.107	-0.091
Eu												1	-0.088	**.908****
Sb													1	-0.221
Ni														1

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

positive correlation coefficients for Hf-Br (r=0.896), Tb-Sr (r=0.927), Fe-Cr (r=0.877), Tb-Zn (r=0.910), Ni-Al (r=0.954), Ni-Hg (r=0.943), and Ni-Eu (r=0.908), while a very significant negative correlation coefficient was found in Eu-Sr (r=-0.875). The TSP fertilizer, which has 46% phosphorus, positively correlates to U, Th, V, As, Cr, Co, Hg, Al, Ni, Fe, Zn, Ca, Na, Br, Br, Se, Ti, Sm, Tb, and Eu. This result is in line with the study of Verbeek et al., which stated that the phosphorus content was positively correlated to Cd, U, V, Sb, Cr, As, and Ni elements [10].

Eighty-five percent of the world's TSP fertilizer production is made from sedimentary phosphate rock, where metals that initially exist in this rock and the manufacturing process highly affect the content of metals in TSP fertilizers [7]. Phosphate rock was proven to contain various metals as constituents in sediments which can be easily transferred into fertilizers during the production process [42]. The long-term use of phosphorus fertilizer has been proven to increase the concentrations of As, Cd, and other trace elements in agricultural soil [35,43]. The long-term use of phosphorus fertilizers in Switzerland increased the concentration of U, Cd, and Th on the soil surface [10].

■ CONCLUSION

The NPK fertilizer contained the highest macro, micro, trace, and non-essential elements compared to other fertilizers. Meanwhile, the TSP fertilizer contained the highest concentration of heavy metals compared to other fertilizers. Fortunately, the concentration of macro, micro, trace, non-essential and heavy metals in all fertilizer samples tested here was within the allowable limits according to Canadian standards. Many of the multi-nutrients and heavy metals analyzed in each fertilizer sample were highly correlated. This finding indicates that those strongly correlated elements form a complex. Considering that some elements and heavy metals that originate from fertilizers can pollute and later accumulate in environmental matrices, it is necessary to monitor the long-term use of inorganic fertilizers against the increase of metal concentrations in the environment to reduce potential health risks to plants and humans. This research provides reliable data that policymakers can use regarding the content of multi-nutrients and heavy metals in fertilizers widely distributed in the market and used by many farmers.

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