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Appraisal of heavy metals and nutrients from phosphate rocks, Khyber Pakhtunkhwa, Pakistan

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This study focuses on fundamental scrutiny of phosphate rock samples in order to investigate the elemental composition (Zinc, Cadmium, Lead, Sodium and Potassium) by Flame Photometry & Atomic Absorption Spectroscopy. The samples have been collected from Hazara Division, Khyber Pakhtunkhwa (KPK), Peshawar. Relative study on heavy metal content and nutrients was performed to find out the comparative resources quality. The sample S5 exhibits highest Cadmium contents while S6 shows higher concentration of other metals. The local resources indicate higher quantity of Lead (Pb). The remedy for this excessive amount of Pb may probably be done by complete separation and disposal of waste phosphogypsum. The phosphate rocks found in the region are good enough to be utilized as raw material for fertilizer manufacturing plants.

Capsule Summary: The elemental analysis of heavy metals and nutrients was performed atomic absorption spectroscopy to determine phosphate rock quality in Pakistan.

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INTRODUCTION

Phosphate is generally employed for the manufacturing of fertilizers. It is the minor constituent of many products like light bulbs, toothpastes, flame-resistant fabrics, detergent manufacturing, livestock and poultry feed etc. (Javied et al., 2008; Mar and Okazaki, 2012; Huang et al., 2017). Phosphate rock (PR) is natural mineral deposits belongs to the species of apatite family. Apatite is a primary phosphate mineral that can differ significantly in physical, chemical, and crystallographic properties (Ahialey et al., 2014; Liu et al., 2017).

Mostly PR deposits include variety of carbonate-fluorapatite, grouped under the collective name of francolite. Sedimentary phosphate deposits display varying compositions and physical forms and found in formations from different ages (Abouzeid, 2008; Dargahi et al., 2016). Igneous phosphates include silica deficient intrusions. The apatite linked with these rocks may probably be of a primary magmatic and hydrothermal or secondary origin. The guano type phosphate deposits are the best known natural fertilizers due to extraordinarily higher quantity of nutrients like nitrogen (N), phosphate PO_4^{3-} and potassium (K) vital for plant development. Guano type rock

Table 1: Phosphate rock reserves and resources of some major producers

Country	Reserves[a] (mmt)*	Resource[b] (mmt)
United states	1,100	49,000
Australia	82	3500
Brazil	260	2800
Canada	15	130
China	3700	16,800
Egypt	100	3400
Israel	180	1600
Jordan	1,500	1800
Morocco	5700	170,000
Russia	200	4300
Senegal	50	250
South Africa	1,500	7,700
Togo	60	1,000
Tunisia	100	1,200
Other countries	950	22,000
World total (rounded)	16,000	290,000

[a]USGS 2010; b. IFDC Resources; mmt: *million metric ton

phosphates are found as hydroxylapatites and carbonate hydroxylapatites (Cevik et al., 2010; Li et al., 2017).

The rock phosphates of varying quality are mined (Table 1) throughout the world (Aydin et al., 2010). Pakistan is rich in mineral contents and KPK is the major producer of PR in Pakistan. The PR deposits exist in Hazara division of KPK.

PR deposits contain gangue minerals and impurities including silica, clay minerals, calcite, dolomite etc. in different combination. The performances of PR for certain direct applications e.g. in agriculture can be influenced by such scums (Macedo et al., 2009; Barkouch et al., 2016). The fertilizer industry is one of the great consumers of PR in addition to the production of animal feed supplements and food products (El-Sheikh et al., 2013; Macedo et al., 2009; Zapata and Roy, 2004). The toxicity of heavy metals [Lead (Pb), Arsenic (As), Mercury (Hg), Antimony (Sb), Cadmium (Cd), Vanadium (V) and nickel (Ni)] depends upon their form or oxidation state. Cr (III) is an important micronutrient while Cr (VI) is toxic.

Sedimentary rocks encompass great accumulation of heavy metals along with environment polluting elements. The quantitative aspects of heavy/hazardous metals in PR sources are variable among different sources and in the same source. The concentration of these metals is largely governed by the soil chemistry and particularly the chemical form of metal. Low pH environment and transfer factor are generally more susceptible for these metal attacks e.g. Cd is the most studied toxic metal owing to the high transfer rate for any crop. Table 2 shows the worldwide distribution of metals in PRs. The quantification of such toxic pollutants is therefore very meaningful for designing the chemical processes employed for production in industry. Toxic heavy metals in surface and subsurface environment are considered growing threats (Khan et al., 1998; Javied et al., 2008; Jiao et al., 2012; Aydin et al., 2010). The soil buildup of different poisonous metals such as Cd, Pb, Cr, and Zn can be related to the application of phosphate fertilizers (Tufail et al., 2006; Yang et al., 2015). The ongoing addition of fertilizers containing heavy metals to the soil can result in their accumulation in the soil over time (Huang et al., 2017). The heavy metals applied with fertilizers tend to accumulate in cultivated soil because heavy metals are non-degradable (Barkouch et al., 2016).

The study area is about 70 km^2 and is situated between 73◦15E to 73◦20E longitudes and 34◦10N to 34◦19N latitudes (Qureshi et al., 2001). Riyala phosphate mine is about 11 km from Qalandrabad and about 24 km from Abbottabad in north east direction. Lagarban is located in north east of the Kakul. The PR reserves of Lagarban are estimated up to 1.14 million tones (Khan et al., 1998). Some other mines in KPK are Thandiani, Banda-pir-khan, Mandrayian, Guldania and Peswal village. The objective of the current study is to find out the level of toxicity owing to the use of these PR in different fields.

MATERIAL AND METHODS

Analytical grade reagents and chemicals purchased from Sigma-Aldrich, United States were employed for experimental work. The experimental procedure consists of sampling, washing, drying, crushing and grinding, digestion of weighed sample into suitable reagent, preparation of solutions and elemental analysis. The detail of samples is provided in Table 3.

The samples were collected in plastic bags and carried to the P.C.S.I.R laboratories. The rock samples were cleaned by washing and air dried. The rock samples were then transferred to Mineral Processing Research Centre (M.P.R.C) of P.C.S.I.R for crushing and grinding. PR is first

Table 2: Global pattern of some elements in phosphate rocks

PR origin	Cd µg/g	Pb µg/g	Zn µg/g	Na µg/g	K µg/g
Algeria	-	-	134	6711	500
Brazil	4	44.5	299	-	-
Egypt	-	-	13.2	1.15	-
Israel	-	-	372	4009	440
Middle East	9	4	315	-	-
Morocco	30	7	345	5362	580
Nigeria	-	-	59	2300	-
North Africa	60	6	420	-	-
Russia	0.1	3	19	3106	4700
Saudi Arabia	2	-	88	-	-
South Africa	-	35	6	-	-
Syria	-	-	269	3882	40
Togo	-	-	143	1086	-
Tunis	11	-	515	10324	1570
USA	7.2	11	403	7770	300

Table 3: Samples along with their origins and place of collection

Sample	Origin	Place of Collection
S_1	Lagarban	Agritech Ltd.
S_2	Banda-pir-khan	Supplier in hattar, Haripur
S_3	Tarnawai	Supplier in hattar, Haripur
S_4	Guldania Q_3	Supplier in Qalandarabad
S_5	Mandrayian	Supplier in Qalandarabad
S_6	Riyala mine (inner region)	Mine
S_7	Mine no.5-B, lease no.12, Gally bane.	Mine

passed through a jaw crusher. The size of rock was reduced to small pieces of rock.

In the second step roll crusher further reduced the size of sample. In the last step, sample is grinded and homogenized in pulverizer and sieved through 30 mesh size. Grounded samples were then dried by keeping in oven at 110 °C for 10 hours to remove moisture if any. The digestion and elemental analysis is performed by following the procedure reported in Sabiha-Javied, (2009).

Multiple sets of standard solutions were prepared and suitable dilutions of each sample were made in order to lay on the calibration curve. For AAS, lamp was warmed-up for 30 min to get the instrument stabilized. Lamp alignment and flame conditions were optimized. The elements were than analyzed accordingly. The elements, Cd, Pb, Zn and K were analyzed using Variant Spectra AA-240 model of AAS while Na was analyzed using Flame photometer.

RESULTS AND DISCUSSION

Analyses of seven (7) samples (Table 3) were carried out to determine the elemental composition of PR. The Cd content of Pakistani PR resources was aligned with the global ranges available for the element (Table 2). The average concentration in local resources was about 4.4 µg/g of rock (Table 4). The worldwide distribution of Cd is 0.1–60 µg/g

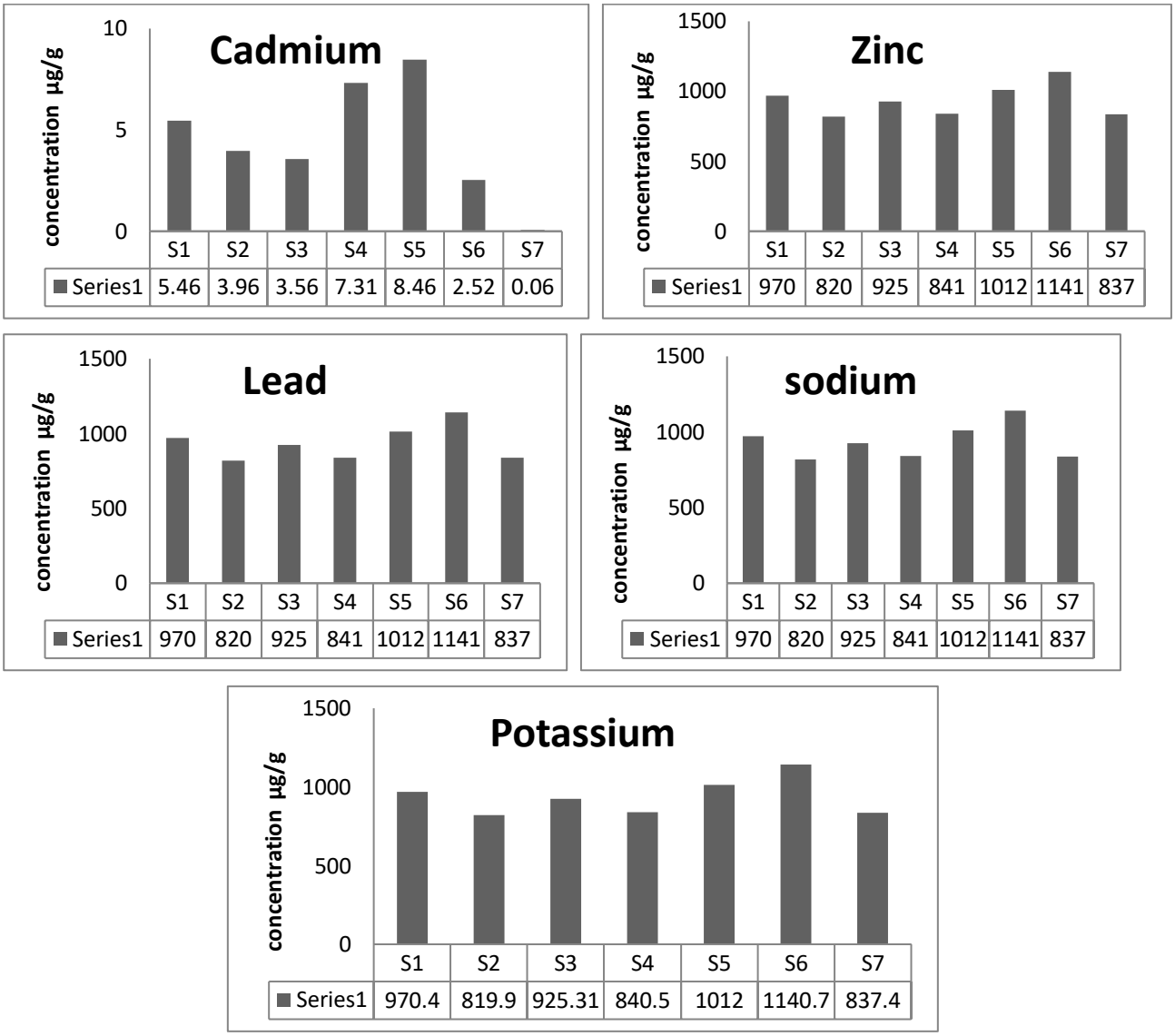

Fig. 1: Comparison of concentration of Cd, Zn, Pb, Na and K in phosphate rocks of different origin.

while the results in our study are compatible with the global range. Various impurities may also be present in crops and soil due to presence of Cd and strictly needed to be addressed. The concentration of Cd is of huge concern regarding phosphate industry and is considered one of deciding factors for the quality of phosphate resources. This largely depends on soil characteristics and irrigation water quality. European importers of PR imply a limit of 10 µg/g of Cd on its import (Conceicaõ and Bonotto, 2006; Liu et al., 2017). Our PR resources are within the European established limit and suggest a very comfortable application of our resources for different manufacturing units (Hacısalihoğlu and Karaer, 2016; Li et al., 2017).

Zn is an essential element and employed as a micronutrient. The range of Zn in local PR determined in the present study is 6.4-52.4. The concentration 25–200 µg/g of Zn is well-thought-out as adequate quantity for agriculture fields (Pantelica et al., 1997; Vaverková, and Adamcová, 2014; Liu et al., 2015; Dargahi et al., 2016). The quantity of Zn calculated in this study 25.7 µg/g of rock lie within the range i.e. 6–515 µg/g of rock.

The concentration of Pb determined in the present study ranged from 6.2-34.1 µg/g. Analysis of Pb has shown that the quantity of Pb in our samples lies within the globally administrated range of 3–44.5 µg/g of rock (Tables 2 and 4). The average amount of Pb contents in local PR samples was 19.2 µg/g of rock. The Pb uptake by the plant depends on soil acidity level. Pakistani soils are relatively more basic; at higher pH the Pb becomes toothless. Moreover, the application of sulphuric acid during different manufacturing processes converts Pb into its sulfate and becomes unavailable for further action in elemental form. The one more plus point is the small transfer factor of Pb to plant; it has not been taken up by the plant up to 300 µg/g in soil. In case it is taken up, it gathers in leaves rather than the fruit (Rosen, 2002). Clay minerals, organic matter and metal

Table 4: Concentration of Cd, Zn, Pb, Na and K in phosphate rock samples

Sample	Conc. Of Cd ±S.D (µg/g)	Conc. Of Zn ±S.D (µg/g)	Conc. Of Pb ±S.D (µg/g)	Conc. Of Na ±S.D (µg/g)	Conc. Of K ±S.D (µg/g)
S_1	5.46±2.61	52.4±2.0	12.4±1.5	4012.2±1.5	970.4±1.7
S_2	3.96±2.73	31.7±1.2	18.7±1.4	3814.9±1.0	819.9±1.4
S_3	3.56±2.66	22.1±1.0	15.81±1.0	3512.2±1.6	925.3±1.5
S_4	7.31±3.13	6.4 ±1.5	6.2 ±1.5	2734.7±1.0	840.5±1.5
S_5	8.46±2.54	18.2±1.0	25.4±1.5	3132.4±1.5	1012.0±1.6
S_6	2.52±3.26	15.3 ±1.8	34.1±1.0	2920.7±1.8	1140.7±1.4
S_7	0.06±2.63	34.4±1.0	22.4±1.5	4020.1±1.5	837.4±1.5
Mean	4.46	25.7	19.8	3449.6	819.9-1140.7
Range	0.06-8.46	6.42-52.4	6.2-34.1	2734.7-4020.1	935.17

hydroxides has strong tendency to absorb Pb at higher pH (Liu et al., 2015; Yang et al., 2015; Gul et al., 2015).

Na is an essential nutrient. The range for Na concentration in present study was determined as 2734.7-4020.1µg/g. The average concentration was found to be 3449.6 µg/g. The comparison of Na concentration in PR samples was performed and it shows that (global range of Na concentration is 1.15–10234 µg/g) the average concentration of sodium estimated in the current work lies within the worldwide distribution of Na in local rocks (Ahialey et al., 2014).

The amounts of K (primary nutrient) in local rock samples were found in acceptable limits. The K and Na are not considered as contaminant or precarious so can be adjusted from other sources. The concentration of K in the present study was 935.17 µg/g of rock which lies well inside the permissible limits (Liu et al., 2015; Dargahi et al., 2016).

CONCLUSIONS

PR samples from local resources were analyzed for elemental composition. The quantity of metals found in current research work is well inside the permissible limits given in literature. The upper limit for a heavy metal (a pollutant) depends on mass of the metal in PR and soil contents. The Pb is the most common pollutant found to be higher in Pakistani PR deposits and requires proper check in the end product.

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