Article
Vol. 21, No. 5, p. 743–752, October 2017
http://dx.doi.org/10.1007/s12303-017-0013-9
pISSN 1226-4806 eISSN 1598-7477
Geosciences Journal GJ

Assessment of heavy metals concentration in phosphate rock deposits, Hazara basin, Lesser Himalaya Pakistan

Faridullah Faridullah[1], Muhammad Umar[2]*, Arif Alam[3], Muhammad Amjad Sabir[2], and Danyal Khan[2]

[1]Department of Environmental Sciences, COMSATS Institute of information Technology Abbottabad 22060, Pakistan
[2]Departmentof Earth Sciences, COMSATS Institute of information Technology Abbottabad 22060, Pakistan
[3]Departmentof Development Studies, COMSATS Institute of information Technology Abbottabad 22060, Pakistan

ABSTRACT: Naturally occurring phosphate rock is the only essential source for the production of fertilizers. Heavy metals and phosphate concentrations are quite higher in phosphate rock formed by sedimentary processes. This detail study was conducted to evaluate the heavy metal concentrations in part of the Hazara region, which is the only source of phosphate fertilizer in the country. Heavy metals are considered as one of the main pollutant responsible for environmental contamination of soil. This study included the concentration of phosphorite in the Hazara region in the three useful forms: total phosphorite, extractable phosphorite and water soluble forms. The phosphorous extracted from sedimentary deposits used to maintain the natural content in agricultural soil which was being depleted due to the regular practice of crop harvest. The data collected during this studies were statically analyzed which refers the significant variations in P, Zn, Cr, Mn, As, Cu, Fe, Ni, & Pb. Zn and Cr concentration in Hazara phosphates. Heavy metals for instance Pb, Cr, Zn and Cu present in higher amount than usable limits and may create environmental pollution (air, surface & groundwater and soil) and health issues of humans. Therefore it is recommended that managing remedial steps are necessary around the mining regions to avoid environmental and health issues.

Key words: heavy metals pollutants, soil, contamination, fertilizer, phosphorites, Lesser Himalaya

Manuscript received August 4, 2016; Manuscript accepted February 9, 2017

1. INTRODUCTION

Rock phosphates got importance in order to provide raw materials used for manufacturing commercial phosphate fertilizers, detergents, animal feed supplements and in chemical industry. But long-continued application of phosphate fertilizers can redistribute and elevate toxic heavy metals for instance Cd, As and Pb in soil profiles (especially in acid soil) and consequently their transfer to the food chain and also raise concentration of these elements in irrigation drainage waters (da Conceicao and Bonotto, 2006). The Rock phosphates contain hazardous elements including heavy metals and radioactive elements, e.g., Cd, Cr, Pb, Mn, Ni, Cu, Fe, U, Th and their daughter products, which are considered to be toxic to soil, human and animal health (Kpomblekou and Tabatabai, 1994). In general, sedimentary rock phosphates contain much higher concentrations of potentially hazardous elements (Cd, Cr, Se, and U) than igneous rock phosphates (Kratz and Schnug, 2005). Researchers in Australia and the UK reported that long-term applications of phosphate fertilizers increased concentration of Cd in surface soil (Huang et al., 2004). Radionuclides may be leached out of the fertilized zone and into groundwater that drains from these fields or transferred via the food chain to humans (Abdel-Haleem et al., 2001). Furthermore mining activities of phosphate rock have been reported to cause heavy metal contamination of the soil in a localized area. Heavy metals such as Cr in mining and milling dust damage the nasal and lung cells. It includes air emissions (greenhouse gases, ammonia and particulate matter etc.), waste water (ammonia and organic nitrogen etc.) and solid waste phosphogypsum (PG) stacks & calcium carbonate etc. PG is a common form of the waste generated by dissolution of phosphate rocks (PR) in H_2SO_4 to produce H_3PO_4 whereas when PR is dissolved in HNO_3 producing fertilizer and waste called calcium carbonate is generated.

The phosphate deposits of Hazara, Lesser Himalaya are

*Corresponding author:
Muhammad Umar
Departmentof Earth Sciences, COMSATS Institute of information Technology Abbottabad 22060, Pakistan
Tel: +92 992 383591-6, Fax: +92 992 383441,
E-mail: umarkhan09@yahoo.com

sedimentary in origin that occur in Cambrian Abbottabad and Tarnawai formations (Umar et al., 2015a) and are the only having economical potential. The deposits exist in an area of about 30 km^2, and mined in some locations including Kakul, Danna, Lambi dogi, Tarnawai, Kaludi-Bandi, Guldanian and Dalola. Around 7.5 × 108 mg/kg of PR of acceptable quality is available at Kakul mine alone. In present study water soluble, extractable and total phosphate of phosphorite deposits exposed in Lesser Himalaya are carried out first time and analyzed the efficient concentration of heavy metals & compared with similar studies carried out in other countries.

2. REGIONAL GEOLOGIC SETTINGS

The study area is a part of tectonically disturbed Hazara region within Lesser Himalayan fold belt. Precambrian–Cenozoic periodic tectonic fluxes (including continent-continent collision of India and Eurasia) were responsible for deformation (Powell, 1979; Umar et al., 2011, 2015a, b). Main Boundary Thrust (MBT), Panjal Fault (PF), Main Mantle Thrust (MMT), Main Karakoram Thrust (MKT) and Kohistan Ladakh Island Arc (KLIA) are important tectonic features of the study area (Fig. 1). Rock units exposed in the area are ranging in age from Precambrian to Holocene. Phosphorites rich Abbottabad Formation is subdivided into four members on the basis of variety of lithologies namely Mahmdagali member (dolomite and limestone rich), Mirpur member (shale, siltstone, sandstone), Sirban member (dolomite, limestone and phosphate) and Mangi di Bandi member (sandstone). Its lower contact is conformable with underlying Kakul Formation of Cambrian age.

The phosphate rock occurred as thin beds, lenses, nodules and bands within carbonate rich strata of Abbottabad and Tarnawai formations. It is usually fine and/or medium to coarse-grained, thinly bedded, massive, pelletal and/or oolitic in nature. Two major deposits contain clean phosphate but another contains siliceous impurities. Commonly phosphate rich beds of good quality with appreciable amount of P_2O_5 (up to 40%) at Lagarban but some horizons are containing silica impurities and hence are considered un-economic.

3. MATERIAL AND METHODS

Twenty seven selected samples of economic value phosphate rock collected during field work from Lagarban, Danna, and

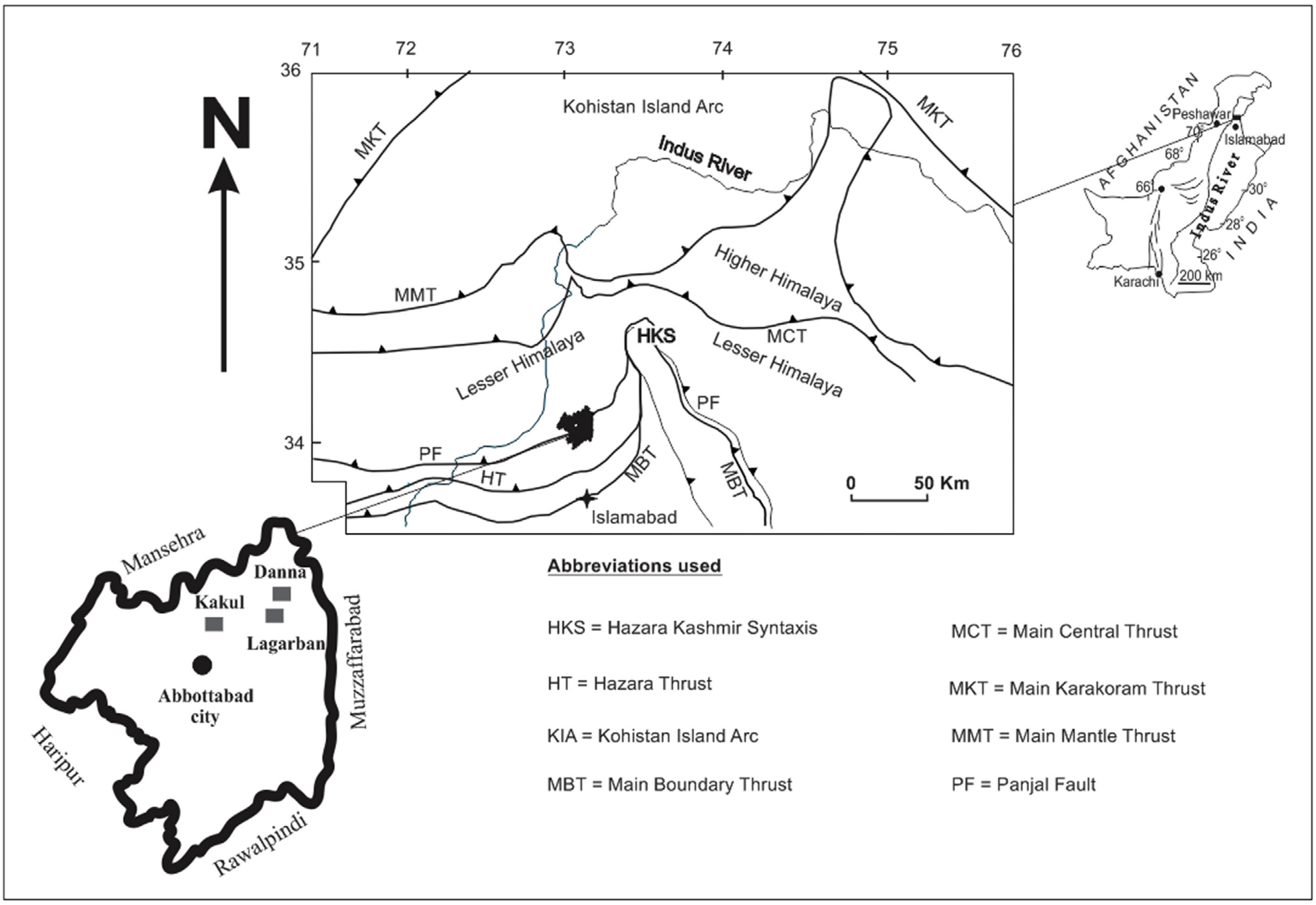

Fig. 1. Map showing major geologic features and location of sampling sites within the study area.

Kakul localities, Hazara Basin within Lesser Himalaya. The concentration of heavy metals and phosphorous were measured in water soluble, extractable and total forms. Phosphate samples were air dried, crushed and sieved (< 0.5 mm) to ensure homogeneity and digested in a mixture of duplicate acids (HNO_3 and $HClO_4$). Total metals i.e., Nickel (Ni), Iron (Fe), Zinc (Zn), Lead (Pb), Copper (Cu) and Chromium (Cr) etc. in the extract of digested rock samples, were determined by atomic absorption spectrophotometer (Ibsram, 1994). Sample weighing 0.25 g was digested with 5 mL concentrated $HClO_4$ by gradual heating on hot plate for an hour. After drying 20% HNO_3 was added to the sample and it was heated again for one hour. The solution was diluted to 50 mL with deionized water and passed through a 0.22 μm filter. The phosphorous was determined on a spectrophotometer using the phosphomolybdate blue method (Murphy and Riley, 1962). Absorbance was determined at a wavelength of 710 nm. The rock samples were extracted for water soluble phophorite and other heavy metals using de-ionized water. A water extract removes only dissolved form of elements but very little of the adsorbed and mineral forms. Extractable phophorite content was determined by the molybdate blue method using spectrophotometer at 710 nm. Five grams sample was taken in a 250 mL Erlenmeyer flask and 100 mL $NaHCO_3$ was added & shaken mechanically for 30 minutes. The suspension was centrifuged for 15 minutes at 2000 rpm. Filtered the supernatant into 200 mL volumetric flask, then diluted with distilled water to the mark. Pipetted 5 mL of the clear extract into a 25 mL volumetric flask and pH was adjusted with H_2SO_4 needed to determine by pipetting 5 mL of $NaHCO_3$ in beaker and titrated it with 5N H_2SO_4. Then added to $NaHCO_3$ extract in the 25 mL volumetric flask, and proceeded according to the sulfomolybdo-phosphate blue color method. A probability level of $P < 0.05$ was considered significant and means were separated by Fisher's least significant difference test.

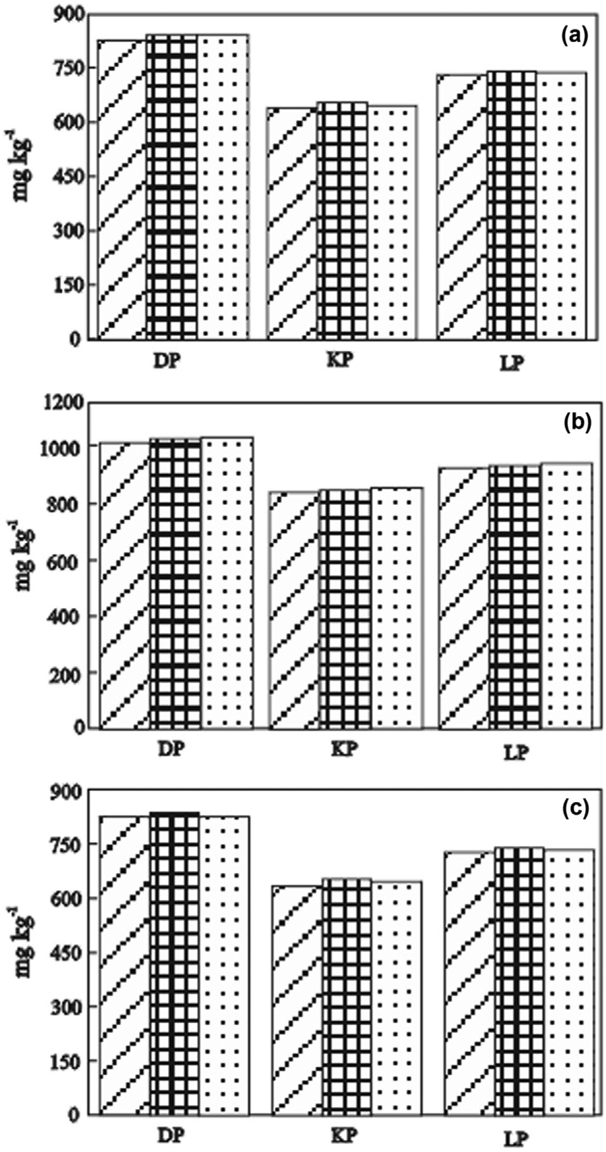

Fig. 2. (a) Total phosphorous; (b) Extractable phosphorous; (c) Water soluble phosphorous in rock phosphate.

4. RESULTS AND DISCUSSION

Heavy metals content is one of the deciding factors for the quality of phosphate fertilizer. Elemental analysis for rock phosphate was carried out to determine the soluble, extractable and total concentration of phosphorous and heavy metals. Significant differences were found in the concentrations of phosphorous and heavy metals in rock phosphate samples analyzed. The samples were collected from Danna, Lagarban and Kakul mines and denoted here as DP, LP and KP respectively. Total phosphorite concentration of Hazara phosphate were considerably varied in the order of Danna > Lagarban > Kakul mines. The maximum concentration of phosphorous was noted in Danna with (1274.33 mg/kg) whereas minimum concentration was found in Kakul with (1057.3 mg/kg) (Fig. 2a). The concentration of extractable P were found in the order of DP (1022.6 mg/kg) > LP > KP (846 mg/kg) (Fig. 2b). Water saturated phosphorous was determined in the order of DP > LP > KP (Fig. 2c). Higher value (831 mg/kg) was noted in DP and lower value was found in KP with (646 mg/kg). The solubility and availability of phosphorous differs widely in rock phosphates depending on their structure. For example, pure fluorapatite is much less soluble than hydroxylapatite or even than carbonate substituted fluorapatites. This very low solubility precludes its direct application as a fertilizer and is classified as unreactive (Bolan et al., 1990; Rajan et al., 1996). Rock phosphates vary considerably in content of heavy metals depending on the geographical location

http://dx.doi.org/10.1007/s12303-017-0013-9

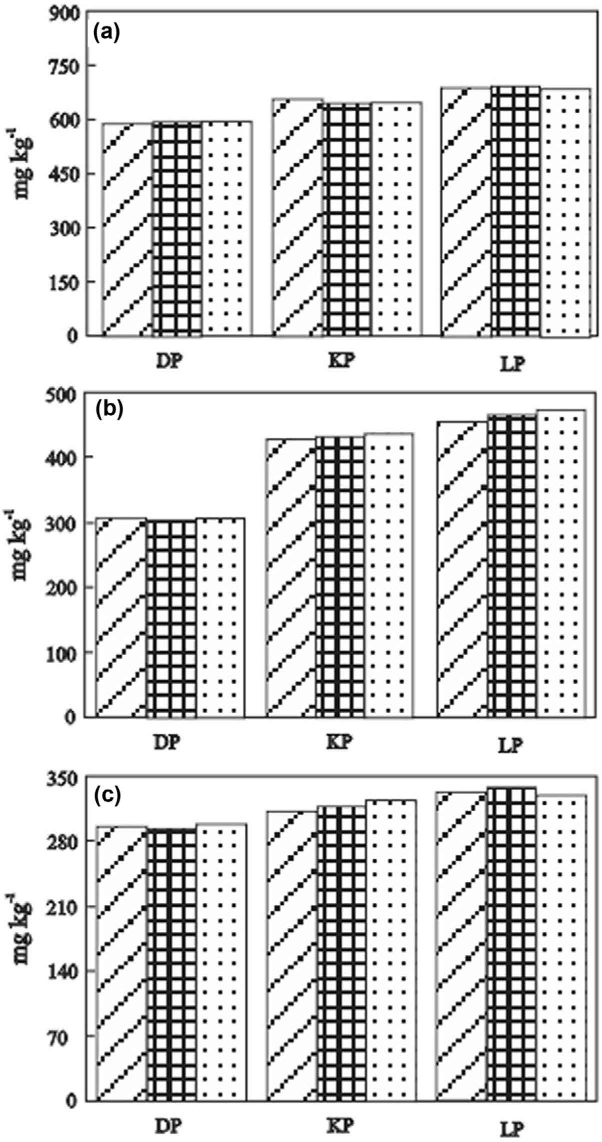

Fig. 3. (a) Total Zn; (b) Extractable Zn; (c) Water soluble Zn in rock phosphate.

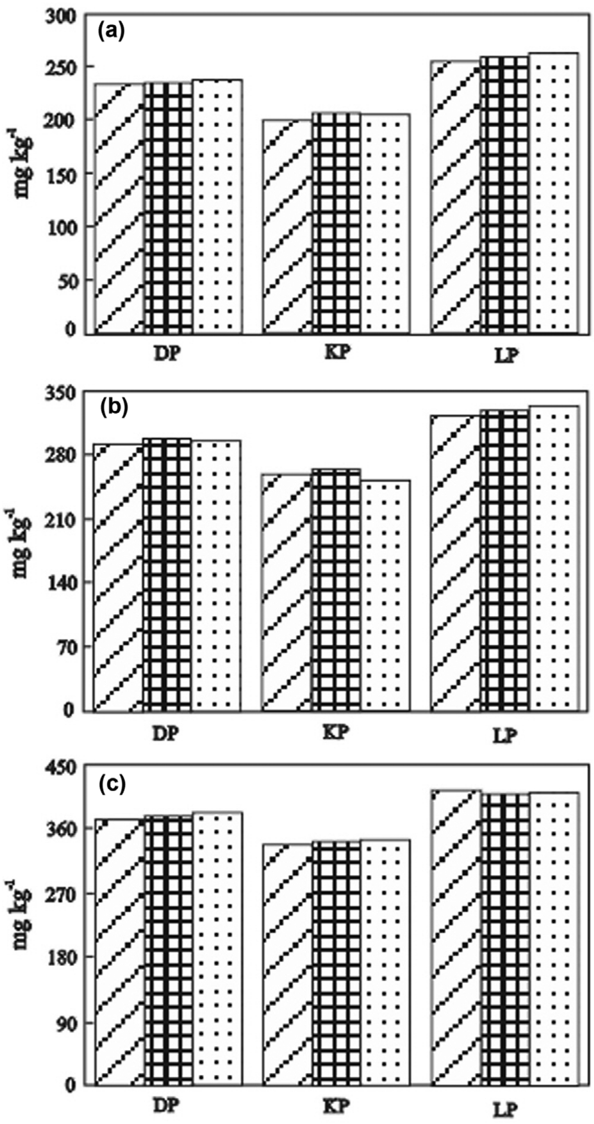

Fig. 4. (a) Water soluble Cr; (b) Extractable Cr; (c) Total Cr in rock phosphate.

(Makweba and Holm 1993; Mortvedt, 1996; Schnug et al., 1996).

The total heavy metal concentration in LP were found in the order of Zn > Mn > Cr > Ni > Cu > Fe > Pb > Cd. The value of total Zn varied in the order of LP > KP > DP (Fig. 3a). The maximum amount of total Zn (689.33 mg/kg) was recorded at Lagarban and the least (593 mg/kg) was recorded at Danna. Extractable Zn at Hazara region were found in the order of LP > KP > DP, the higher concentration Zn (465.0 mg/kg) were found at Lagarban and the lowest concentration Zn (304.67 mg/kg) were observed in Danna (Fig. 3b). The water soluble Zn in the Hazara phosphates were in the order of LP > KP > DP (Fig. 3c). The greater value of water soluble Zn (332.67 mg/kg) was observed at Lagarban whereas minimum concentration (294 mg/kg) was recorded at Danna. The acceptable range of Zinc concentrations in phosphate rock is 6–515 mg/kg, while the determined zinc concentration in present study is under usable limits except samples collected from Danna where little higher values were recorded (i.e., up to 593 mg/kg), so care should be taken in this case.

Although Cr is required in trace amount for sugar and lipid metabolism but its larger amount can be toxic. Water soluble Cr contents in the rock samples of Hazara region was found in the order of LP > DP > KP (Fig. 4a). The amount of water soluble Cr was found in the range of 258.67 mg/kg to 235.0 mg/kg. Samples from the KP, Cr contents (203.33 mg/kg) were found in lower amount. The value of extractable Cr (328.0 mg/kg) was found greater in the Lagarban deposit, whereas lowest concentration of Cr (257.67 mg/kg) was observed in the Kakul phosphates and was marginally lower than extractable Cr

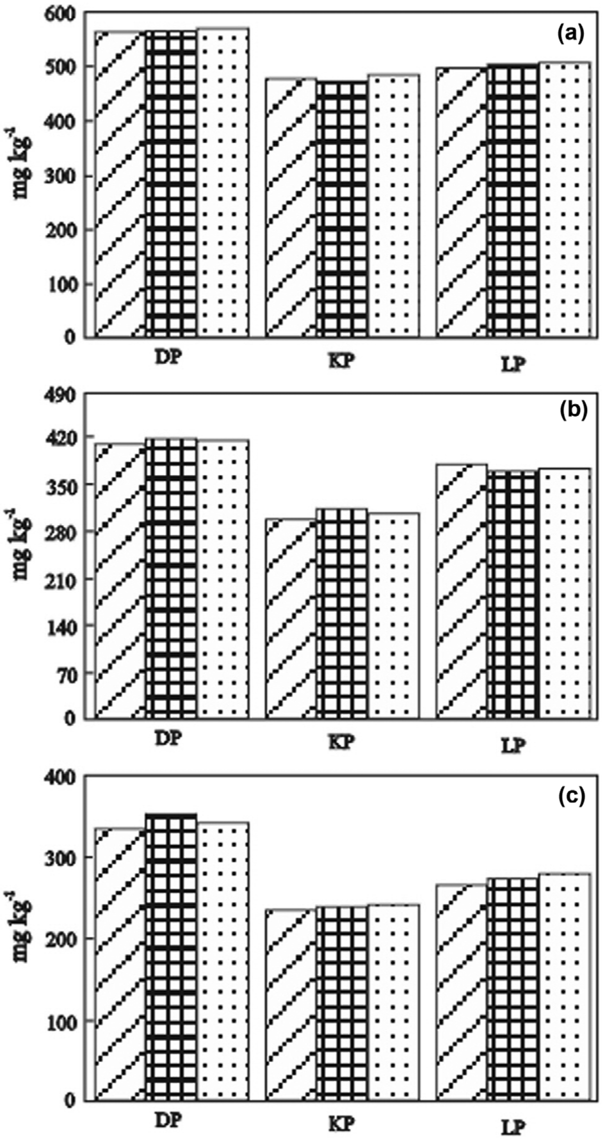

Fig. 5. (a) Total Mn; (b) Extractable Mn; (c) Water soluble Mn in Hazara phosphate.

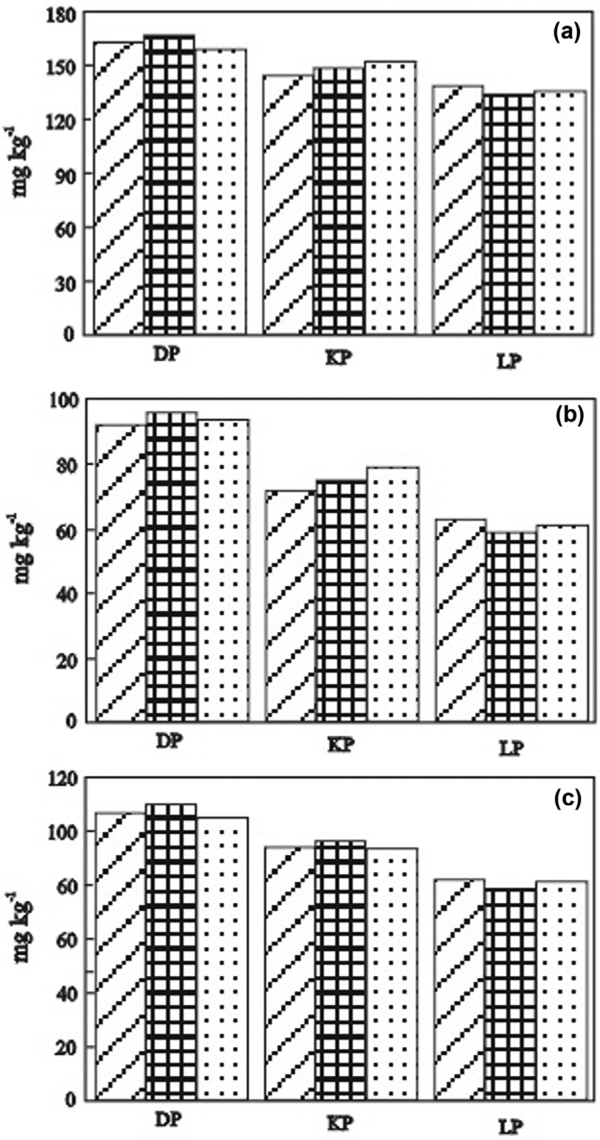

Fig. 6. (a) Total Fe; (b) Water soluble Fe; (c) Extractable Fe in phosphate rocks, Hazara region.

(295.0 mg/kg) in Danna. Concentration of total & extractable Cr was noted as LP > DP > KP (Fig. 4b). Acid digested Cr (410 mg/kg) was found at Lagarban, the minimum concentration (341.6 mg/kg) was observed at Kakul (Fig. 4c). Cr concentration in Hazara phosphate samples indicates higher values than usable limits (1–233 mg/kg).

Nevertheless the possible addition of heavy metals and toxic organic compounds, excess of labile organic matter and leachable phosphorous or presence of pathogenic microorganisms continues to be of the concern (McBride, 2003). Amount of total Mn (566.69 mg/kg) in Danna was noted to be higher than Lagarban (502.67 mg/kg) whereas least was observed from Kakul (477.33 mg/kg) (Fig. 5a). The order of Mn in Hazara phosphorite were noted as DP > LP > KP. Extractable Mn (415.33 mg/kg) was found higher at Danna while the minimum concentration of Mn (305.0 mg/kg) recorded in samples taken from Kakul mines (Fig. 5b). Water soluble Mn (342.7 mg/kg) was found higher at Danna and slightly decreased at Lagarban (272.0 mg/kg) and Kakul (237.0 mg/kg) (Fig. 5c). The PCC and PG waste is contaminated by the solution process, containing both radioactivity and heavy metals in proportion to that was in the phosphate rock (Righi et al., 2005). Mn concentration recorded in present investigation is under the usable limits and may not be toxic for soil and plants. In the Hazara phosphates significant amount of total Fe varied in the order of DP > KP > LP. The total Fe (163 mg/kg) was found higher at Danna and the lowest total Fe (136.3 mg/kg) in Lagarban mines (Fig. 6a). Fe was found maximum in both water soluble (Fig. 6b) and extractable (Fig. 6c) forms at

http://dx.doi.org/10.1007/s12303-017-0013-9

Danna (107 mg/kg) followed by Kakul (94.3 mg/kg) and Lagarban (61 mg/kg).

Cu concentration was also noted much higher in Lagarban phosphorite samples as compared to Danna and Kakul. In the Hazara region Cu concentration was found highest in samples collected from Lagarban area. The concentration of Cu in the Hazara region were noticed by differences in order of LP > DP > KP. Water soluble Cu concentration varied in the order of LP > DP > KP. The greater concentration of Cu was observed at Lagarban with value (69.33 mg/kg) whereas the minimal (35.33 mg/kg) in Kakul (Fig. 7a). Extractable Cu concentration varied in the order of LP > DP > KP. Lagarban has the maximum concentration of extractable Cu with (135.0 mg/kg) and minimum concentration was found in Kakul with (93.33 mg/kg) (Fig. 7b). With small quantities, certain heavy metals are nutritionally essential for a healthy life (e.g., iron, copper, manganese, and zinc). Total Cu concentration varied in the similar order LP > DP > KP. Lagarban phosphate (220.0 mg/kg) has the maximum concentration of total Cu, minimum concentration of total Cu found in Kakul (147.0 mg/kg) (Fig. 7c). Heavy metals are also common in industrial application such as in the manufacturing of pesticides, batteries, alloys, steel and more. The present investigation reveals that LP bears slightly higher concentration than global limits (23–130 mg/kg).

Water soluble Pb concentration were found in the order of DP > KP > LP. Danna (64.67 mg/kg) has the maximum concentration of water soluble Pb and the minimum concentration was found in Lagarban with (40.6 mg/kg) (Fig. 8a). Extaractable Pb noted

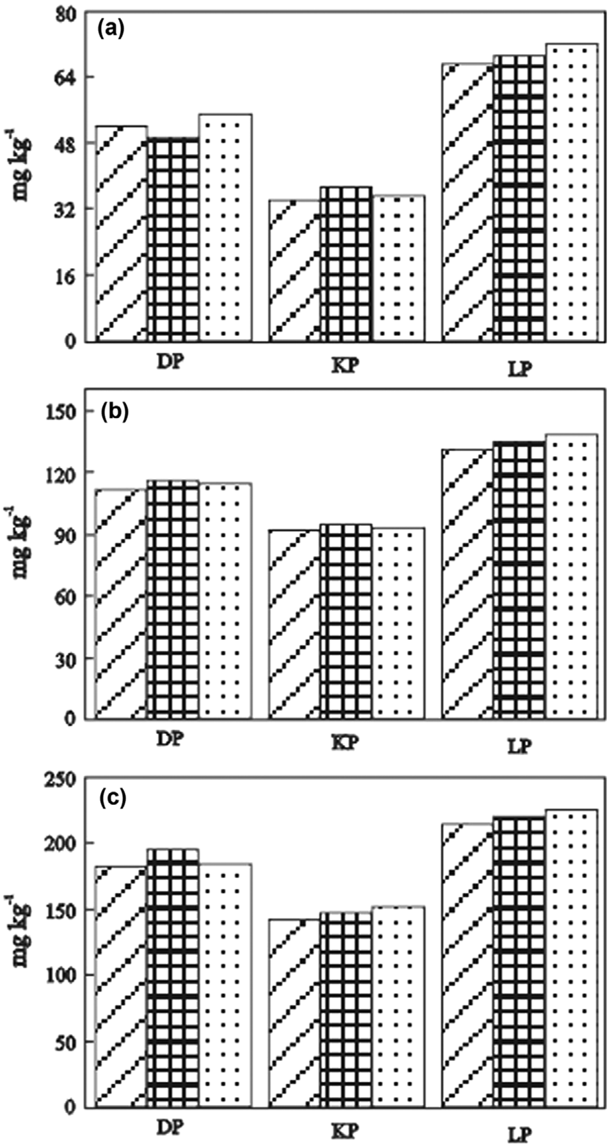

Fig. 7. (a) Water soluble Cu; (b) Extractable Cu; (c) Total Cu in Hazara phosphate.

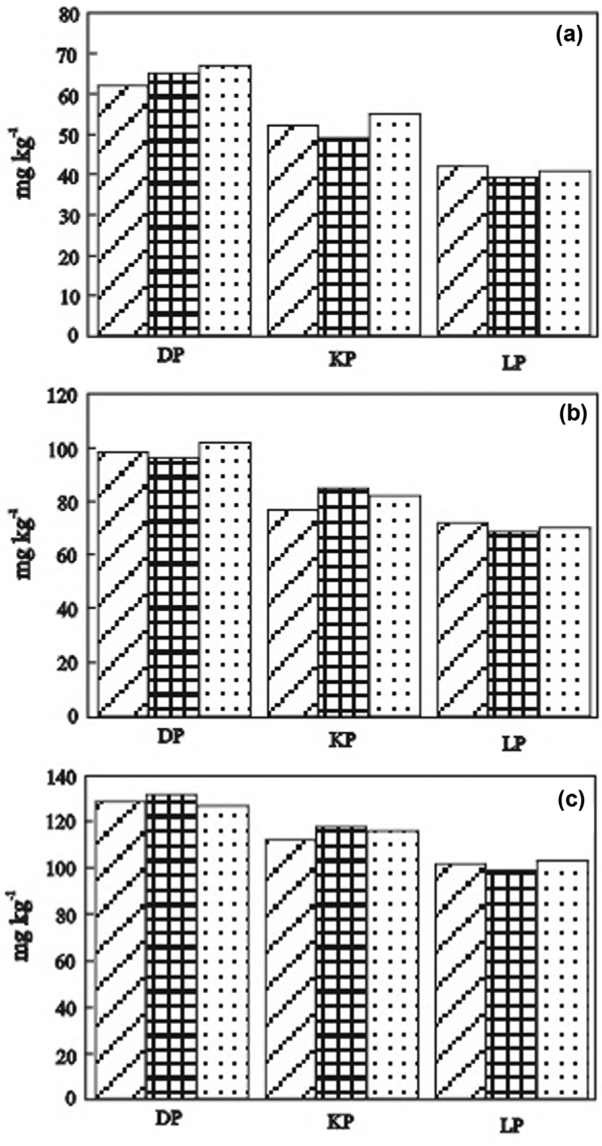

Fig. 8. (a) Water soluble Pb; (b) Extractable Pb; (c) Total Pb in rock phosphate.

from Hazara region varied in the order of DP > LP > KP. Dunna (98.67 mg/kg) has the maximum concentration of extractable Pb whereas the minimum concentration was found in Kakul (81.33 mg/kg) (Fig. 8b). Toxic levels of Pb reduces the rate of photosynthesis and total chlorophyll production. Total lead (Pb) concentration was observed in the order of DP > KP > LP. Danna (129.33 mg/kg) has the maximum concentration of and the minimum concentration was found in LP (101.3 mg/kg) (Fig. 8c). The ingestion of lead (Pb) in plants at higher pH of soil the lead (Pb) turns immobilized (Rosen 2002). The Pb values of Hazara phosphates are higher than the usable global limits (3–44.5 mg/kg) and may be harmful for soil, plants and human health.

Water soluble Ni concentration was found in the order of Lagarban > Danna > Kakul. LP (106.67 mg/kg) has the maximum

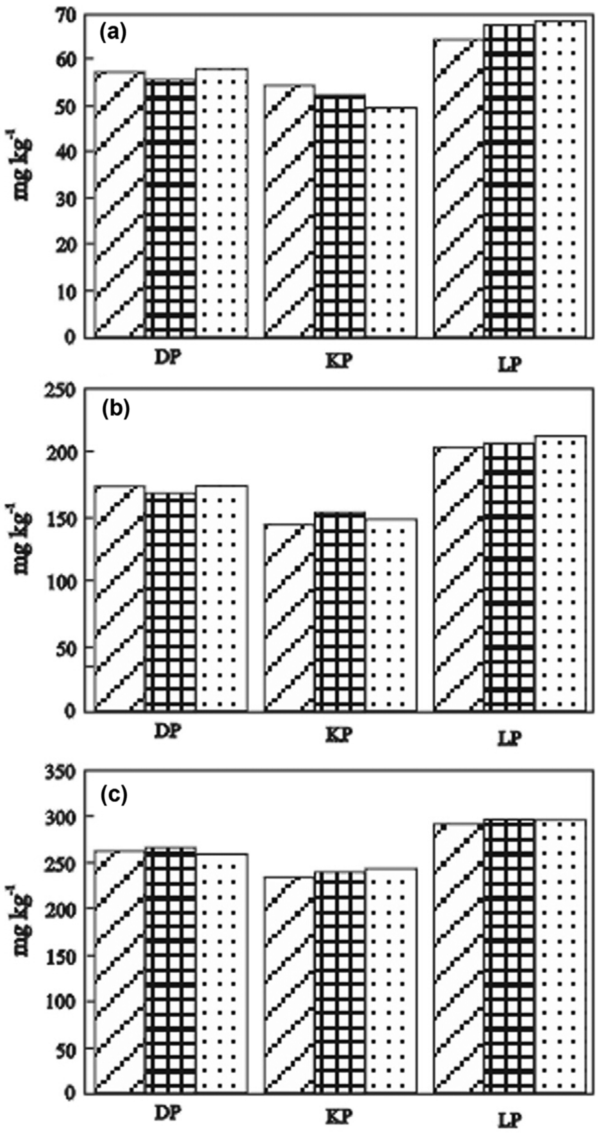

Fig. 9. (a) Water soluble Ni; (b) Extractable Ni; (c) Total Ni in Hazara region.

concentration of water soluble Ni whereas the minimum concentration was found in Kakul (80.3 mg/kg) (Fig. 9a). Extractable Ni were noted in the order of LP > DP > KP. Lagarban has the maximum concentration of extractable Ni (201.6 mg/kg) whereas the minimum concentration was found in Kakul (148.7 mg/kg) (Fig. 9b). The total Ni concentration were found in the order of LP > DP > KP. Lagarban has the maximum concentration of total Ni (294.67 mg/kg) whereas the minimum concentrations were found in Kakul (238.6 mg/kg) (Fig. 9c). Higher concentration of Ni recorded in this study are considered as toxic as Ni content are exceeded the tolerable limit as 116.5 mg/kg (Goyer, 1996).

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., Be, Cr), neurotoxicity (e.g., Pb), gastroenteritis, kidney and liver damage (e.g., Al), anemia and stomach and intestinal irritation (e.g., Cu), and Cancer (e.g., As, Cr-VI). The phosphate rock samples collected from Hazara deposits, Pakistan and Jordan, were used for the manufacturing of PFs in Pakistan. Various methods were applied for the analysis, atomic absorption spectrometry was used for the determination of Al_2O_3, Fe_2O_3 and MgO, flame photometry was used for the analyses of Na_2O and K_2O, titrimetric method for CaO and gravimetric quinoliummolybdo phosphate method for P_2O_5 etc. The analysis of these rocks for their major chemical composition showed the higher value for P_2O_5.

Many researchers reported that long-term applications of P-fertilizers increased concentration of Cd in surface soil (Huang et al., 2004). Cd concentration was found lowest in Hazara Region then other heavy metals studied. Water soluble Cd concentration varied in the order of DP > LP > KP. The greater concentrations of water soluble Cd were found in DP (23.63 mg/kg) and LP (23.47 mg/kg) with marginal difference (Fig. 10a), whereas the lowest concentration was found in Kakul (18.57 mg/kg). Extractable Cd concentration varied in the order of LP > KP > DP. Lagarban has the highest concentration of extractable Cd with (35.37 mg/kg) and the minimum concentration was found in Danna (27.47 mg/kg) (Fig. 10b). The total Cd concentration was found in the order of LP > DP > KP. Lagarban (66.57 mg/kg) have the greater total concentration of Cd and the lower total concentration was found in Kakul (52.07 mg/kg) (Fig. 10c). Cadmium concentration in Lagarban phosphate of present study was found slightly higher than maximum global limit 60 mg/kg (Taher and Abdelhalim, 2013). Global usable limits of Cd concentration in phosphate rocks is 0.1–60 mg/kg (Conceicao and Bonotto, 2006), but there is no danger to use phosphate fertilizer noted in this study.

The degree of toxicity of trace ingredients, which ultimately harm the environments may be resulted due to long term use of phosphate fertilizers as well as soil treatments to the agri-

http://dx.doi.org/10.1007/s12303-017-0013-9

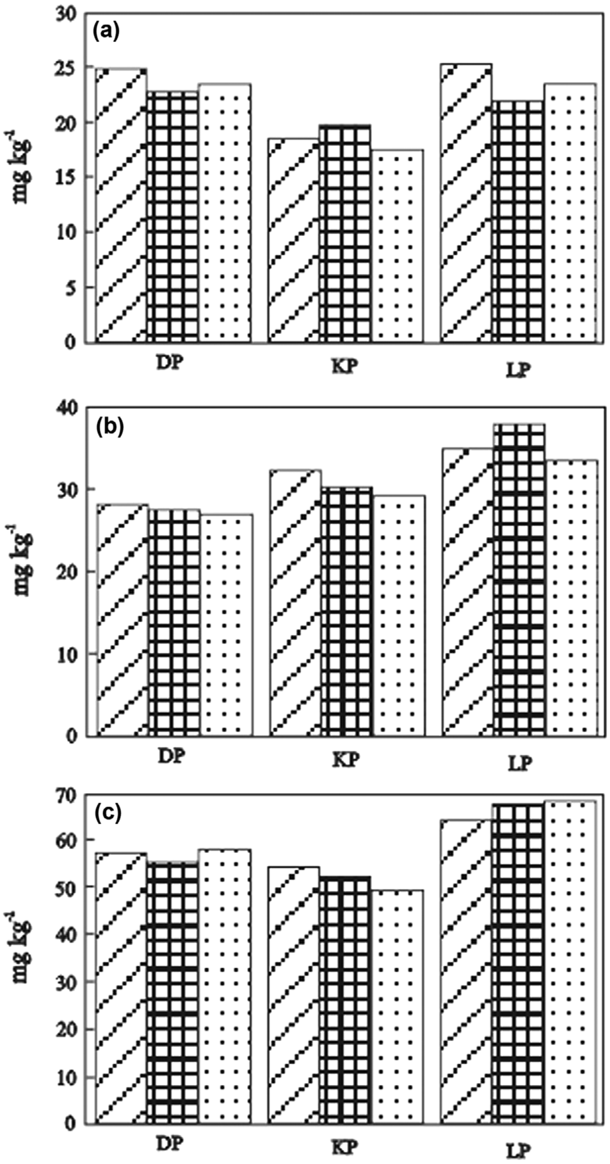

Fig. 10. (a) Water soluble Cd; (b) Extractable Cd; (c) Total Cd in phosphate rocks in study area.

cultural lands. The possible effects of fertilizers on environments is dependent on the number of factors such as nature of elements released, amounts used, toxicity & mobility of these elements and ease to incorporate these elements into the biota (Sattouf, 2007). Furthermore the quantity and quality of toxic elements released can effectively be used to estimate the potential environmental contamination risk in the soil (Raven and Loeppert, 1997). Due to non-degradable nature of the heavy metals present in the fertilizers cause their accumulation in agriculture soil (Voet et al., 2000; Abdel Haleem et al., 2001). Long applications of rock phosphates (contains relatively high heavy metals) as fertilizer could endanger human as well as animal health because of the heavy metals accumulation through food chain, which can ultimately cause chronic health troubles (Sattouf, 2007; Islam et al., 2007). Waseem et al. (2016) reviews the heavy metal contamination in several areas of Pakistan over the past few years, particularly to assess the heavy metal contamination in water (groundwater, surface water, and waste water), soil, sediments, particulate matter, and vegetables. The listed contaminations affect the drinking water quality, ecological environment, and food chain. Moreover, the toxicity induced by contaminated water, soil, and vegetables poses serious threat to human health. Waseem and Arshad (2014) observed from his study that most of the toxic metals in biological fluids/tissues in general population of Pakistan have higher background values comparatively. For example the mean values of toxic metals like As, Cd, Cr, Ni, and Pb in blood of general population were found as 2.08 mg/L, 4.24 mg/L, 60.5 mg/L, 1.95 mg/L, 198 mg/L respectively. Similarly, the urine mean values of 67.6 mg/L, 3.2 mg/L, 16.4 mg/L, 6.2 mg/L and 86.5 mg/L were observed for As, Cd, Cr, Ni, and Pb respectively.

To minimize the risks associated with the transfer of heavy metals from P-fertilizers into the environment, rock phosphates of such origins are used which is low in heavy metal contents. Rock phosphates from different origin contain a distinctive heavy metal assemblage which is characteristic of the formation processes or indicative of subsequent modification by diagenesis or weathering (Weissberg and Singers, 1982). In general, sedimentary rock phosphates contain much higher concentrations of potentially hazardous elements (As, Cd, Cr, Pb, Se and U) than igneous origin. Sometimes As and Pb concentrations may be lower in sedimentary than igneous rock phosphates. The rock phosphates are either applied directly to the soil, especially in organic farming or manufactured to produce water-soluble phosphorus fertilizers. It is reported that sedimentary rock phosphates are suitable for direct application as fertilizers only under certain conditions (Chien, 1993; Rajan et al., 1996). The contamination of rock phosphates with heavy metals does limit the suitability of rock phosphates as a source for agriculture phosphorous in organic farming. The safe management of this farming requires monitoring and measurement of radionuclide and toxic heavy metals in applied rock phosphates. Therefore it is suggested to ensure the uses of phosphorous and other major nutrients applied in a right quantity depending on the soil conditions at the correct time. The heavy metals like As, Cr, Pb, Hg, Ni, and V has prime significance as observed in recent years, because their entrance into the human food chain particularly Cd, impairs the function of liver and kidneys (Von Geldmacher et al., 2004). The quality of fertilizer is dependent upon heavy metals released from phosphate rocks. Therefore all measuring steps should be used in order to protect environment as well as public health e.g., Phytoremediation and electrokinetics (Raskin et al., 1997).

5. CONCLUSIONS

Concentration of heavy metals and phosphorous of the Hazara phosphate sedimentary deposits was carried out in total, water soluble and extractable forms for the purpose of their environmental effects especially soil. The results of this study exhibit that heavy metals concentration reduces in order of Zn, Mn, Cr, Ni, Cu, Fe, Pb, Cd and Zn, Mn, Cr, Ni, Fe, Cu, Pb, Cd in samples taken from Danna-Lagarban and Kakul mines, respectively. The results showed that Hazara phosphate deposits have significant amount of phosphorite for the production of phosphate fertilizers but it contains higher amount of number of heavy metals particularly Zn, Pb, Cu and Cr. Higher concentration of these heavy metals may cause number of problems related to soil, environment and human health e.g., soil immobilization, weak plant growth, disorder in plant metabolism, neurotoxicity and gastroenteritis. To reduce the environmental risks in air, soil, surface & groundwater and food chain careful use and remedial measures should be taken in mining vicinities.

REFERENCES

Abdel-Haleem, A.S., Sroor, A., El-Bahi, S.M., and Zohny, E., 1995, Heavy metals and rare earth elements in phosphate fertiliser components using instrumental neutron activation analysis. Applied Radiation and Isotopes, 55, 569–573.

Bolan, N.S, White, R.E., and Hedley, M.J., 1990, A review of the use of phosphate rocks as fertilizers for direct application in Australia and New Zealand. Austrian Journal of Experimental Agriculture, 30, 297–313.

Chien, S.H., 1993, Solubility assessment for fertilizer containing phosphate rock. Fertilizer Research, 35, 93–99.

da Conceicao, F.T., and Bonotto, D.M., 2006, Radionuclides, heavy metals and fluorine incidence at Tapira phosphate rocks, Brazil, and their industrial (by) products. Environmental Pollution, 139, 232–243.

El-Mrabet, R., Abril, J., Periáñez, R., Manjón, G., García-Tenorio, R., Delgado, A., and Andreu, L., 2003, Phosphogypsum amendment effect on radionuclide content in drainage water and marsh soils from South-western Spain. Journal of Environmental Quality, 32, 1262–1268.

El-Taher, A. and Abdelhalim, M.A.K., 2013, Elemental Analysis of Phosphate Fertilizer consumed in Saudi Arabia. Life Science Journal, 10, 701–708.

Goyer, R.A., 1996, Toxic effects of metals. In: Klaassen, C.D. (ed.), Casarett & Doull's Toxicology: Basic Science of Poisons (5th edition). McGraw-Hill, New York, p. 691–736.

Huang, B., Kuo, S., and Bembenek, R., 2004, Availability of Cadmium in some phosphorus fertilizers to field-grown lettuce. Water, Air, and Soil Pollution, 158, 37–51.

Ibsram, 1994, Methodological Guidelines for IBSRAM's Soil Management Networks (2nd edition). International Board for Soil Research and Management, Bangkok, 243 p.

Islam, E., Yang, X., He, Z., and Mahmood, Q., 2007, Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. Journal of Zhejiang University – Science, B8, 1–13

Kpomblekou, K. and Tabatabai, M.A., 1994, Metal contents of phosphate rocks. Communications in Soil Science and Plant Analysis, 25, 2871–2882.

Kratz, S. and Schnug, E., 2005, Schwermetalle in P-Düngern. In: Haneklaus, S. (ed.), Recent Advances in Agricultural Chemistry. Landbauforschung Völkenrode, Sonderheft, Bundesforschungsanstalt für Landwirtschaft, Braunschweig, 286, p. 37–45.

Makweba, M.M. and Holm, E., 1993, The natural radioactivity of the rock phosphates, phosphatic products and their environmental implications. Science of the Total Environment, 133, 99–110.

McBride, M.B., 2003, Toxic metals in sewage sludge-amended soils: has promotion of beneficial uses discontinued the risk? Advances in Environmental Research, 8, 5–19.

Mortvedt, J.J., 1996, Heavy metal contaminants in inorganic and organic fertilizers. Fertilizers Research, 43, 55–61.

Murphy, J. and Riley, J.P., 1962, A modified single solution method for the determination of phosphate in nature water. Analytical Chimica Acta, 27, 31–36.

Powell, C.M.A., 1979, A speculative tectonic history of Pakistan and surroundings – some constraints from the Indian Ocean. In: Farah, A. and de Jong, K.A. (eds.), Geodynamics of Pakistan. Geological Survey of Pakistan, Quetta, p. 5–24.

Rajan, S.S., Watkinson, J.H., and Sinclair, A.G., 1996, Phosphate rocks for direct application to soils. Advances in Agronomy, 57, 77–159.

Raskin, I., Smith, R.D., and Salt, D.E., 1997, Phytoremediation of metals: using plants to remove pollutants from environment. Current Opinion in Biotechnology, 8, 221–226.

Raven, K.P. and Loeppert, R.H., 1997, Trace element composition of fertilizers and soil amendments. Journal of Environmental Quality, 26, 551–557.

Righi, S., Luciallib, P., and Bruzzi, L., 2005, Health and environmental impacts of a fertilizer plant Part I: Assessment of radioactive pollution. Journal of Environmental Radioactivity, 82, 167–182.

Rosen, C.J., 2002, Lead in the home garden and urban soil environment communication and educational technology services. University of Minnesota Extension, Minneapolis, 4 p.

Schnug, E., Hanklaus, S., Schnier, C., and Scholten, C., 1996, Issues of natural radioactivity in phosphates. Communication Soil Science and Plant Analysis, 27, 829–841.

Sattouf, M., 2007, Identifying the origin of rock phosphates and phosphorus fertilizers using isotope ratio techniques and heavy metal patterns. Ph.D. Thesis, Braunschweig University of Technology, Braunschweig, 178 p.

Tufail, M., Akhtar, N., and Wagas, M., 2006, Radioactive rock phosphate: The feed stock of phosphate fertilizers used in Pakistan. Health Physics, 90, 361–370.

Umar, M., Khan, A.S., Kelling, G., Kassi, A.M., 2011, Depositional environments of Campanian-Maastrichtian successions in the Kirthar Fold Belt, southwest Pakistan: Tectonic influences on late Cretaceous sedimentation across the Indian Passive margin. Sedimentary Geology, 237, 30–45.

Umar, M., Sabir, M.A., Farooq, M., Khan, M.M.S.S., Faridullah, Jadoon, U.K., and Khan, A.S., 2015a, Stratigraphic and sedimentological attributes in Hazara basin Lesser Himalya, north Pakistan: their role in deciphering minerals potential. Arabian Journal of Geosciences, 8, 1653–1667.

Umar, M., Betts, P., Khan, M.M.S.S., Sabir, M.A., Farooq, M., Zeb, A., Jadoon, U.K., and Ali, S., 2015b, Signatures of late Neoproterozoic Gondwana assembly and Maronian glaciation in Lesser Himalaya: A palaeogeographical and stratigraphical approach. Acta Geologica Polonica, 65, 1–19.

Voet E., Guinee, J.B., and Haes, H., 2000, Heavy Metals: A Problem Solved? Methods and Models to Evaluate Policy Strategies for Heavy Metals. Kluwer Academic Publishers, Dordrecht , 242 p.

Von Geldmacher, M., Mallinckrodt, V., and Schaller, K.H., 2004, Acute and chronic toxicity of metals and compounds in man. In: Merian, E., Anke, M., Ihnat, M., and Stoeppler, M. (eds.), Elements and their Compounds in the Environment. Wiley-VCH Verlag, Weinheim, p. 415–432.

Waseem, A., Arshad, A., Iqbal, F., Sajjad, A., Mehmood, Z., and Murtaza, G., 2014, Pollution status of Pakistan: A retrospective review on heavy metal contamination of water, soil, and vegetables. BioMed Research International. http://dx.doi.org/10.1155/2014/813206

Waseem, A. and Arshad, J., 2014, A review of Human Biomonitoring studies of trace elements in Pakistan. Chemosphere, 163, 153–176.

Weissberg, B.G. and Singers, W.A., 1982, Trace elements and provenance of phosphate rocks. New Zealand Journal of Science, 25, 149–54.