



Total and extractable soil selenium contents variation within and across the parent materials

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Article published on October 30, 2016

Key words: Multiple regression equation, Parent materials, Extractable selenium, Soil properties, Total selenium.

Abstract

Selenium is an essential trace element for humans and animals by affecting them through its toxicity and deficiency. Selenium contents in soils depend on the source of parent material the soils are derived from. Total soil selenium as well as phosphate-buffer extractable selenium varied with type of parent material and weathering stage. Three replicated soil profiles at three different weathering stages (i.e. least weathered, moderately weathered and relatively more weathered) were sampled at genetic horizons level from alluvium, loess, sandstone and shale parent materials. Total selenium varied between 270 to 7050 $\mu\text{g kg}^{-1}$, and phosphate buffer extractable selenium ranged from 25 to 90 $\mu\text{g kg}^{-1}$ soil in the dataset. Total and phosphate-buffer extractable selenium distribution changed differently with soil genesis in each parent material. In shale and loess soils total selenium increased toward the surface in relatively more developed soils whereas in alluvium and sandstone soils weathering effect was negligible. The mean phosphate-buffer extractable selenium was significantly high in the shale derived soils followed by the loess, alluvium and sandstone. Multiple regression equation predict that crystalline iron, total selenium, Al_a, and cation exchange capacity are the main controlling factors for phosphate buffer extractable selenium.

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Introduction

Selenium (Se) is an essential trace element and, for humans and animals (Mac Farquhar *et al.*, 2010). Selenium contents in soils depends on the source of parent materials the soils are derived from, and soil forming processes which redistribute selenium (Mayland *et al.*, 1989; Cuvardic, 2003). Similarly, pedogenic processes control the spatial distribution of selenium contents and the continuity of lithological properties (Hartikainen, 2005b; Adriano, 2001).

Shale inherently contains more selenium minerals, and hence high contents of selenium are found in shale derived soils (Jefferis, 1984; Rosenfeld and Beath, 1964). The sedimentary rocks have high selenium contents than the igneous rocks. Among the igneous rocks, granites, rhyolites, rhyolitic pumices, and the sedimentary limestone represent the low selenium rocks whereas in and esites, basalts, and Upper Cretaceous argillites have high selenium (Wells, 1967). Fine textured argillaceous clay, iron oxides, and humic compounds provide exchange sites causing to increase selenium in shale parent material (Huayu and Zhisehng, 1998). Selenium contents are also associated with an increase of clay and silt in soils (Wang and Chen, 2003). Clay fraction controls the selenium with and without metal oxides and organic matter removal followed by silt and sand fractions (Wang and Chen, 2003).

Table 1. The selected soils with USDA classification.

Parent material	Least weathered soil	Moderately weathered soil	Weathered soil
Loess	Rajar, Typic Ustorthents	Rawalpindi, Udic Haplustepts	Chakwal, Typic Haplustalfs
Alluvium	Shahdra, Typic Ustifluvents	Argan, Fluventic Haplustepts	Gujranwala, Typic Haplustalfs
Sandstone residuum	Qazian, Lithic Ustipsamments	Balkasar, Typic Haplustalfs	Kahuta, Udic Haplustalfs
Shale residuum	Ghoragali, Typic Udorthents	Tirnul, Typic Haplustepts	Murree, Typic Hapludolls

The soil properties were determined including i.e. pH, redox potential, CaCO₃ content, dithionite extractable iron, dithionite extractable aluminum, oxalate extractable iron, cation exchange capacity, total and dissolved organic carbon. Soil pH was measured from saturated soil paste (McLean, 1982),

Scarce information on variation in total soil selenium and phosphate buffer extractable selenium contents at different weathering stages in each parent material. It is hypothesized that phosphate selenium contents changed with parent material and soil genesis (weathering stage).

The objectives of the study were to understand the variation in phosphate buffer extractable selenium and total selenium at different weathering stages in each parent material and phosphate buffer extractable selenium relationship with soil properties.

Material and methods

Soil sampling and characterization

The soils at different stages of weathering were taken from alluvium, loess, sandstone and shale parent materials. Replicated profiles for each soil series were dug (Table 1). The soil was sampled from each genetic horizon level and passed through 2 mm sieve after air drying. The loess parent material is deposited during Pleistocene period in sub-humid to semi-arid climate and occupies level, sloping, erosional surfaces. Alluvium parent material is derived from Himalayas and deposited during Pleistocene period to present. The sandstone and shale-sandstone admixture comprise of Siwalik formation of Pliocene period and the Murree formation of Miocene period host residual soils where genesis is driven by surface relief.

redox potential was measured from 1:1 of soil to water suspension, and calcium carbonate was determined by CH₃COOH consumption method (Loeppert *et al.*, 1984). Total organic carbon was determined by wet digestion using K₂Cr₂O₇ solution (Walkley, 1947), and dissolved organic carbon (DOC) was determined by extracting soluble organic carbon in K₂SO₄,

digestion in $K_2Cr_2O_7$ and concentrated H_2SO_4 , and measurement of excess $K_2Cr_2O_7$ with $Fe(NH_4)_2(SO_4)_2$ Ferrous ammonium sulfate (Nelson and Sommers, 1982).

Dithionite extractable iron was measured by extracting with $C_6H_5Na_3O_4 \cdot 2H_2O$, and $NaHCO_3$ buffer in the presence of $Na_2S_2O_4$ (Mehra and Jackson, 1960) and amorphous iron content from soil was extracted with acidified $(NH_4)_2C_2O_4 \cdot H_2O$ solution (Jackson *et al.*, 1986). Crystalline iron content was calculated by subtracting amorphous iron from dithionite iron contents.

Soil total selenium

Soil total selenium was determined by wet digestion with acid mixture (1:1) of nitric acid and hydro fluoric acid. One gram finely ground soil was digested and samples were destroyed at $160^\circ C$ in a drying box for 6 h. After adding 5 mL of 10% HCL the sample was evaporated for a while, solution was made to 50 mL volume with de-ionized and stored at $4^\circ C$ until selenium analysis on atomic absorption spectrophotometer coupled with hydride vapor generator (Hagrova *et al.*, 2005). Sodium selenate was used for standard reference to evaluate the recovery percentage of the method which was above 97%.

Extractable (bioavailable) soil selenium

Twenty five milliliter of 0.1 molar phosphate buffer ($KH_2PO_4 + K_2HPO_4$) of pH 7 was added to the 5 gram soil and shaken for 24 hr on end to end mechanical shaker. Supernatant was filtered through $0.45 \mu m$ after centrifugation.

The filtrate of the sample was stored at $4^\circ C$ until the selenium analysis on atomic absorption spectrophotometer coupled with hydride vapor generator (Hagrova *et al.*, 2005).

Statistical analysis

The variance in the soil parameters and total selenium were ascribed to soil parent material at different depths collectively.

The multivariate analysis was implemented using Proc General Linear Model in SAS version 9.4 (SAS Institute Inc., 2014). The parent material and soil (parent material) were class variable and the soil depths were multiple dependent variables. Stepwise multiple regression analysis was to correlate phosphate buffer extractable selenium and soil properties that determine phosphate buffer extractable selenium in soils derived from various parent materials.

Result and discussion

Soil characteristics

The soils are derived from residuum of shale and sandstone of Miocene epoch, the Pleistocene loess, and the alluvium of Holocene and Pleistocene epochs. All the soils are moderate to weakly differentiated, low in organic carbon, extractable iron, calcareous to decalcified up to 90 cm depth with CEC between 20 to $37 \text{ cmol}_c \text{ kg}^{-1}$ soil. The shale derived soils had high total organic carbon as these soils occur in high rainfall and coniferous forest, leading to greater accumulation of total and dissolved at the surface horizons.

The extractable iron (dithionite extractable iron) and amorphous iron (oxalate extractable iron) were also greater in the shale soils than alluvium, loess and sandstone. Most soils were medium to strongly calcareous caused by decalcification except for Haplustalfs in alluvium and loess. Most soils had pH between 6.5 to 8.2 buffered by soil $CaCO_3$ contents.

The shale and loess soils had high redox potential (Eh) than alluvium and sandstone. Cation exchange capacity was highest in the shale soils due to high argillaceous clay contents and increased with advance weathering in each parent material (Table 2).

Table 2. The basic characteristics for the soils developed in different parent materials.

Parent material	Clay	CaCO ₃	CEC	TOC	DOC	Eh	pH	Fe _{Crys}	Fe _o	Total Se	Available Se
	g 100g ⁻¹	%	Cmol _c kg ⁻¹	g kg ⁻¹	mg kg ⁻¹	mV		-----g kg ⁻¹ -----		-----µg kg ⁻¹ -----	
Alluvium	26c	7.6b	21.3c	2.7b	39a	246c	7.59a	11.97b	0.54b	468b	45b
Loess	31b	6.9bc	28.2b	2.9b	38a	260b	7.66a	9.18c	0.81a	518b	51a
Sandstone	24c	5.5c	15.9d	3.0b	41a	244c	7.44b	7.45d	0.48b	320b	37c
Shale	40a	9.8a	37.5a	5.1a	44a	287a	7.30b	21.47a	0.82a	1578a	55a

CaCO₃, soil CaCO₃ equivalent (Loeppert *et al.*, 1984); CEC, cation exchange capacity (Rhoades, 1982); TOC, total organic carbon by wet oxidation (Nelson and Sommers, 1982); CBD-Fe, citrate bicarbonate dithionite-extractable iron (Mehra and Jackson, 1958) and FeO, oxalate extractable iron (Jackson *et al.*, 1986); DOC, dissolved organic carbon (Olsen and Sommers, 1982). Cryst Fe, crystalline iron calculated from subtraction of amorphous iron from dithionite iron contents. Means followed by the same letter within each column are statistically similar at $p > 0.05$

Soil total selenium

Total selenium content in the soils ranged from 270 to 7050 $\mu\text{g kg}^{-1}$, and the highest variability was associated with the source of parent material. The shale derived soils had the highest total selenium found in the range of 740 to 7050 $\mu\text{g kg}^{-1}$ soil whereas the loess, alluvium and sandstone derived soils had significantly lower values than shale that were at par with each other (Table 2). The variations in total selenium relates to lithology (Cuvardic, 2003). The shale inherently contains more selenium minerals causing the total selenium in shale derived soils to increase (Jefferis, 1984; Rosenfeld and Beath, 1964; Gissel-Nielsen *et al.*, 1984). The igneous rocks granite, rhyolite and rhyolitic pumices are low selenium rocks and andesite and basalt are high selenium rocks (Wells, 1967) in other words the high siliceous rocks have low selenium contents than mafic rocks which explains the low values of selenium in the sandstone and alluvium.

Total selenium contents differed with depth in the parent materials as the hypothesis of no depth x parent material interaction was rejected (Wilk's lambda F 11.37, df 12, $p \geq 0.0001$). The interaction was associated with significantly high total selenium content at the surface of the shale derived soils contributed by total organic carbon selenium (Fig. 1). Selenate-selenium ions are sorbed by ferric and aluminum ions complexed by organic matter (Pezzarossa *et al.*, 1999).

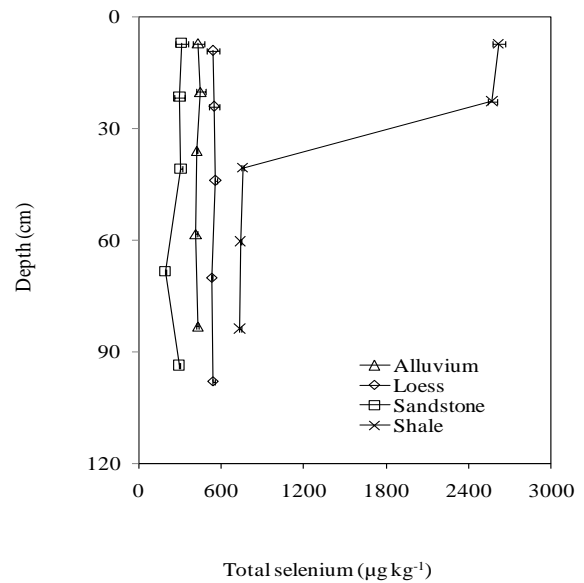


Fig. 1. Distribution of total selenium in different parent materials indicating increased total selenium towards the surface in shale.

The soil genesis changed total selenium distribution with depth differently in each parent material. The hypothesis of no depth x soil (pm) interaction was rejected with test statistics wilk's lambda F 6.53, df 32, $p \geq 0.0001$. In shale and loess soils, total selenium increased toward the surface in relatively more developed soils. Murree soil profiles had high total selenium at the surface due to high organic carbon (Eich-Greatorex *et al.*, 2007). The Hapludoll had a mollic epipedon causing the mean to increase several folds. The Typic Udorthents (Ghoragalli soil) also had high organic carbon at the surface. The Murree and Ghoragalli soils occur under coniferous forest in subhumid to humid climate leaving organic carbon accumulation and, consequently, the high mean selenium in the shale (Jhonsson, 1992). Although less pronounced, the Alfisols of the loess as well had greater selenium at the surface. The vegetation type is more important than the direct effect of precipitation on organic selenium accumulation (Jobbagy and Jackson, 2000). Pedogenesis in the alluvium and sandstone caused a little or no change in total selenium level in the profiles. The Haplustalfs and Ustifluvents/Psamments had no significant difference throughout the depth (Fig. 2).

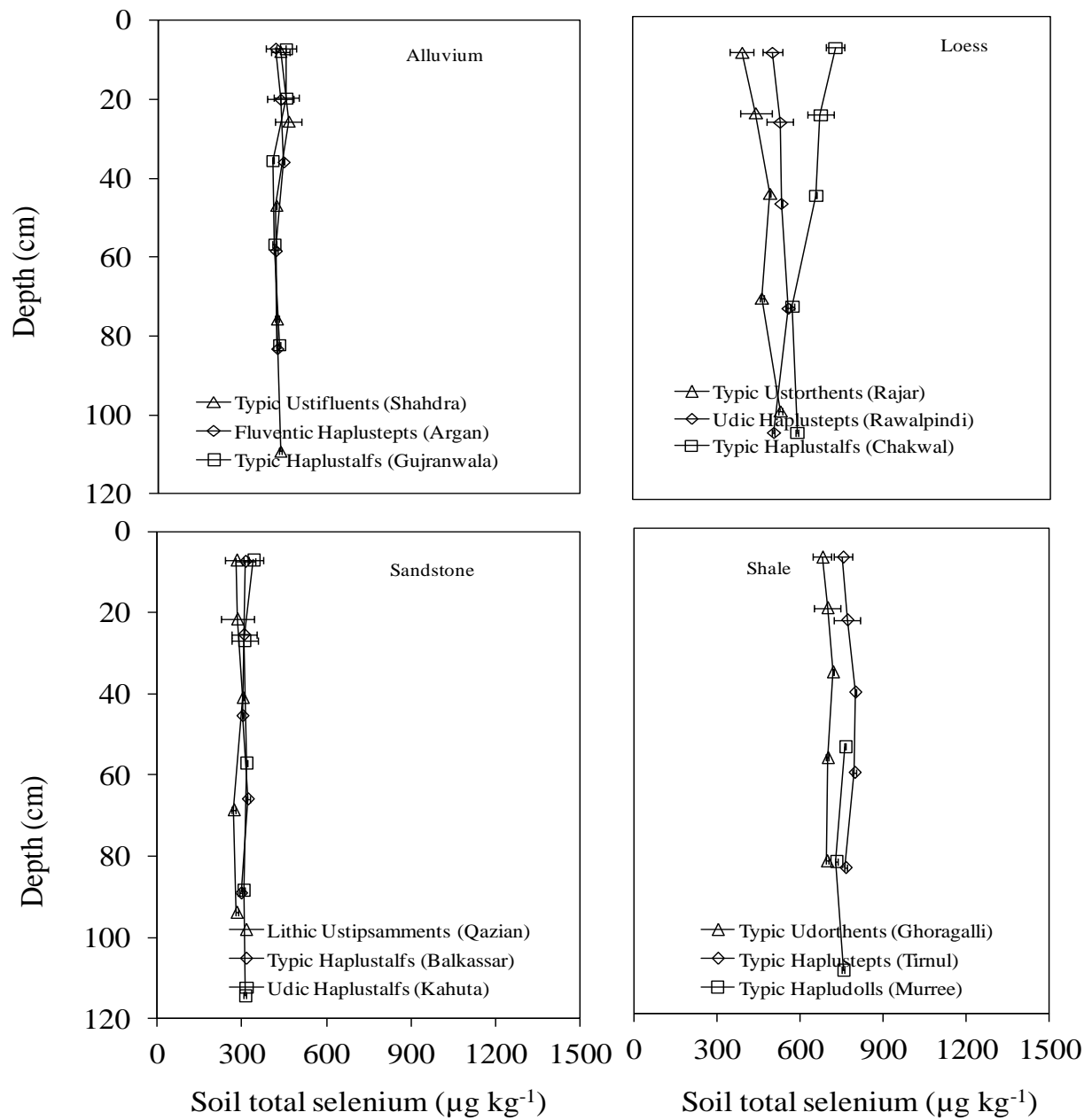


Fig. 2. Distribution of total selenium contents in the soils at different weathering stages in each parent material.

Total soil selenium had a significant correlation ($p < 0.0001$) with crystalline iron contents ($r = 0.68$), amorphous iron ($r = 0.59$), clay ($r = 0.55$) and total organic carbon ($r = 0.49$). Selenium has a strong relationship with iron (Ryser *et al.*, 2005). Soil selenium and iron minerals have three aspects of their relationship: (a) selenium is incorporated into the crystal structure as isomorphous substitution (Pyrite),

(b) occluded in crystalline iron oxides structure or co-precipitated, (c) adsorbed on the surface of iron oxides (Mrurphy, 1988; Balistreri and Chao, 1987; Strawn *et al.*, 2002; Diener and Neumon, 2011). The relationship of total soil selenium was stronger with crystalline than amorphous iron oxides (Fig. 3) indicating more occlusion or precipitation than surface adsorption, contrary to the findings of Hingston *et al.* (1968).

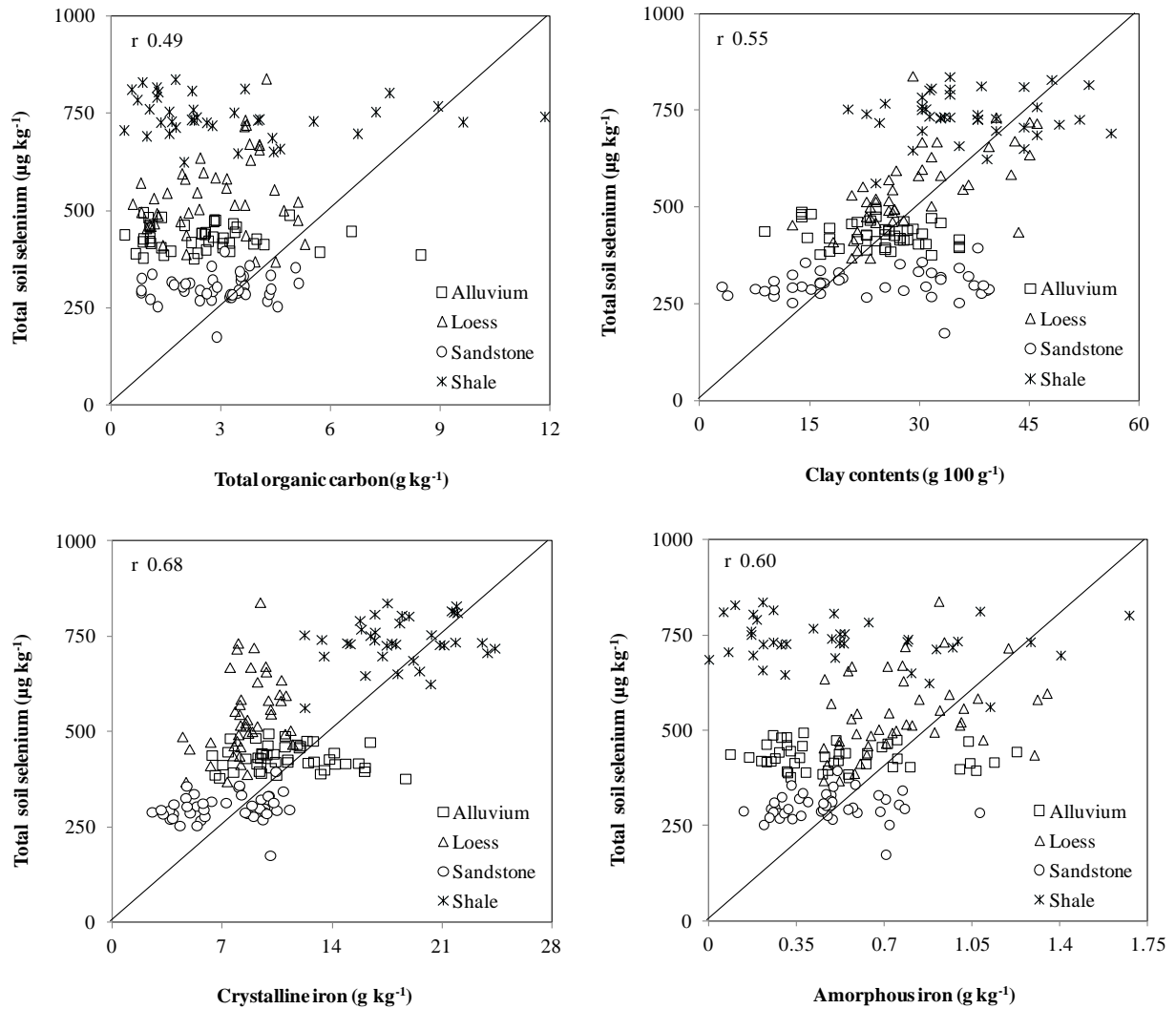


Fig. 3. Relationship of total soil selenium with total organic carbon, clay content, crystalline and amorphous iron contents.

Conforming to previous studies the selenium contents are positively correlated with organic matter and clay contents (Yamda *et al.*, 2009; Xing *et al.*, 2015; Supriatin *et al.*, 2015). The argillaceous clays increase as the mafic character of the rocks increases resulting from concentration of selenium containing primary minerals in the absence of quartz. The iron oxides are as well concentrated in the clay size fraction.

The positive role of organic matter in total selenium was through concentration of selenium soil biota. Organic selenium in these soils is maximum 20% of total selenium as opposed up to of 80% (Rayman, 2004), which explains the low of correlation with total selenium.

Extractable (bioavailable) soil selenium

The bioavailable selenium extracted with phosphate-buffer at pH 7 (Hagrova *et al.*, 2005) ranged from 25 to 90 $\mu\text{g kg}^{-1}$ soil, and was high in the shale derived soils followed by a significantly low mean in the loess, alluvium and sandstone derived soils.

The hypothesis of no “depth x parent material” and no “depth x soil (pm)” interactions could not be rejected suggesting that phosphate buffer extractable selenium changed a little with depths. Consequently, the difference remained significant among the parent materials at different stages of development in each parent materials at different stages of development throughout the respective profile depth (Fig. 4 and Fig. 5).

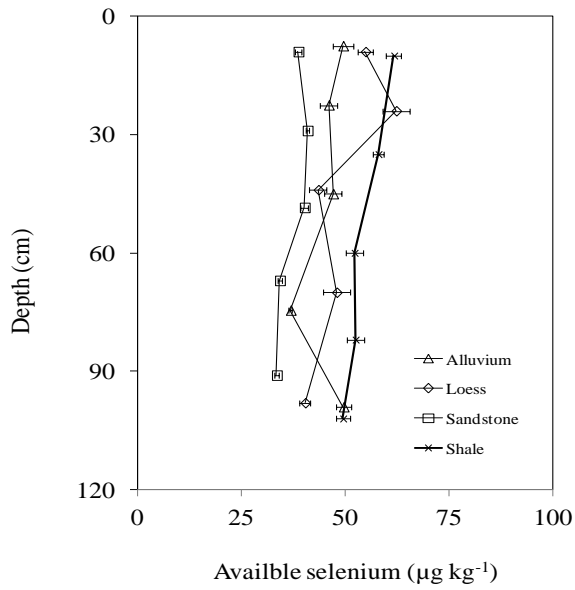


Fig. 4. Distribution of available selenium contents in different parent materials.

The relatively more weathered soils had increased phosphate-buffer extractable selenium in each parent material. Phosphate-buffer extractable selenium increases with soil weathering (Mayland *et al.*, 1989; Kulp and Pratt, 2004; Matamoros-Velozza *et al.*, 2011). Phosphate-buffer extractable selenium in the soils had positive correlation with total selenium content.

Cation exchange capacity and the redox potential (Fig. 6). Phosphate-buffer extractable selenium had poor had a little relation with poorly crystalline iron oxides (data not depicted) that are commonly secondary precipitates of iron released from primary minerals while pyrite oxidation has been postulated to control available extractable selenium during shale weathering (Matamoros-Velozza *et al.*, 2011).

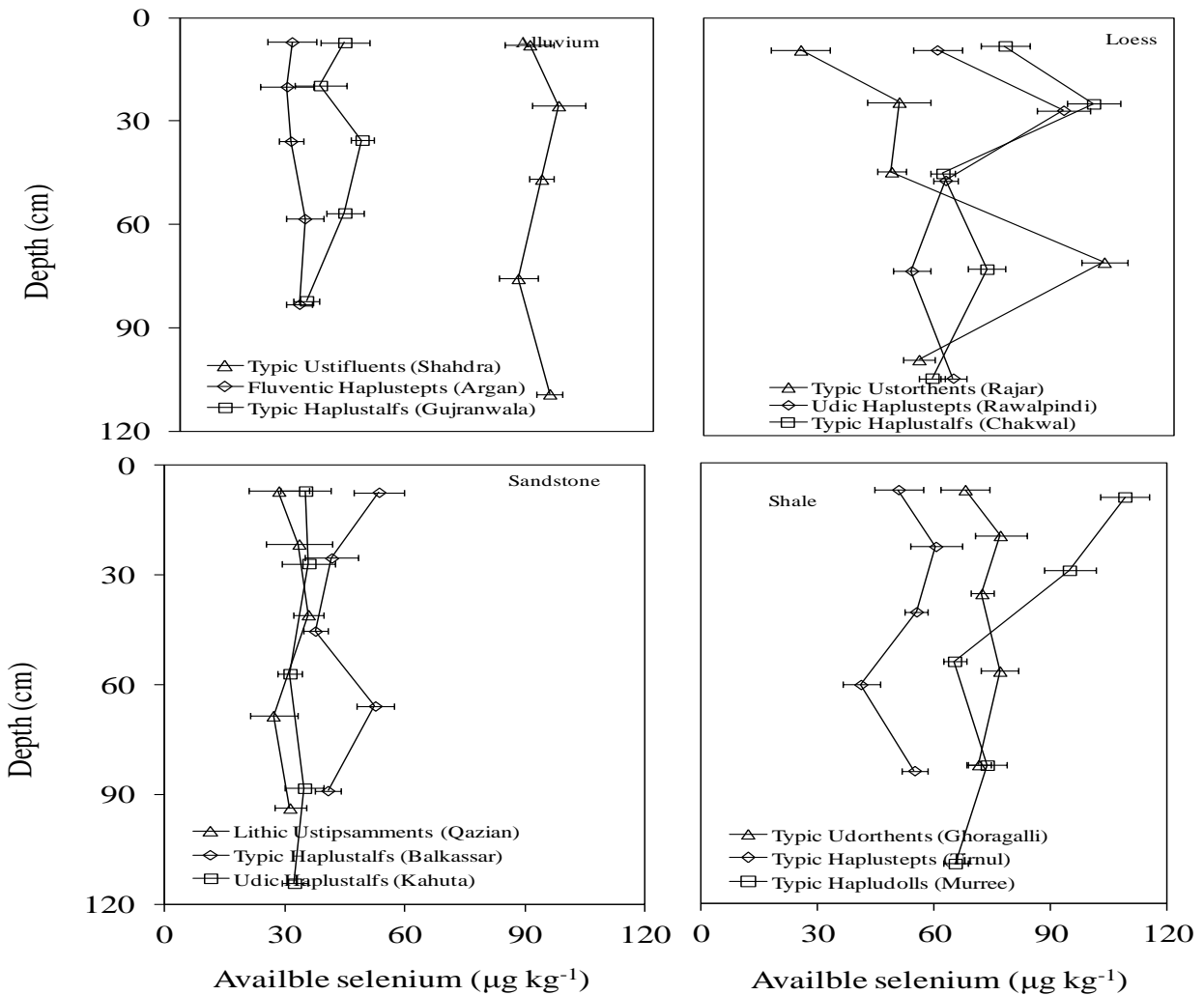


Fig. 5. Distribution of available selenium contents in the soils at different weathering stages in each parent material.

While shale contains argillaceous clay and the sandstone and lighter textured alluvium largely quartz, selenium contents and cation exchange capacity increased with an increase in the mafic character of soil parent materials (Gray and Murphy, 2002). Cation exchange capacity also increases with weathering due to mineral transformation coinciding with the release of selenium under oxidation.

The studies reported an increase in bio-available selenium with total soil selenium (Fordyce, 2005). The phosphate buffer extractable selenium increase with Eh implies that oxidized soils (weathered) have more phosphate-buffer extracted selenium than the less weathered soils (Hagrova *et al.*, 2005).

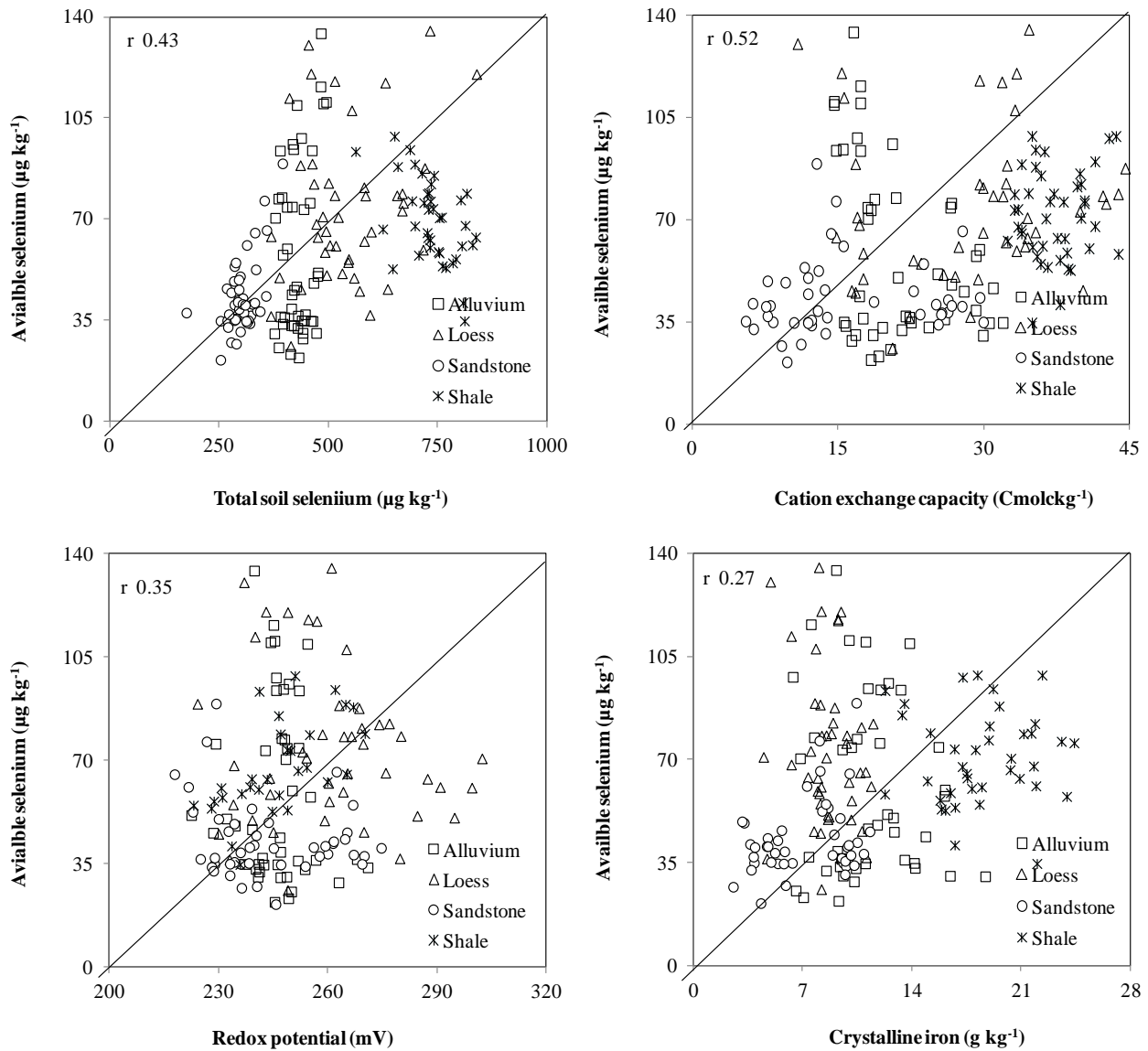


Fig. 6. Relationship of Phosphate buffer selenium with total selenium, CEC, Eh, crystalline and amorphous iron contents.

The regression equation to predict extractable selenium with some uniform predictor-variables (different intercept for the parent materials), had final model r^2 0.27 and two predictor-variables viz. CEC and total selenium, thus justifying different equations for each parent material which proved to be useful (Table 3).

The distribution of residuals was even with high r^2 in case of the alluvium and shale.

The loess and sandstone had low r^2 and error biased with the concentration level (Fig. 7) where the models predicted higher values than observed at low concentration and low values at high concentration.

CaCO₃, soil CaCO₃ equivalent (Loeppert *et al.*, 1984);
 CEC, cation exchange capacity (Rhoades, 1982);
 TOC, total organic carbon by wet oxidation (Nelson
 and Sommers, 1982); CBD-Fe, citrate bicarbonate

dithionite-extractable iron (Mehra and Jackson,
 1958) and DOC, dissolved organic carbon (Olsen and
 Sommers, 1982). FeCrys, crystalline iron calculated
 from subtraction of amorphous iron from dithionite
 iron contents.

Table 3. Regression equations with different parameters estimate for each parent materials.

Parent material	Regression equations	r ²
Alluvium	Selenium P-buffer = -151.10 + 6.13FeCrys + 38.91FeO - 2.78Clay + 6.40CaCO ₃ + 1.66CEC + 0.24Se _{Total}	0.78
Loess	Selenium P-buffer = 387.28 - 8.33TOC - 8.59Fe _{crys} - 0.61Eh - 0.90Clay - 4.4CaCO ₃	0.38
Sandstone	Selenium P-buffer = 156.19 + 14.47Al _d - 0.38Eh - 11.4pH + 0.17Se _{Total}	0.50
Shale	Selenium P-buffer = 44.92 + 5.505TOC - 6.41pH + 0.54Clay - 0.51DOC + 0.56 CaCO ₃ + 1.22CEC	0.90

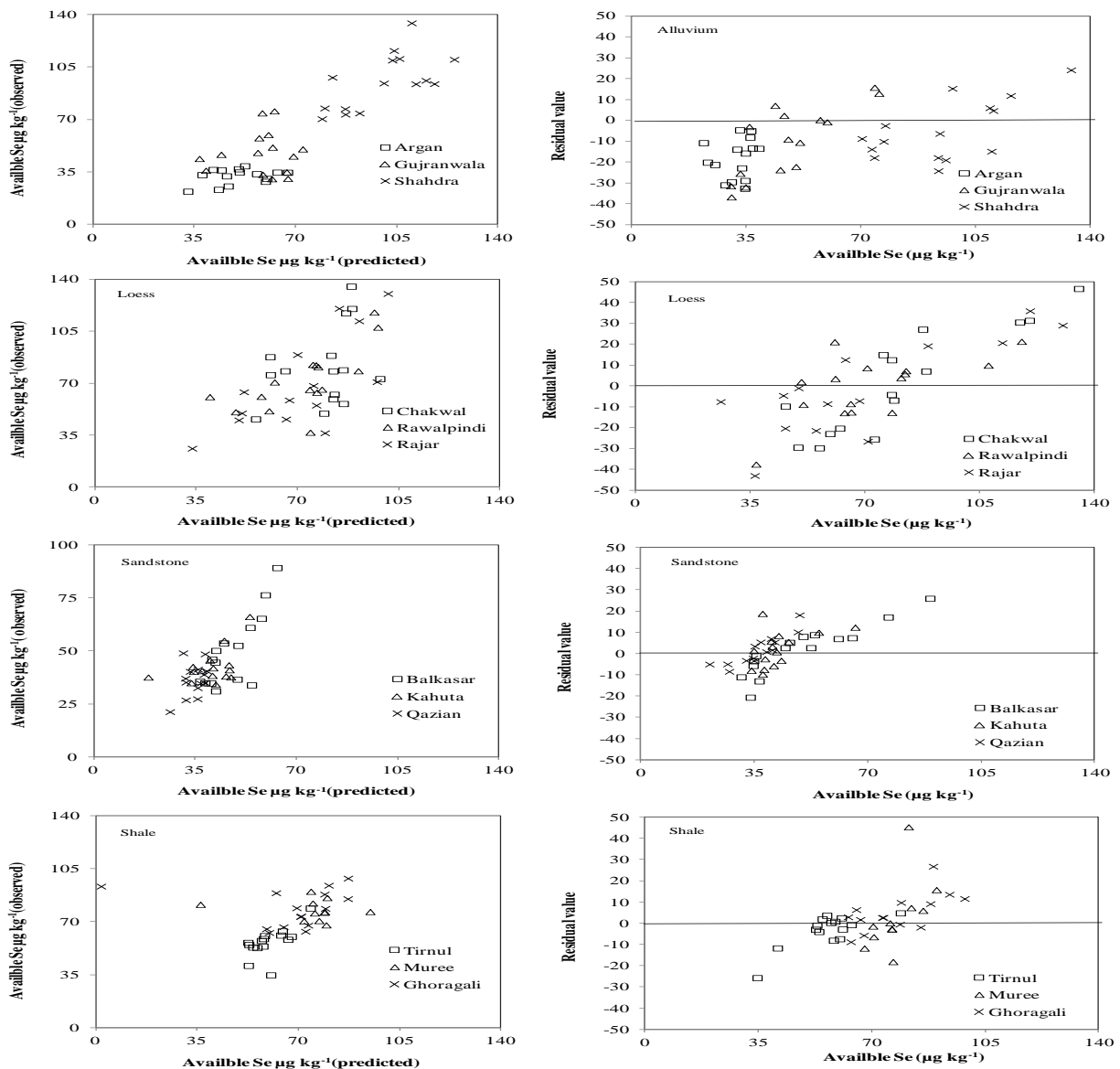


Fig. 7. Available selenium plot against the predicted and residuals.

Conclusions

Total and phosphate-buffer extractable selenium contents varied within the soil parent materials where the highest concentration was in shale. Soil genesis caused total to increase in loess while phosphate buffer extracted selenium increased with weathering in all the parent materials. Depth effect was negligible both for extractable and total selenium except that the surface of the Hapludoll of shale with mollic epipedon had high total selenium. Phosphate buffer extractable selenium positively correlated with crystalline iron, total selenium, redox potential (Eh), and cation exchange capacity. The positive correlation between redox potential and phosphate buffer extracted selenium implies that oxidized soils or highly weathered soils have more bioavailable selenium than reduced or least weathered soils. Regression equations to predict available selenium from soil parameters differed with the soil parent materials

Acknowledgment

This work was possible by financial assistance of Higher Education Commission of Pakistan through the 5000 fellowships Program.

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