SOIL QUALITY AND GROWTH PERFORMANCE OF CROPS OF AGROECOSYSTEMS IN THE VICINITY OF FLUORITE MINING

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Abstract. This study investigated the influence of fluoride on the number of macrofauna species on the soil surface and in the upper soil layer (0-10 cm depth) and crop growth performance on agricultural lands in the vicinity of fluorite mining activities in District Loralai, Balochistan, Pakistan. Results demonstrated that ants were sensitive to the fluoride above the concentration of 55 mg kg^{-1} soil; whereas, grasshoppers, crickets, spiders and toothed earwigs were tolerant to high fluoride concentrations (e.g. 74 mg kg^{-1} soil). The concentration of fluoride in soil was positively correlated with the concentration of fluoride in vegetables (R^2 = 0.75; $P \leq 0.05$ for leaves, R^2 = 0.48 $P \leq 0.05$ for fruits, R^2 = 0.81 $P \leq 0.05$ for stems and R^2 = 0.61 $P \leq 0.05$ for roots). Crop growth performance parameters such as yield and nutrient efficiency ratios concerning nitrogen and phosphorus had no obvious relationships with the concentrations of soil organic matter or fluoride in soil. These results conclude that concentration of fluoride in soil might have had negative influence on soil fauna and crop growth performance as no relationship was found between these parameters with the soil quality indicator i.e. soil organic matter.
Keywords: *farming systems, nitrogen use efficiency, phosphorus use efficiency, soil fauna, soil organic matter*

Introduction

Mine tailings from mining activities, negatively influence surrounding ecosystems, by contaminating air, water and soil, through dispersion of metal(oids) (Gil-Loaiza et al., 2016). Moreover, mine tailings as abandoned dumping sites, generally possess acidic pH, which is threatening to the surrounding vegetation including agricultural lands (Mendez et al., 2014; Zhang et al., 2014) and further increases the bioavailability of heavy metals in soil (Takac et al., 2010). Empirical evidences suggest that mining activity causes contamination of agricultural soils from high distances (Djebbi et al., 2017; Gao et al., 2017). For example, findings of Limei et al. (2008) showed that the rice-cultivated agricultural lands in Chenzhou City, China, which were at 23 km to 63 km distances from mining activities, had concentration of cadmium, that exceeded many times its critical concentration in rice, soil and vegetables. Fluorite mining also adversely affects soil quality of agroecosystems through irrigation, which contains fluoride contamination (Davies, 1994).

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Balochistan province of Pakistan is famous for deposits of coal, chromite, copper, gypsum, fluorite, celestite, iron, barite, limestone, marbles etc. (Malkani, 2011). Loralai has approximately 50000 tons of fluorite deposits and the fluorite mining in this region is in progress (Malkani et al., 2017). Fluorite has been excavated from three sites in Loralai; whereas, local people of this region rely on livestock and agriculture. Extensive fluorite mining can have influence on crops and soils of agricultural lands of this region. The objectives of this study are to assess 1) concentration of fluoride in agricultural soils and crops and 2) soil quality and crop growth performance of agricultural lands. The hypotheses of this study are; 1) soils of agricultural lands of this region have contamination of fluoride and the concentration of fluoride in crops has a positive relation with the concentration of fluoride in soil, 2) fluoride contamination of soils of agricultural lands has disturbed vegetation-soil ecosystem relationship as growth performance of crops has no positive relationship with soil quality indicators (e.g. organic matter).

Materials and methods

Study area

Loralai district is the part of Zhob division, which is located in the northeast of Baluchistan province, Pakistan. This area is also called as Bori and occupies an area of 8155 square kilo meters. It lies between the latitudes of 67°41'18"- 69°44'22"East and 29°54'50"- 30°41'28" North. This region has Mediterranean type arid climate, with summer temperature of 40 to 45 °C and winter temperature of 3 to 10 ^{o}C. Rainfall mostly occurs in winter to spring, occasionally summer season also receives rainfall. Snowfall also occurs in winter. The yearly mean temperature is 28.1 ^{0}C. January is the coldest month, and July is the warmest month in the year. Dargai, Baharvala and Mahiwal are the fluorite mining sites of Loralai.

Sampling procedure

Two sets of samples were collected. First set of samples involved sampling of vegetables and soils from agricultural lands at various distances from mining sites (*Figure 1*). This sampling was carried out to measure the concentration of fluoride in soil and vegetables. The second set of samples involved sampling of vegetables and soils from the agricultural lands that are close to mining sites (*Figure 2*). The second set of sampling was carried out to measure aboveground vegetable biomass, nitrogen (N), phosphorus (P) and nitrogen and phosphorus efficiency ratios of tested vegetables, macrofauna of surface soil and upper soil layer (0-10 cm depth) and physico-chemical properties of soils.

For the first set of samples, at each selected site (cropland), 5 spots were selected randomly at various distances within a given cropland, crops were cut down above the soil surface. The soil samples were collected from the same spot, from 0-15 cm depth, using 5 cm diameter and 10 cm height soil corer. Samples of vegetables and soil were taken during the field visit in June 2– 2019 to March 17 2020. A control for soil and vegetables was chosen from five fields from the city Duki, which is located 63 km away from Loralai. The coordinates of vegetable and soil samples of data set 1 and 2 are given in supplementary *Table A1* and in the maps as *Figure 1* for data set 1 and *Figure 2* for data set 2. For the second set of samples, 17 croplands were selected (*Figure 3*). At each selected site (cropland), five spots were selected randomly at various distances. At each spot, 0.5 x 0.5 m plots were marked with colored rope, within that square area, crops were

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cut down above the soil surface and were collected in zip-lock plastic bags. The soil samples were collected from the center of each plot after harvest of vegetation, from 0-10 cm depth, with the same procedure as described above. Soil samples were collected in zip-lock plastic bags and were stored in refrigerator at 4^{o}C until used for chemical analysis.

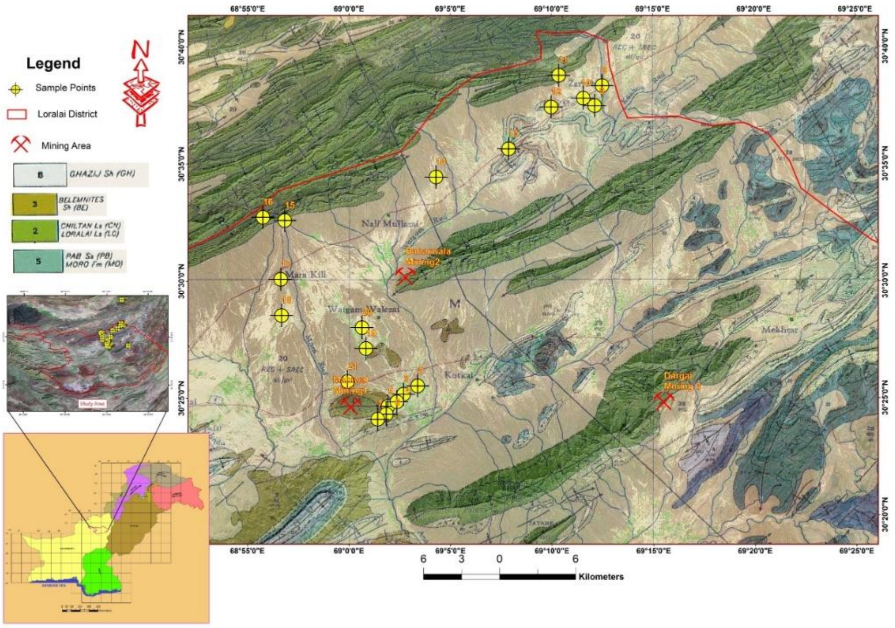

Figure 1. *The names of villages as sampling sites, mentioned in yellow circle are as follows; 1) Tor Thana, 2) Terrag, 3) Kotakai, 4) Chamaza, 5) Saper Chamaza, 6) Chijan Wa, 7) Sagri, 8) Shabozai, 9) Mahiwal, 10) Cheena Alizai, 11) Nali Walizai, 12) Agberg, 13) Tangi Sar, 14) Zarra, 15) Kochan, 16) Zara Kalam, 17) Darai, 18) Marra Tangi, 19) Juma Killi, 20) Manzaki*

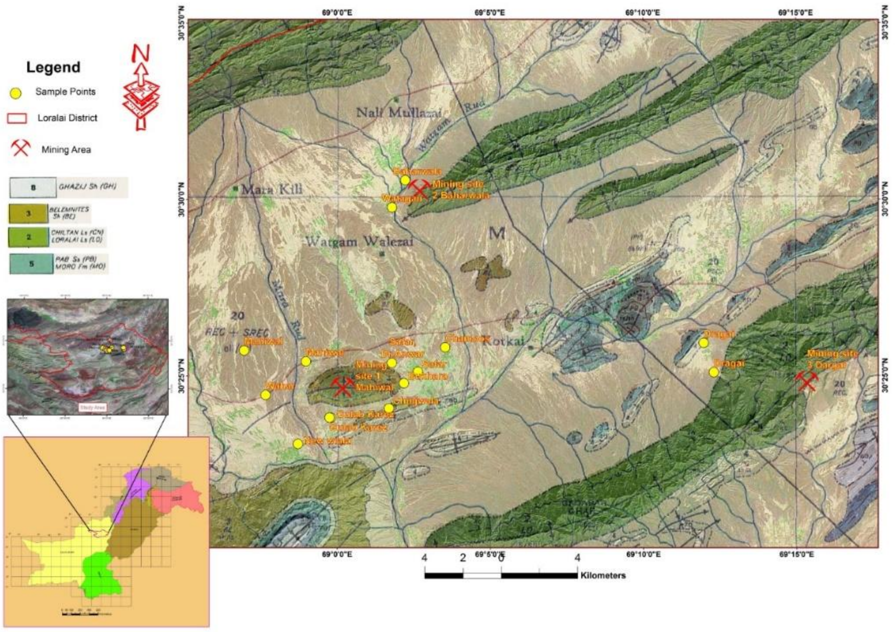

Figure 2. *Coordinates of data set 1 and data set 2*

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Table 1. *Mean ± SD water soluble fluoride in soil (mg kg^{-1} in 0-15 cm depth soil), leaf, fruits, stem and root tissues (mg kg^{-1})*

Sampling sites (villages with their names)	Fluoride in soil	pH of soil	Vegetable	Fluoride in leaf	Fluoride in fruit	Fluoride in shoot	Fluoride in root
Cheena Alizai	23.3±0.96^{a}	6.24	Spinach	17.47±0.67^{a}	--	11.7±0.57^{a}	8.53±0.54^{a}
Tor Thana	14.19±0.54^{b}	6.65	Potato	13.42±0.55^{b}	4.77±0.12^{a}	4.52±0.12^{b}	8.11±0.12^{b}
Kachi Alizai	13.52±0.34^{c}	6.96	Onion	3.55±2.90^{d}	3.20±0.15^{c}	2.09±0.09^{e}	5.78±0.09^{c}
Aghberg	8.6±0.35^{g}	6.63	Cabbage	2.90±0.09^{e}	2.51±0.16^{d}	1.33±0.09^{f}	3.09±0.07^{f}
Mahiwal	11.0±0.36^{e}	6.91	Garlic	5.09±0.10^{c}	1.77±0.10^{f}	2.02±0.04^{e}	3.62±0.22^{e}
			Wheat	1.71±0.13^{g}	1.22±0.12^{h}	2.14±0.12^{e}	3.52±0.09^{e}
Sagri	12.78±0.26^{d}	--	Carrot	3.60±0.08^{d}	3.45±0.08^{b}	3.88±0.07^{c}	5.27±0.11^{d}
Shabozai	9.23±0.18^{f}	6.97	Pea	2.85±0.07^{e}	1.20±0.05^{h}	2.92±0.05^{d}	3.03±0.04^{f}
Nali Walizai	7.42±0.44^{h}	6.95	Cauliflower	2.45±0.04^{f}	1.50±0.06^{g}	1.45±0.06^{f}	5.53±0.06^{cd}
			Mustard	1.51±0.11^{g}	1.95±0.10^{e}	2.96±0.11^{d}	3.75±0.31^{e}
Control site**	4.07	6.10	Spinach	4.20	0.00	1.77	1.58
Control site	4.46	6.34	Potato	1.48	0.31	1.00	0.94
Control site	3.47	5.98	Union	0.40	0.29	0.22	1.01
Control site	3.75	6.46	Cabbage	0.37	0.30	0.24	0.75
Control site	3.90	6.19	Garlic	0.97	0.26	0.32	1.91

Within column, values with different uppercase letters are significantly different at P≤0.01. – represents no data. ** control site (Duki city) was 63 km away from Loralai

Figure 3. *Croplands of study site for sample set 2*

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Macrofauna that were found on the surface of soil within each plot, as well as in the soil samples from upper soil layer (0-10 cm depth), were collected in 5% formalin-containing bottles. One bottle was used for one sampling site (cropland) as a pool sample of five replicates of a given sampling site. The sampling for data set 2 for vegetation, soil and soil fauna was carried out from 2 – 13 September 2019.

Chemical analysis of plant samples

Vegetables of data set 1 were rinsed with deionized water (Fluoride 0 ppm) to remove dust particles and oven-dried for 48 hours at 60°C. Samples were homogeneously grinded. Samples were thereafter analyzed for the concentration of fluoride with potentiometric ion selective electrode method (McQuaker and Gurney, 1977; D'Alessandro et al., 2008). Briefly, fluoride was extracted from the plant samples with HNO_3, followed by aqueous KOH. A fluoride-specific ion electrode was used to determine the concentration of fluoride in the solution. These were registered in an ion analyzer instrument which was calibrated with standards of known concentrations of NaF in distilled and deionized water. The supernatant was mixed at 1:1 ratio with a total ionic strength adjustment buffer (TISAB-IV) to dissociate F-Complexes and stabilize pH. The buffer was prepared by mixing 84 ml conc. HCl, 242 g TRIS (hydroxymethyl aminomethane, and 239 g sodium tartrate (FW=230.08), in about 500 ml water, cooled, and transferred to 1-liter volumetric flask and made to I L.

The vegetables of data set 2 were oven-dried at 60°C for 48 hours and the dry biomass was calculated. The analysis of nitrogen and phosphorus was carried out by digesting plant samples in sulfuric acid with repeated addition of hydrogen peroxide (30%) (Wolf, 1982). The concentration of nitrogen was assessed by Kjeldahl method of Jones (1991). The digested samples were analyzed for the concentration of phosphorus by vanadomolybdate phosphoric acid yellow color method of Cottenie (1980). The nitrogen efficiency and phosphorus efficiency ratios, as indicators of nutrient use efficiency for these nutrients (Baligar et al., 2001) were calculated as;

$$Nutrient\ efficiency\ ratio\ (NER\ or\ PER) = \frac{Plant\ biomass}{Concentration\ of\ N\ or\ P\ in\ plant\ tissue} \quad \text{(Eq.1)}$$

Chemical analysis of soil samples

The chemical analysis of soil samples of data set 1 was done at Geo Science Advance Research Laboratory, Geological Survey of Pakistan; whereas chemical analysis of soil samples of data set 2 for the concentration of fluoride was carried out at the Quaid-e-Azam University, Islamabad. The air-dried soil samples were crushed, passed through 2 mm mesh size sieve to remove pebbles and other debris. Thereafter, samples were burned in crucibles by fusion with 10 mL NaOH, and placing in furnace for 30 minutes at 600^{0}C. These fused samples were dissolved with 20 mL deionized water followed by their mixing in TISAB buffer solution to determine the concentration of fluoride with the ion selective electrode method (Zhang et al., 2010). The organic matter and soluble inorganic phosphorus of soil was analyzed according to the protocol described in Estefan et al. (2013) and D'Angelo et al. (2001), respectively. The pH and electrical conductivity were analyzed with ORION ion analyzer (5-Star series). Macrofauna were analyzed in the Department of Zoology, University of Balochistan, Pakistan.

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Statistical analysis

The data sets of individual research parameters (except for soil fauna due to pooled samples) were screened for normal distribution with D'Agostino-Pearson K2 test before analysis of variance (ANOVA). The differences between mean values of a given data set were analyzed using least significance difference test. The relationship of concentration of water soluble fluoride in soil with the concentration of fluoride in various tissues of tested vegetables was measured with Pearson correlation coefficient (Pearson's *r*). Data analysis was performed on CoStat and Microsoft Excel software.

Results

The concentration of water soluble fluorite in 0-20 cm depth of soil (sample set 1) ranged from 7.42 – 23.3 mg kg^{-1} soil and 0-10 cm depth the range was 37 – 74 mg kg^{-1} soil (sample set 2). The concentration of fluoride in leaves, fruits, stems and roots of tested crops showed positive and significant relationship with the concentration of water soluble fluoride in soil (*Figure 4*). The 17 croplands sampled had diverse cropping systems; however, almost all croplands were under mouldboard tillage practice. The application of manure with synthetic fertilizer and the addition of ash of crop residues in soil were common practices (*Table 1*). The concentration of soil organic matter varied significantly between croplands and ranged between 3.59 – 12.6 mg kg^{-1} soil (*Table 2*). The number of soil fauna m^{-2} and total number of species per cropland varied between sampling sites (*Table 3*). Total of 25 different species of soil fauna were observed (*Table 3*). The number of soil fauna m^{-2} between sampling sites ranged from 0 – 6 while number of species of soil fauna between sampling sites ranged from 0 – 8 (*Table 3*). The growth performance parameters of crops i.e. biomass, NER and PER varied significantly between croplands (*Table 4*). The lowest NER and PER were found in garden pea of Dargai F2 field, whereas the highest NER and PER were found in maize of Gulab karez 2 and chili of Mahiwal F1 fields respectively (*Table 4*). No relationship was observed between SOM and the NER and PER of crops except for garden pea of Dargai F2, which had the lowest SOM and lowest NER and PER. Likewise, no relationship was observed between number of soil fauna and species with NEW and PER of crops (*Table 5*).

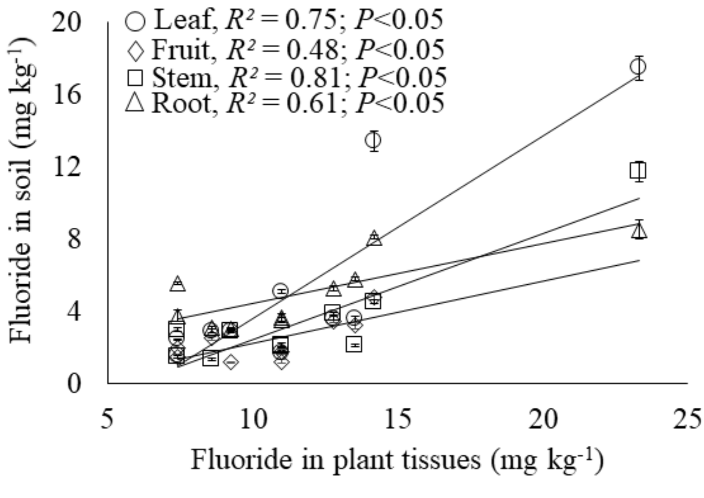

Figure 4. *Regression analysis to measure relationship between concentration of fluoride in soil and concentration of fluoride in leaves, fruits, stems and roots of tested crops*

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Table 2. *Type of harvested crop, cropping history and fertilizer management of study sites*

Sampling villages with their names	**Age (yrs)**	**Crop sampled and tested**	**Cropping history of agricultural land**	**Fertilizer management**
Mahiwal F1	~ 50	Chili	Crop rotation, (Vegetable-cereals) fallow period for a season or year	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Mahiwal F2	~ 50	Cauliflower	Crop rotation, (vegetables-cereals) fallow period for a season or year	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Bukhara F1	> 100	Ladyfinger	Crop rotation (cereals-vegetables) fallow period for a season or year	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Bukhara F2	> 100	Tomato	Crop rotation, (vegetables-cereals) fallow period for a season or year	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Chapri F1	> 100	Chili	Crop rotation, (cereals- vegetables)	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Chamoos	~ 30	Chili, ladyfinger, bringel	Intercropping, crop rotation, (vegetables-cereals)	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Chapri F2	6 yrs	Chili	Crop rotation, (cereals-vegetables)	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Mahiwal F3	~ 50	Carrot	Tree-based intercropping + crop rotation	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Gulab Karez F1	~ 60	Carrot	Crop rotation (cereals-vegetables)	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Gulab Karez F2	~ 60	Maize	Crop rotation (vegetables-cereals)	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Chinjwala	~ 60	Chili	Crop rotation (cereals-vegetables)	Manure + synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Wahar	~ 30	Cauliflower	Crop rotation (cereals-vegetables)	Synthetic fertilizer but also amend manure every 2-3 yrs, deep tillage, ash of plant residues returned to field after burning for cooking
New Wiala	~ 20	Maize	Crop rotation	Fallow period of 2-3 yrs, synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Baharwala	~ 30	Cauliflower	Crop rotation (vegetables-cereals)	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Watagan	6	Carrot	Crop rotation (cereal-vegetables)	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Dargai F1	2	Chili	Crop rotation	Synthetic fertilizer, deep tillage, ash of plant residues returned to field after burning for cooking
Dargai F2	1	Garden pea	No crop rotation	Synthetic fertilizer, deep tillage

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Table 3. *Soil organic matter (g kg^{-1}), water soluble fluoride (mg kg^{-1} soil in 0-10 cm depth soil) and olson P (mg kg^{-1}) of soils collected from study field sites*

Field site	Vegetable	Soil type*	F	SOM	Olson P
Mahiwal F1	Chili	Loamy	43	9.34 ± 1.00[b]	1.09 ± 0.51[ab]
Mahiwal F2	Cauliflower	Loamy	37	7.75 ± 0.85[b]	0.26 ± 0.58[ab]
Bukhara F1	Ladyfinger	Sandy loam	51	3.59 ± 0.56[e]	1.13 ± 0.32[ab]
Bukhara F2	Tomato	Sandy loam	40	3.62 ± 0.98[cde]	1.86 ± 1.34[a]
Chapri F1	Chili	Sandy loam	62	12.5 ± 1.37[a]	1.02 ± 0.65[ab]
Chamoos	Chili, ladyfinger, eggplant	Loamy	41	7.40 ± 0.58[b]	1.49 ± 0.66[ab]
Chapri F2	Chili	Sandy loam	50	4.33 ± 1.28[cde]	1.38 ± 1.33[ab]
Mahiwal F3	Carrot	Loamy	48	6.84 ± 1.22[bc]	1.33 ± 0.60[ab]
Gulab Karez F1	Carrot	Sandy loam	54	6.23 ± 2.15[bcde]	1.52 ± 0.54[ab]
Gulab Karez F2	Maize	Sandy loam	63	7.28 ± 1.86[b]	3.32 ± 1.29[a]
Chinjwala	Chili	Sandy loam	68	12.6 ± 1.36[a]	1.42 ± 0.62[ab]
Wahar	Cauliflower	Loamy	71	10.8 ± 1.79[ab]	2.59 ± 0.93[a]
New Wiala	Maize	Riverbank deposits	59	5.64 ± 0.51[cd]	0.62 ± 0.32[b]
Baharwala	Cauliflower	Riverbank deposits	74	7.52 ± 1.54[bc]	1.41 ± 0.39[a]
Watagan	Carrot	Sandy loam	68	7.62 ± 0.60[b]	1.00 ± 0.41[ab]
Dargai F1	Chili	Loamy	63	8.77 ± 0.83[b]	0.86 ± 0.54[ab]
Dargai F2	Garden pea	Loamy	59	4.04 ± 068[de]	1.00 ± 0.60[ab]

Within column, values with different letters are significantly different at $P \leq 0.05$. *soils of all tested sites had gravels

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Table 4. *Number of soil fauna (m^{-2}), number of fauna species and types of soil fauna found in different study field sites*

Field site (village names)	Vegetable	Number of soil fauna (m^{-2})	Total number of species	Names of animals
Mahiwal F1	Chili	6	6	*Trimeroptropis Sp., Orthoptera tetrigigae, Orthoptera tetrigigae, Acheta domesticus, Iridomyrmex purpureus,* Family-lycosidae
Mahiwal F2	Cauliflower	3.2	5	*Schistocera geregaria Trimeroptropis Sp., Iroxals afghana Iridomyrmex purpureus Euborellia annulipes*
Bukhara F1	Ladyfinger	2.0	3	*Orthoptera tetrigigae* Family-lycosidae *Iridomyrmex purpureus*
Bukhara F2	Tomato	2.0	5	*Schistocera geregaria Trimeroptropis Sp., Iroxals afghan, Orthoptera tetrigigae, Hepyllus ecclesiasticus,*
Chapri F1	Chili	4.0	6	*Euborellia annulipes, Pepsis thibse, Oniscus asellus,* Family- Carabidae, *Dysdera corocata,* Family-lycosidae
Chamoos	Chili, ladyfinger, eggplant	4.4	8	*Schistocera geregaria Orthoptera tetrigigae Iridomyrmex purpureus Euborellia annulipes Oniscus asellus, Coccinella septempuntata, Blattela germanica,* Family-lycosidae
Chapri F2	Chili	3.6	5	*Trimeroptropis sp., Iroxals afghan, Orthoptera tetrigigae Euborellia annulipes,* Order-Lepidoptera
Mahiwal F3	Carrot	2.4	4	*Trimeroptropis sp., Iroxals afghan, Orthoptera tetrigigae* Order- Lipidoptera
Gulab Karez F1	Carrot	5.2	7	*Schistocera geregaria Trimeroptropis sp., Iroxals afghana Orthoptera tetrigigae Iridomyrmex purpureus, Camponotus pennsylvanicus, Pyrgomorpha conica*
Gulab Karez F2	Maize	0	0	--
Chinjwala	Chili	0	0	--
Wahar	Cauliflower	2.8	4	*Schistocera geregaria Trimeroptropis sp., Iroxals afghana Orthoptera tetrigigae*
New Wiala	Maize	0	0	--
Baharwala	Cauliflower	4.0	7	*Schistocera geregaria Trimeroptropis sp., Iroxals afghana, Orthoptera tetrigigae, Gryllus sp.(gryllinae) Dysdera corocata, Vostox sp.*
Watagan	Carrot	5.2	6	*Trimeroptropis sp., Orthoptera tetrigigae, Coccinella septempuntata Camponotus pennsylvanicus, Agelenopsis sp., Pyrgomorpha conica*
Dargai F1	Chili	2.8	4	*Schistocera geregaria Trimeroptropis sp., Acheta domesticus, Gryllus sp.(gryllinae)*
Dargai F2	Garden pea	4.0	6	*Trimeroptropis sp., Iroxals afghan, Orthoptera tetrigigae Iridomyrmex purpureus, Camponotus consobrinus* Family-Apidae

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Table 5. *Mean ± SD dry biomass of vegetables (t ha^{-1}), total N, total P, nutrient efficiency ratio of crops for N and P*

Sampling sites (villages with their names)	Vegetable	Dry biomass	Total N	Total P	NER	PER
Mahiwal F1	Chili	147 ± 33.4^{ab}	26.4 ± 3.9^{ab}	2.68 ± 1.2^{c}	5.6 ± 1.4^{bc}	0.71 ± 0.47^{a}
Mahiwal F2	Cauliflower	118 ± 58.9^{ab}	29.2 ± 7.5^{ab}	5.06 ± 2.9^{bc}	4.1 ± 2.2^{bcd}	0.30 ± 0.20^{abc}
Bukhara F1	Ladyfinger	88.8 ± 36.5^{b}	16.4 ± 2.1^{c}	4.36 ± 1.2^{bc}	5.3 ± 1.7^{bc}	0.23 ± 0.14^{abc}
Bukhara F2	Tomato	135.7 ± 37.6^{ab}	20.7 ± 6.6^{abc}	3.89 ± 2.2^{bc}	6.9 ± 2.1^{bc}	0.46 ± 0.34^{abc}
Chapri F1	Chili	165 ± 35.9^{ab}	23.9 ± 1.2^{b}	6.39 ± 2.5^{bc}	6.8 ± 1.1^{b}	0.31 ± 0.20^{abc}
Chamoos	Chili, ladyfinger, eggplant	123 ± 50^{abc}	20.5 ± 6.5 ^{abc}	6.46 ± 2.7^{bc}	5.9 ± 2.2^{bcd}	0.23 ± 0.14^{abc}
Chapri F2	Chili	188 ± 42.2^{ab}	28.6 ± 6.7^{ab}	5.18 ± 1.6^{bc}	6.9 ± 2.6^{bc}	0.40 ± 0.19^{abc}
Mahiwal F3	Carrot	177 ± 53^{ab}	36.1 ± 7.5^{a}	8.28 ± 5.1^{abc}	5.1 ± 1.8^{bcd}	0.39 ± 0.46^{abc}
Gulab Karez F1	Carrot	98.7 ± 32^{b}	30.8 ± 4.9^{ab}	7.04 ± 2.8^{b}	3.1 ± 0.7^{cd}	0.16 ± 0.08^{c}
Gulab Karez F2	Maize	234 ± 50^{a}	13.5 ± 1.9^{c}	5.77 ± 3.5^{bc}	17.4 ± 3.9^{a}	0.55 ± 0.28^{abc}
Chinjwala	Chili	160 ± 39.3^{ab}	25.8 ± 2.3^{ab}	3.9 ± 1.3^{bc}	6.2 ± 1.7^{b}	0.51 ± 0.42^{ab}
Wahar	Cauliflower	106 ± 50.6^{ab}	24.8 ± 10.4^{abc}	5.9 ± 3.9^{bc}	5.5 ± 4.1^{bcd}	0.32 ± 0.30^{abc}
New Wiala	Maize	100 ± 22.4^{b}	13.6 ± 1.9^{c}	4.9 ± 1.7^{bc}	7.3 ± 1.4^{b}	0.23 ± 0.12^{abc}
Baharwala	Cauliflower	123 ± 18^{b}	28.0 ± 6.6^{ab}	4.6 ± 1.5^{bc}	4.6 ± 1.4^{bcd}	0.29 ± 0.12^{abc}
Watagan	Carrot	101 ± 18.7^{b}	25.8 ± 2.9^{ab}	6.1 ± 3.1^{b}	3.9 ± 0.8^{bcd}	0.19 ± 0.09^{bc}
Dargai F1	Chili	140 ± 31.2^{ab}	25.0 ± 9.4^{ab}	6.6 ± 1.3^{b}	5.6 ± 1.3^{b}	0.21 ± 0.04^{c}
Dargai F2	Garden pea	35.8 ± 8.2^{c}	25.9 ± 10.5^{abc}	12.6 ± 2.4^{a}	1.7 ± 1.1^{d}	0.02 ± 0.01^{d}

Within column values with different letters are significantly different ($P \leq 0.05$)

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Discussion

The concentration of fluoride in the soils ranged between 7.42 – 23.3 mg kg^{-1}; whereas, the concentration of fluoride in edible parts of vegetable crops ranged between 1.2 – 11.7 mg g^{-1} plant tissue. The data collected from the soil and vegetables of local gardens in the Kpogame and Hahotoe phosporite mining area, Togo West Africa, Tanouayi et al. (2016) reported that the concentration of fluoride in soil ranged between 5.1 – 11.2 mg g^{-1} soil. The concentration of fluoride in vegetables (eggplant, carrot, onion, cucumber, chili pepper) ranged between 1.6 – 20.6 mg g^{-1} plant tissue (Tanouayi et al., 2016). The concentration values for fluoride, in the soils of agricultural lands of our study site, are lower than the published reports. We attribute this to the fact that, soils of agricultural lands of Loralai mining sites are transported. However, because the concentration of fluoride in irrigated waters are very high (1.5 – 18.9 mg L^{-1}, data unpublished), and the possible deposition of this heavy metal from air, as has been frequently reported for other heavy metals from mining activities (Bislimi et al., 2021; He et al., 2021), these factors might be the reason of still high concentration of fluoride in soils and vegetables.

As hypothesized, concentration of fluoride in soil had a significantly positive influence on its concentration in all tissues of crops (i.e. leaf, fruit, stem and roots) (R^2 = 0.75, 0.48, 0.81 and 0.61 for leaf, fruit, stem and root tissues of crops respectively; P<0.05). Our results are consistent with published empirical evidences, which demonstrated positive relationship between the concentration of heavy metals in soil with their concentration in edible plant tissues (Avila et al., 2017; Kaninga et al., 2020, Kaninga et al., 2021; Filimon et al., 2021) including fluoride (Bhat et al., 2015). The set limit for fluoride concentration in edible parts of crops (leafy vegetables, corn and maize) by FAO/WHO is 1.5 mg kg^{-1} plant tissue (FAO/WHO, 2011). Our data show fluoride concentration in the range of 1.2 – 11.2, depending on the concentration of fluoride in soil samples. Filimon et al. (2021) found that the concentration of copper (Cu) and lead (Pb) in leafy vegetables such as celery roots, sorrel and dill, grown in the agricultural lands near Bor Copper Mining site, Eastern Serbia Europe, exceeded the safe limit of Cu 40 mg kg^{-1} plant dry weight and Pb 0.3 mg kg^{-1} plant dry weight, set by WHO/FAO. Empirical evidences support our finding that concentration of heavy metals in soil from mining activities directly increase their concentration in crops.

A negative relationship was found between concentration of fluoride and number of soil surface or soil fauna and number of ants. The sites Baharwala, Wahar and Dargai F1 had water soluble fluoride concentration as 74, 71 and 63 mg kg^{-1} soil respectively. Interestingly, in these sites, presence of ants was not observed; however, macrofauna such as *Schistocera geregaria Trimeroptropis sp.*, *Iroxals afghan* and *Orthoptera tetrigigae* were the most common in these highly polluted soils. These species were however found in other soils also, which indicates their high tolerance to fluoride toxicity. The ants such as *Iridomyrmex purpureus*, *Camponotus pennsylvanicus* and *Camponotus consobrinus* were found in the soils of study sites Mahiwal F1, Mahiwal F2, Bukhara F1, Dargai F2, Gulab Karez F1 and Chamoos. The concentration of fluoride in these soils were 43, 37, 51, 59, 54 and 41 mg kg^{-1} soil respectively. This finding shows that these ant species can tolerate concentrations of fluoride less than 55 mg kg^{-1}. The sites such as Gulab Karez F2, Chinjwala and New Wiala had fluoride concentrations as 63, 68 and 59 mg kg^{-1} soil and no macrofauna was found, which may be due to fluoride toxicity. Our findings are in agreement to the results of Madden and Fox (1997) regarding high sensitivity of ants to fluoride concentration.

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Soil organic matter plays an important role in the health of soil and crop growth performance (Kane et al., 2021; Wulanningtyas et al., 2021). No relationship of SOM was seen with crop growth performance. For example, two sites; Chapri F1 and Chinjwala had the highest concentration of SOM (12.5 and 12.6 mg kg^{-1} respectively) but it did not positively influence the NER or PER of crops. These sites also had high concentration of fluoride in soil (62 and 68 mg kg^{-1} soil, respectively), which may explain this result. Contrary to these sites, PER of crop of Mahiwal F1 site was significantly higher. This site had lower SOM but also had lower concentration of fluoride (43 mg kg^{-1} soil) and also had higher abundance of soil fauna. These factors may explain high crop growth performance of this site than most of other sites. The difference in NER and PER between crops and their no relationship with SOM and concentration of soil fluoride may be due to differential tolerances of crops to heavy metal toxicity (Kumar et al., 2016) besides diverse management history, irrigation water and difference in soil texture. The croplands that had loamy texture generally had the highest number of soil fauna and greater number of species of soil fauna such as Mahiwal and Chamoos croplands and the crops of these sites tend to have higher PER. Another interesting observation can be seen regarding age of a cropland. The newly grown croplands such as Chapri F2 and Dargai F2 had the lowest concentration of SOM, the lowest yield t ha^{-1} and lower NER and PER but this observation was not consistent for other new fields such as Chapri F2, Watagan and Dargai F1.

Conclusions

The concentration of fluoride in vegetables was positively related to its concentration on soil. Ants were sensitive to the high concentration of fluoride in soil. Grasshoppers, crickets, spiders and toothed earwigs were tolerant to the high concentration of fluoride. No clear relationship between concentration of fluoride in soil and crop growth performance parameters (biomass yield, NER and PER) was found. Likewise, relationship of SOM with soil fauna and crop growth performance parameters was also not observed. Future research is required to assess soil quality and crop growth performance parameters of croplands of this region, and the same needs to be done on croplands of other regions, within same climatic zone, but with no mining activity. Such study will help get an insight into influence of fluoride mining on agroecosystem processes.

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APPENDIX

Table A1. *Coordinates of data set 1*

Sampling site	Latitude	Longitude
Tor Thana	30°26’33.6”	69°06’10.8”
Terrag	30°25’32.8”	69°03’22.9”
Kotakai	30°25’11.3”	69°02’41.4”
Chamaza	30°24’51.8”	69°02’21.4”
Saper Chamaza	30°24’40.3”	69°01’55.3”
Chijan Wa	30°24’20.2”	69°01’50.1”
Sagri	30°24’07.5”	69°01’24.6”
Shabozai	30°38’22.0”	69°12’29.9”
Mahiwal	30°37’30.0”	69°12’8.0”
Cheena Alizai	30°37’48.7”	69°11’34.2”
Nail walizai	30°38’48.8”	69°10’21.6”
Agberg	30°37’27.0”	69°09’58.1”
Cheena Alizai	30°35’42.0”	69°07’43.8”
Zarra	30°34’31.2”	69°4’16.1”
Kochan	30°32’29.8”	68°56’53.2”
Zara kalam	30°32’48.5”	68°55’57.1”
Darai	30°30’07.9”	68°56’35.2”
Marra tangi	30°28’30.7”	68°56’37.9”
Juma Killi	30°27’07.9”	69°00’50.1”
Manzaki	30°28’04.3”	69°00’37.8”
Control site 1**	31° 21’ 00’’	69° 34’ 07’’
Control site 2**	31° 21’ 33’’	69° 33’ 59’’
Control site 3**	31° 23’ 10’’	69° 34’ 58’’
Control site 4**	31° 25’ 07’’	69° 35’ 06’’
Control site 5**	31° 25’ 40’’	69° 35’ 14’’

**Duki city, Balochistan, Pakistan, 63 kilometers away from Loralai

Table A2. *Coordinates of data set 2*

Sampling site	Latitude	Longitude
Mahiwal F1	30°42’37.9”	68°98’34.1”
Mahiwal F2	30°42’36.3”	68°98’28.3”
Bukhara F1	30°41’35.1”	67°03’63.6”
Bukhara F2	30°41’32.6”	69°03’61.6”
Safar F1	30°41’90.0”	69°04’37.4”
Chamoos	30°43’02.5”	69°05’87.2”
Safar F2	30°42’29.2”	69°02’96.7”
Mahiwal F3	30°42’67.4”	69°99’49.8”
Gulab karez F1	30°39’71.1”	68°99’65.0”
Gulab karez F2	30°39’70.7”	68°99’57.1”
Chinjwala	30°40’15.1”	69°02’80.9”
Wahar	30°40’77.9”	68°96’09.5”
New wiala	30°38’47.0”	68°97’85.4”
Baharwala	30°50’91.4”	69°03’69.6”
Watagan	30°49’63.7”	69°02’97.4”
Dragai F1	30°41’83.5”	69°20’50.0”
Dragai F2	30°43’22.5”	69°19’94.9”
Mining site 1 Mahiwal	30°41’16.0”	69°00’30.1”
Mining site 2 Baharwala	30°50’47.6”	69°04’49.2”
Mining site 3 Dargai	30°41’39.7”	69°25’57.4”

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