

Article

Lead Extraction Methods in Roadside Soils and Its Relationship with Soil Properties

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Abstract: Lead (Pb) is an environmental pollutant, and its concentration in the soil environment has received greater attention. Studies on the interrelation of Pb and major soil properties using different extraction methods have been poorly documented. The lead extraction method is important to be identified, which may accurately reflect Pb extractability from soils. Therefore, a study was conducted to investigate the Pb pollution of roadside soils. Four extractants: ammonium acetate (NH₄OAc), hydrochloric acid (HCl), diethylenetriaminepentaacetic acid (DTPA), and sodium hydroxide (NaOH). Soil samples were sieved for three particle sizes: finer to coarser particles (0.5 to 2 mm). Results showed that there were substantial differences for Pb concentrations among sampling sites depending on the extracting reagents: HCl > DTPA > NH₄OAc > NaOH. The extractability of Pb from soil was apparently enhanced with the increasing strength of a reagent used for the soil solution. The NH₄OAc extractable Pb concentrations in the surface soil samples from the Abbottabad area ranged from 67.9 to 246.7 mg kg⁻¹, and in Haripur, the Pb concentrations ranged from 97.6 to 242.5 mg kg⁻¹. At 20% HCl solution, the average Pb concentrations were 2.6 times higher than the NH₄OAc solution in the topsoil of Abbottabad area. The roadside soils contained Pb concentrations higher than the permissible limits. The control soil samples (from a distance of 200 m) exhibited Pb concentrations in the relative range of 28.5 to 61.7 mg kg⁻¹. Pb concentrations in the topsoil and subsoil were found to be apparently inconsistent. The concentration of Pb was higher in the soil containing a higher amount of organic matter and clay content. The soil pH and particle size were inversely related to extractable Pb in the soil. Higher Pb pollution in the soil could be associated with the higher traffic density.

Keywords: extraction methods; Karakoram highway; lead; roadside soil; soil characteristics

1. Introduction

Industrialization, urbanization, and other human activities have enhanced the environmental pollution caused by organic and inorganic pollutants, and it has adversely affected the living organisms [1,2]. Inorganic chemicals are accumulated in soils as nutrients and potential toxic elements [3]. Heavy metals are non-biodegradable, and their concentrations in the environment last for longer periods [1]. The use of gasoline containing Pb as an

additive is a major source of Pb in the environment [4]. Other main sources of lead (Pb) in the soil environment are auto exhausts, paints, and contaminated water and food [5]. Lead contamination in roadside soils is usually related to the exhaust emissions of automobiles operating with leaded gasoline [6]. There is a strong association between roadside Pb pollution and transportation [7,8]. The spatial distribution of Pb in the roadside soil is very strong but inversely correlated with the distance from the road [9]. Gzyl [10] attributed high concentrations of Pb and Cd in soils and vegetables to vehicular emissions. In Turkey, lead has been banned in gasoline since 2006, but a still significant concentration of Pb is present in urban soil due to having a prolonged half-life. Lead contamination of roadside soil and vegetation is considered to arise from motor vehicle exhaust [11], which is considered the largest source of Pb contamination [9]. Lead has been reported as a toxic heavy metal associated with several health problems [5].

The people working in the manufacturing and processing industries, i.e., lead smelters and refineries and battery, painting, ceramic, and printing workshops are exposed to the Pb contamination. Lead is an inorganic pollutant that dangerously affects unborn and young children causing various diseases and also affecting the performance of the central nervous system [12]. Lead induces a variety of biochemical and physiological dysfunctions in humans and animals [13]. Lead exposure may cause hematological, renal, cardiovascular, neurological, developmental, and behavioral disorders [14].

A range of extraction reagents is used to ascertain the mobility and solubility of trace element fractions in the soil. The heavy metals fractionation by different extracting agents is important to know to understand the fundamental reactions of heavy metals in soils [15]. The distribution of metal in different forms depends on the chemical properties of an element [16]. Several extraction methods have been reported for the extraction of heavy metals [17–19]. Tessier et al. [20] reported the fractions of heavy metal in water-soluble, exchangeable, carbonate-bounded, iron–manganese oxide-bound, organic matter-bound, and residual forms. Different kinds of extractants are used to extract heavy metals from soils. These extractants are water, acid, oxidizing agent, chelating agent, or surfactant. Various agents have been utilized to remove heavy metals from soils such as inorganic salts (potassium phosphate, potassium chloride, potassium nitrate, potassium sulfate, or sodium perchlorate) [21,22], inorganic acids (sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid or mixed acid) [23], organic acids (citric or acetic acids) [24], and alkaline agents (e.g., sodium hydroxide) [25,26]. Extraction methods differ due to the extraction conditions, chemical nature and concentration of leaching solutions, solution/soil ratio, operational pH, and extraction time [27]. Single extraction procedures have mainly been developed for the extraction of cationic trace metals.

Several studies have been conducted on Pb contamination in roadside soil and vegetation [24,28]. However, existing reports on the Pb pollution within the roadside soils due to highway traffic and vehicles in the Hazara Division have not been reported. The Karakoram Highway (KKH) (China-Pakistan Friendship Highway) is a 1300 km long highway that extends from Hasan Abdal in the Punjab province of Pakistan to the Khunjerab Pass in Gilgit-Baltistan, where it leads into China. Huge traffic density prevails on this highway. Lead contamination in soils could be an unknown threat to agricultural production in the area along KKH. Since soil properties influence the extraction of Pb from soils, the concentration of Pb differs with the type of extractant in a soil condition. Moreover, it is important to identify an extraction method that may accurately reflect the extractability of Pb in soils in relation to soil properties. Studies on the interrelation of Pb and major soil properties using different methods have also been poorly documented. Therefore, this research was conducted to investigate Pb contamination in the soil along the Karakoram highway in Hazara division and its relationship with land characteristics using different extraction methods. The study investigated both Pb contamination in roadside soil and assessed the suitability of a reagent for the determination of the total amount of extractable Pb in the soil. During this study, standard chemical extraction of Pb from soils was carried out using different concentrations of hydrochloric acid (HCl), ammonium acetate (CH₃COONH₄)

buffered solution, diethylenetriaminepentaacetic acid (DTPA), and alkaline agent of sodium hydroxide (NaOH) solutions to investigate the concentration of Pb in the roadside soil.

2. Materials and Methods

2.1. Study Area Description

Hazara is a region in the northeastern part of the Khyber Pakhtunkhwa province of Pakistan. It is located east of the Indus River and comprises eight districts: Abbottabad, Battagram, Haripur, Kolai-Palas, Mansehra, Upper Kohistan, Lower Kohistan, and Torghar. Hazara lies close to the crossroads formed by the River Indus and the Grand Trunk Road. Haripur is in a hilly plain area at an altitude of 520 m and has an average temperature of 37.9 °C in summers and 6.5 °C in winters. The annual precipitation is about 564 mm, and humidity in the air ranges between 27% and 56%. The Karakoram Highway begins at the Haripur area and goes north through the Hazara division toward China via the northern areas. This study involves random soil sampling at different distances from the roadside. The dominant soil order in Haripur is aridisol, while inceptisol soil order is found at Abbottabad. Soils were sampled from sides of southern part of Karakoram Highway from more than twenty locations of the Abbottabad and Haripur Districts of Hazara Division, Pakistan (Figure 1).

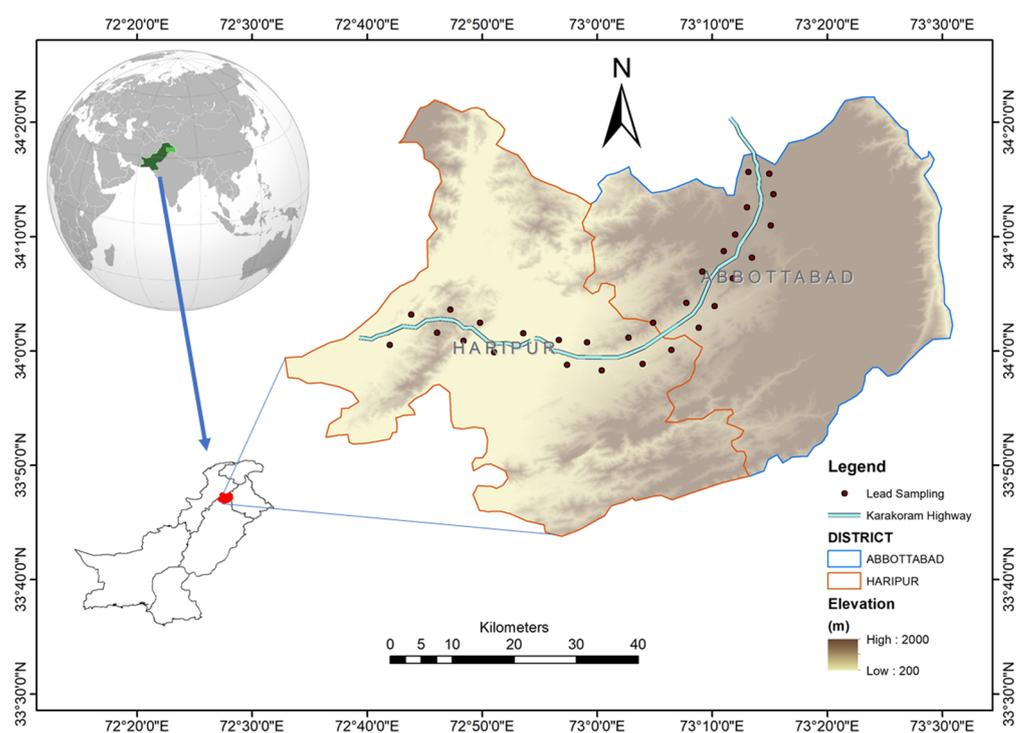


Figure 1. Map showing study area and southern part of Karakoram Highway (KKH). It is the highest paved international road in the world running between Western China and Pakistan.

2.2. Soil Analyses

From each site, i.e., a subplot (5 m × 5 m), a soil sample was taken from different soil layers (0~15; 15~30 cm depths). Four to five discrete samples were collected from each site and combined into a single homogenized composite sample for analysis. There were twenty composite soil samples collected randomly from roadside. The samples were properly mixed in plastic bags. From the sampling site, a composite soil sample was also taken from the fields 200 m away from the road. That was considered control soil since deposition of roadside dust or auto exhaust may be negligible at a distance of 200 m. Soil samples were collected randomly from the surface depth from each site with an auger. The samples were kept in polythene bags to keep them in moist condition.

Materials such as stones, granules, plant parts, and leaves were removed from the samples. The soil samples were air-dried and ground, then passed via 0.5 mm, 1 mm, and 2 mm sieves. Samples were analyzed for their different chemical and physical properties, i.e., pH, electrical conductivity (EC), texture (sand, silt, and clay), organic matter, total calcium (Ca), total magnesium (Mg), total potassium (K), etc., using standard methods. The pH was determined by using a pH meter (HANNA HI 8520) by taking soil and water in the ratio of 1:5 and then shaking for an hour [29]. Electrical conductivity (EC) of the soil was determined by using soil and water (1:5) and shaking for an hour and then measuring with an EC meter (4320 JENWAY) [29]. Organic matter was determined by the dry combustion method [30]. Soil texture was determined using a hydrometric method [31]. Samples were digested in a mixture (3:1) of HNO₃ and HClO₄, and the contents of Ca, Mg, and K were determined using an atomic absorption spectrophotometer (AAS) (Model Analyst 700, Perkin Elmer) [32]. The accuracy of the analytical procedures was evaluated by the analysis of the standard reference material (SRM).

2.3. Lead Extraction Methods

A set of sieves was used for the separation of soil particle fraction. Soil particles were divided into three fractions, i.e., 0.5 mm (finer particles), 0.5 to 1 mm (medium particles), and 1–2 mm (coarse particles) of soil. Lead extraction procedures as detailed below were applied in the three sieved soil samples collected from each site to ascertain the differences in extractable Pb content in soils as influenced by soil particle size. The extraction of lead from three soil fractions was performed using the following extraction methods denoting four main groups of extractants: (1) inorganic acid (hydrochloric acid (HCl)), (2) salts (CH₃COONH₄ (ammonium acetate; buffered solution)), (3) organic chelating agents (diethylenetriaminepentaacetic acid (DTPA)), and (4) alkaline agent (sodium hydroxide (NaOH)). The extractions were conducted at a 1:25 soil-to-solution ratio [33]. In 50 mL centrifuge tubes, a series of 25 mL of extraction solutions of different concentrations were used, i.e., NaOH at 0.04, 0.2, 0.4, 1, 2, 4, 8, and 12%, whereas HCl, CH₃COONH₄, and DTPA were used at five different concentrations (0.1, 1, 5, 10, 20%). These reagents with relative concentrations were prepared with the proper dilution. At 20°C, the suspensions with 2.0 g of soil sample were shaken for 6 hrs in a constant temperature chamber. The suspension was centrifuged at 3000 rpm for 30 min. and then filtered, and the filtrate was brought to a volume of 50 mL. The concentration of Pb was measured using AAS.

2.4. Statistical Analyses

All statistical analyses were conducted by using the SAS program, version 8.02 [34] (SAS Institute 1999). Mean separation of Pb concentrations in soils via different extracting agents was performed using a least significant difference (LSD) at $p < 0.05$. A relationship between the Pb contents extracted through four extraction methods across three particle size fractions of soils to the soil properties was also determined.

3. Results and Discussion

3.1. Descriptive Statistics of Soil Parameters

Physicochemical properties of the roadside soils are summarized in Table 1. Significant differences in the soil properties were observed among the soil samples of both the Haripur and Abbottabad areas. Irrespective of the sample, the pH ranged from 6.89 to 8.13 in the Abbottabad area, whereas its values ranged from 7.63 to 8.14 in the Haripur area, and EC in soils ranged from 98 to 224 $\mu\text{S cm}^{-1}$. Organic matter content in the soil obtained ranged from 1.2 to 4.4%. The majority of soil samples exhibited a higher amount of sand as compared to clay and silt soil particles. Clay content in soils was found more in the Abbottabad areas than the Haripur areas. The average amounts of the nutrients varied such that $\text{K} > \text{Ca} > \text{Mg}$ in the Haripur area. Potassium concentrations ranged from 91.4 to 181.9 mg kg^{-1} soil in Abbottabad areas. A lower amount of K was found in the Haripur areas. The changes in the elemental concentrations in soils could be attributed to their

chemical and physical properties and their mutual interactions. Calcium contents ranged from 46 to 94 mg kg⁻¹ in plain areas of Haripur, whereas it ranged from 15 to 47 mg kg⁻¹ in the Abbottabad areas. Average concentration of Mg was 80 mg kg⁻¹ in the Abbottabad areas and 69.9 mg kg⁻¹ in the Haripur areas.

Table 1. Soil characteristics of roadside soil samples (0–15 cm) of Abbottabad and Haripur areas.

Sites	pH	EC	OM	Ca *	Mg *	K *	Clay	Silt	Sand
		μS cm ⁻¹	%	mg kg ⁻¹				%	
Abbottabad areas									
S1	7.56 ± 0.03	137.0 ± 2.3	4.2 ± 0.1	25.2 ± 1.2	119.4 ± 2.4	122.1 ± 4.5	34.0 ± 1.2	15.0 ± 0.3	51.0 ± 1.2
S2	7.78 ± 0.02	166.1 ± 2.4	4.1 ± 0.1	30.7 ± 1.4	80.5 ± 3.3	101.7 ± 2.7	18.0 ± 2.0	15.5 ± 0.4	66.5 ± 2.0
S3	7.59 ± 0.04	154.6 ± 1.8	4.3 ± 0.2	15.8 ± 0.9	80.5 ± 2.1	112.4 ± 3.7	17.0 ± 0.9	22.4 ± 0.5	60.6 ± 1.3
S4	6.89 ± 0.03	104.7 ± 2.0	3.9 ± 0.2	45.5 ± 2.2	67.8 ± 2.1	145.6 ± 3.4	39.0 ± 1.2	24.0 ± 0.4	17.0 ± 1.0
S5	7.88 ± 0.02	119.1 ± 2.4	4.2 ± 0.1	18.7 ± 1.0	90.5 ± 3.1	181.9 ± 4.0	48.0 ± 2.0	35.0 ± 0.4	17.0 ± 0.7
S6	8.13 ± 0.02	224.4 ± 3.4	1.2 ± 0.02	47.1 ± 2.4	41.1 ± 2.0	91.4 ± 3.8	19.0 ± 1.1	28.0 ± 1.0	53.0 ± 2.8
Haripur areas									
S1	7.97 ± 0.03	98.9 ± 2.6	4.1 ± 0.2	46.1 ± 2.1	79.3 ± 1.7	83.4 ± 3.2	22.0 ± 0.7	34.0 ± 1.2	44.0 ± 2.0
S2	7.68 ± 0.02	187.4 ± 2.0	4.4 ± 0.3	88.1 ± 2.0	61.0 ± 1.8	67.3 ± 2.8	37.5 ± 0.8	30.0 ± 2.0	32.5 ± 1.2
S3	7.87 ± 0.02	166.1 ± 3.4	4.2 ± 0.1	71.1 ± 2.3	68.4 ± 2.1	74.9 ± 3.1	24.0 ± 1.0	30.5 ± 1.7	45.0 ± 2.0
S4	7.67 ± 0.02	171.0 ± 3.2	2.8 ± 0.1	72.9 ± 2.0	72.6 ± 1.6	92.7 ± 2.6	42.5 ± 2.1	20.0 ± 0.4	37.5 ± 1.1
S5	8.14 ± 0.02	101.6 ± 3.1	4.0 ± 0.2	94.0 ± 2.1	47.0 ± 1.0	73.8 ± 2.6	17.5 ± 2.1	25.0 ± 0.7	57.5 ± 1.0
S6	7.63 ± 0.04	111.4 ± 3.2	4.1 ± 0.2	78.5 ± 1.2	88.9 ± 3.1	53.6 ± 1.7	17.5 ± 0.6	30.0 ± 0.9	52.5 ± 2.7

± values indicate standard errors. * Ca, K, Mg concentration representing total form.

3.2. Extraction of Lead from Soil Using Different Methods

Soil samples collected from roadside sites were examined for Pb concentration using four extraction methods. Results of the study area showed that there were significant differences in Pb concentrations among sampling sites and extraction methods. The extraction efficiency of Pb was associated with the concentration of the extracting solution. Lead concentrations in soil varied among extracting agents, and the concentrations depended on the reagents used in the order of HCl > DTPA > NH₄OAc > NaOH, irrespective of the strength of a reagent in the soil solution (Figures 2–6). With the increasing strength of a reagent solution, the extractability of Pb was significantly enhanced in the soil. The amount of NH₄OAc extractable Pb in the topsoil samples of the Abbottabad area ranged from 67.9 to 246.7 mg kg⁻¹ and in the Haripur area, the Pb concentrations were recorded from 97.6 to 242.5 mg kg⁻¹. At 20% HCl solution, the average Pb concentrations were 2.6 times higher than NH₄OAc reagent in the topsoil of the Abbottabad area. The average concentration in the topsoil of the Abbottabad area was found from 67.8 mg kg⁻¹ in 0.1% to 246.3 mg kg⁻¹ in 20% NH₄OAc solution, whereas the average concentration of Pb in the topsoil of the Haripur area ranged from 338 mg kg⁻¹ in 0.1% to 662 mg kg⁻¹ in 20% HCl solution. Lead is usually transferred from the atmospheric segment of the roadside environment to the soil compartment, and thus, Pb is concentrated in the upper portion of the soil.

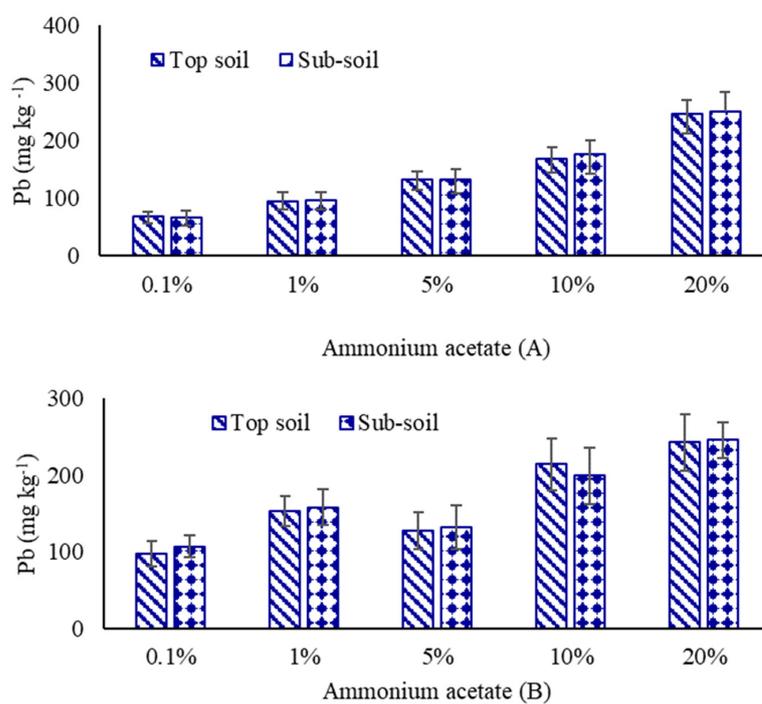


Figure 2. Changes in ammonium acetate extractable Pb in topsoil and subsoil collected from roadside areas of (A) Abbottabad and (B) Haripur.

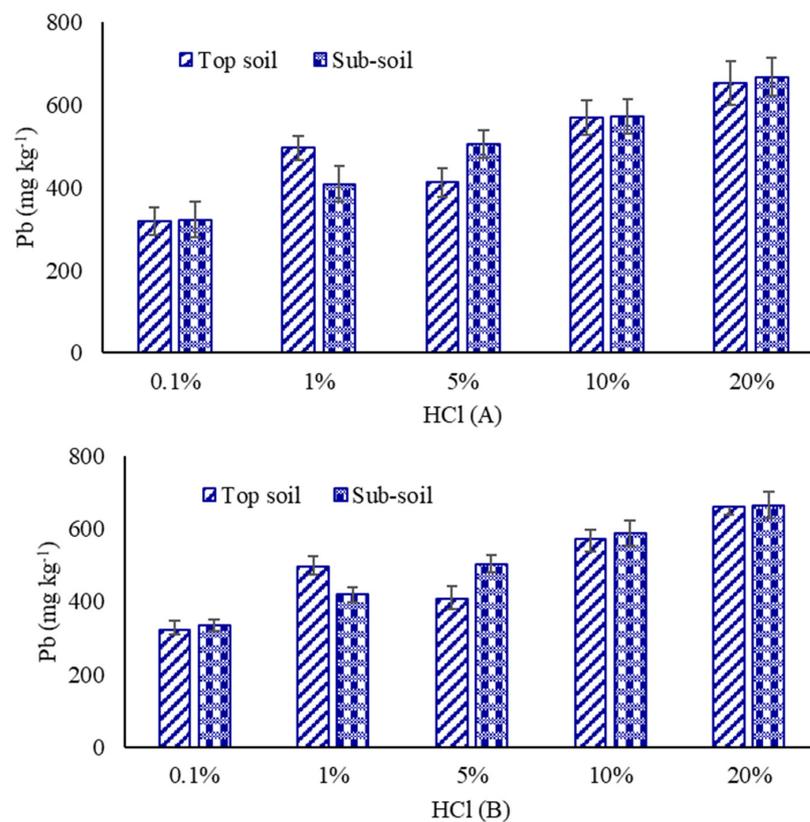


Figure 3. Changes in HCl extractable Pb in topsoil and subsoil collected from roadside of (A) Abbottabad and (B) Haripur.

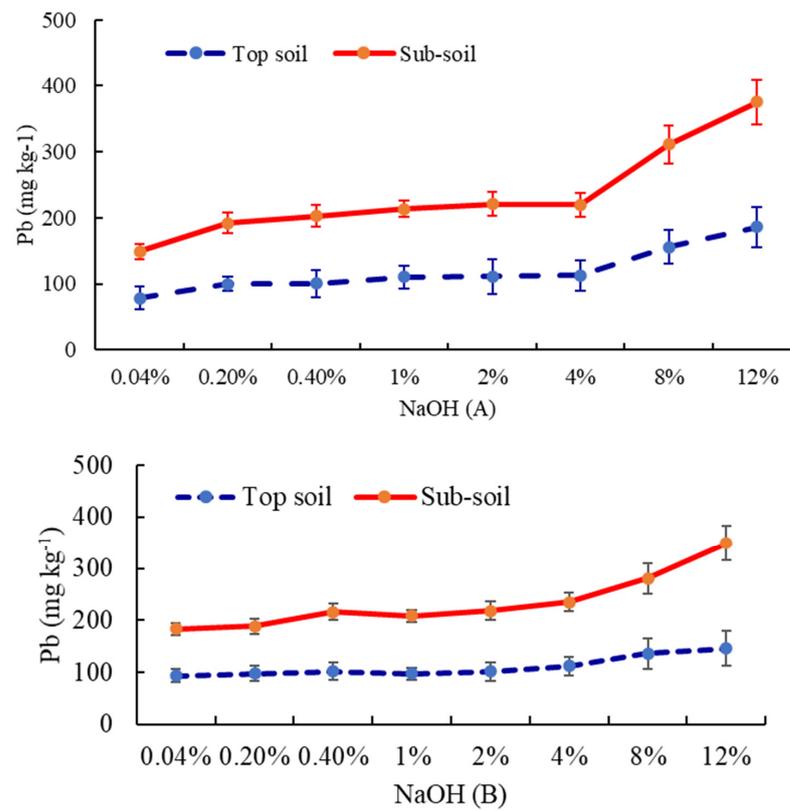


Figure 4. Changes in the NaOH extractable Pb in the topsoil and subsoil samples near roadside of (A) Abbottabad and (B) Haripur areas.

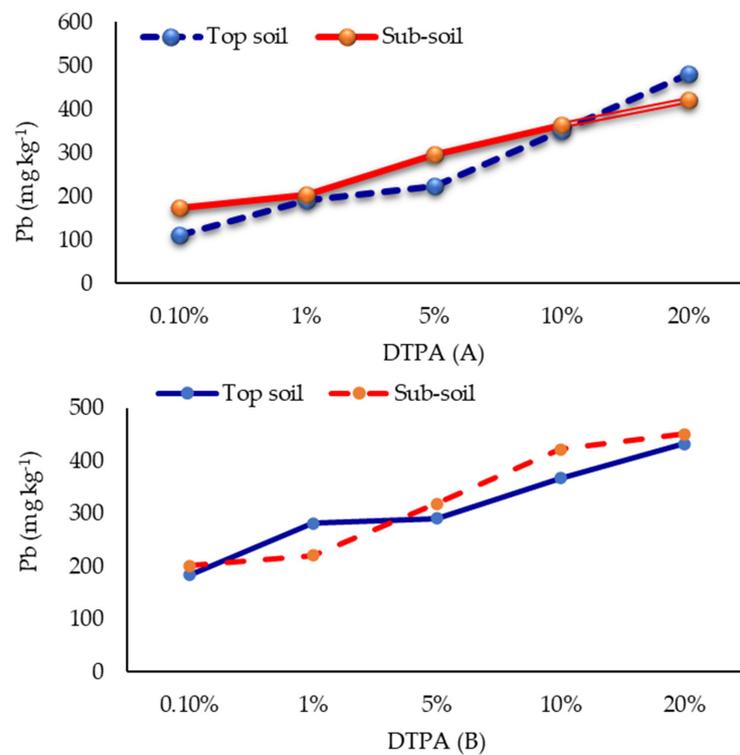


Figure 5. Changes in DTPA extractable Pb in topsoil and subsoil samples near roadside of (A) Abbottabad and (B) Haripur areas.

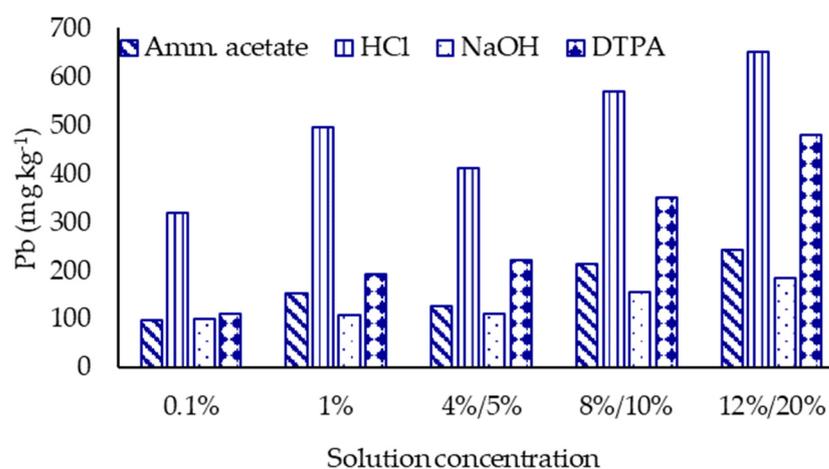


Figure 6. Comparison of Pb extraction methods from the surface soil samples along the roadside of Abbottabad areas (0–15 cm; n = 6).

The roadside soils retained higher Pb concentrations than the permissible limits, i.e., 10–70 mg kg⁻¹, as reported by FAO/WHO [35]. Soil samples collected from a longer displacement away from the road gave a lesser amount of Pb in the soil. Studies on the roadside soil Pb concluded that the Pb concentrations are directly related to traffic volume and inversely correlated with perpendicular distance from the roadway. Higher accumulation of Pb in nearby roadside soil could be associated with the traffic movement and wind direction. This study indicated a considerable contamination of Pb in the roadside soil environment, whereas control soil samples taken at a distance of 200 m showed an average Pb concentration of 28.5 to 61.7 mg kg⁻¹. Therefore, this can be confirmed that the sampling distance from the roadside particularly influenced the Pb concentrations in the soil. The Pb contamination of roadside soil could vary due to traffic load variations. The distribution of heavy metals in the roadside soil was very strong and conversely correlated with an increasing distance from the road [9].

Moreover, the type of road traffic volume and the time of use reportedly influenced the Pb contents in the soil, irrespective of the distance [36]. At approximately 200 m distance, a constant level of Pb in several soil samples was obtained, which may confirm the lost effects of the roadway on the Pb contamination in soils. A comparison of Pb concentrations in soils also strongly implicates automobiles as the active and main source of Pb contamination in the soil environment. The vehicles in congested traffic areas move slowly due to the traffic jams, and this situation may enhance Pb contamination in the environment. The quality guidelines for soil Pb concentrations developed in different countries indicate wide variations [37]. The limit for the total concentration of Pb in soil was 200 mg kg⁻¹ [37], while the Dutch reference value was reported as 35 mg kg⁻¹ [38]. In France, the soil threshold level of Pb is 100 mg kg⁻¹ [39]. The current levels of Pb have fallen drastically due to the complete or gradual phasing out of leaded gasoline in some countries [40].

The study predicts that Pb pollution in soils under the influence of heavy traffic could also pollute edible crops. The penetration of heavy metals such as Pb into the food chains may bring an ecological issue and health hazard for the residing community near roadsides. Therefore, the crops grown in the contaminated land should be carefully assessed before their consumption by human beings. Lead concentration pattern in the topsoil and subsoil was found to be inconsistent. Few soil samples exhibited a higher concentration of Pb in the subsoil samples due to the Pb accumulation after leaching from the topsoil. Lead contents have been reported to be accumulated in the surface soil [41]. Accumulations of Pb in the soil were associated with the amount of organic matter, which was reported as an important sink for Pb in the soils [42]. Results showed that there were tangible differences in the Pb concentrations among the sampling sites both in the Abbottabad and Haripur areas. The differences found in the Pb concentrations in soils could depend on the land

configuration of sampling areas and depth of the soil. Except for NH_4OAc extractable Pb, the concentrations of Pb were higher in the subsoil as compared to the topsoil, irrespective of the sampling site. A higher amount of clay and organic matter content prevailed in the soil samples of the Abbottabad areas when compared with the Haripur areas. The changes in Pb concentration in soil could be attributed with the changes in the physicochemical properties of soils. The solubility of Pb in soil has been found to be pH-dependent. A high soil pH may precipitate Pb as hydroxide, phosphate, or carbonate and promote the formation of relatively stable Pb–organic complexes [43]. Lead status of roadside soils has been varied due to the sampling site, distance, and wind direction. Lead concentration of soil near the roadside was observed as substantially higher than the soil sample of distant sites from the road. The possible sources of Pb in soils have been reported to be the runoff from the road and atmospheric deposition [44]. Therefore, more deposition of Pb near traffic movement can occur.

Simple linear regression between the amount of Pb present in the soil versus soil properties is plotted in Figure 7. Lead concentration in the soil relatively depended on the soil properties such as soil organic matter, pH, and texture. Lead concentration was higher in the soil where the amounts of organic matter and clay content were apparently in excess. The soil pH was inversely related with the extractable amount of Pb from the soil, irrespective of the sampling area. This study may also confirm a relatively higher affinity of Pb toward organic matter contents in soil. Regression plots showed a higher relationship of Pb concentration in soil with organic matter and clay percentages in the soil by the following equations: $y = 119.76x - 54.73$; $R^2 = 0.76$ and $y = 16.59x - 205.84$; $R^2 = 0.79$, respectively. Garcia-Miragaya [45] also reported a negative relationship of soil pH with the release of Pb from soils. The extractability of Pb was correlated with clay contents in the soils. Soil texture affects the chemical characteristics of soil, including the formation of Al–organic matter bonded stable *P* and leaching of *P* from soils [46], which may be related to the extractability of Pb. The sorption behavior of Pb in soils appeared to be varied from soil to soil and was influenced by the soil properties, such as pH, organic matter, cation exchange capacity (CEC), and clay contents [47]. Generally higher pH value of the soil decreased the mobility of trace elements and enhanced the adsorption capacity of soil. Christensen [48] reported that each unit increase in pH resulted in a twofold decrease in the concentrations of heavy metal in soils. Different soil factors such as pH, redox potential, and CEC are involved for the immobilization of elements in soil [49]. In the natural environment, the pH of the soil has an enormous influence on soil biogeochemical processes. Soil pH is a master soil variable that influences soil biological, chemical, and physical properties and processes that affect plant productivity [50,51].

Lead concentration was also oppositely related to the particle size of the soil (Figure 8). The concentration in the soil particles was found in the order of finer (0.5 mm) > medium sized (0.5–1.0 mm) > coarser (1–2.0 mm). The greater particle size of the soil produced a lower Pb concentration in the soil and vice versa. In the finer soil, the higher amount of clay and organic matter apparently enhanced the extractability of Pb from soil samples. Higher Pb pollution in the soil surrounding the roadside could be linked with the higher density of traffic. The extent of Pb retention in the soil is relatively associated with the several factors, i.e., soil properties, parent material, topography, vegetation cover, drainage pattern and soil management practices, etc. This study demonstrated that particle size distribution is related to the concentration of Pb in the soils. Invariably, reports of roadside soil Pb showed that the Pb concentrations are positively correlated with the volume of the traffic and inversely related to the horizontal distance from the roadside. Soil Pb adjacent to an old road with a lower traffic volume may exceed the Pb concentration in soil compared with a young road with higher traffic volume [52]. The lower mobility factor of Pb in the soil and its retention for a longer time could lead to the higher contamination of Pb in the roadside soils. Therefore, soil sampling at different depths and the distance from the roadside could be considered a crucial factor for the monitoring and assessment of heavy metals contamination in the soils.

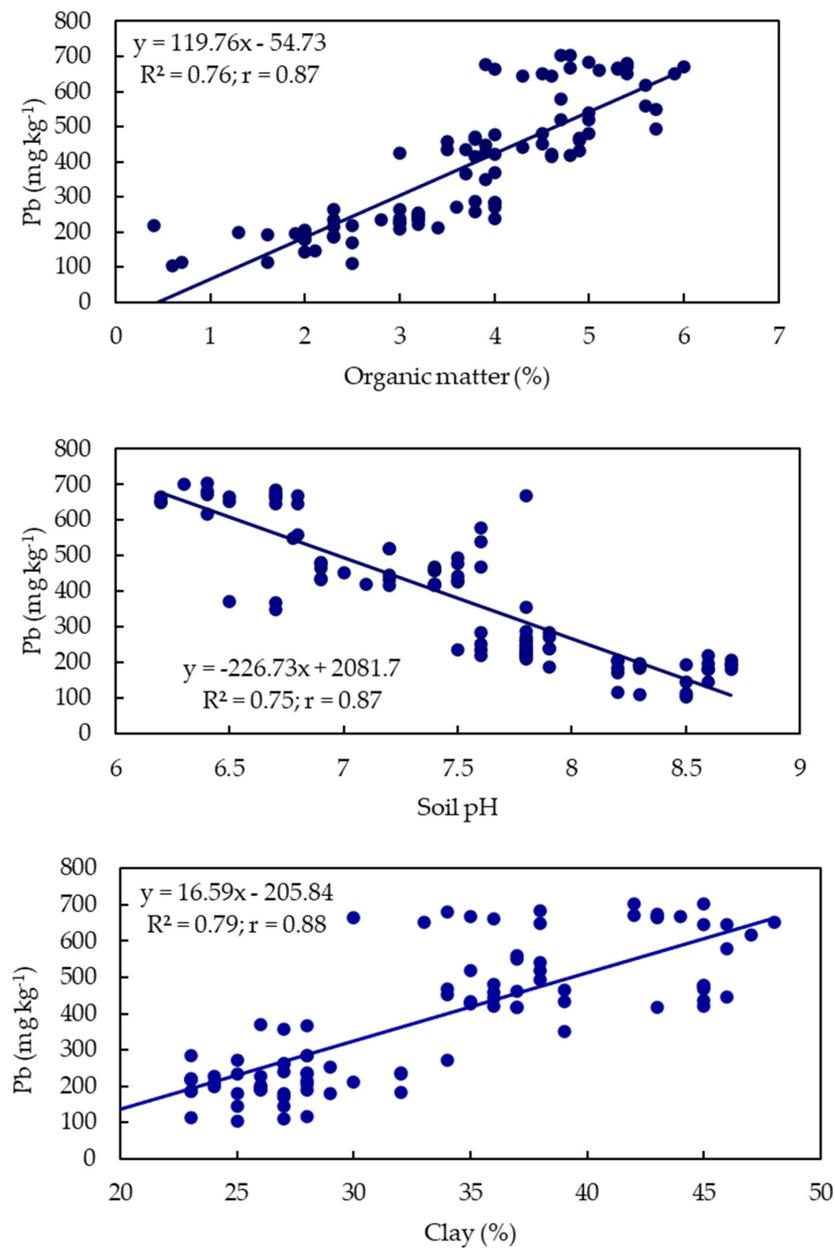


Figure 7. Regression plot for the extractable Pb versus organic matter, pH, and clay contents of the surface soil (n = 6).

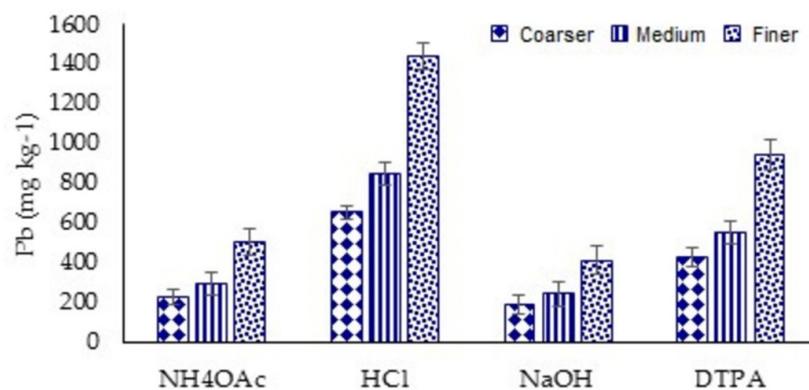


Figure 8. Extractability of Pb as affected by extracting agents (20%) and particle size of surface soil of the Abbottabad areas.

The concentration of Pb in the soils was related to the particle size distribution in soils since fine particles of soils contained a higher amount of Pb contaminant in mineral soil [53]. Lead containing dust particles has a relatively short residence time in the atmosphere and deposits early in the near roadside. This may further contribute the accumulation of Pb on the roadside soils [54]. Yousefi et al. [55] reported that industrialization, population, density of vehicles and motor traffic, mode of public transportation, age of vehicles, condition of tires and brake pads, and corrosion of vehicle's bodies; sampling conditions; geometric properties and the quality of the streets; and fuel additives are the factors that influence the amount of Pb in the soil. The atmospheric, soil, and vegetative components of the roadside environment contain higher levels of Pb originated from the combustion of gasolines via vehicles [56]. Culbard et al. [57] reported the Pb concentrations in the roadside dust of urban areas in the UK as being between 45 and 9660 mg kg⁻¹ of total lead with the geometric mean value of 786 mg kg⁻¹. In the recent years, the Pb content in the gasoline has been markedly decreased in the UK after the introduction of the regulations for the reduction in Pb content from 0.64 g L⁻¹ in 1966 to 0.14 g L⁻¹ in 1986. This situation has declined the Pb contamination in the environment via motor vehicles [11]. During the analytical study of 233 samples, 130 samples contained Pb up to 200 µg g⁻¹, while 70 samples showed Pb concentration ranging from 200 to 400 µg g⁻¹, and 33 samples gave Pb in the range of 400 to 1200 µg g⁻¹ [11]. Khan et al. [58] reported contamination of the roadside soils with Pb due to long-term exposure to traffic and a substantial amount of Pb concentration in the roadside soils compared to the reference soils. Moreover, the contamination levels of soils were found in the order of primary road > secondary road > tertiary road > reference site.

Lead recovered from soil with HCl and DTPA reagents was higher as compared to the other two reagents, probably due to the ability of Pb to form stable organo-metallic complexes in soil. These results also suggest that Pb extraction was partially dependent upon several soil factors. This phenomenon may be controlled and affected by soil depth, sampling site, pH, cation exchange capacity, organic matter content, texture, chemical composition of soil, and soil process such as leaching and organic creation process. The Mehlich-3 solution showed more capacity of extraction of micronutrients in comparison to the other extractants [59]. Acid reagents and chelates produced higher amounts of micronutrients after extraction by the Mehlich-3 solution than by the DTPA-TEA [60], and by diluted acids (e.g., Mehlich-1 and HCl) [61]. Diluted acid solutions may only partially solubilize soil's heavy metal, while chelating agents such as DTPA or EDTA reduce the Cu activity in solution by complexation, causing the dissolution of the labile forms of Cu in soils [62].

4. Conclusions

It is concluded that Pb concentrations in roadside soil samples depended on the extracting reagent used, i.e., HCl > DTPA > NH₄OAc > NaOH. The extractability of Pb from soil was enhanced with the strength of a reagent in the soil solution. The roadside soils contained Pb concentrations higher than the permissible limits. The control soil samples (from a distance of 200 m) exhibited Pb concentrations in the relatively lower range of 28.5 to 61.7 mg kg⁻¹. The concentration of Pb was higher in the soil samples containing higher amounts of organic matter and clay. The soil pH was inversely related to the extractable Pb in the soil. Lead concentration was oppositely related to the particle size of the soil. Higher Pb pollution in the soil under the influence of the Karakoram Highway could be associated with the higher traffic density. Determination of Pb concentration in the roadside soils and natural vegetation in relation to soil properties is further suggested. More studies are also required on the investigation of Pb in soils in relation to Pb contamination in edible crops grown in the contaminated soils to avoid detrimental health effects.

Further research is required to identify the use of a suitable chemical reagent and cheaper extraction method for the determination of potentially toxic elements such as Pb in contaminated soils. Proper assessment of Pb in the soils and edible crops grown in the vicinity of main roads is essential for secure health implications. Remediation

of Pb-contaminated soils using a feasible technique is also suggested for a sustainable crop production.

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