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Changes in Selected Elements of Soils Under Simulated Acid Rain Conditions

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Abstract: Acid rain has been considered a major polluting agent harmful to both terrestrial and aquatic ecosystems. A study was carried out to examine the variations of different elements in Abbottabad soil, Pakistan. The acidification process increases the extraction of different elements from the soil. The extracted concentration of Mg increased in the CL soil after the addition of 1*N* HNO_3 (1:5) by 46.7%, with 1*N* H_2SO_4 by 56.3%, and the mixture of both acids 68.1% than untreated CL soil. The average Na concentrations (mg kg^{-1}) of soil suspension (1:5) were achieved among acids as HNO_3 (17.2) > HNO_3 plus H_2SO_4 (15.4) > H_2SO_4 (14.8) > no treatment (8.5). The greater strength of acid released more amounts of an element from the soil. This study indicated a distinct alteration in the composition of soil by acidification practice.

Keywords: acid rain; chemical properties; sandy loam soil; clay loam soil.

1. Introduction

Acid rain is an environmental issue, which leads to the acidification of waters and soils [1]. A large amount of fossil-fuel combustion causes the emission of SO_x and NO_x to the atmosphere, Coal- and oil-fired power plants and transportation sources, such as vehicles and ships, are the sources of acid deposition [2]. The main anthropogenic sources of SO_2 emissions are coal and petroleum, including several industrial processes [3]. Similarly, natural phenomena contribute acid-producing gases to the atmosphere via volcanoes. Biological processes also produce these gasses on the land, wetlands, and oceans. Acid rain creates harmful effects on plants and aquatic animals. The damage that occurs to the ecosystems from acidic deposition is dependent on the buffering ability of that ecosystem. This buffering ability is dependent on several factors, the two major ones being soil chemistry and the inherent ecosystem sensitivity to acidification. The ecosystems may be damage indirectly due to alteration. The soil system is a very complex and dynamic feature on planet Earth [2, 3].

Plants need healthy soil for growth. Long-term changes in the chemistry of soils may occur due to the phenomena of acid rain. Subsequently, this acid rain peculates in the soil and has the ability to strip away vital plant nutrients through chemical reactions and causing a potential threat to plant productivity. [4]. reported a rapid decline of soil pH was attributed to long-term atmospheric acid deposition (nitrogen and sulfur) [5]. It concluded that acid rain reduces the leaf area and the sunflower's overall plant growth [6, 7]. It reported reduced growth and yield of several crop species due to simulated acid rain under glasshouse conditions.

It has been reported that the H^+ ion in the acidic water displaces the cations from their binding states, reduces the cation exchange capacity, and enhance the concentrations of cations in the soil solution. Sulfate and nitrate ions in the acid rain increase the leachability of cations from the soil. The cations like K^+, Na^+, $Ca^{2+,}$ and Mg^{2+} are leached from soils and become unavailable to plants [2, 8]. Heavy metals such as Cu, Pb, and Cd, are attached to the negatively charged surface of soil particles and can be displaced by the presence of H^+ ions [9].

Acid rain may be able to enhance the heavy metal mobilization in soil ecosystems. Research studies have been done to understand the effects of acid rain on plants and the lithosphere. However, its effects on the water extractability of selected elements in soil were discussed in detail. Therefore, this study's objective was to determine the influence of simulated acid rain on the solubilization of selected elements in the soil.

2. Materials and Methods

This research was conducted in the Lab of LiScient Department at COMSATS Institute of Information Technology Abbottabad, Pakistan, to determine the influence of acid rain on soils' chemical composition under laboratory conditions. Two types of soils, sandy loam soil and clay loam soil, were sampled from the Abbottabad area. Soil samples were oven-dried at 105^{o}C and then sieved using a 2 mm sieve. Soil physicochemical parameters like pH, electrical conductivity (EC), texture, organic matter, and micro-and macro-elements (K, Ca, Mg, Na, Mn, Fe, and Cr) were examined before the soil treatment. These soils were treated with the following diluted acid concentrations to ascertain elemental changes from NE-SW direction.

1. 1*N* HNO_3, 0.1*N* HNO_3, 0.01*N* HNO_3,
2. 1*N* H_2SO_4, 0.1*N* H_2SO_4, 0.01*N* H_2SO_4,
3. Combined treatments (1:1) of 1*N*, 0.1*N*, and 0.01 *N* of both H_2SO_4 and HNO_3

The above synthetic acid rains were selected based on the study of [1]. Five g of each soil was treated and shaken on an end-over-end shaker, separately with 25 mL (1: 5) and 50 mL (1:10) of each diluted acid as detailed above for at least 2 hours. Each treatment was triplicated to ensure the validity of the outcome. The treated samples were centrifuged at 3000 rpm for 15 min. and then filtered with a 0.45 µm membrane filter. Micro- and macro-elements in the filtrate were identified with an atomic absorption spectrometer (Model AAnalyst 700, Perkin Elmer [16]. Total carbon was figure out by dry combustion using Nelson and Sommersmethod [10]. Soil samples were weighed into porcelain crucibles and ashed in the muffle furnace at 550 ^{o}C for 2 h to determine total carbon. Total carbon was assessed to calculate the organic matter by multiplying with 1.72. The pH and electrical conductivity (EC) of the soils (1:5) were estimated thru the pH meter (Model: HANNA HI 8520)and EC meter (Model: 4320 JENWAY), respectively. The particle size distribution of the soil was measured utilizing the pipette method [11]. The details of different chemical properties of soil are enlisted in Table 1. Data were analyzed, and results were expressed on an oven-dry basis. Mean separation was done using LSD at $P < 0.053$.

3. Results and Discussion

The study indicated that all acidic water treatments boost major and minor elements' solubility than control soil irrespective of the metal species. Elemental concentrations were varied as Ca > Mg > Fe > Na >Mn> Cr. The dilution of soil at 1:10 ratio of soil-water extracted more cations concentrations than the soil-water suspension of 1:5. Irrespective of an acid's strength, the release of elements differed among acid treatments as H_2SO_4> HNO_3> mixture of HNO_3 and H_2SO_4. Elemental concentrations were significantly affected by diluted acids. The level of cation concentrations in soils was positively linked with the strength of the acid. Besides, the magnitude of cations concentrations in the soil solution was largely dependent on acid concentration. Furthermore, the difference in the metal concentrations was recognized between soil types. Irrespective of the type of element, clay loam (CL) soil gave a higher amount of heavy metals than sandy loam (SL). This could be related to greater innate accumulation or retention of these elements. The sorption behavior of heavy metals in soil varied from soil to soil. It could also influence soil properties, pH, organic matter, cation exchange capacity (CEC), and clay contents. In both types of soil, a strongly acidic solution effectively released the heavy metal compared to distilled water.

The influence of simulated acid rain on Ca's extractability in the soil differed: H_2SO_4>HNO_3> mixture of H_2SO_4 and HNO_3 (Figure 1). Calcium concentration in the soil solution was obtained after acid treatment of 1N HNO_3, 1N H_2SO_4, and their mixtures 45.1, 48, and 50 mg kg^{-1} in sandy loam, after shaking of 1:5 soil-water suspension with the comparison of control soil where the Ca was 26.6 mg kg^{-1}. Acid water treatment of 1N HNO_3, 1N H_2SO_4, and their mixture differed in 1:5 soil-water suspension of CL soil, i.e., 56.2, 60.4, and 50 mg kg^{-1} with the comparison of untreated soil where Ca was 31.2 mg kg^{-1}. These treatments differed for SL soil [1:10 soil-water suspension] as 50.2, 53.0, and 55.3 mg kg^{-1} than control soil where the Ca content was 29.4 mg kg^{-1}. The CL soil gave a higher amount of Ca instead of soil. Calcium concentration (mg kg^{-1}) differed in CL as 1N H_2SO_4(66.7) > 1N HNO_3 62.2 > mixed acids (55.6) > control (34.4).

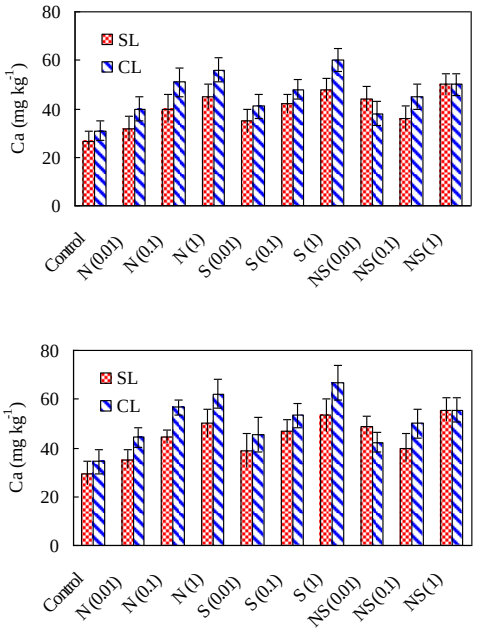

Figure 1. Solubility of Ca in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10).

Therefore, Magnesium concentration in the extract elevated for clay loam after shaking with water (1:5) by 46.7% with 1*N*HNO_3, 56.3% with 1*N*H_2SO_4, 68.1% with the mixture of both acids as compared to untreated SL soil. HNO_3 acid solution of different strength released the Mg (mg kg^{-1}) as 27.6 (1*N*HNO_3) > 24 (0.1*N*HNO_3) > 18.3 (0.01*N*HNO_3) > 12.5 (control) in SL soil (Figure 2). Magnesium concentration (mg kg^{-1}) in CL soil was approximately 18.7 (control) < 27.8 (0.01N HNO_3) < 35.7 (0.1N HNO_3) < 39.0 (1N HNO_3) after shaking with 1:5 soil water suspension. Magnesium (mg kg^{-1}) was recorded in the H_2SO_4 treatment with value of16.3 (0.01*N*) < 23.4 (0.1*N*) < 29.6 (1*N*) in SL soil. These treatments provide Mg (mg kg^{-1}) in CL soil as 25.1 (0.01N) < 32.5 (0.1*N*) < 45.7 (1*N*) after 1:5 shaking for two hours. The concentration of Mg (mg kg^{-1}) was differed among mixed acid treatments of HNO_3 and H_2SO_4 as 18.8 (0.01*N*) < 25.3 (0.1*N*) < 35 (1*N*) for SL and 24.8 (0.01*N*) < 34.4 (0.1*N*) < 42.5 (1*N*) for CL soil (1:5). Shaking of diluted soil solution (1:10) increased the concentration of Mg (mg kg^{-1}) across all acid treatments. For instance, the concentration of Mg (mg kg^{-1}) was differed among HNO_3 treatments as 19.4 (0.01*N*) < 25.8 (0.1*N*) < 30.1 (1*N*) for SL and 29.9 (0.01*N*) < 38.3 (0.1*N*) < 41.9 (1*N*) for CL soil (1:10). The Mg (mg kg^{-1}) varied among H_2SO_4 treatments as 17.5 (0.01*N*) < 25.2 (0.1*N*) < 31.8 (1*N*) for SL and 27.6 (0.01*N*) < 34.5 (0.1*N*) < 49.1 (1*N*) for CL soil (1:10). The higher extraction of heavy metals in acid in clay loam soil could be attributed to the enrichment of the adsorbed cations. This phenomenon could also be associated with chemical changes that attributed as a result of acidic solution.

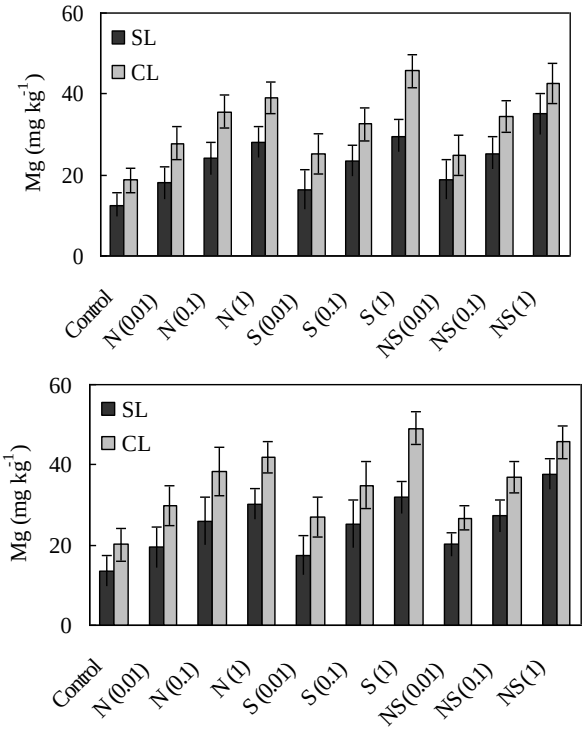

Figure 2. Mg solubility in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10).

The average Na concentration (mg kg^{-1}) of soil suspension (1:5) was achieved among acids: as HNO_3 (17.2) >HNO_3 plus H_2SO_4 (15.4) >H_2SO_4(14.8) > no treatment (8.5) regarding normality of acid. The concentration of Na (mg kg^{-1}) was enhanced in 1:10 suspension and was varied as HNO_3 (19.5) >HNO_3 plus H_2SO_4 (17.4) >H_2SO_4(17.1) > no treatment (9.8). The amount of elements in the extractions was directly related with the concentrations of acid (Figure 3). Clay loam soil released more Na than SL. HNO_3 treated soil showed a concentration of Na as 9.2 (0.01*N*) < 14.3 (0.1*N*) < 18.0 (1*N*) for SL and 15.3 (0.01*N*) < 22.1 (0.1*N*) < 23.9

(1*N*) for CL soil (1:5). The dilutions of H_2SO_4 treated SL soil showed Na level as 10.2 (0.01*N*) < 12.5 (0.1*N*) < 15.0 (1*N*) and 10.3 (0.01*N*) < 17.2 (0.1*N*) < 25.3 (1*N*) for CL soil (1:5). The SL soil which were treated with mixed acids showed Na level (mg kg^{-1}) as follows 11.1 (0.01*N*) < 14.4 (0.1*N*) < 17.8 (1*N*) and 9.3 (0.01*N*) < 15.6 (0.1*N*) < 24.1 (1*N*) for CL soil (1:5). When we compared samples shaken soil with distilled water, the acids with I N strength has extracted the concentrations of elements more than 2-times, regardless of the type of an element.

Table 1. Physico-chemical properties of soils used for the experiment.

Property	Unit	Sandy loam soil	Clay loam soil
Sand	%	67	38
Silt	%	27	28
Clay	%	6	34
Organic matter	%	2.6	3.2
EC (1: 5)	dS m^{-1}	1.3	1.6
pH	-----	8.4	8.3
Soluble Ca	mg kg^{-1}	26.6	31.0
Soluble Mg (water)	mg kg^{-1}	12.5	18.7
Soluble Na	mg kg^{-1}	6.0	11.2
Soluble Fe	mg kg^{-1}	10.1	13.1
Soluble Mn	mg kg^{-1}	3.7	4.8
Soluble Cr	mg kg^{-1}	1.3	2.0

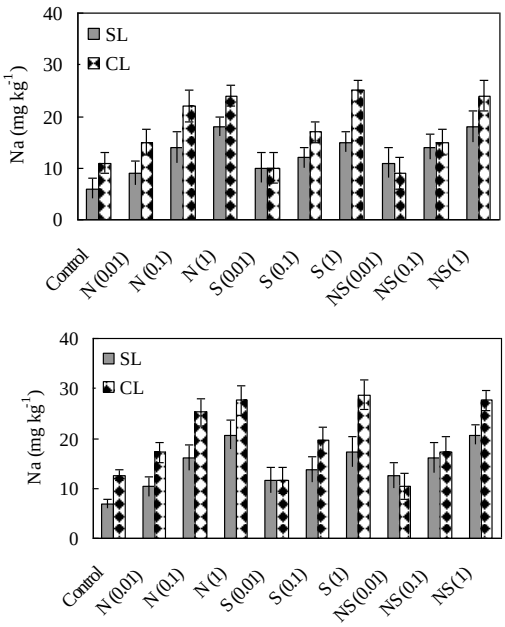

Figure 3. Solubility of Na in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10)

The Fe concentrations (mg kg^{-1}) in SL soil in 1:5 suspensions were obtained among HNO_3 acid with the normality (*N*) of 1, 0.1, and 0.01 as 24.5, 18.3, and 15.3. (Figure 4). The same acid in the CL soil solubilized the Fe as 23.4, 20.3, and 16.7. There was a slight variation of Fe in diluted H_2SO_4 than HNO_3 dilutions. H_2SO_4 extractions were found with Fe level as 23.6 (1N), 18.8 (0.1N) and 16.1 (0.01) I SL soil. The extractions of CL soil among three treatments of H_2SO_4 were found: 24.1 (1*N*), 21.3 (0.1*N*), and 17.4 (0.01*N*). Overall, the normality of acid, the mean value (mg kg-1) of Fe among acids varied as 11.6, 19.8, 20.3, and 20.6 in control, HNO3, H2SO4, and mixed acids the ratio of 1:5 dilutions. Fe values (mg kg^{-1}) were enhanced in 1:10 dilutions and varied as 13.7 (control) < 23.2 (HNO_3) < (H_2SO_4) 24.0 < (mixed acids) 24.3.

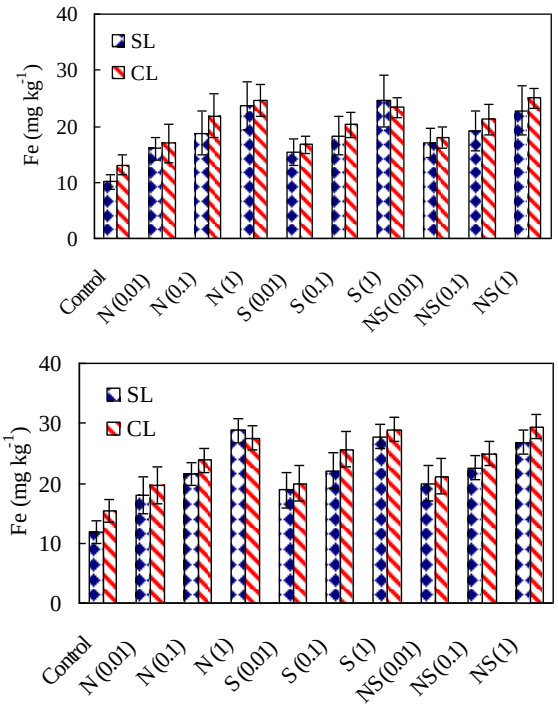

Figure 4. Solubility of Fe in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10).

The extractability of Mn was profoundly affected by the saturation of soil with acids (Figure 5). The SL soil differed as H_2SO_4>HNO_3> mixture of H_2SO_4 and HNO_3. Manganese concentration in the soil solution was obtained among the acid treatment of 1*N* HNO_3, 1*N*H_2SO_4, and their mixtures 10.3, 11.4, and 10.4 mg kg^{-1} in sandy loam after shaking of 1:5 soil-water suspension when compared with the control soil where the Mn was 3.8 mg kg^{-1}. Acid water treatment of 1*N*HNO_3, 1*N*H_2SO_4, and their mixture differed in 1:5 soil-water suspension of CL soil as 15.3, 15.6, and 16 mg kg^{-1} during comparison with untreated soil where the Mn was 4.8 mg kg^{-1}.

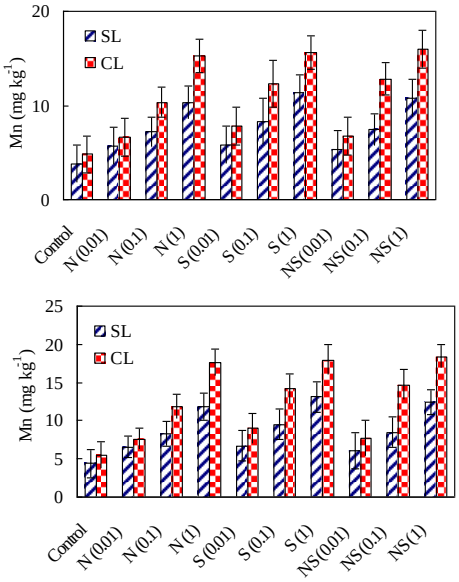

Figure 5. Mn solubility in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10).

Across all normalities, Mn (mg kg^{-1}) in the acid treatments differed for 1:5 soil-water suspension as H_2SO_4 (10.2), HNO_3 (9.2), and a mixture of H_2SO_4 and HNO_3 (9.8) than control soil where the Mn content was 4.3 mg kg^{-1}. The CL soil gave a higher amount of Mn than SL soil. Manganese concentration (mg kg^{-1}) differed in CL as H_2SO_4(11.7), HNO_3 (10.6), mixed acids (11.3), and control (4.9) in 1:10 diluted treatments. Soil pH and organic matter are the soil factors that control heavy metal availability [12]. Acid rain enhanced the leaching of heavy metals from the contaminated soil. Also, it caused the heavy metal fractions to become more labile [1].

The significant changes in Cr concentrations of soils were noticed with the application of acids (Figure 6). The release pattern of Cr was similar to other metals in both soil. Strong acidity level extracted more amount of Cr rather than weaker acid. The higher concentration of Cr in the CL soil could be attributed to its higher concentration in the irrigation water. In general, acid treatments may increase the risk of heavy metals in runoff or water bodies. It has been reported that heavy metal solubility was the organic material function in soil treatment [13, 14,15]. It was reported that acidification of soils lowered the cation exchange capacity, affected the grain size distribution, and altered the consistency and strength properties. This study indicated that acid rain could increase heavy metal concentrations in the soil solution.

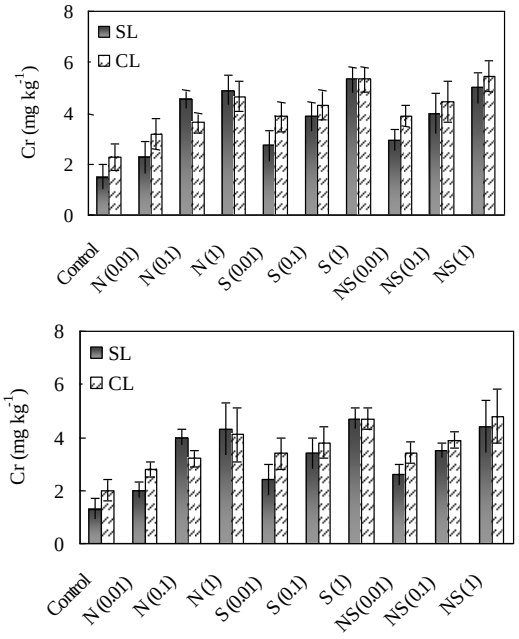

Figure 6. Solubility of Cr in soils as affected by simulated acid rainwater after shaking at two soil-water ratios (1:5 and 1:10).

4. Conclusions

In summary, it can be concluded that the shaking of the Abbottabad soils. Pakistan, with the acid solution, can alter the extractability of heavy metals. Heavy metal concentrations increased with soil acidification. Furthermore, the concentrations of cations in the soil were varied as Ca > Mg > Fe > Na >Mn> Cr. Clay loam soil showed a higher concentration of elements in the solution than sandy loam soil. Soil-water suspension of 1:10 extracted more cations than the 1:5 ratio. The extraction of elements differed among acid treatments. Like, H_2SO_4> HNO_3> mixture of HNO_3 and H_2SO_4, across all normalities. The concentrated acid solubilized more concentration of element (1*N*> 0.1*N*> 0.01*N*). This study found an alteration of soil composition with acidification.

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Conflicts of Interest

The authors declare no conflict of interest.

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