

GROUND WATER QUALITY ASSESSMENT IN INDUSTRIAL ZONES OF CENTRAL PUNJAB, PAKISTAN

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ABSTRACT: Solid and liquid waste generation has increased tremendously in this era of industrialization. A large amount of domestic and industrial waste is disposed off without segregation practices. Inadequate waste management practices and lack of technologies endure contamination of ground water table, surface water resources and water supply infrastructure. The heavy metals and microbial byproducts present in leachates which deteriorate ground water quality and consequent health effects are prevalent and ever-increasing in industrial urban areas of Pakistan. The current study assesses the effects of leachate on water from open dumping sites of two cities (Gujranwala and Sialkot) during pre- and post-rain season. We have collected and analyzed ground water samples for the assessment of metals and compared with global and national quality standards. It was found that most of the pre-rain samples had pH value near to or higher than WHO/NEQS standards in both cities, while TDS, EC, hardness, nitrate, sulfates, chlorides and phosphates concentrations were found to be within WHO/NEQS permissible standards. The heavy metals (Zn, Fe, Cu, Cr, Ni, Cd, Co and Pb) were detected in higher concentration than NEQS/WHO standards, which was an indication of detrimental effects on ground water quality. It has been detected that all parameters had significantly increased and the concentration of most of the metals were above WHO standards in post rainfall season. Increase in concentration of heavy metals especially, Cd, Zn, Fe, Cr, Cu, and Ni was the indication of deleterious effects on ground water quality originated from dumping sites. Hence it is deduced from the study that continuous disposal of all categories of solid waste in open dump sites could not only result in degradation of water quality but such a higher level of contamination could have damaging effects on human health and other organisms.

Key words: Leachate, Monsoon rain, Heavy metals, Open dumping sites, Water contamination.

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INTRODUCTION

The rapid socio-economic development has interrupted physical and ecological environment due to exponential increase in population and socio-economic activities, worldwide (Xie *et al.*, 2005; Nduka *et al.*, 2016). The imbalance of basic facilities in rural and urban towns, result in mass migration of population clusters towards major cities. The socio-economic activities resulting in establishment of industrial zones and generation of mammoth amount of industrial and domestic waste. The solid waste is commonly managed through recycling, landfill site development, open dumping and burning on landfill sites. Whereas, liquid waste is either treated for reuse by waste water treatment and disposal on agricultural or range land or discharged in water bodies or disposing off on or below the land surface through injection process. When an unknown and untreated disposal of industrial wastes takes place on open dumps or landfills or discharged in water bodies on hope of dilution or natural treatment phenomenon. Moreover, industrial effluents are normally discharged

into low lying areas, ponds, or municipal waste drains without any treatment hence pose a public health concern. Such solid and liquid waste disposals cause either groundwater contamination through seepage, or could lead to streams, rivers, and ultimately in nearby seas through runoff process (Shah, 2014). Samples of effluent collected from textile, dyeing, calendaring, steel industry, hospitals and clinical laboratories, foundries and tanneries in Punjab, Pakistan were found with excessive amount of soluble salts, i.e., nitrogen (N), phosphorous (P), potassium (K) and heavy metals, i.e., cadmium, chromium, cobalt, copper, iron, manganese, nickel, and zinc, to name a few (Murtaza *et al.*, 2010; Khan *et al.*, 2019). The infiltration of rainfall and intervening running water channels through dump-yards cause chemical mixing the waste products which produces leachate. Nevertheless, groundwater contamination over the years has already documented an extensive health risks to nearby population and environment where such practices are in vogue till filing this (Papadopoulou *et al.*, 2007; Maqbool *et al.*, 2011; Shah, 2014). Such waste disposal sites could result in leaching and mobility of

contaminants into water resources, which is categorized as one of major environmental problem in developing world (Castaneda *et al.*, 2012; Lawal *et al.*, 2013). The perception of people living in the vicinity of dumping sites is limited about hazardous effects of waste on human health and environment (Paoli *et al.*, 2012; Ali *et al.*, 2015).

Solid waste leachate has organic matter, trace elements and xenobiotic organic contaminants along with toxic, carcinogenic chemicals and infectious microbial contaminants (Matejczyk *et al.*, 2011). Water bodies contamination originating from disposed products (Oman and Junestedt, 2008a; Sultana *et al.*, 2018) including both industrial and household wastes through direct induction or dispersion of chemicals with municipal solid waste (Oman and Junestedt, 2008b).

The groundwater and surface water reservoirs most used by humans which are highly vulnerable to untreated water, leachate contamination, metal invasion, and other pollution (Gorde and Jadhav, 2013; Sener *et al.*, 2017; Tian *et al.*, 2016). The monitoring and periodical assessment of groundwater quality help to indicates seasonal variability in its composition and possible source of contamination. Water-rock interactions exist commonly in shallow depths of aquifer, which may be endangered by natural or anthropogenic activities especially due to tanneries and nickel plating industry (Naseem *et al.* 2018). The ground water quality become anomalous when untreated or ill-treated industrial waste has an access to the water resources. Hence, current study was designed to determine the effects of leachate on ground water in vicinity of dumping sites and any comparative evaluation of ground water quality by collecting pre-rain and post-rain samples.

In Pakistan, heavy metal pollution is contributed largely from industries such as tanneries, construction material units, automobiles industry alongside agricultural practices that uses metal laden fertilizers and are believed as main sources of heavy metal contamination (Khan *et al.*, 2020). The groundwater quality is examined for the presence of heavy metals due to their toxicity. The heavy metals neither biodegrade nor leave the environment and go through a global ecological phase (Ahmadipour *et al.* 2014). Some heavy metals, i.e., Copper (Cu), Zinc (Zn) and Nickel (Ni), play a vital role in bio-geochemical systems, while Cadmium (Cd) and Lead (Pb) are non-essential to biological system (Jamal *et al.*, 2013). Though, the heavy metals are constituent material of most sediments, rocks and earth's crust (Nowrouzi and Pourkhabbaz, 2014).

Although various studies worldwide have reported similar contaminations and their health effects on neighboring as well as distant populations due to underground accumulation or movement through underground water (Nasir *et al.*, 2012; Kouidri *et al.*, 2016); Khan *et al.*, 2020), few studies have been found in

research database regarding effects of monsoon rain pattern on movement of contaminants vertically underground or horizontally to nearby water supply in and around small and medium size industrial cities of Pakistan (Ullah *et al.*, 2008; Ali *et al.*, 2015). Such comparison becomes more imminent in and around Industrial cities of Pakistan, particularly in Punjab province, where large population has been involved in cottage industry related to leather and sports goods and electronic manufacturing, and are dumping waste in their neighborhoods in abundance, beside municipal solid waste disposal without treatment. Hence, current study was designed to determine the effects of leachate on ground water in vicinity of dumping sites in Central Punjab and to develop comparative evaluation of ground water quality by collecting pre-rain and post-rain samples.

MATERIAL AND METHODS

a. **Study Area and sampling sites:** The current study was conducted in Gujranwala, its surrounding towns, and Sialkot, both are industrialized cities of Pakistan besides their burgeoning population due to employment opportunities. A huge amount of waste is dumped from residential cottage industry and medium-sized industrial sources on dumping sites in Municipal territory and at landfill sites in the suburban areas without any treatment, surveillance or environmental monitoring. The ground water samples were collected from four different dumping sites located at Gujranwala Metropolitan Area (Site A and B coded as GA and GB) and Sialkot (Site A and B in residential and industrial zones of Sambrial, Sialkot Metropolitan Area coded as SA and SB) as shown in figure 1. **Sample collection:** The water samples were collected from 12 different locations (SA1, SA2, SA3, SB1, SB2, SB3, GA1, GA2, GA3, GB1, GB2, GB2 and GB 3) within 1km of dumpsites, in both industrial cities. The water samples from each site (about 1 liter) were collected pre-rain season, during dry months of winter and post-rain water samples from all sites after one-week of heavy winter rain in the study area. The samples were stored in a dark and cool place (4-5°C). The water samples about 500 mL were preserved in bottles at pH 2 by adding 2-3 drops of conc. HNO₃ (US EPA, 2009) for heavy metal analysis and remaining 500 ml sample from each bottle was used for analysis of other physico-chemical parameters.

b. **Physico-chemical Analysis of Water Samples:** The parameters including pH, TDS, EC, odour, colour, taste, turbidity, hardness, sulfates, nitrates, chlorides and phosphates were quantified by following standard methods for examination of water and wastewater (APHA, 2005). The amount of heavy metals (Cu, Cr, Ni, As, Zn, Pb, Co, Cd, Fe and Hg) in digested sample was

analyzed following the standard methods (APHA, 2005), using atomic absorption spectrophotometer (Perkin Elmer 2100). The reasonably good data density was subject to

basic statistical analysis through ANOVA by using SPSS (Version 19).

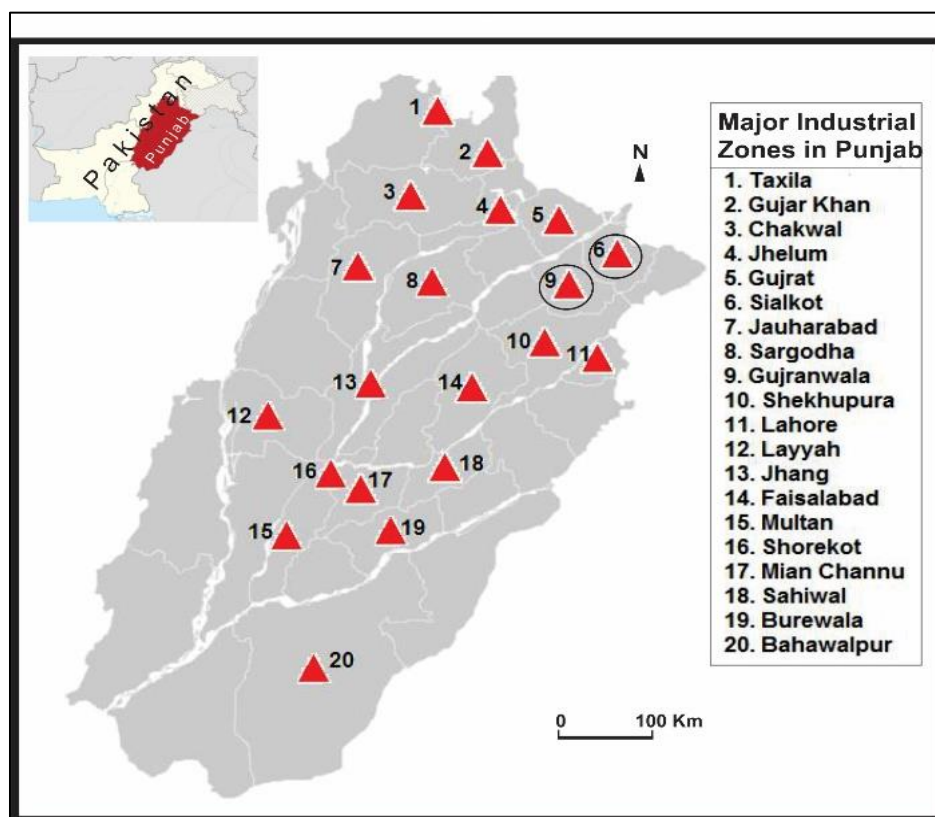


Figure-1. The base map depicting the major industrial zones of Punjab province, Pakistan. (The locations of open dumping sites in Industrial cities Sialkot and Gujranwala are encircled).

RESULTS AND DISCUSSIONS

a. Physico-chemical Analysis of Ground Water

pH: Quality of ground water is affected by *soil leachates* (Castaneda *et al.*, 2012). The color, odor, taste and turbidity was non objectionable and within the WHO/NEQS values (WHO, 2004; Pak EPA, 2008). The maximum pH value 8.61 ± 0.38 was recorded in the water sample SA3 collected from dumping site A of Sialkot while the minimum value 7.61 ± 0.38 was recorded in SB1 during pre-rain season but a decrease in pH value was observed during post-rain season and its maximum value was 8 ± 0.27 in SA1 and minimum value 7.3 ± 0.27 was found in SB1. The highest pH value in GB1 (8.71 ± 0.38) but lowest value in GB2 (8.36 ± 0.38) was found in the water sample collected from dumping site B of Gujranwala during pre-rain season but a decrease in pH value was observed during post-rain season and its highest value (8.43 ± 0.27) and minimum value (7.8 ± 0.27) was found in GA3 and GB3 respectively. It was also observed that the most of pre-rain samples had pH value

near to or higher than WHO/NEQS standard (WHO, 2004; Pak EPA, 2008) for pH of drinking water in both cities but the pH value of post-rain samples was less the stipulated value prescribed by WHO.

Total Dissolvable Solids (TDS): The TDS in pre-rain water samples of Sialkot was found in range (115 ± 5 – 385 ± 13 mg/L) and in the SA3 and SB1 respectively but a significant increase in TDS value was examined in water samples collected after the rain and the maximum TDS value 576 ± 15 mg/L and minimum value 142 ± 8 mg/L was observed in SB1 and SA1 respectively. The similar trend was observed in case electrical conductivity in which rain had increased its maximum value 770 ± 26 mg/L to 1152 ± 30 mg/L found both in SBI and minimum value 230 ± 10 mg/L in SA3 to 284 ± 16 mg/L in SA1 respectively. The maximum hardness of pre-rain water samples was 104 ± 4 mg/L in SB1 and minimum hardness 58 ± 6 mg/L was determined in SA3 while the post-rain samples had maximum hardness 118 ± 6 mg/L and minimum hardness 75 ± 6 mg/L in SB1 and SA1 respectively. The TDS in pre-rain water samples of Gujranwala was found between GB2 (501 ± 15 mg/L) and

GA3 (345 ± 11 mg/L) but variations in TDS was examined within GB2 (376 ± 7 mg/L) and GA3 (562 ± 30 mg/L) in water samples collected after the rain from Gujranwala. However, in case of electrical conductivity, rain had increased its maximum value (1002 ± 30 mg/L) to (1152 ± 60) mg/L found in GA3 and minimum value (690 ± 22) mg/L to (752 ± 14) mg/L in GB2 respectively.

Water Hardness: The maximum hardness of pre-rain water samples was (96 ± 8 mg/L) in GA3 and minimum hardness (79 ± 8 mg/L) was assessed in GA2 while the post-rain samples had maximum hardness (124 ± 7 mg/L) and minimum hardness (101 ± 8 mg/L) in GB2 and GA2 respectively ground water samples collected from Gujranwala. TDS, EC and hardness values were found to be within WHO/NEQS standards (WHO, 2004; Pak EPA, 2008). It was also observed that the nitrate, sulfates, chlorides and phosphates concentrations were comparatively higher in post-rain samples than pre-rain and found to be significantly different in each site and overall ground water samples collected from Gujranwala had higher nitrate, sulfates, chlorides and phosphates concentrations as compared to samples collected from Sialkot. Furthermore, nitrate, sulfates, chlorides and phosphates concentrations were found to be within WHO/NEQS permissible standards (WHO, 2004; Pak EPA, 2008).

b. Heavy Metals in Ground Water Samples

Chromium: The maximum concentration of chromium 0.2 ± 0.07 mg/L and minimum concentration 0.07 ± 0.2 mg/L was found in SA2 and SB3 respectively in ground water samples collected before rain from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest concentration 1.1 ± 0.05 mg/L and lowest 0.79 ± 0.1 mg/L of chromium in SA2 and SB2 respectively and its concentration was comparatively higher than pre-rain due values due to the run off and mobility from tannery areas soil to ground water (Figures 2 and 3). The highest concentration level of chromium in pre-rain samples collected from Gujranwala was 0.08 ± 0.5 mg/L assessed in GA1 and minimum level in Gujranwala was 0.01 ± 0.01 mg/L in GB3 while highest concentration 0.9 ± 0.2 of post-rain samples and lowest concentration 0.6 ± 0.02 mg/L was found in GB1 and GB3 respectively which was relatively higher than pre-rain samples (Figures 4 and 5). The chromium level in current study was found to be higher than examined by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Copper: The copper had highest concentration 2.8 ± 0.3 mg/L and lowest concentration 1.5 ± 0.2 mg/L in SA1 and SB3 respectively in ground water samples collected before rain from locality of dumping sites of Sialkot while highest copper concentration 3.9 ± 0.3 mg/L and lowest 2.7 ± 0.5 mg/L was present in SA1 and SB3

respectively in water samples collected after rain from Sialkot (Figures 2 and 3). The maximum concentration level of copper in pre-rain samples collected from Gujranwala was 2.9 ± 0.5 mg/L assessed in GA3 and minimum level in Gujranwala was 2.1 ± 0.01 mg/L in GA1 while highest concentration 4.1 ± 0.3 mg/L of post-rain samples and lowest concentration 3.5 ± 0.3 mg/L was observed in GA3 and GA2 respectively which was relatively higher than pre-rain samples (Figures 4 and 5). Copper concentration level in all ground water samples from both cities except SB3 pre-rain sample collected from "B" duping site of Sialkot was higher than the permissible limits of WHO/NEQS (WHO, 2004; Pak EPA, 2008). The over dose of copper can cause neurological complications, hypertension, liver and kidney dysfunction (Gowd and Govil, 2008; Rao *et al.*, 2001). The copper concentration in ground water samples of Sialkot was lower than the Gujranwala and its value were significantly different in each site. The copper level in current study was found to be higher than examined by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Nickle: The samples collected before rain had nickel had highest concentration 0.7 ± 0.4 mg/L and lowest concentration 0.01 ± 0.007 mg/L in SB1 and SA2 respectively in ground water samples collected from dumping sites of Sialkot while highest nickel concentration 1.6 ± 0.5 mg/L and lowest 0.51 ± 0.03 mg/L was present in SB1 and SA2 respectively in water samples collected after rain from Sialkot (Figures 2 and 3). The highest concentration level of nickel in pre-rain samples collected from Gujranwala was 0.58 ± 0.01 mg/L assessed in GB3 and minimum level in Gujranwala was 0.51 ± 0.03 mg/L in GA2 while highest concentration 0.94 ± 0.6 mg/L of post-rain samples and lowest concentration 0.6 ± 0.01 mg/L was observed in GB1 and GA1 respectively which was relatively higher than pre-rain samples (Figures 4 and 5). The nickel concentration level in all ground water samples from both cities was higher than the stipulated values of WHO/NEQS (WHO, 2004; Pak EPA, 2008). Nickel is considered as one of the most mobile of the heavy metals when released to water, mainly in polluted waters having organic material will keep nickel soluble (Khan, 2011). The nickel concentration in ground water samples of Sialkot was higher than the Gujranwala and its value were significantly different in each site. The primary source of nickel in drinking-water is the leaching of metals in water network (WHO, 2005). Nickel is recognized to affect non-occupationally exposed individuals (Boustani *et al.*, 2012).

The toxicity and carcinogenicity of some nickel compounds in experimental animals, as well as in the occupationally exposed people, are well documented and reported (Cempel and Nikel, 2006). The nickel level in

current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Zinc: The maximum concentration 2.22 ± 0.09 mg/L of zinc and minimum concentration 1.21 ± 0.05 mg/L of zinc was observed in SA1 and SB3 respectively in ground water samples collected in dry season from dumping sites of Sialkot while highest zinc concentration 4.3 ± 0.8 mg/L and lowest 2.57 ± 0.2 mg/L was analyzed in SA1 and SB3 respectively in water samples collected after rain from Sialkot (Figures 2 and 3). The pre-rain ground water samples had maximum concentration level 2.23 ± 0.2 mg/L of zinc in GA3 and minimum level in Gujranwala was 1.01 ± 0.5 mg/L in GA2 while highest concentration 3.17 ± 0.3 mg/L of post-rain samples and lowest concentration 2 ± 0.3 mg/L was assessed in GA1 and GB3 respectively which was relatively higher than pre-rain sample (Figures 4 and 5). The zinc concentration level in all pre-rain and few post-rain ground water samples from both cities was within the WHO/NEQS limits (WHO, 2004; Pak EPA, 2008) while most of post-rain samples had zinc concentration higher than or near to the stipulated values of WHO/NEQS. The zinc level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Cobalt: The highest cobalt level 0.9 ± 0.5 mg/L and lowest cobalt level 0.07 ± 0.1 mg/L was found in SB1 and SA3 respectively in ground water samples collected in dry season from dumping sites of Sialkot while highest cobalt level 1.2 ± 0.5 mg/L and lowest 0.11 ± 0.007 mg/L was analyzed in SB3 and SA3 respectively in water samples collected after rain from Sialkot (Figures 2 and 3).

The ground water samples had maximum cobalt level 1 ± 0.1 mg/L and minimum level 0.5 ± 0.1 mg/L in pre-rain GB2 and GA3 respectively in Gujranwala but highest concentration 1.13 ± 0.04 mg/L of post-rain samples and lowest concentration 1.03 ± 0.3 mg/L was assessed in GA1 and GB3 respectively which was relatively higher than pre-rain samples (Figures 4 and 5). WHO/NEQS limits for cobalt are not available. Furthermore, cobalt concentration in ground water samples of Sialkot was comparatively lower than the Gujranwala and its values were significantly different in each site. The cobalt level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Cadmium: The maximum concentration of cadmium 0.47 ± 0.04 mg/L and minimum concentration 0.28 ± 0.2 mg/L was found in SB3 and SA3 respectively in ground

water samples collected before rain from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest concentration 0.57 ± 0.05 mg/L and lowest 0.49 ± 0.04 mg/L of cadmium in SA2 and SA3 respectively and its concentration was comparatively higher than pre-rain due values due to the run off and mobility from dumping sites to ground water (Figures 2 and 3). The highest concentration level of cadmium in pre-rain samples collected from Gujranwala was 0.4 ± 0.02 mg/L assessed in GB1 and minimum level in Gujranwala was 0.02 ± 0.02 mg/L in GA2 while highest concentration 0.5 ± 0.05 mg/L of post-rain samples and lowest concentration 0.3 ± 0.03 mg/L was found in GA1 and GB3 respectively which was relatively higher than pre-rain samples (Figures 4 and 5). The cadmium concentration in all ground water samples from both cities was higher than or the stipulated values of WHO/NEQS (WHO, 2004; Pak EPA, 2008). The major target organs for cadmium are the kidney and liver where it accumulates in high concentrations which lead to chronic kidney dysfunction (Taiwo 2010). The cadmium level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Iron (Fe): The highest concentration 0.8 ± 0.4 mg/L and lowest concentration 0.1 ± 0.05 mg/L of iron was examined in SB1 and SA1 respectively in ground water samples collected before rain from locality of dumping sites of Sialkot while highest iron concentration 2.4 ± 0.4 mg/L and lowest 1.12 ± 0.1 mg/L was found to be in SB1 and SA1 respectively in water samples collected after rain from Sialkot (Figures 2 and 3). The maximum concentration level of iron in pre-rain samples collected from Gujranwala was 1.03 ± 0.5 mg/L assessed in GA3 and minimum level in Gujranwala was 0.11 ± 0.4 mg/L in GB3 while highest concentration 2.29 ± 0.6 mg/L of post-rain samples and lowest concentration 1.11 ± 0.6 mg/L was observed in GA3 and GA2 respectively which was relatively higher than pre-rain samples (Figures 4 and 5).

The iron concentration level in most of the ground water samples collected from both cities was found to be higher than permissible limits of WHO/NEQS (WHO, 2004; Pak EPA, 2008) except few pre-rain ground water samples from "A" dumping site of Sialkot was within the WHO/NEQS limits (WHO, 2004; Pak EPA, 2008) and its value were significantly different in each site. The level of iron may enhance the level of iron in blood which can damage the cells of the gastrointestinal tract, preventing them from regulating iron absorption (El-Harbawi *et al.*, 2010). The iron levels play a major role in producing atherosclerosis through interaction of iron and cholesterol in promoting oxidative damage, causing both atherosclerosis and neuro degeneration and disorders (Sullivan, 2007; Perez *et al.*, 2010). Ong and Halliwell, (2004) reported the

involvement of iron in Alzheimer's disease. The iron level in current study was found to be high as compared to previously reported by Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

Lead: The lead concentration in all samples in both cities was within WHO/NEQS standards (WHO, 2004; Pak EPA, 2008). The presence of high concentration of heavy metals like Cd, Zn, Fe, Cr, Cu and Ni was the indication of deleterious effects on ground water quality by dumping sites.

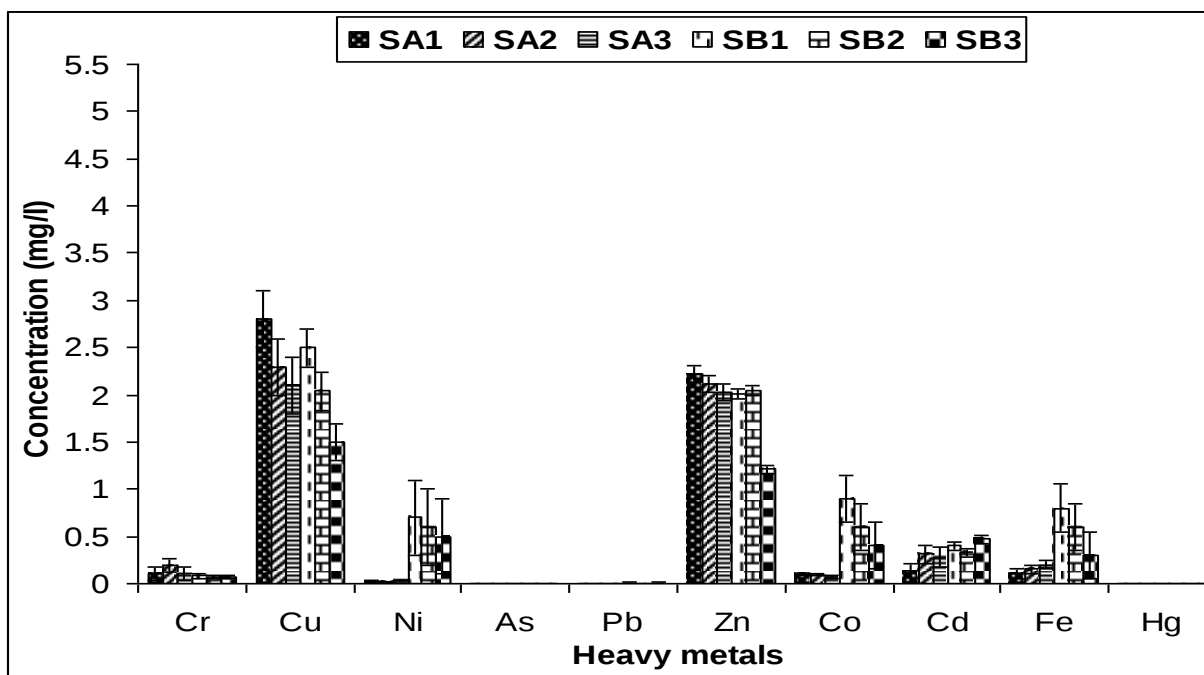


Figure 2. Heavy metals in pre-rain ground water samples collected from Sialkot Industrial Zone.

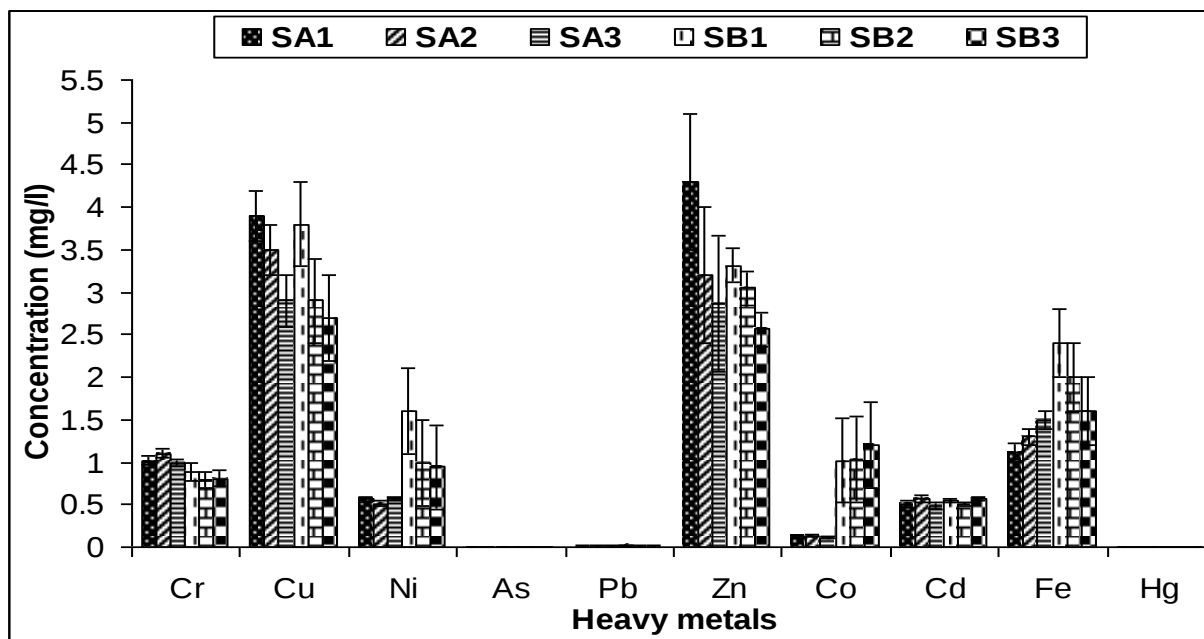


Figure-3. Heavy metals in post-rain ground water samples collected from Sialkot Industrial Zone.

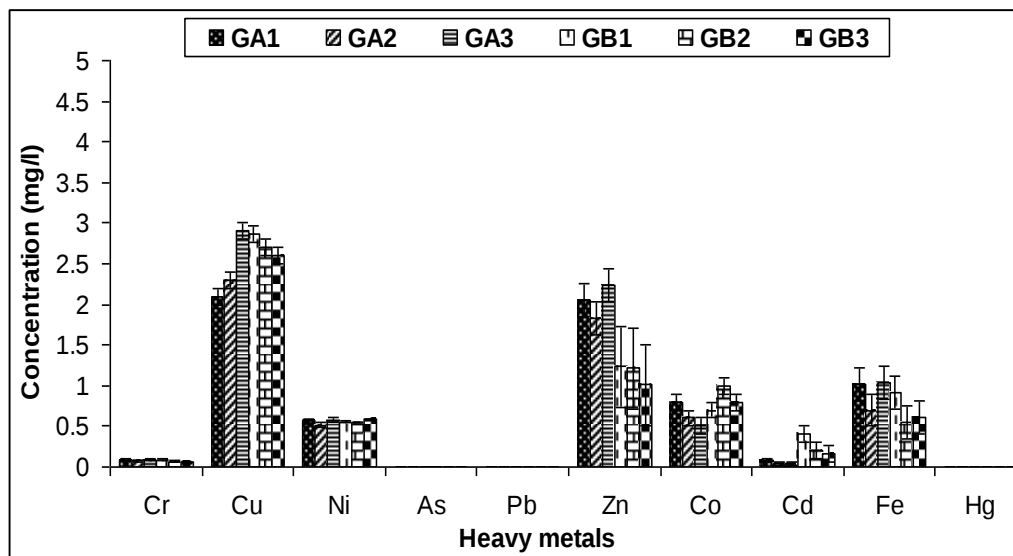


Figure-4. Heavy metals in pre-rain ground water samples collected from Gujranwala Industrial Zone.

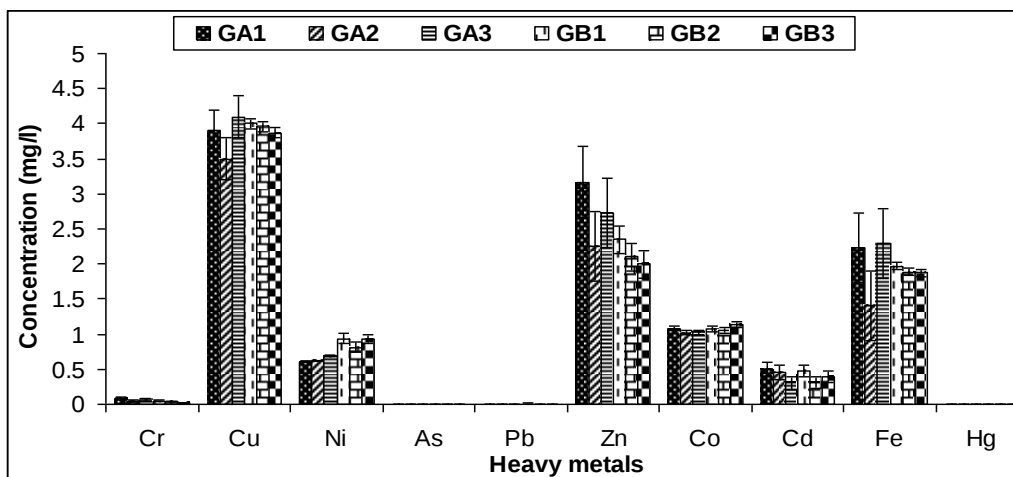


Figure 5. Heavy metals in post-rain ground water samples collected from Gujranwala Industrial Zone.

Therefore, results of study deduced that continuous disposal of all categories of solid waste in open dump sites could result in degradation of quality of the groundwater and envioning subsurface. The people living in that area are at risk of toxic effects of heavy metals on their organ system due to accumulation of metals. Water samples collected from both cities were not fit for drinking due to high contamination level of heavy metals. An efficient water purification system is recommended to avoid hazards due to higher level contamination on human and other organisms. Moreover, soils in receipt of released leachates could also become potential source of contaminants entry into crops and the human food web. The groundwater quality assessment is essential to ensure sustainability in the environment. Furthermore, it is suggested that shallow geophysical investigations can be employed to industrial and

household dumpsites to study penetration of leachate and burial impacts on aquifer contamination in and around industrialized urban and sub-urban areas in developing economies to chalk out mitigation strategies for preserving human and environmental health.

Conclusion: The rain had significantly increased the concentration of most of the parameter tested for water quality. The presence of high concentration of heavy metals like Cd, Zn, Fe, Cr, Cu, Ni was the indication of deleterious effects on ground water quality by dumping sites.

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