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RISK ASSESSMENT AND ESTIMATION OF HEAVY METALS IN ROCK SAMPLES OF LAKI FORMATION, LOWER INDUS BASIN-PAKISTAN

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Abstract

In the present study, chromium (Cr), lead (Pb), nickel (Ni), copper (Cu), cadmium (Cd), and zinc (Zn) have been estimated from the Laki formation in the lower Indus basin of Pakistan using Atomic Absorption Spectrophotometer. Eight different rock samples were collected from drill holes of wells with different depths to estimate heavy metals like Cr, Cu, Cd, Pb, Ni, and Zn. These metal concentrations ranged from 0.560 ppm to 2.235, 0.030 ppm to 0.365 ppm, 0.020 ppm to 0.060 ppm, 0.01 ppm to 0.70, 1.400 ppm to 2.810 ppm, 0.2530 ppm to 0.4055 ppm, respectively. These samples are a health risk for lead, cadmium, nickel, and chromium but not for zinc and copper. This study indicates that drilling, grinding or destroying these rocks is a health risk associated with the labour and the local community.

1. Introduction

Heavy metals consist of elements lighter than carbon and apply to most cases. Heavy metals include transitional metals like zinc, lead, and copper (Mil-Homens *et al*, 2006). Too many metals harm the ecosystem, such as the lead in gasoline, industrial waste, and acid rain's ability to leach metal ions from the soil into bodies of water. Waste-derived fuels are especially prone to contain heavy metals (Duffus, 2002). Significant sources of toxic metals are wastewater and the associated garbage. The USEPA pinpoints that 81% of the metals come from various regulated industries, and about 19% come from consumer households (U.S. Environmental Protection Agency, 1986). The two essential by-products of municipal treatment units are 70.00% to 90.00% of cadmium, lead, chromium, copper, and zinc are separated as solid wastes (Briggs & Ficke, 1977). Heavy metals like cadmium, lead, and mercury are highly toxic, even in very low concentrations. These deposits in body tissues for lengthy periods may harm human health (Jennett *et al*, 1973). The order of harmfulness of heavy metals for humans trails the order Co < Al < Cr < Pb < Ni < Zn < Cu < Cd < Hg (Mansourri & Madani, 2016). The amount of dose, emission rate, and exposure time all affect how dangerous heavy metals are to humans. Mercury, lead, and cadmium are heavy metals that have recently attracting greater attention (Valavanidis & Vlachogianni, 2010). Aerosols and dust particles can be inhaled to expose one to lead, as can lead-tainted food and drink. Human bones, heart, liver, kidneys, brain, and nervous system are all affected by lead poisoning (Flora *et al*, 2006). Initial poisoning from lead exposure is linked with memory loss, headache, dullness, and being petulant (Harvey, 2002). Lead poisoning may lead to anaemia and haemoglobin disruption (Järup, 2003). The WHO mentioned harmless limits of Pb in wastewater and soils used for cultivation are 0.01 and 0.1 ppm, respectively (Chiroma *et al*, 2014; Ayeni, 2014). Prolonged noxiousness of Cd in children comprises harm to pulmonary, skeletal, and digestive systems and the growth of malignancies of the kidneys, prostate, and heart (Lim *et al*, 2010; WHO, 2011). Smoking cigarettes, consuming contaminated food, being exposed to it at work, and working in primary metal industries are all ways that people get exposed to cadmium (Paschal, *et al*, 2000). The WHO permitted the safe limit of Cd in wastewater and soils for cultivation purposes is 0.003 ppm (Aneyo *et al*, 2016). Chromium is extensively consumed in papers, pulp, pigments, preservatives, paints, metallurgy, and electroplating (Jaishankar *et al*, 2014). The chromium enters the environment through fertilizers and sewage (Ghani & Ghani, 2011). The WHO recommends a safe level of 0.003 ppm of Cd in agricultural soils and wastewater (Wolińska *et al*, 2013). Nickel is a white silvery metal used to make alloys like steel, electronic items, coins, and other uses (Davis, 2000). Humans are exposed to Ni via atmosphere, diet, or water (Duda-Chodak & Blaszczyk 2008). Inhalation was an easy way of exposure to Ni concerning health hazards. However, the gastrointestinal route was less important due to its restricted gastric absorption. The toxicity of some nickel compounds in the pulmonary system in experimental animals and the occupationally exposed population was well documented (Cempel & Nikel, 2006). On disclosure to Ni, levels of Ni-poisoning in the body tissues enhanced and even in urine. The harmful impacts of Ni on human health may comprise allergy, skin issues, and organ cancer (Seilkop & Oller, 2003). The permissible range for Ni in wastewater and cultivated lands are 0.02 and 0.05 ppm, respectively, recommended by WHO (Chiroma *et al,* 2014; Ayeni, 2014). Although copper is a necessary component of human life, excessive amounts can harm health. Acute copper poisoning can result in short-term gastrointestinal distress with symptoms like nausea, vomiting, and abdominal pain. It was observed that liver poisoning could occur at high doses enough to cause mortality. Young teenagers' intelligence declines after prolonged exposure to high copper concentrations (Jaishankar *et al,* 2014). Zinc may pollute water due to a higher concentration of zinc in the used water of industrial plants. Such used water is not accurately purified—consequently, zinc-polluted sludge accumulates on the banks of rivers. Zinc may enhance the acidity of water. Zinc can deposit in the bodies of fish residing in contaminated water bodies. As zinc enters the bodies of these fish, it can travel up in the food chain. Abdominal pain, nausea, and vomiting are the initial signs of zinc poisoning. Additionally, tiredness, anaemia, and lightheadedness can occur (Porea *et al,* 2000). Living organisms require various concentrations of heavy metals. Humans require iron, copper, manganese, molybdenum, cobalt, and zinc. In higher concentrations, these metals can be harmful. Other heavy metals, including lead, are toxic without known stimulating effects on organisms. Its accumulation with time in the bodies of organisms can cause serious health risks. Certain elements, even cadmium, are usually poisonous and are helpful for certain microorganisms or under specific conditions (Davis *et al,* 2003). This research work aims to estimate the concentration of different heavy metals (Cr, Ni, Cu, Pb, Cd, and Zn) at varying depths of the gas well of the Laki formation, Lower Indus Basin, Pakistan. The rock samples were collected from the gas well. The quantitative analysis exhibits the concentration of other heavy metals in rock samples and associated health risks. The study successfully builds a compelling case by connecting the prevalence of heavy metals to their potential impact on human health.

2. Experimental Work

2.1 Geology of the Study Area

Kirthar basin exhibits largely the same lithological units as the Sulaiman basin during the Mesozoic and Quaternary but varies in Tertiary strata. Malkani (2012) reported the revised stratigraphy of the Sulaiman basin. Kirthar. i.e., the Lower Indus Basin and Sulaiman Basin have the same lithology during the Mesozoic and Quaternary. However, they differ in Tertiary strata, such as; the Paleocene Ranikot Group exhibits Khadro and Lakhra formations. Early Eocene Laki Group exhibits Sohnari and Laki formations, and the Late Eocene Kirthar Group shows Kirthar and Gorag formations; the Oligocene Gaj Group represents Gaj formations and the Miocene-Pliocene Vihowa Group (Manchar group) that are wrapped in the valleys and plains by the eolian, colluvial, Subrecent and Recent fluvial deposits (Malkani, 2012). The Laki Formation was named by Cheema *et al*. (1977) and derived from the Laki Series of Noetling (1903). It is now being divided into two members. The lower Chat limestone member (including basal dominant limestone unit of Chat member of Nagappa 1959) consists of the main limestone with minor shale intercalations. The upper Meting shale member (following Meting shale named after Meting village 30 km SW of Kotri by Nuttal 1925, and Meting shale member of Brouwers and Fatmi (1993) consists of terrestrial or estuarine reddish-brown lateritic clays, gypseous shales, reddish-brown soft sandy limestone, sandy claystone, and calcareous sandstone (Shah, 1977). The physical parameters of the samples used in this study are given in the Table 1. These samples depth ranges from 310 to 625 m. Geology shows that all the samples are from the Laki formation, and lithology shows that these are intercalated, which means 20-40% shale in their structure. These samples' Total Organic Carbon (TOC) ranges from 0.24% to 5.22%. The highest TOC is observed in the 7^{th} sample, while the lowest TOC is observed in the 3^{rd} sample. The Table 1 also also gives information on the number of free hydrocarbons (gas and oil) in the sample.

Table 1. Physical parameters of rock samples.

Sr. No.	Depth (m)	Formation	Lithology	Total Organic Carbon (%)
1	310-15	Laki	Intercalation of shale	0.54%
2	330-35	Laki	Intercalation of shale	0.5%
3	350-55	Laki	Intercalation of shale	0.24%
4	370-75	Laki	Intercalation of shale	0.52%
5	390-95	Laki	Intercalation of shale	0.34%
6	580-85	Laki	Intercalation of shale	1.26%
7	600-05	Laki	Intercalation of shale	5.22%
8	620-25	Laki	Intercalation of shale	0.76%

2.2 Chemicals

Experiment chemicals are Nitric acid (HNO_3), 98%, and Hydrochloric acid (HCl), 99%.

2.3 Preparation of Samples

First, rock samples were crushed to a fine powder using a pestle and mortar and then taken into the crucible. The rock samples were in the furnace at 700 °C for 5-6 hours. Putting rock samples in a furnace is to completely burn and remove all organic matter from rock samples. After this, rock samples were taken in a china dish. These samples were oven-dried overnight at 60-70 ºC. The rock samples were dried in an oven to remove moisture. 2 grams of each sample were taken, digested in 20 ml Aqua Regia (15mL HCl+ 5 mL HNO3), and placed on a hot plate till dry to get maximum digestion. After digestion, the samples were diluted 10 times with a 10% HCl Solution. The solution was filtered in pre-weighed filter paper to separate all impurities.

2.4 Preparation of stock solution and working standards

Thus, stock solution of all metals prepared. From standard solution, dilutions of 1 ppm, 2 ppm, 4 ppm and 8 ppm prepared.

2.5 Analysis of samples

Firstly, we ran the standard solution of each heavy metal like Cr, Cu, Ni, Pb, Cd, and Zn through Atomic Absorption Spectrometer. Then, we ran the differently prepared samples to determine the heavy metals and in our samples.

3. Results & Discussion

The concentration of Pb (0.01-0.70 ppm), Cu (0.030-0.365 ppm), Cd (0.020-0.060 ppm), Cr (0.560-2.235 ppm), Zn (0.2530-0.4055 ppm), and Ni (1.400-2.810 ppm). As shown in Figure 1, sample C2 has the highest lead concentration. i.e., 0.7ppm and C3 has the lowest concentration of lead. WHO safe limit of lead in soil is 0.1 ppm. Three out of Eight samples. i.e., C3, C4, and C5 contain a permissible lead concentration. Five other samples have concentrations of lead above the WHO limit. These samples and dust created from them can cause serious health risks.

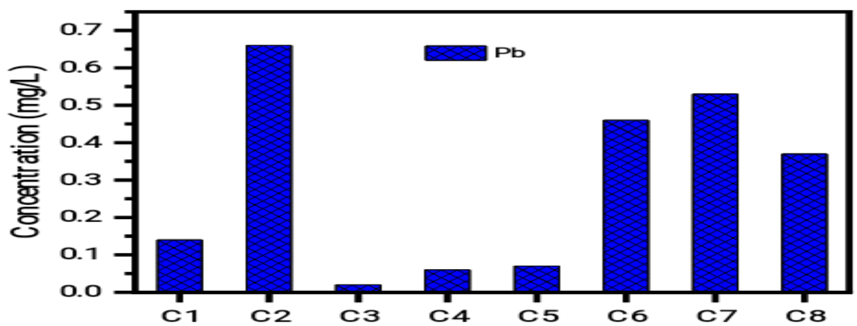

Figure 1: pb concentration in rock sample

It is evident from Figure 2 that Sample C8 shows the lowest concentration of copper, and C2 shows the highest concentration. The highest concentration limit of copper is 50 ppm. All samples are within the limit. Therefore, none of these samples is a health risk concerning copper.

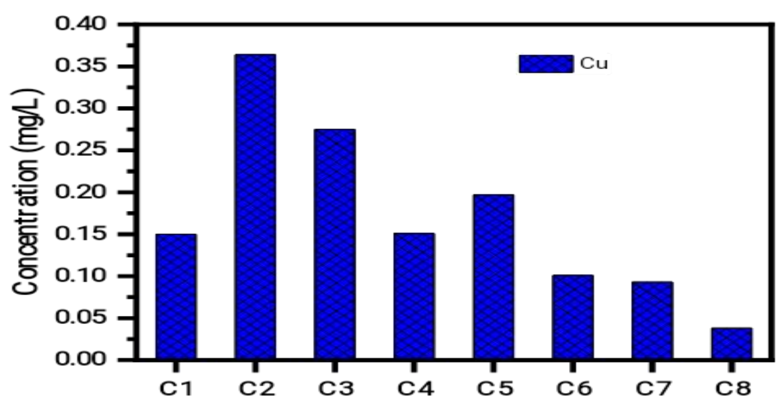

Figure 2: Cu concentration in rock samples.

Figure 3 shows the highest cadmium concentration in sample C8 and the lowest in C1, while the WHO safe limit for cadmium is 0.003 ppm. All samples contain Cd above 0.2 ppm, which may cause serious health issues to the community living in these areas.

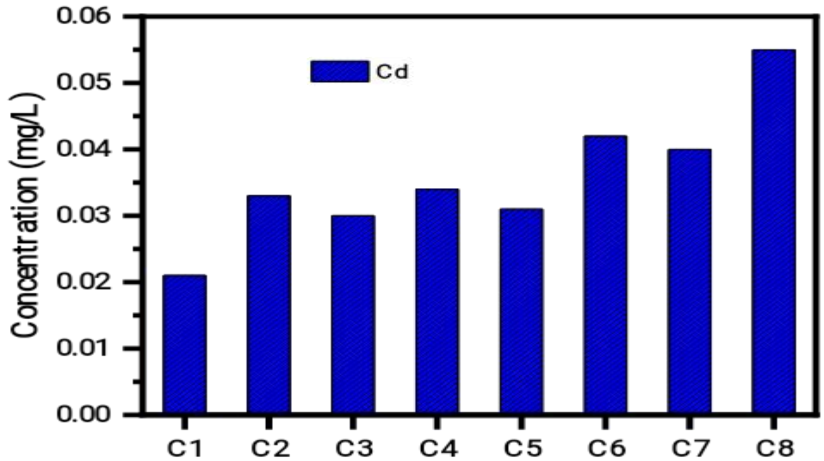

Figure 3: Cd concentration in rock samples

The highest chromium concentration is found in the C5 sample, and the lowest is found in the C3 sample (Figure 4). The permissible limit for Cr is 0.1 ppm, as directed by WHO. All samples have chromium above this limit. These samples are a serious health risk for human health.

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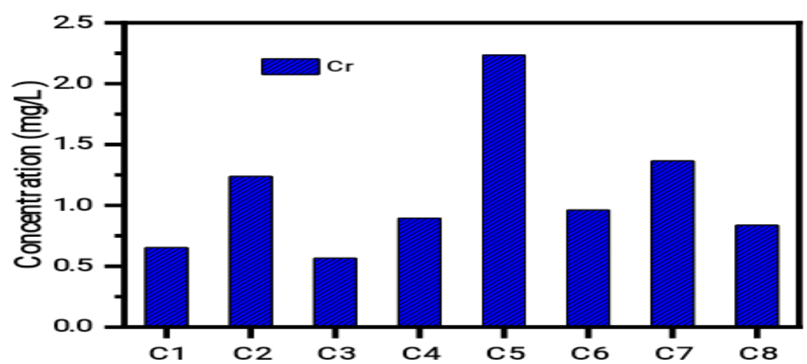

Figure 4: Cr concentration in rock sample

The zinc concentration in all samples falls within 0.25-0.405 ppm, Figure 5. The lowest is C3 and the highest is C8 (WHO safe limit for zinc is 10 ppm). None of these samples crosses this limit. Therefore, all samples are within the safe limit of zinc concentration (Figure 5).

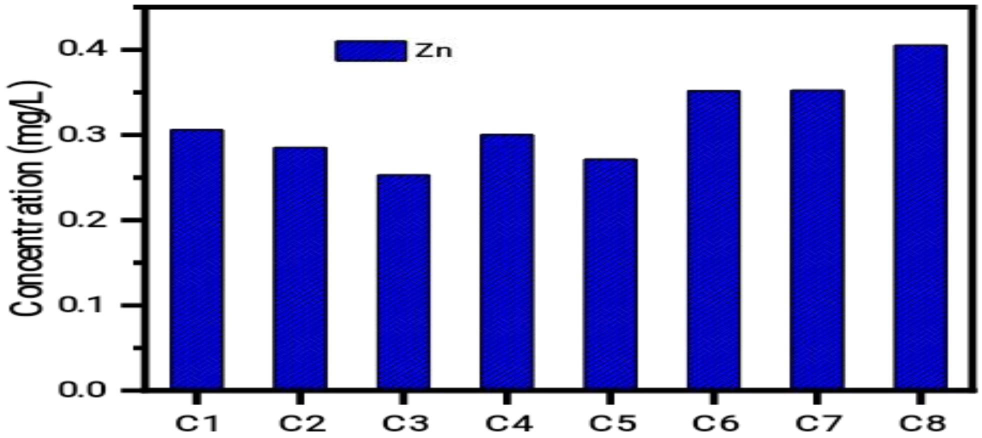

Figure 5: Zn concentration in rock samples

Nickel is as lowest as undetectable in six samples except for C1 and C3 (Figure 6). Nickel is safe for human health but not above 0.05 ppm. Two samples fall above this range. These samples will pose health risks associated with the nickel.

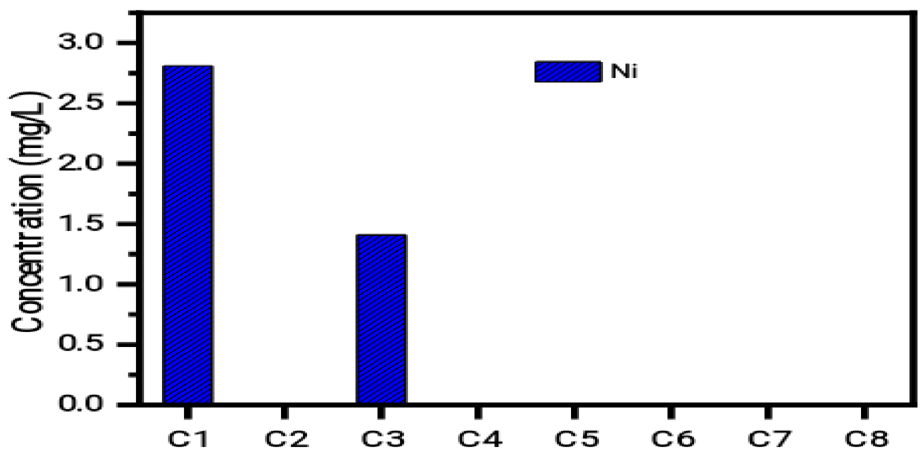

Figure 6: Ni concentration in rock samples

These elements in human and natural environments play an important role in different biological processes. It has become clear that the concentration of these metals is prevalent worldwide and may even have such importance, harming almost one billion people. Remarkable initiatives have occurred during the last thirty years in understanding the clinical effects of these metal deficiencies and their role in physiology, biochemistry, and many other fields. Metals, i.e., Cr, Pb, Ni, Cu, and Cd, greatly impact humans and their habitat. Their deficiency and excess amount cause serious effects on human health and the environment. The outcome provides valuable insights into the potential health risks associated with the studied metal concentrations and their implications.

4. Conclusions

Finally, this research estimated the amount of Pb, Cu, Cr, Cd, Zn, and Ni in different Rock samples of Laki formation, Lower Indus Basin, Pakistan. Most of these metals are essential constituents of the human body. The heavy metals' concentration in different Laki areas varied from 0.010-0.70 ppm. Based on the concentration of these heavy metals in this study in the samples, a comparison was drawn with World Health Organization (WHO) recommended safe limits for human health. Out of these six metals, three are seriously threatening human health. These are Lead, Cadmium, Chromium, and Nickel. However, Copper and Zinc are within WHO limits. Therefore, no health risk to humans arises due to these metals. It was drawn that there is a health risk while drilling, cutting, grinding, or locating these samples of Laki formation.

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