Analysis and Distribution of Lead, Cadmium, Molybdenum and Aluminum Contamination in Surface Waters around the Copper Mine

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Abstract

The objective of this study is to investigate distribution patterns of Lead (Pb), Aluminum (Al), Molybdenum (Mo), and Cadmium (Cd) along the Shoor River and determine sources and the degree of pollution in wet and dry seasons. Metal concentrations in water samples were extracted by cloud point extraction method and determined by flame atomic absorption spectroscopy. Based on the results, the highest concentration was found on the dam (Mo: 2.5, Al: 0.90, Cd: 1.00 and Pb: 0.77 mg/L) and before dam (Mo: 1.10, Al: 0.78, Cd: 0.82 and Pb: 0.8 mg/L), subsequently. But metal concentration significantly decreased in the water after the dam (Mo: 1.00, Al: 0.77, Cd: 0.35, and Pb: 0.42 mg/L). According to the results, cadmium and lead in the copper mine were maximum and will diminish by keeping distance from the mine. Mean comparison of all water samples in both wet and dry seasons showed a significant difference ($p<0.05$) between Lead and Molybdenum concentration in two seasons, but there was no difference between the Aluminum content and Cadmium in dry and wet seasons. Metal concentration, was enhanced by decreases in pH Comparison the concentration of heavy metal with WHO' standards indicates that Molybdenum (1.10mg/L), and Cadmium (0.52mg/L) concentration is higher than standards.

Keywords: copper mine, heavy metals, river contamination, surface water

1. Introduction

Water resources are the main component of earth and play an important role in both human and animal health. Protecting these resources is inspired in most countries. Some heavy metals such as Fe, Zn, Ca, and Mg have been considered essential metals and have a known biological function in the body, but others like Cd, Pb, and Hg are considered non-essential. Both essential and non-essential metals are toxic when dosed above a critical level [6]. Since heavy metals cannot be degraded, contamination of aquatic systems by them can be critical because of their persistence in the environment [17]. Metals are constantly come into the environment by volcanoes, rocks and also by multiple anthropogenic activities, such as using of fuels, mining, industrial and agronomical activities. The river near mines is an important sink for heavy metal pollution. Metals enter river water from mining areas in different ways [13]. Contaminants generally enter the rivers, and then they enter in the food chain and accumulate in the different organs of plants, animals, and humans progressively [3]. By entrance of metal pollutants into a river (naturally or anthropogenic), they can be dissolved or precipitated [4].

Depending on physicochemical conditions, the dissolved pollutants may be precipitated [15]. Due to the problems mentioned, much research has intensified on measurement of water pollution in different parts of the world [7, 9, 10, 19]. There were a lot of reports about river contamination in Iran. For example, the sediments from the Haraz River (north of Iran) and its delta are rather polluted with Cd, As, Sr, and Pb [11]. Urban, industrial, and domestic sewage in the Shiraz urban area increased heavy metal concentrations in the water and sediment of Khoshk River [15].

Contamination of heavy metals in domestic water is a danger to human health [1]. Heavy metal cytotoxicity is created by the generation of reactive free radicals. They can oxidize sulfhydryl groups of proteins, lipid peroxidation, DNA damage, and many other effects [5, 8]. Heavy metal contamination in the soil polluted by Sarcheshmeh Copper Mine has been reported previously [14]. Because of the importance of these rivers as a source of human consumption and agriculture and few studies on the heavy metal contamination in them, this study tries to investigate the distribution patterns of water heavy metals along river and determines the degree of ecosystem pollution in wet and dry seasons.

2. Materials and Methods

2.1 The Study Area

Sarcheshmeh copper mine is located at 29° 58 N, 53° 55' E, 160 km southwest of Kerman city. This deposit is the fourth-largest copper mine in the world and is estimated to contain 1 billion tons of copper and much less for Mo[16]. Shoor River (around 35 Km) is the main recipient of industrial and mineral waste of the Sarcheshmeh copper complex. It ends in the sedimentary dam about 18 km north of the mine site (Fig.1). Overflow dam is one of the main agents of water pollution. Furthermore, there are several headwaters around the mine that supply river water.

2.2 Water Sampling

A total of 66 water samples were collected in two seasons. Water samples were collected in late April and early May in wet season and late September to early October in dry season. Sampling along the way was carried out by half-liter bottles on the sides' river and in the middle of the river. Twenty-five water samples every 3 Km were collected along the river in each season. Ten water samples were collected far from the study area as a control.

2.3 Apparatus and Materials

Material: Nitric acid (Merck), hydrochloric acid (Merck), distilled water, TAN (1-(2-triazo)-2-naphthol) (Merck), methanol (Merck), Millipore filters paper at a size of 0.45 µm, blue band filter paper

Apparatus: Atomic absorption spectroscopy equipped with a graphite furnace (Varian Spectra 220 GTA), thermostatic bath (Bain Marie), centrifuge, Milli-Q® system.

2.4 Analytical Method

Water samples were analyzed to calculate the concentration and distribution of heavy metals. Metal concentrations in water samples were determined after extracting by the cloud point extraction method [2]. Analysis was done by atomic absorption spectrometry equipped with a graphite furnace (GFAAS). The pH and EC were measured by a calibrated pH and EC meter. It should be noted that in the current research, the maximum level allowed for these metals is too high for normal graphite furnace measurement. Therefore, samples would require dilution before measurement. Considering this matter, the values found for the analytical characteristics are presented in Table 1. In addition, the accuracy and recovery of the proposed method were assessed by analyzing water samples taken far away from the mining area as control samples for all metals. Recoveries were changed between 90 to 110% for determining heavy metals.

2.5 Mapping of Dispersion Water Pollution

In this paper, the GIS software *ILWIS* 2.1 was used to analyze and create groundwater pollution-sensitive zone map. Kriging method and Spherical model were used for estimating residential exposure to pollution. Green color represents a good quality or low pollution, yellow-reddish color indicates an intermediate state and red has been selected for areas where water quality is undesirable and highly polluted.

2.6 Statistical Analysis

The normal distribution tests were carried out using SPSS software version 18, by Duncan multiple range tests, t-test, and one-sample t-test.

3. Results and Discussion

Shoor is a seasonal river that provides water for agricultural and industrial use. Table 2 shows the mean concentrations of Pb, Al, Mo and Cd in

Table 1: Analytical characteristics of the water samples determination by GFAAS

Analytical characteristics	Heavy metals			
	Mo	Al	Cd	Pb
Worked concentration range (µg /L)	1.58-29.82	4.05-13.91	0.45-9.98	2.43-29.89
Limit of detection (µg /L)	0.21	0.28	0.16	0.52
Limit of quantification (µg /L)	0.70	0.93	0.53	1.73

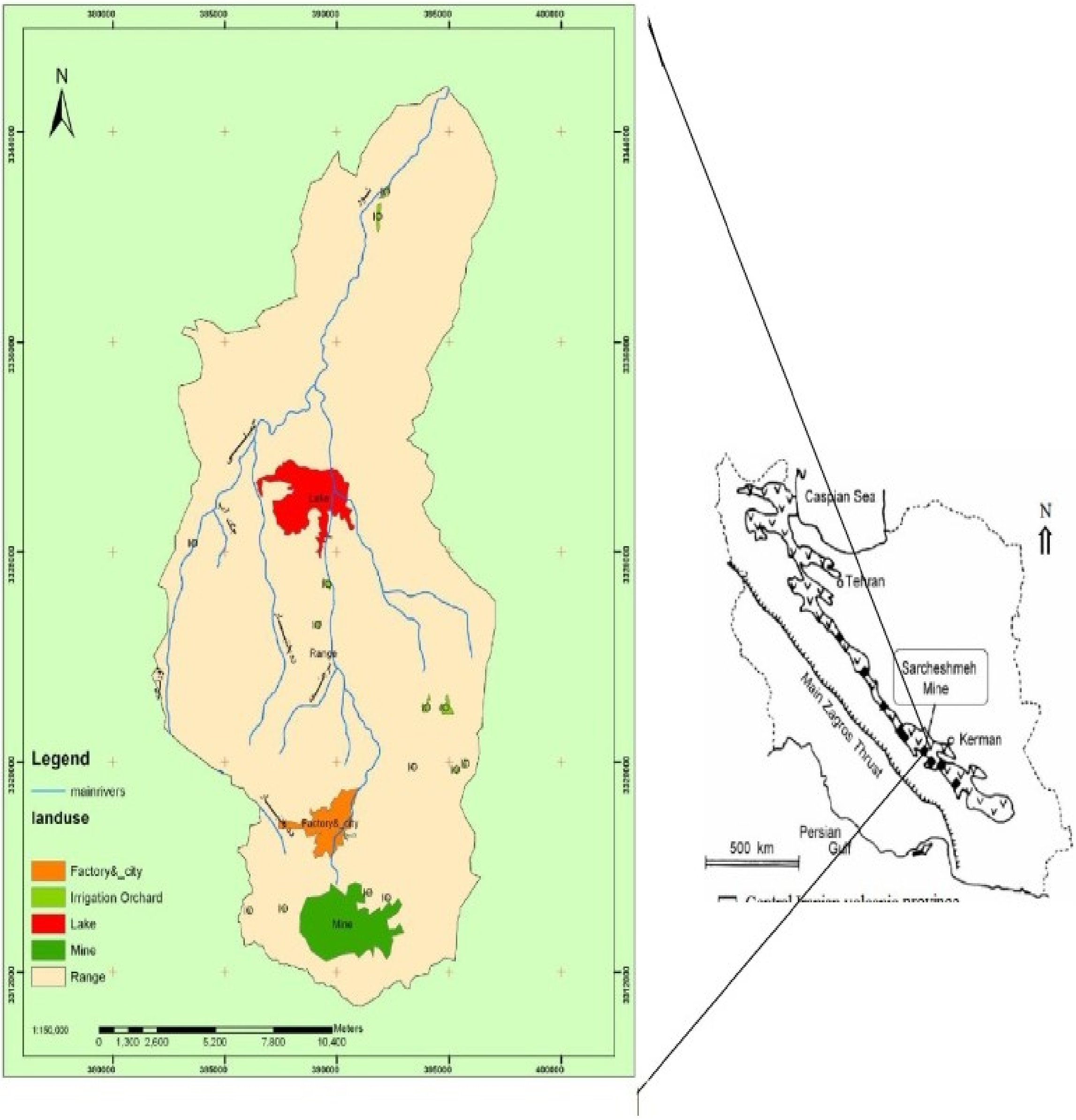


Fig.1: Map of Sarcheshmeh mining and headwaters around it

Shoor water. Based on the results, the highest concentration was found on the dam (Mo=2.50, Al=0.90, Cd=1.00 and Pb=0.77 mg/L) and before dam (Mo=1.10, Al=0.78, Cd=0.82 and Pb=0.80 mg/L), subsequently. It is due to the accumulation of mine waste. But metal concentration significantly decreased in the water after the dam (Mo=1.00, Al=0.77, Cd=0.35 and Pb=0.42 mg/L). Because of metals deposition in the dam, their concentration is reduced in water after it. According to the results, cadmium, aluminum, and lead were maximum in the copper mine and will diminish by keeping distance from the mine. Due to the entrance of mine sewage, the greatest concentration of molybdenum was between the copper mine and dam. Molybdenum concentration will diminish by keeping distance from the dam because they were deposited in it.

Mean comparison of all water samples in both wet and dry seasons indicated that there is a significant difference ($p<0.05$) between Pb and Mo concentration in two seasons. But there was no difference between the content of Al and Cd in dry and wet seasons (Table 3).

The variations of pH and EC in water samples of different locations in Shoor River were shown in Table 2. In this research, metal concentration was enhanced by decreases in pH. The precipitation of metal is essentially dependent on two factors: the metal concentration and the pH of the water. The acidity of the aqueous system

Table 2: The mean concentrations of Pb, Al, Mo and Cd in different location of Shoor water samples ($p<0.05$)

Sampling location	Mo(mg/L)	Al(mg/L)	Cd(mg/L)	Pb(mg/L)	pH	EC (dS m^{-1})
control	0.67±0.13^{c}	0.75±0.07^{b}	0.18±0.02^{b}	0.42±0.44^{b}	7.0	0.40
before dam	1.12±0.10^{b}	0.78±0.07^{ab}	0.72±0.13^{b}	0.80 ±0.07^{a}	9.5	0.27
after dam	1.01±0.08^{bc}	0.70±0.07^{b}	0.35±0.05^{b}	0.42±0.02 ^{b}	7.8	0.39
dam	2.59±0.58^{a}	0.90±0.16^{a}	1.00±0.40^{a}	0.77±0.09^{a}	10.	0.36

Table 3: Pb, Al, Mo and Cd concentrations of water samples in wet and dry seasons ($p<0.05$)

Metals	season	Mean(mg/L)± SE	Sig.
Mo	dry	0.98±0.16	0.13
	wet	1.35±0.15	
Al	dry	0.78±0.05	0.47
	wet	0.69±0.07	
Cd	dry	0.54±0.13	0.27
	wet	0.51±0.08	
Pb	dry	0.58±0.06	0.01
	wet	0.63±0.05	

affected the mobility of heavy metals [18]. Rastmanesh et al. reported that there is a high negative correlation between metal mobility and pH. It suggests that by decreasing metal mobility, pH increased [12].

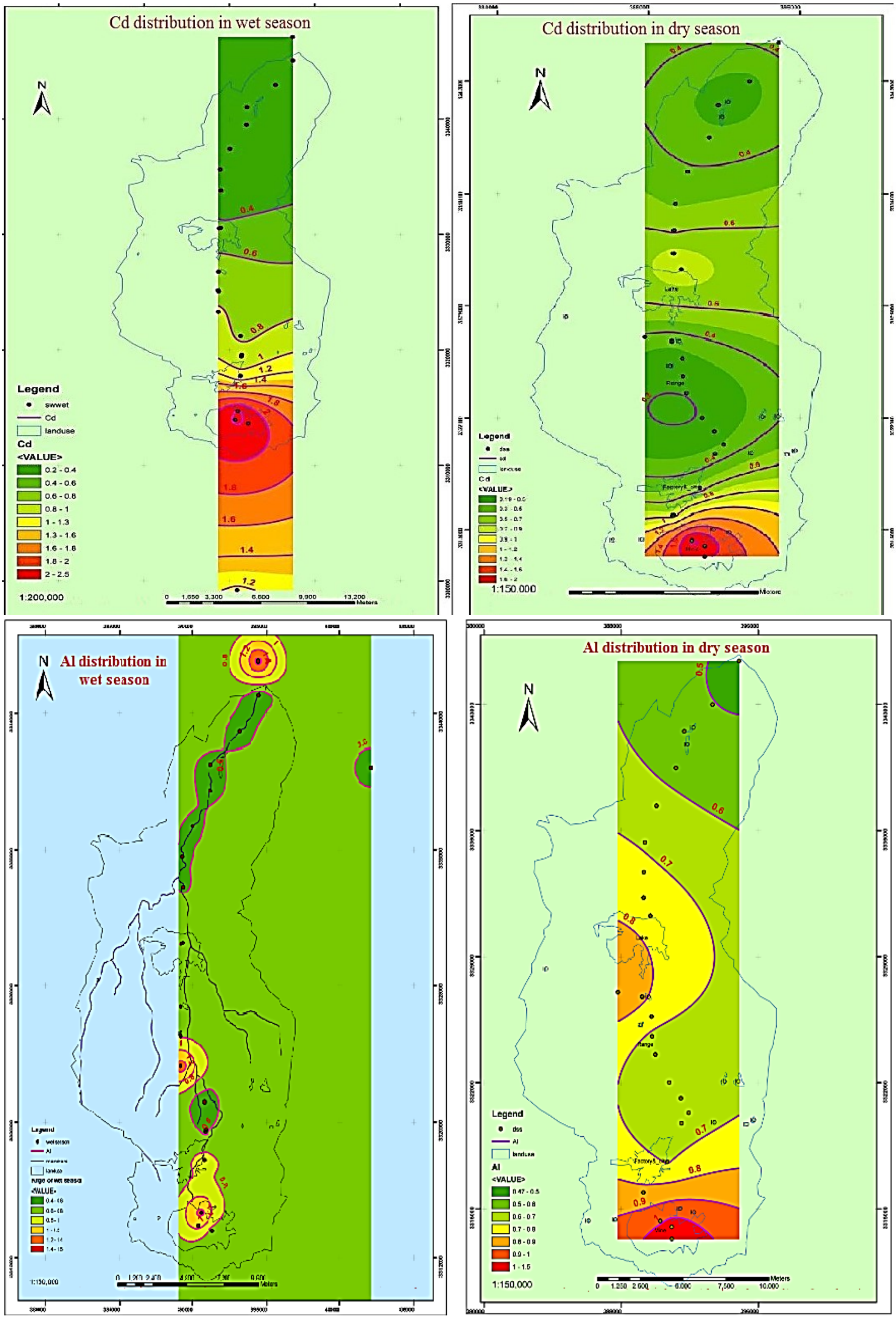
A comparison of the concentration of heavy metal in this area with WHO standards indicate that Mo and Cd concentration is higher than standards (Table 4). Mo is necessary for human beings and animals at low concentrations; however, a high concentration of Mo can lead to toxicity. Cadmium (Cd) is harmful to health. The results showed that Mo and Cd can lead to tissue injury and have a synergistic effect on kidney injury [20]. In the study of Karbassi, the bulk concentrations of Pb, Cd, Zn, Cu, Fe, Ca and, Al in Shoor River bed sediments were determined and Cd and Zn indicated the highest pollution index [20].

4. Conclusions

As a consequence, the copper mine and the factory are the main sources of pollution in this region. Surface water around them was contaminated by Al, Cd, Mo, and Pb elements. The concentration of these elements diminished from the copper mine to Rafsanjan city (Fig.2).

Table 4: Comparison of heavy metals concentration in water samples with WHO standards

	Mo(mg/L)	Al(mg/L)	Cd(mg/L)	Pb(mg/L)
Concentration (mean±SE)	1.11±0.10	0.73±0.04^{b}	0.52±0.07^{b}	0.61±0.03
WHO standard	0.01	5	0.01	5


Cd distribution in wet season
N
Legend
swwet
Cd
landuse
Cd
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0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1
1 - 1.3
1.3 - 1.6
1.6 - 1.8
1.8 - 2
2 - 2.5
1:200,000
0 1,650 3,300 6,600 9,900 13,200
Cd distribution in dry season
N
Legend
1:150,000
Meters
Al distribution in wet season
N
Al distribution in dry season
N
Legend
dss
Al
landuse
Al
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0.5 - 0.6
0.6 - 0.7
0.7 - 0.8
0.8 - 0.9
0.9 - 1
1 - 1.5
1:150,000
0 1,250 2,500 5,000 7,500 10,000
Meters

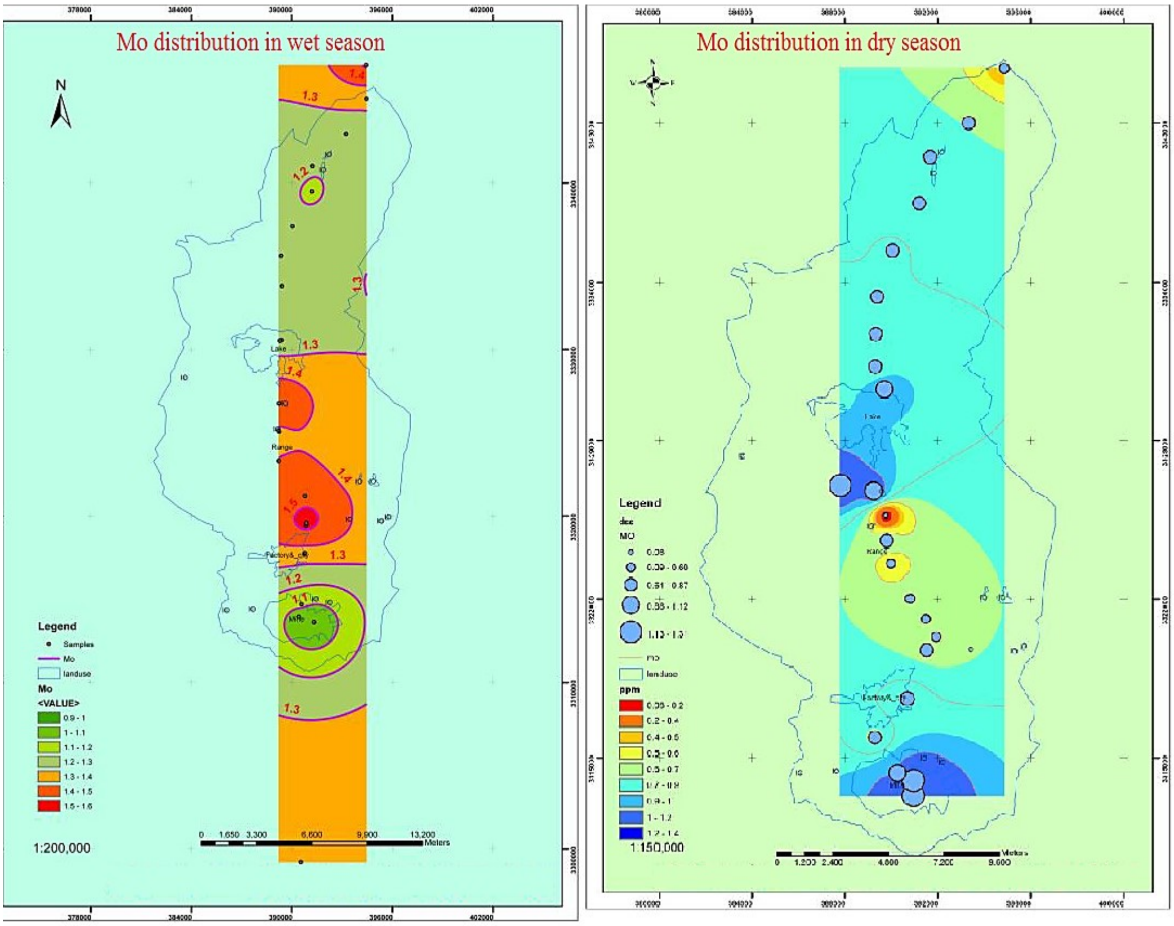

Fig 2: Distribution maps of studied Heavy metals (Pb, Al, Cd, Mo) in dry and wet seasons

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