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Study of groundwater contamination by five heavy metals at Draa Lasfar functional mine region in Marrakech city – Morocco –

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Abstract

The aim of the study was to create awareness on the effect of mine dumpsite on groundwater in developing countries, especially Morocco. In order to achieve this objective, water samples were obtained from 08 randomly selected hand dug wells in the Draa Lasfar area near Marrakech city in July and August 2004. From these samples, pH and conductivity were determined using a pH/conductivity meter, while the concentrations of the heavy metals (Al, Cd, Cu, Pb and Zn) were determined using atomic absorption spectrophotometer (AAS). The study showed that the groundwater in the study area was generally alkaline (7.74 ± 0.23) and contained Al (147.9 ± 27.7 µg / l), Cd (3.3 ± 0. 5 µg / l), Cu (26.1 ± 2.4 µg / l), Pb (44.0 ± 10.0 µg / l) and Zn (67.1 ± 37.8 µg / l) concentrations that are higher than the permissible limits recommended by the World Health Organization (200, 3, 200, 10, 10 and 500 µg/l, respectively). The study concluded that the groundwater sources within 1 km radius of a major landfill will be vulnerable to the effect of landfill, if they are not adequately protected.

1- Introduction

Water is not only a resource, it is a life source. It is well established that water is important for life. Water is useful for several purposes including agricultural, industrial, household, recreational and environmental activities. Despite its extensive use, in most parts of the world water is a scarce resource (Vanloon and Duffy, 2005). It is generally obtained from two principal natural sources ; Surface water such as fresh water lakes, rivers, streams and groundwater such as borehole water and well water (McMurry and Fay, 2004; Mendie, 2005; Caroline and Wilfred, 2013).

The ground water is defined as water that is found underground in cracks and spaces in soil, sand and rocks. This source has two distinct functions; firstly, it is a significant source of both urban and rural population's water supply and secondly it sustains many wetland ecosystems (Abdul Jameel and al., 2012).

As the urbanization process continues, water pollution problems have become increasingly evident and have led to serious ecological and environmental problems. Industrial production without adequate regard for environmental impacts has increased water and air pollution. and has led to soil degradation and large scale global impacts such as acid rain, global warming and ozone depletion.

Due to the anthropogenic activities soil and water quality gets contaminated. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Therefore, they tend to accumulate in soils and sediments. Metals are essential for human growth, but if consumed in excess may cause physiological disorders. Elevated concentrations of heavy metals in water may cause phytotoxicity, direct hazard to human health, indirect effects due to transmission through the food chain or contamination of ground- or surface-waters (Momodu and Anyakora, 2009).

Heavy metals in water refers to the heavy, dense, metallic elements that occur in trace levels, but are very toxic and tend to accumulate, hence are commonly referred to as trace metals. The major anthropogenic sources of heavy metals are industrial wastes from mining sites, manufacturing and metal finishing plants, domestic waste water and run off from roads. Many of these trace metals are highly toxic to humans, such as Hg, Pb, Cd, Ni, As and Sn. Their presence in surface and

underground water at above background concentrations is undesirable. Some heavy metals such as Hg, Pb, As, Cd, Fe, Co, Mn, Cr etc... have been identified as deleterious to aquatic ecosystem and human health (Abdul Jameel and al., 2012).
This study was carried out to determine the spatial and seasonal variations of heavy metal deposition in groundwater in a mining area near Marrakech city in Morocco in order to assess the extent of pollution generated by the mining activity and to identify the key mechanism responsible for this contamination and its relation to this mining activity.

Keywords: Mining extract zone, contamination, heavy metals, well water, Marrakech-Morocco.

2- Experimental procedures

2.1. Study area

The Draa Lasfar mine is located in northwest of the Mrabtine zone at approximately 10 Km in the west of Marrakech city (figure1), it's located a few hundred meters from the Tensift River, close to a rural community of about 5790 ha, which 65% are occupied by farmland. Draa Lasfar consists on deposit of pyrite mineral discovered in 1953 although their commercial exploitation did not begin until 1979. Mineral was processed by flotation after primary and secondary crushing and grinding, producing 60 Mt of products in the first two years (1979 and 1980). Industrial activity stopped in March 1981, although it restarted in 1999 due to its great resource of polymetallic components (As, Cd, Cu, Pb and Zn). During its exploitation, tailings were discharge all around the mine area posing a risk for the environment.

2.2. Sampling methods and sample preparation

Water samples were collected from eight wells once four weeks for one month between July and August 2003.
Water was taken from wells which are falling within 1 km radius of industrial unit of Zn and Pb extraction. Samples were taken directly from wells in sterile glass bottles of 250 milliliters capacity (Divya et al., 2011), after rinsing the bottles three times with sample water. In order to collect the samples directly from well, bottle with a string attached to neck was used. Another long clean string was tied to the end of sterile string and the bottle was lowered into the water allowed to fill up. Then the bottle was raised and stoppered. The collected samples were transported to laboratory in ice within an insulated container and analyzed within 24 hours of collection.
A total of 96 well water samples, 24 each week during four weeks and analyzed for physical parameters like temperature and pH and chemical parameters like Chemical Oxygen Demand (COD).

Temperature and pH of each sample was measured using mercury filled glass thermometer and digital pH meter respectively. Measurement of COD was made photometrically in Spectroquant NOVA 60 (Merck. Germany) after digesting the samples in preheated Thermoreactor TR 320 (Merck, Germany). Concentration of nitrate and lead in not filtered water samples was measured photometrically in Spectroquant NOVA 60 and expressed in mg/l.
Metal contents of the water samples were analyzed by AAS (Model: ECILTM AAS−4141). For the determination of heavy metals, the water samples were digested with 20 ml aqua-regia (HCl/HNO3 3:1 volume ratio) in a beaker (open beaker digestion) on a thermostatically controlled hot plate. Then 5.0 ml hydrogen peroxide was added to the sample to complete the digestion and the resulting mixture was heated again to near dryness in a fume cupboard and filtered by Whatman no. 42 filter paper and the volume was made up to 50 ml by double distilled water (Kard and al., 2008).
Estimation of aluminium, copper, zinc, lead and cadmium was carried out using Atomic Absorption Spectrophotometer (Divya et al., 2011).

3- Results and discussion

The summary of the estimated results of laboratory analyses conducted on the samples are in Table 1.
Table 1 shows that the groundwater resource is not suitable for domestic purposes for which it is presently used in some of the residential areas in the studied region. The waters are generally acid (6.2 ± 0.5) and contain the investigated heavy metals at an

amount that is above the maximum recommended (WHO, 2006) limits, except Al, Cu and Zn.

Specifically, the pH of the groundwater samples showed that the water sources around the landfill were within a wide range of 5.4 and 7.2.
Samples from the residential area were between slightly acid to alkaline. The lowest pH (5.4) in the investigated groundwater sources was recorded in a borehole within the residential area; in a firm that shares a wall boundary with the landfill.
In the present study, pH was not within the acceptable range of pH for drinking water (6.5-8.5)(WHO, 2006).
It's known that pH value is mainly influenced by volume of water, soil type, presence of chemicals and application of acidic fertilizers (Divya et al., 2011).
During the studied period (dry season: summer), these low values of pH may be justify by the death and decay of plants due to lack of sufficient water which increases the organic acid content of water in turn causing acidity. These lower pH values during dry season could be due to relative high photosynthesis of micro and macro vegetation resulting in production of more CO_2 shifting the equilibrium towards alkaline side (Kumar et al., 2010). This could be attributed to the presence of luxuriant vegetation inside most of the wells during rainy season.
The effects of acidic waters on human health and the environment have been widely reported. For example, acidic waters have been known to be aggressive and enhance the dissolution of iron and manganese causes unpleasant taste in water (Edwards et al., 1983).
Water sampled were generally characterised by high electric conductivity, quite above the World Health Organization's standard limits of 1.0 µS.m-1.
Studied groundwater sources within the residential area contain high conductance value probably as a result of decreased volume of water and runoff in the dry season.

- Chemical Oxygen Demand

Higher values of COD were observed during summer. Higher values of COD indicate the presence of oxidizable organic matter. The entry of industrial effluents and the agricultural runoff might be responsible for increased level oxidizable organic matter (Sisodia et al., 2006). The higher COD could be due to death and decay of plants and subsequent increase in organic matter during summer (Kumar et al., 2010).

- Copper

Mean copper concentration was in the range of 22.6 ± 4.3 – 29.6 ± 5.3 µg/,l and was under WHO guidelines, 2006 (200 µg/l) for Cu in drinking water.
This low concentration of Cu in the groundwater is likely due to the fact that Cu is easily chemisorbed on or incorporated in clay minerals of soils (Rodriguez et al., 2009). This chemisorption can be justified by that copper is characterized by high complex constant organic matter thus it can be hypothesized that Cu is bound to labile organic matter such as lipids, proteins, and carbohydrates.

- Lead

- Mean lead concentration was in the range of 32.6 ± 16.9 – 63.2 ± 22.4 µg/l and was above WHO guidelines, 2006 (10 µg/l) for lead in drinking water. This mining extract zone being an industrial area is subjected to the discharge of effluent containing lead to nearby water bodies.
Analysis of waste products generated by this mine extract industry showed that significant amount of lead is generated by this industrial unit in their waste products. The effluents rich in lead are discharged to water bodies nearby and subsequently affect the groundwater quality of the area. Combined effect of decreased amount of water in summer and strong leaching during winter might have contributed to higher lead concentration during these two seasons.

- Zinc

Mean zinc concentration was in the range of 24.9 ± 3.8 - 131.4 ± 4.9 µg/l, and was within the limit of 500 µg/l as prescribed by WHO guidelines. 2006. The zinc concentration in studied water during summer can increase when depletion of water leads to greater concentration of this metal (Buragohain et al., 2010).

- Cadmium

Mean cadmium concentration varied from 1.17±0.1 to 1.93±0.4 µg/l, within the limit of 3µg/l as prescribed by WHO guidelines, 2006.
Many studies (Pichard et al., 2004) have insisted on the high capacity of cadmium to bind to suspended

particles of water and to form sedimentary deposits containing high concentration of cadmium (Lapaquellerie et al., 1995), thereby promoting a reduction in its concentration in waters.

- Aluminium

Elementary aluminum is insoluble in cold and hot water. In pH range between 5.5 and 8.8 aluminium is insoluble and $Al(OH)_3$ is predominant. It is also possible that aluminum polymerized and formed poly-cations such as $Al_2(OH)_2(H2O)_8^{4+}$ and $Al_{13}(OH)_{32}^{7+}$ (Habs et al., 1997). These structures can be enough to rush out and train with them aluminum, which reduces both mobility and content of this element in waters (Pichard et al., 2004).

4- Conclusion

Well water quality in the study zone showed seasonal variation for temperature some parameters (pH, COD, concentration of nitrate, aluminium, copper, zinc, lead and cadmium) and exceeded in most cases the limits prescribed by WHO guidelines 2006. In order to improve quality of well water and consequently to protect people and animals from the perils of well water contamination, it is crucial to initiate measures to check the pollution from industrial effluents and to establish on-site regular well water quality monitoring network stations.

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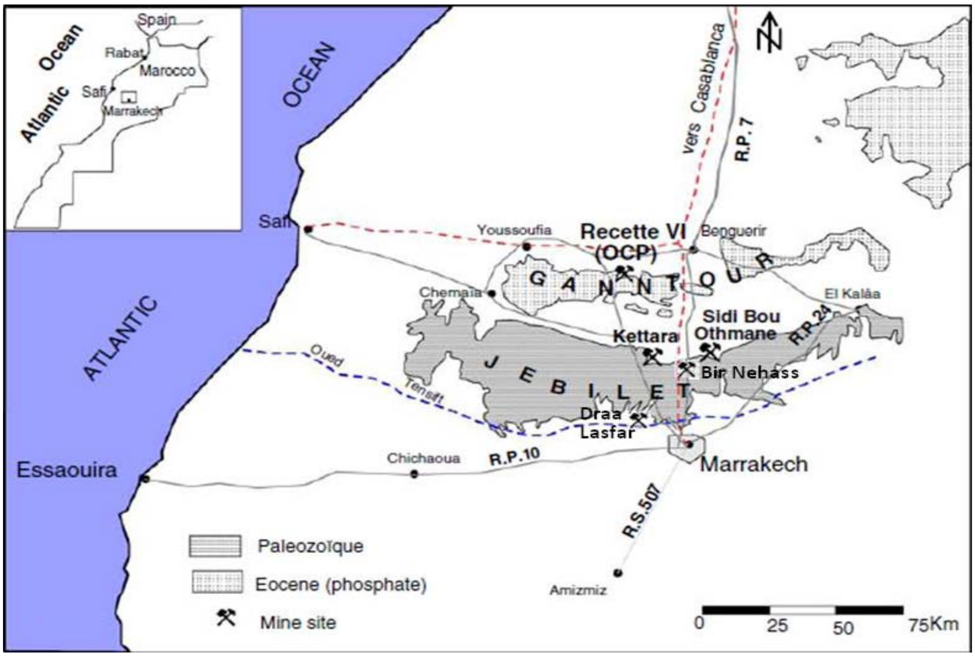

Figure 1: Drâa Lasfar mine geographic situation in Marrakech region