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Short Communication

A New Approach to Understanding Well Water Contamination by Heavy Metals at a Mining Extract Region in Marrakech, Morocco

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Abstract

Environmental pollution by heavy metals originating from functional mines can become a very important source of contamination both in soil and water. We studied the seasonal variation of physicochemical parameters of well water at the Draa Lasfar mining extract area in Marrakech, Morocco. A total of 144 samples (36 each during winter, spring, summer, and autumn) were collected during 2012-13 and analyzed for temperature, pH, total hardness, chemical oxygen demand (COD), and concentrations of nitrate and heavy metals like lead, zinc, and cadmium. Significant differences between seasons were observed for temperature, COD, and concentrations of nitrate, zinc, and cadmium. The highest temperature (28.72º±3.16) was recorded during summer. COD and zinc concentration was maximum during summer (167.25±31.05 mg/l, 131.4±12.0 µg/l, respectively). Highest nitrate (2.67±0.75 mg/l) concentrations were recorded during spring. Highest lead (632.14±82.54 µg/l) and cadmium (1.93±0.36 µg/l) concentrations were recorded during winter.

Keywords: mining extract zone, contamination, heavy metals, well water, Marrakech, Morocco

Introduction

Of all the natural resources, water is unarguably the most essential and precious. It is a universal solvent and as a solvent it provides ionic balance and nutrients that support all forms of life [1]. It is generally obtained from two principal natural sources: surface water such as freshwater lakes, rivers, and streams, and groundwater such as borehole water and well water [2].

In Morocco, the major source of water used to meet domestic, agricultural, and industrial needs is groundwater, which is defined as water 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 the urban and rural populations' water supply, and secondly it sustains many wetland ecosystems.

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Unfortunately, industrialization and human activities have partially or totally turned our environment into dumping sites for waste materials. As a result, many water resources have been rendered polluted and hazardous to life [3]. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish.

Deposition of heavy metals in groundwater from anthropogenic activities has been implicated in an increase in heavy metal concentration above recommended levels [4, 5]. The term "heavy metal" is not altogether clearly defined, but in the case of water pollution these are metals such as arsenic, cadmium, iron, cobalt, chromium, copper, manganese, mercury, molybdenum, nickel, lead, selenium, vanadium, and zinc. While heavy metals do tend to have a high atomic mass and so are heavy in that sense, toxicity seems to be a further defining factor as to what constitutes a heavy metal and what does not.

Heavy metals are important components of agro-allied products such as pesticides, herbicides, and fertilizers, and manufacturing and other synthetic products such as paints and batteries. Mining activities and industrial, municipal, and domestic wastes have been reported to be important sources of heavy metal pollution in groundwater [6].

Excessive concentrations of heavy metals in groundwater is of great concern because of its non-biodegradability. Therefore, their persistence in the environment portends a health hazard to plants and animals, consequently triggering ecological imbalance in the ecosystem [7].

Another concern that high concentrations of heavy metals raise is their ability to bioaccumulate across the food chain, with members that are high up the food chain having concentrations of such metals several times higher than what is obtainable in the departure point of the contamination (groundwater) [8, 9]. In Morocco, groundwater is the main source of water in most rural communities. It has good microbiological and biological properties in general and as such requires minimal treatment. Actually, a variety of human activities – notably industrial and mining process – have been responsible for the wider diffusion of heavy metals into this type of water [10].

This study was carried out to determine the spatial and seasonal variations of heavy metal deposition in groundwater in a mining area near Marrakech, Morocco, in order to assess the extent of pollution generated by mining activities and to identify the key mechanism responsible for this contamination and its relation to the mining activity.

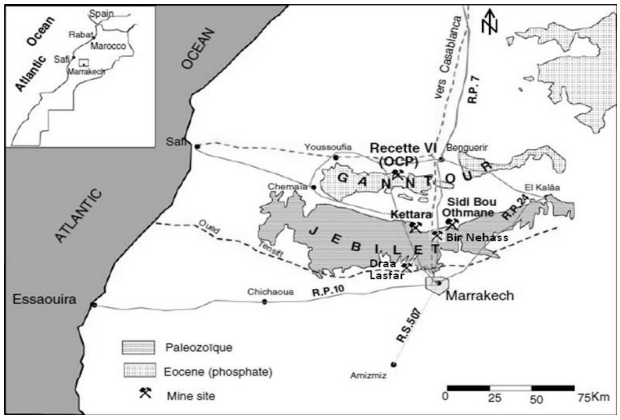

Fig. 1. Drâa Lasfar mine geographic situation in Marrakech region.

Experimental Procedures

Study Area

The Draa Lasfar mine is located northwest of the Mrabtine zone approximately 10 km west of Marrakech (Fig. 1). It is located a few hundred meters from the Tensift River, close to a rural community of about 5,790 ha, 65% of which is farmland. Draa Lasfar consists of a deposit of pyrite discovered in 1953, although their commercial exploitation did not begin until 1979. The 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, Fe, Pb, and Zn). During its exploitation, tailings were discharged all around the mine area, posing a risk to the environment.

Sampling Methods and Sample Preparation

Water samples were collected once a month for 12 months between April 2012 and April 2013. Water was taken from wells within a 1 km radius of industrial units of Zn and Pb extraction. Samples were taken directly from wells in 250 ml sterile glass bottles [11] after rinsing the bottles three times with sample water. A string was attached to the bottle neck in order to collect samples directly from a well. Another long clean string was tied to the end of a sterile string and the bottle was lowered into the water allowed to fill. Then the bottle was raised and stoppered. The collected samples were transported to a laboratory on ice within an insulated container and analyzed within 24 hours of collection.

A total of 144 well-water samples (36 each during June-August, March-May, September-December, and January-March) were collected in 2012 and 2013 and analyzed for physical parameters like temperature and pH, and chemical parameters like total hardness and chemical oxygen demand (COD).

Temperature and pH of each sample was measured using a mercury-filled glass thermometer and digital pH meter, respectively. Total hardness of the samples was estimated using a total hardness test kit. Measurement of COD was made photometrically using a Spectroquant NOVA 60 (Merck, Germany) after digesting the samples in a preheated Thermoreactor TR 320 (Merck, Germany).

Table 1. Physical quality of well water.

Parameters	Seasons			
	Winter	Spring	Summer	Autumn
pH	6.71±0.24	6.56±0.14	6.03±0.17	5.78±0.21
Temperature (ºC)	27.5±2.07	28.02±3.16	28.72±2.26	28.37±2.68

Table 2. Chemical quality of well water.

Parameters	Mean concentrations during four seasons			
	Winter	Spring	Summer	Autumn
Total hardness	302.56±31.39	296.28±37.14	423.67±27.88	376.15±23.75
COD	96.87±17.37	117.26±57.41	167.25±31.09	115.68±43.16
Nitrate	2.11±0.47	2.67±0.71	1.63±0.23	1.15±0.43
Copper (µg/l)	90.4±16.47	102.74±21.30	136,82±31.91	119.52±12.45
Lead (µg/l)	632.14±82.54	335.45±62.71	512.64±60.85	433.52±71.57
Zinc (µg/l)	80.12±5.51	86.72±6.42	131.42±7.45	103.91±9.25
Cadmium (µg/l)	1.93±0.36	1.68±0.19	1.78±0.37	1.56±0.24

Concentration of nitrate and lead in unfiltered water samples was measured photometrically in a Spectroquant NOVA 60 and expressed in mg/l.

Metal contents of the water samples were analyzed by AAS (Model: ECILTM AAS-4141). For determining 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 [12].

Estimation of zinc, lead, and cadmium was carried out using atomic absorption spectrophotometry [11].

Results and Discussion

Results of analysis are shown in Tables 1 and 2.

pH

pH of well water was in the range of 5.78±0.22-6.71±0.24, and significant difference between seasons was not observed. pH is mainly influenced by volume of water, soil type [11], presence of chemicals, and application of acidic fertilizers.

In the present study, pH was not within the acceptable range of pH for drinking water (6.5- 8.5; [13]).

– Acid pH of well water during autumn may be due to dissolved carbon dioxide and organic acids such as fulvic and humic acids, which are derived from decay and subsequent leaching of plant materials. During dry seasons (summer) there may be death and decay of plants due to lack of sufficient water, which increases the organic acid content of water, in turn causing acidity. The higher pH values during the rainy season could be due to relatively low photosynthesis of micro and macro vegetation resulting in production of less CO_2.
– Shifting the equilibrium toward the alkaline side [14]. This could be attributed to the presence of luxuriant vegetation inside most of the wells during the rainy season.

Temperature

Temperature ranged from 27.5-28.1. The lowest temperature was recorded during winter and the highest was recorded during summer, which was in accordance with ambient temperature pattern [15, 16].

Total Hardness

Total hardness was in the range of 296.28±37.14-423.67±27.88 mg/l, with no significant seasonal variation. Higher total hardness could be due to the discharge of effluents and untreated waste [17] from the local extracting mine industry to nearby surface water sources. The highest value of total hardness was observed during summer, which could be due to the low water level and high rate of evaporation during summer [18].

Chemical Oxygen Demand

COD ranged 96.87±17.37-167.25±31.05, and showed significant difference between seasons. Lowest and

highest values were observed during winter and summer, respectively. 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 levels of oxidizable organic matter [18]. The higher COD could be due to the death and decay of plants and subsequent increases in organic matter during summer [13]. The lower COD observed during winter could be due to the effect of dilution increased by rain in this season.

Nitrate

Mean nitrate concentration of well water was in the range 1.15±0.43-2.67±0.75 mg/l, which was within WHO guidelines (2006) for nitrate. Nitrate detected in well water samples might have originated from decaying organic matter [19], the discharge of sewage and industrial wastes, and runoff from agricultural fields containing nitrate fertilizers [14]. Mean nitrate concentration was lowest during autumn and highest during spring. The highest concentration during spring might be due to the application of nitrogenous fertilizers to agricultural land during the rainy season and subsequent seepage through soil.

Copper

Mean copper concentration was in the range of 90.4±16.47-136.82±31.91 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 [20]. This chemisorption can be justified by the fact 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 335.45±62.71-632.14±82.54 µg/l, and was above WHO guidelines (2006, 0.01 mg/l) for lead in drinking water. This mining extract zone being an industrial area is subject to the discharge of effluent containing lead to nearby water bodies.

Analysis of waste products generated by this mine extract industry showed that a significant amount of lead is generated by this industrial unit in their waste products. Effluents rich in lead are discharged to water bodies nearby and subsequently affect the groundwater quality of the area. This showed a significant seasonal variation: spring samples showed the lowest concentration while winter and summer seasons showed highest concentrations. The combined effect of a decreased amount of water in summer and strong leaching during winter might have contributed to higher lead concentrations during these two seasons.

Zinc

Mean zinc concentration was in the range of 80.12±5.51-131.42±7.45 µg/l, and was within the limit of 500 µg/l as prescribed by WHO guidelines (2006). The analysis report pointed out that a significant amount of zinc is generated by this industrial unit, which in turn deteriorates groundwater quality. The concentration was highest during summer, when depletion of water leads to greater concentration of metals [21].

Cadmium

Mean cadmium concentration varied from 1.56±0.24-1.93±0.36 µg/l, and showed significant difference between seasons. Analysis of waste products showed that this industry discharged some amount of cadmium in their waste products, deteriorating groundwater quality. Cadmium concentration was found to be highest during winter, which might be due to leaching during this season.

Conclusions

Well water quality in the study zone showed seasonal variation for temperature in some parameters (pH, COD, concentrations of nitrate, 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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