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ORIGINAL RESEARCH PAPER

ANALYSIS OF SEASONAL VARIATION ON DEGREE OF CONTAMINATION WITH HEAVY METALS IN AARJATE VILLAGE, MOROCCO. AN INDEX APPROACH

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Abstract: Water samples from wells and samples from soil nearby them were taken during dry (June-September 2013) and wet (December 2013, January - February 2014) seasons and concentrations of Cd, Cu, Mn, Ni, Pb and Zn were determined. Contamination Factor for each heavy metal and Nemerow pollution index were calculated showing a decrease in contamination degree from summer to winter for soil and an increase in case of groundwater. Vertical transfer of pollutants from top soil to groundwater was assessed using Hierarchical Cluster Analysis, significant correlations between concentrations and composition of soil being found. In case of Ni, the variables corresponding to the concentrations from soil and groundwater were part of the same cluster, in both seasons, the distribution maps of concentrations confirming the pattern of transfer.

Keywords: *contamination factor, groundwater, Hierarchical Cluster Analysis, Nemerow index, soil, vertical transfer*

INTRODUCTION

Due to their persistence, toxicity and non-biodegradable nature, heavy metals are regarded as a serious concern in relation to human health effects [1]. Cd is toxic to humans because it has the ability to mimic the metabolic functions of zinc (an essential element), thus modifying the activity of enzymes in the body. Cd exposure may cause kidney problems and deterioration of bones, and prolonged exposures (occupational) can cause lung, stomach or prostate cancer [2-5]. Pb has the ability to mimic the metabolic functions of Ca, and inhibits the activity of most enzymes. Also it can affect the functioning of the intestinal tract and can cause anemia and renal dysfunction. In case of children, even in small amounts, it can cause brain damage and nervous system disorders [3, 5, 6]. Cu, Mn and Zn are essential elements, but both deficiency and excess have adverse effects on human health [3, 5, 7, 8].

Intensification of agriculture through excessive application of agrochemicals favors the enrichment of agricultural soil with heavy metals: Cd, Pb, Mn, Zn from fertilizers; Cu, Mn, Pb, Zn from pesticides; Cd, Cu, Pb, Ni, Zn from manure [9]. Due to their characteristic: most metals do not undergo microbial or chemical degradations, soil is acting as a sink, the transfer of heavy metals in case of agricultural soils being mostly through plant uptake, air transfer, or vertical transfer during rainfall [10], to deeper layers of soil and groundwater. In all cases, humans are in contact with heavy metals through food chain (soil-plant-human, or soil-plant-animal-human), inhalation or drinking water [11].

Aarjate Village is located in Rabat Salé Zemour Zaer Region, at 25 km from the City of Rabat - the capital of the Kingdom of Morocco. The village is covering an area of about 151.86 km^2, with an average elevation of 130.84 m above sea level. The climate belongs to semiarid Mediterranean climate, with dry warm to hot summers and mild to cold wet winters. The economy of the area is dominated by agriculture (cereals, vegetable gardens and orchards) and cattle breeding [12] and the water from wells is used by inhabitants for drinking and also for irrigation [11].

There is no assessment conducted in this area in the region regarding heavy metals concentrations in soil or groundwater. So, the aim of this current research conducted from June 2013 to February 2014, was to assess the concentrations of heavy metals, to identify the way seasonal variation may influence them and to identify locations where a risk of contamination is manifesting and to which extent.

MATERIALS AND METHODS

The sampling was performed in each season, during the time of the highest agricultural activities. The water samples were collected from 25 wells located inside the farms and on the crop fields. They were stored in sterile-polyethylene bottles and preserved with 1% nitric acid [13]. The soil samples were collected at the depth of 0-25 cm, from an area of 10x10m having the well in center and mixed to form a single sample for each location. The soil was air dried, sieved through a 2mm mesh [14] and digested with aqua regia (3:1 $HCl:HNO_3$) [15].

The heavy metals (Cd, Cu, Mn, Ni, Pb, Zn) concentrations were determined using atomic absorption spectrometer Varian, AA 240 FS [16], with reagents from Merck.

The measurements of soil components (clay, slit, sand) were performed according to the gravimetric methods [17].
Descriptive, comparative and Hierarchical Cluster Analysis (HCA), were conducted using SPSS 20 software. Because in Morocco there are no national standards or threshold established for heavy metals concentrations, for comparison analysis limits from World Health Organization (WHO) were used [11]. Raw values were standardized to z_scores prior cluster analysis. For HCA the Ward method with Squared Euclidean Distance was applied to the variables in order to assess the similarity degree between them [18-21]. The distribution maps were generated in ArcMap application from ArcGIS 10 software using Ordinary Kriging interpolation method [1, 22, 23].

RESULTS AND DISCUSSIONS

Seasonal variation

Concentration's range and the mean for the heavy metals determined in top soil and groundwater are summarized in Table 1. *% exceeding* was calculated for all elements as the percentage of values which are exceeding the WHO limits from the total number of samples.

Table 1. *Range, average and percentage of samples exceeding the World Health Organization (WHO) thresholds for the heavy metals concentrations from ground water and top soil in Aarjate Village, Morocco*

n[a] = 25		groundwater (mg·L^{-1})		soil (mg·kg^{-1} dried soil)	
		Summer	Winter	Summer	Winter
Cd	range	0.000 – 0.004	0.00 – 0.004	0.71 – 6.45	0.52 -4.83
	mean	0.001	0.001	2.256	1.995
	%exceeding[b]	4%	8%	16%	8%
Cu	range	0.000– 0.012	0.00 – 0.026	10.55 –23.33	9.14 – 22.57
	mean	0.003	0.005	15.334	14.542
	% exceeding[b]	0%	0%	0%	0%
Mn	range	0.000 – 0.088	0.00 – 0.041	72.62 -743.36	65.94 – 780.80
	mean	0.01	0.008	235.320	236.449
	% exceeding[b]	0%	0%	0%	0%
Ni	range	0.000 – 0.063	0.00 - 065	5.69 – 35.63	4.88 – 132.71
	mean	0.007	0.016	17.800	22.058
	% exceeding[b]	8%	32%	0%	4%
Pb	range	0.000 – 0.010	0.00 – 0.01	3.63- 96.22	6.01 – 76.25
	mean	0.002	0.001	30.562	26.354
	% exceeding[b]	0%	0%	0%	0%
Zn	range	0.0056 – 0.404	0.0190 – 53.5	17.73 – 65.14	14.77 – 47.54
	mean	0.046	17.914	32.319	31.531
	% exceeding[b]	0%	48%	0%	0%

[a] n= number of sampling locations per season
[b] % exceeding = percentage of locations where WHO thresholds are exceeded

It can be observed that the values and percentage of exceeding of WHO limits [11] are increasing for groundwater from summer (dry season) to winter (wet season), while for soil, they are decreasing, with an exception for Ni. Also, in ground water values over the thresholds are registered for Cd, Ni (both seasons) and Zn (only winter), while for soil there are registered for Cd (both seasons) and Ni (only winter).
The data are highlighting a possible vertical transfer from top soil to groundwater of pollutants, favored by the large quantities of rain during wet season.

Vertical transfer

Vertical transfer of heavy metals from top soil to ground water is depending of soil composition, soils with high content of clay and slit favoring the accumulation, while sandy soils are more easily passed by water during rainfalls, and thus favoring the transport to the deeper layers and groundwater [10].
Concentrations for heavy metals from soil and groundwater from each season were analyzed in relation with soil content using Hierarchical Cluster Analysis applied to the variables. The dendograms (Figure 1) are confirming the results from the literature, the concentrations measured in soil being correlated with the clay (zp_A_t) and slit components (zp_L_t), and the concentrations from groundwater being in the same cluster with the sand component (zp_S_t).
Ni concentrations from soil and groundwater have a different behavior, being part of the same cluster, linked with the clay (zp_A_t) and slit components (zp_L_t), with a degree of similarity over 75% in summer and around 70% in winter. These and the increase of number of values exceeding WHO limits in groundwater highlight the possibility of vertical transfer of Ni from upper soil layers.

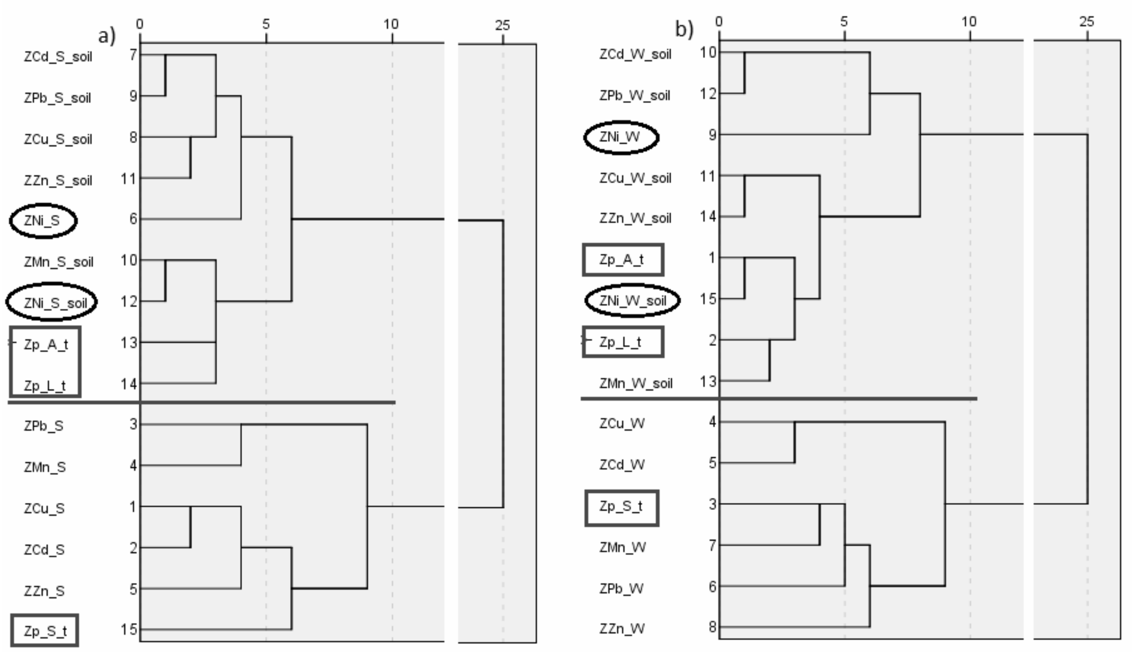

Figure 1. *Dendograms using Ward Linkage resulted from HCA applied on soil composition and soil and groundwater heavy metals concentrations determined during a) summer season and b) winter season in Aarjate Village, Morocco*

The distribution maps for Ni in soil (Figure 2a) show a location of maximum values in the eastern part of the village, the pattern of Ni concentrations distribution in groundwater (Figure 2b) following the slope of the terrain from the high accumulation area in the North-East to the lower grounds near the river.

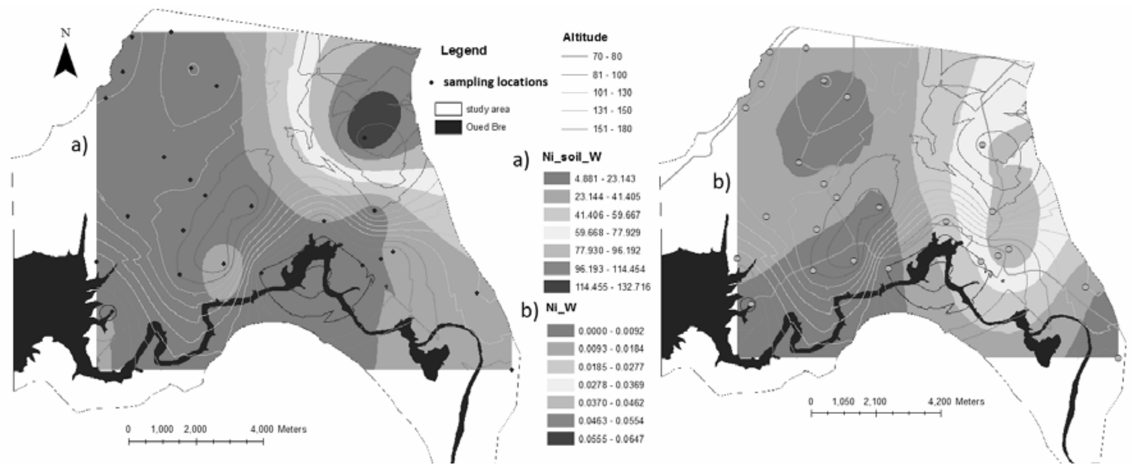

***Figure 2**. Distribution maps of Ni concentrations determined from top soil (a) and groundwater (b) during winter (wet season) in Aarjate Village, Morocco*

The increase of values determined for Ni in soil (Table1) in winter may be explained through an addition of contaminants during activities specific to the season and through the chemical behavior of Ni in aqueous solutions. In order to determine the sources of contamination, further investigations are needed, taking into account the extension of the study area and a monitoring program of the quality of agricultural soil and of the water from the wells used by the inhabitants.

Degree of contamination of soil

In order to assess the degree of contamination with heavy metals of soil and groundwater in Aarjate Village, Morocco, Nemerow composite index [24] was used. The algorithm takes into account not only the relation between the pollution indexes for each heavy metal, but also the maximum value of them (Equation 1).

$$PI_{Nemerow} = \sqrt{\frac{\left(\frac{1}{m}\sum_{i=1}^{m} P^i\right)^2 + \left(P^i_{\max}\right)^2}{2}} \tag{1}$$

where: $PI_{Nemerow}$ represents Nemerow pollution index; m is number of heavy metals taken into account; P^i is individual pollution index calculated for heavy metal i; P^i_{max} is maximum value of individual indexes P^i.

The quality of soil environment is classified into 5 grades: $PI_{Nemerow}<0.7$, "safety domain"; $0.7\leq PI_{Nemerow}<1.0$, "precaution domain"; $1.0\leq PI_{Nemerow}<2.0$, "slightly polluted domain"; $2.0\leq PI_{Nemerow}<3.0$, "moderately polluted domain"; and $PI_{Nemerow}>3.0$, "seriously polluted domain" [25].

Nemerow algorithm was applied to Contamination Factors (C_f) as individual pollution index (Equation 2).

$$C_f = \frac{C}{C_r} \tag{2}$$

where: C_f represents the Contamination Factor for a specific heavy metal, C is the determined concentration of the heavy metal, and C_r represents the reference level.

The index C_f was suggested by Hakanson in 1980 as a sedimentological risk index used to describe the contamination of a given toxic substance in a lake or a sub-basin [26], but it was successfully used on soil assessment, also [24, 27]. The classes used to describe the Contamination Factor are: $C_f < 1$ meaning *"low contamination"*; $1 \leq C_f < 3$, *"moderate contamination"*; $3 \leq C_f < 6$, *"considerable contamination"*; and $C_f \geq 6$, *"very high contamination"* [26].

Because in Morocco no national thresholds considering the contamination of agricultural soil are established, the limits proposed by World Health Organization (WHO) were used as reference level for C_f.

For soil, values in the *"moderate contamination"* category were obtain for Cd in summer (16% of samples) and for Cd and Ni in winter (8% and 4% respectively). Considering the total pollution based on Nemerow index, the majority of locations can be classified in *"safety domain"* (76% of samples in summer and 80% in winter). In *"precaution domain"* category, there are 16% of samples in dry season and 12% in wet season, the rest of 8%, in both seasons, are not exceeding the *"slightly polluted domain"*.

For groundwater, in summer Cu, Mn and Zn have values only in *"low contamination"* category, while 12% of samples for Cd, 20% for Pb and 4% for Ni can be classified in *"moderate contamination"*. Another 4% of samples for Ni are in *"considerable contamination"* category. In winter, the percentages of samples in higher contaminated categories are increasing: 12% for Cd, 12% for Pb, and 28% for Ni in *"moderate contamination"* category; 4% of samples for Ni and 4% for Zn are in *"considerable contamination"* category, while Zn values rise up to *"very high contamination"* category for 44% of locations. Considering the total pollution based on Nemerow index, 64% of samples in summer and 24% in winter can be classified in *"safety domain"*, 28% of samples in summer and 20% in winter are in *"precaution domain"*, and in *"slightly polluted domain"*: 4% of samples in summer and 8% in winter. *"Moderately polluted domain"* is reached in summer by only 4% of locations, while in winter 48% of samples can be classified in *"seriously polluted domain"*.

CONCLUSIONS

Locations where the concentrations of heavy metals were exceeding WHO thresholds, both in ground water and in soil, were identified. The degree of contamination calculated using pollution indexes is rising to *"slightly polluted domain"* in soil, in both seasons, and to *"seriously polluted domain"* in groundwater during rainy season.

Seasonal variation were identified, the value of concentrations and also the percentage of exceeding the WHO limits increasing in groundwater from summer to winter, and decreasing in soil.

Results of Hierarchical Cluster Analysis applied to the heavy metals concentrations and clay, slit and sand components of soil, as variables showed correlations between the

concentrations measured in soil with the clay and slit components, and between the concentrations from groundwater with the sand component, in both seasons, highlighting the possibility of vertical transfer of pollutants from top soil to groundwater.
In case of Ni, vertical transfer is confirmed by the correlation between variables and by the spatial pattern of concentrations distribution in groundwater.

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