



# Application of Multivariate Statistical and Geochemical methods for Assessing of Groundwater pollution near controlled Landfill in Oum Azza area, NW Morocco

Benabbou A.<sup>1,2</sup>, Benhoussa A.<sup>1</sup>, Fekhaoui M.<sup>2</sup>, El blidi S.<sup>2</sup>, El Abidi A.<sup>3</sup> and Bounagua M.<sup>4</sup>

<sup>1</sup>Science Faculty, Zoological Laboratory, Mohamed V Agdal University, Rabat, MOROCCO

<sup>2</sup>Scientific Institute, Pollution, Environmental Toxicology and Health Hazards laboratory, Mohamed V Agdal University, Rabat MOROCCO

<sup>3</sup>National Institute of Health, Department of toxicology, Health Ministry, Rabat MOROCCO

<sup>4</sup>Chemical Laboratory, Science Faculty, Mohamed V Agdal University, Rabat MOROCCO

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## Abstract

The concentration of various physico-chemical parameters including heavy metals was studied in the water samples collected around the controlled landfill (Rabat, Morocco); in order to assess the hydrochemical hydro-chemical quality of groundwater and to study the possible impact of leachate percolation on groundwater quality. The high level of hardness and low concentration of heavy metals demonstrate strong mineralization of groundwater. In exception, lead shows in some wells higher concentrations than the WHO standard. The Piper diagram was used to identify geochemical processes occurring in the Oum Azza area. The Principal Component Analysis (PCA) technique was used to identify natural and anthropogenic factors, which are at the origin of three main classes of water proved including; calcium bicarbonate water  $Mg - HCO_3^- - Ca^{2+} - Mg^{2+}$ , sodium chloride- water  $Cl - Na$  and  $Cl - Ca^{2+}$  water. The results of PCA, hydro-chemical and geochemical interpretation suggest that the great variation in groundwater quality is influenced by the nature of the rock host which modifies significantly the water chemistry, with high concentration of  $NO_3^-$ ,  $NO_2^-$ ,  $NH_4^+$ , suggesting the possible negative impacts of the landfill leachate on groundwater quality. The excess of lead metal may have occurred from the percolation of leachate in the nearby landfill, processing the urban and industrial waste from the municipalities of Rabat. This investigation demonstrates that the hydrochemistry quality of groundwater of Oum Azza could be traced back to both natural and anthropogenic processes.

**Keywords:** Groundwater, mineralization, heavy metals, controlled dump-site.

## Introduction

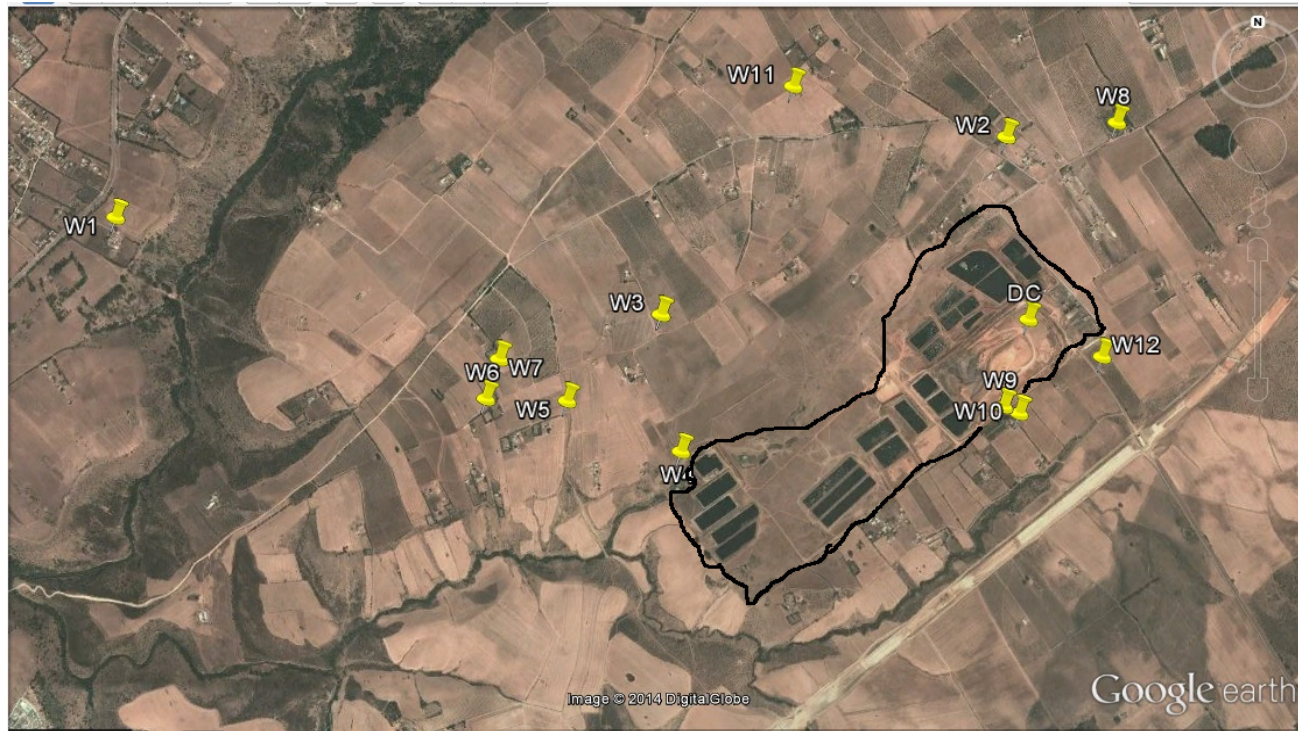
Landfill sites have been a major environmental concern in Morocco, mainly attributed to rapid industrialization and explosive population growth generating five million tons of waste annually. In recent years, a growing number of studies stressed the critical situation of the quality of several Moroccan groundwater reservoirs; especially the pollution caused by the leachate in uncontrolled and controlled landfill sites<sup>1-4</sup>. Indeed, it has a complex and liquid nature that add to the pollution load<sup>5-10</sup>, which is increasingly considered to be a major source of groundwater pollution<sup>2,11</sup>. Subsequently, the impact of landfill leachate on the surface and groundwater became subject of multiple studies using different approaches to assess groundwater leachate contamination. This can be done either by the experimental determination of the impurities, or by their estimation with mathematical modeling<sup>12-14</sup>.

In the present work, a multivariate analysis approach based on Principal Component Analysis (PCA); and geochemical methods were used to assess the impact of the controlled landfill on groundwater quality. A sampling campaign was conducted to measure concentration of various physico-chemical parameters,

including heavy metals in groundwater samples; collected from twelve wells on Oum Azza area (Rabat, Morocco) nearby the landfill.

## Materiel and Methods

**Study area:** The study area Oum Azza (figure-1), is located in the northwest of Morocco, characterized by semi arid climate; the annual precipitation is approximately 555 mm. Major rainfalls occur in October-April, while dry season spawning the rest of the year. The mean monthly temperatures vary between 12.6°C and 32.5°C. The study area is occupied by low-intensity agricultural land and is endowed with a waste treatment center, which provides an environmental advantage to the area. Howbeit, we cannot ignore the risk of eventual percolation of leachate into groundwater. The area is marked by the predominance of primary fields, indeed the bedrock of the main formations in the region, flush locally over much of the plateau consists mainly of schist Visean age (Primary) fractured and cut by veins of quartzite. The carbonate minerals (calcarenes, limestones) are the predominant mineral. The major tectonic phase that affect the stand since carboniferous does not allow to precisely highlighted a particular type deformation.



**Figure-1**  
**Map showing the sampling location taken by Google earth.**  
**W: well, DC: controlled Landfill**

**Sampling and analytical methods:** For this study; twelve groundwater samples were collected in June 2010. In order to avoid evolution of samples and obtain representative values of ambient condition; the pH and electrical conductivity (E.C) were measured in situ immediately after sampling.

Whilst the rest of parameters; nitrate, nitrite, ammonium, sulfate and orthophosphate were analyzed by spectrometry according to AFNOR standards NFT 90-013, NFT 90-012, NFT 90-015, NFT 90-040, NFT 90-023, using a jascov-530 molecular absorption spectrometer controlled by a computer. Sodium and potassium concentration were measured using flame photometer, according to AFNOR standards NFT 90-042. Alkalinity and hardness were measured using titration method. Organic matter was determined by oxidation with potassium permanganate in an acid hot medium. The dosage of Chloride was carried out by the standards titration method (Mohr method). Calcium and magnesium was determined by the complex method using ethylenediamine tracetac acid. The concentrations of cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb) and zinc (Zn) were determined using SpectrAA-20 (Varian) atomic absorption spectrometer.

## Results and Discussion

**Physico-chemical characteristics of groundwater:** Table 1 gives summary of the results obtained from this study for the chemical composition of the groundwater samples. The pH is

slightly neutral, with values ranging from 6.38 to 7.0. The E.C of groundwater is in the range of [623  $\mu\text{s}/\text{cm}$  - 2200  $\mu\text{s}/\text{cm}$ ], which indicates the high mineralization of groundwater. This strong mineralization observed in water samples near the landfill, is an indication of its influence on the water quality. lead to the assumption in its effect on the water quality.

The high values of total hardness 35°F confirmed the severe charge by calcium and magnesium; which classified waters in the category "very hard water".

The order of abundance of cations is  $\text{Ca}^{2+} > \text{Na}^{+} > \text{Mg}^{2+} > \text{K}^{+}$ , the majority of samples exceed the desirable limit of Ca (75mg/L) which is derived from minerals formation of underlying carbonate like calcarenites. However, all samples are below health guidelines of Mg (50mg/L), except samples W9 and W10. The concentration of ions is as follow:  $\text{HCO}_3^{-} > \text{Cl}^{-} > \text{SO}_4^{2-} > \text{NO}_3^{-}$ . Concerning Cl ion, our result show that the concentration in the majority of the samples exceed the limit of Cl (250mg/L).

Therefore, all the values of sulfates are conform to within the standards of WHO (250mg/L). Bicarbonate ions represent the first dominant anions in the study area. The richness of this element is due firstly to the dissolution of bicarbonates, and secondly is derived from carbon dioxide gas from both the atmosphere and the soils.

**Table-1**  
**Statistical summary of physico-chemical parameters**

Variable	WHO	Max	Min	Mean
pH	6.5-8.5	6.38	7.44	7.03
C.E	750	1945	474	1131
Cl <sup>-</sup>	250	372	71	202.94
Mg <sup>2+</sup>	30	55.94	10.70	30.238
Ca <sup>2+</sup>	75	206	29.65	91.96
Na <sup>+</sup>	50	229.8	40.60	127.85
K <sup>+</sup>	100	10.50	0.50	3.78
NO <sub>3</sub> <sup>-</sup>	50	2.21	60	21.76
NH <sub>4</sub> <sup>+</sup>	0.2	3.96	0	0.45
NO <sub>2</sub> <sup>-</sup>	0.2	0.32	0	0.04
PO <sub>4</sub> <sup>2-</sup>	0.5	0.48	0.09	0.23
SO <sub>4</sub> <sup>2-</sup>	250	60.94	4.29	28.20
Hardness	50	61.40	11.80	35
Pb (ug/L)	10	20.04	13.45	7.58
Cd (ug/L)	3	< 2	< 2	< 2
Cr (ug/L)	50	1.07	0.2	0.65
Zn (ug/L)	5000	0.19	0.0026	0.04
Cu (ug/L)	2000	0.007	4.87	2.40

Other anthropogenic emissions of carbon dioxide also increase bicarbonate in groundwater bodies as well; such as dioxide carbon gas originating from controlled dump-site nearby, as a result of oxidation of organic matter and bicarbonates from sulfate reduction of organic materials in the aquifer<sup>15</sup>; as shown in equations 1 and 2<sup>16</sup>.



The amount of nitrate concentration is higher than the standard fixed by WHO (50mg/L), especially in well 6 (60mg/L). The absence of minerals source of nitrate in the study area cannot explain the increase concentrations of NO<sub>3</sub><sup>-</sup>; it should be ascribed to some non-natural processes, such as proximity to the controlled dump-site, septic tank and fertilizers application<sup>17-22</sup>. Mor<sup>16</sup>, have reported that the increasing of NO<sub>3</sub><sup>-</sup> concentration in groundwater could be due to wastewater dump at the disposal site and likely indicate the impact of leachate.

The presence of nitrite varied from 0.04 mg/L to 0.32 mg/L, it exceed the standard limit (0.1mg/L). The concentration of NH<sub>4</sub><sup>+</sup> ranged from 0.45 mg/L to 3.96 mg/L, the values exceed the standards of WHO (0.5mg/L); they likely indicate their origin from leachate. A very low concentration of orthophosphate was also observed in water samples and its concentration varied from 0.09 mg/L to 0.48 mg/L.

With regard to heavy metals being analyzed, Cu and Zn are characterized as undesirable metals in drinking water. Following WHO<sup>23</sup> recommendations, concentrations above 2mg/L and 5mg/L in water respectively, are unacceptable for drinking purposes. Nevertheless, the copper concentration of all samples of this investigation ranged from 0.2 to 8.92 ug/L; significantly below the WHO (2000ug/L) recommended health-based guideline value. Similarly, Zn shows low concentration, the rang being 0.0026ug/L to 0.19 ug/L. The situation likely indicates that those metals may be absorbed by the soil or by organic matter.

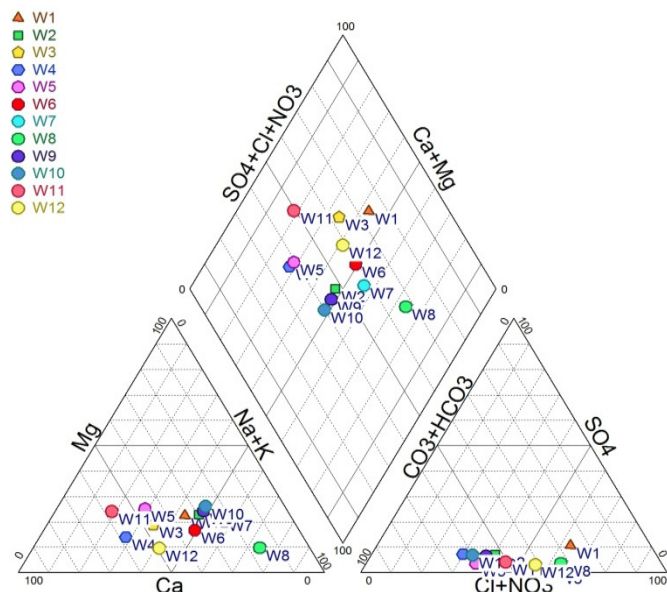
The Pb, Cd, and Cr metals, are characterized as toxic for drinking water. All samples respected the indicated limits of those pollutant metals, respectively, excepted the wells W<sub>2</sub>, W<sub>8</sub> and W<sub>12</sub> which indicate respectively the higher values of Pb than the WHO recommended; 12.22 ug/L, 13.88 ug/L and 10.88 ug/L.

This excess may be occurred from the percolation of leachate in the nearby landfill, which processes the urban and industrial waste from the municipalities of Rabat. Indeed, leachate is the main vector of transmission of metal pollution from waste disposal sites<sup>24</sup>. Waste can also be a source of emergence of lead<sup>25,26</sup>. Moreover, most of the urban waste contains this pollutant, such as batteries, paints and paper cardboards. Fevrier<sup>27</sup> showed that the majority of metal pollutants may undergo when they pass through the soil, by bio-physico-chemical transformations, which have the effect of promoting their mobility and transport.

The metal mobility is also controlled by physical sorption mechanisms, and landfills have an inherent *in situ* capacity for minimizing the mobility of toxic heavy metals<sup>28</sup>. Heavy metals remain in the waste or at the waste-rock interface as a result of redox controlled precipitation reactions<sup>29</sup>. This mechanism reduces the migration of the heavy metals into groundwater. Generally, the concentration of those elements does not exceed the standards. However, there is health-hazard risk; by bioaccumulation effect, especially as water wells are used for irrigation and animal watering.

**Hydrochemical water type:** The concentration of major cations and anions; obtained from the groundwater analysis, are displayed on the Piper diagram (figure-2). It shows the dispersion of anions and cations; contained in water samples, indicating that those variables could be associated either to lithological heterogeneities or human activities. Three main types of water were identified; The first type is HCO<sub>3</sub><sup>-</sup> - Ca<sup>2+</sup> - Mg<sup>2+</sup> (W<sub>2</sub>, W<sub>9</sub>, W<sub>10</sub>, W<sub>5</sub>, W<sub>4</sub>, W<sub>11</sub>), the second type is Cl-Na (W<sub>7</sub>, W<sub>8</sub>) and last one is Cl-Ca (W<sub>6</sub>, W<sub>1</sub>, W<sub>3</sub>, W<sub>12</sub>). The appearance of Cl-Ca facies reflects the exchange of sodium in the water by calcium. Moreover, the abundance of ions HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> is broadly derives from weathering processes including the dissolution of carbonate and calcarenites minerals that are abundant in the studied area . The hydrochemistry of

groundwater was controlled primarily by water-rock interaction than by the anthropogenic pollution.



**Figure-2**  
**Piper diagram for water samples**

**Multivariate statistical analysis: PCA:** The PCA method has been extensively used to define the evolution and the origin of chemical parameters of groundwater, and also to group the commonly collected water quality data and exhibits the correlations between chemical parameters. In this investigation, PCA was used to extract two principal components that control the chemical variability in groundwater.

Figure-3 shows the position of Wells and the correlation of chemical parameters in the plane defined by the axes of components 1 and 2. The components Pc1 and Pc2 explains 23% and 18.23% of the variance, respectively. The ACP performed shows that the groundwater isolates in groups of a different quality, according to their chemical potential. Therefore, the water samples were gradually passed into nitrogen -rich waters to highly mineralized water.

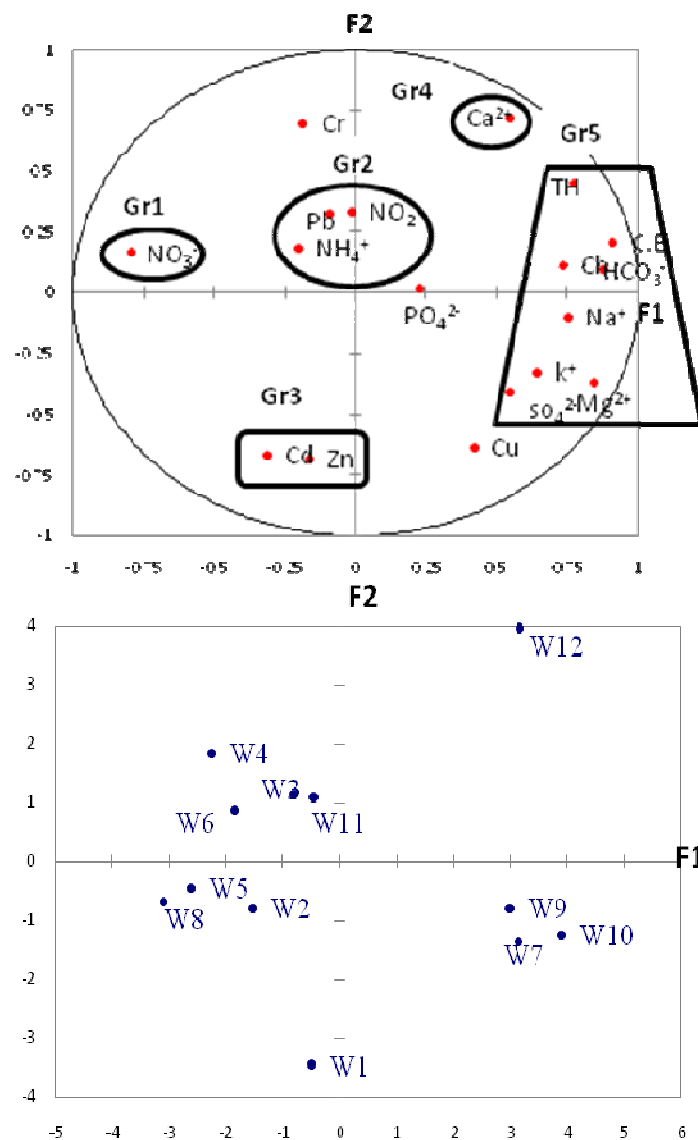
The lecture of the position of wells and the loading of chemical parameters in the plane is defined by the axes of components 1 and 2 shows the individualization of following groups (figure-3)

Group 1 includes the well W6, it is characterized by the greatest amount of nitrate, reflecting the advanced organic pollution.

Group 2 and group 3 occupies a middle position on the negative side of axis F1, and opposed according the axis F2. The group 2 involves the wells W3 et W11, it is characterized mainly by the pollution from NH<sub>4</sub> and NO<sub>2</sub>. Whilst, the group 3 is characterized by the highest levels of Zn and Cd, it involves the well W1.

Group 4 contains the well W<sub>12</sub>, it is characterized by high levels of calcium, with modest mineralization.

Group 5 it is located on the positive side of the F1 axis, it is represented by wells W10, W7 and W9, characterized by high concentrations of bicarbonate, chloride and, by its hardness, which evokes a strong mineralization, that reaches 2,200 us / cm.



**Figure-3**  
**Parameters Circle of correlation for the first two components, Plane factorial F.F2 of wells**

PCA highlights the physico-chemical qualitative differences of the studied water. The presence of a strongly mineralized pole that characterizes water wells P7, P9 and P10 located in the Paleocene limestone; reflects the high concentrations of chloride, calcium and bicarbonate, which can be attributed mainly to the dissolution of calcium carbonate (CaCO<sub>3</sub>) and

magnesium carbonate ( $MgCO_3$ ). However, high concentrations of sodium and low levels of magnesium, argue in favor of adsorption of calcium and release of sodium.

The waters of the other wells deviate from mineralized pole to individualized and defined groups with different chemical characteristics, with less mineralization and high organic load, likely related to Landfill Leachate Oum Azza nearby.

In conclusion, the study shows that mineralization of groundwater is governed mainly by the hydrogeochemical reactions between water and crossed lithological formation. However, the negative impact of the nearby landfill, is probably involved in the acquisition of the metal composition of some wells, particularly the lead metal. Indeed, in the environment the natural processes contribute rarely to these great concentration. The problems of metallic elements related to the acute toxicity are rare. More worrying are the long term effects of micropollution which relate these toxic elements in water at very low levels, such as Cd and Cr.

## Conclusion

The different, but complementary, approaches used, such as PCA, geochemical and hydrochemical methods, have generated several important results. Analyzed groundwaters are highly mineralized with significant alkalinity. Those waters are characterized by high hardness that makes them inappropriate for human consumption. Moreover, the waters were divided into three main hydro-facies; calcium and magnesium bicarbonate water -  $HCO_3^- - Ca^{2+} - Mg^{2+}$ , sodium-chloride water  $Cl^- - Na^+$ , and chloride water  $Cl^- - Ca^{2+}$ . We also note that the mineralization of groundwater is mainly governed by natural processes including; the water-rock interaction and ionic exchange phenomenon. Indeed, the crossed geological limestone matrix plays a significant role in the variation of groundwater hydrochemistry. However, high concentrations of pollution indicators  $NO_3^-$ ,  $NO_2^-$  and  $NH_4^+$  in well W6 can be the source of contamination of water by effluent waste from the nearby controlled landfill.

Except lead, the concentration of these elements does not exceed accepted standards. Nevertheless there is health-hazard risk of local population; by bioaccumulation effect, especially as water wells are used for irrigation and animal watering. Hydrochemical groundwater quality in Oum Azza area, is influenced by both natural and anthropogenic factors.

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