Impact of the household solid waste discharge and the sewage waste water plant of the city of Khouribga (MOROCOO) on the physico-chemical properties of water in nearby wells.

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Abstract: Our study focuses on monitoring the spatial evolution of a number of physico-chemical parameters of wells waters located at different distances from the discharge of the city of Khouribga (S0 upstream station, S1, S2 et S3 are respectively located at 5.5, 7.5, 11 Km away from solid waste discharge of the city). The absence of a source of drinking water in this region involves the population to feeding on its groundwater wells. Through the results, we note that most of the analyzed parameters exceed the potable water standards from S1. At this source of water, we find that the conductivity (1290 $\mu mScm^{-1}$; Standard 1000 $\mu mScm^{-1}$), Total Hardness TH (67.2°F/ Standard 50° F), Ca^{2+} (146 mg l^{-1} standard 60 mg l^{-1}), Cl^- (369 mg l^{-1} standard 150 mg l^{-1}), NaCl (609 mgl^{-1}), Methyl orange alakanity "M. alk" (280 mg l^{-1}) greatly exceed the drinking water standards. By following these parameters, it is obvious that some values have decreased in the downstream stations, while others become important. We find that the conductivity is always higher than 950 $\mu mScm^{-1}$; the TH registers 72°F in S3; Ca^{2+} is in the range of 153 mg l^{-1} in S3, Cl^- and $NaCl^-$ reached 426 mg l^{-1} and 702 mg l^{-1} respectively in S2, M alk becomes higher and reaches 430 to 350 in S3. At the wells S2, we found that the nitrites are well beyond the standard 1.05 mg l^{-1}. Whereas, at the control station S0, the values are lower or at the limit of drinking water standards: conductivity (452 $\mu mScm^{-1}$), TH (34 F°), Ca^{2+} (68 mg l^{-1}), Cl^- (157 mg l^{-1}), $NaCl^-$ (258 mg l^{-1}), M alk (220 mg l^{-1}). Thus, the diagnosis reveals the presence of a high pollution caused by the leachates of the household waste discharge and by the effluents of the sewage waste water plant (SWWP). The phenomenon of the water hardness could, also, be generated by the processes of erosion, leaching and soil infiltration in the region (phosphate layers, intercalated layers of marl and limestone), phenomenons also caused by the acidity due to this surrounding pollution. The source S1 is the nearest surrounding site of the discharge and the most affected by the phenomenon of pollution, especially, it is near to a superficial water source S'1 polluted by the effluents coming from the sewage waste water plant of the city. In the light of these data, we can deduce that the consumption of this water from S1 does not conform the standards of drinking waters, and could affect the human health.

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1. Introduction

Springs and groundwater are traditionally the preferred water for drinking, because they are better protected from pollution than surface water. However, certain minimal characteristics are required so that they can be of use to the production of drinking water, which must satisfy standards of physico-chemical and biological quality. The production of drinking water from natural water usually requires appropriate treatment adapted to correctible quality parameters to meet drinking water standards. On the other hand, the diffusion of the hydric transmission diseases as the typhoid and the dysentery is related to the state of the consummate waters. While, an overdose in chlorine for the disinfection and the purification of the water may lead to the production of organo-halogenes compounds which, eventually, can cause mutagenic and carcinogenic effects (Guergazi and Achour, 2005).

Since the antiquity, the human activities did not stop modifying the natural conditions of the aquatic ecosystems. Other changes are mainly caused by the natural biogeochemical processes (Meybeck and Helmer, 1992).

In Morocco as all around the world, for several years, these ecosystems are gradually degraded under the influence of the strong expansions of the human activities (agricultural, industrial and other) (Ben Said, 1994; Talami et al., 1997; Cherifi, 2001; Tazi et al., 2001).

In the city of Khouribga, given the climatic and geomorphologic characteristics of the region, the available resources of waters are very limited. The absence of important relief decreases the pouring of the winter rains which come from the west. So, the weak availability of the subterranean resources is due to the hydrogeological nature, since, the infiltrated quantities of water are for their major part drained towards the plain of Tadla where they feed the deep groundwater (Samihi, 2009).

This scarcity of water is aggravated by the industrial need for phosphates washing, that is the equivalent of the half of the city's needs of potable water. Fortunately, a new SWWP was built to allow the treatment of waste water of Khouribga for the production of 5 millions m^3/year for the wash of the phosphate.

On the other hand, few studies were realized in the region about the preservation of the quality and the subterranean water resources. The sources of pollution caused by the various human activities in the city are numerous and diversified. The dumping of the solid waste and the disposal of urban waste water can engender a big risk of pollution (Seiler et al. 1999; Kass et al. 2005; McArthur et al. 2012; Badri et al. 2012).

In fact, the dumped waste, in the contact of the rainwater, undergoes biological and physico-chemical transformations giving leachates (Tränkler et al. 2005; Kulikowska and Klimiuk, 2008). Several studies showed that these leachates constitutes one of the main vectors of the pollution besides of the solid pollution itself (Al-Yaqout et al. 2003; Alkassasbeh et al. 2009). They transfer, an important organic, mineral pollution, which is sometimes toxic (Loizidou and Kapetanios, 1993; Kerbachi and Belkacemi, 1994).

The evaluation of the impact of an anthropological pollution and the degree of the deterioration of the quality of the water is possible through the measure of a set of physico-chemical and bacteriological parameters. In the case of a deterioration considered important, water will not be considered as potable for human consumption. It can then be used as such for other purposes (irrigation,…) or it will have to undergo appropriate treatment to recuperate its drinkability.

We, thus, have studied the characterization and the spatial evolution of the quality of the water of wells according to their distance with regard to the household waste discharge and the sewage waste water plant SWWP. The objective is to determine the effect of these various kinds of pollution on the quality of subterranean waters and also to define globally the efficiency of the auto-purifier power of water sources in prospected zones.

2. Material and Methods

Area of study

The Khouribga province (world capital of phosphate production) is located in the center of Morocco at 120 km southeast of Casablanca. It covers a total area of 4250 km^2, which present 0.6 % of the national territory. The population of the province is 499 144 inhabitants, about 1.67% of the national population (RGPH, 2004). Half of it (about 53%) is concentrated in the urban zone of the city. However, the water system is less important because the permeability of limestone does not allow a normal flowing (Bleuchot, 1969).

Discharge and SWWP of Khouribga city

The hazardous household solid waste discharge site is located at about 2 km from the exit of the city, with an area of 41 ha. The site looks like an old quarry of the OCP (PFD, 2011). The waste production is estimated at 124,100 tons per year generated by a population estimated of about 200 000 inhabitants (196 000 in 2005). The sewage waste water plant SWWP is neighboring the discharge and also emplaced at 2km in outskirts, this SWWP purified about 5 millions m^3 of waste water/year.

Climatic conditions of the region

The average annual rainfalls are of about 568 mm. The temperature is in the average of 25 °C. The maximum registered is 40.2 °C in July –August, and decreases since mid-September until February (4.7°C) (PFD, 2011). The wind direction is generally from NW to SW. The most violent of them occur in the summer (between 10 and 30 m/s). Since spring, drying winds (type chergui) are frequent and give rise sometimes to important temperature increase, but of limited duration. The average duration of wind exposure is 5 hours in winter and 12 hours in summer. The warmer months, when evapotranspiration is the highest, are: July and August. The humidity in summer can reach very low values (up to 10% of relative humidity) (PFD, 2011). The values of the groundwater temperature in the region are between 25 °C and 30 °C. The level of water depth starts from 50 m to 100 m.

Choice of stations: water source sampling

The waters studied are the groundwater, the samples of which have been collected from the wells at different distances from the discharge and SWWP:

- In the S0 station, the water has been sampled from a well situated in the upstream (in the outskirts of the city of Khouribga) before the zone of the household waste discharge and sewage waste water plant SWWP, this station is considered as a standard station.
- The other samples are taken from stations or wells situated at various distances from the discharge and the SWWP, because the general slope of the groundwater is directed westward (Hazan and Ferre, 1964):
- S1 at 5.5 km, S2 at 7.5 km, S3 at 11 km southwest from the discharge and SWWP.
- S'1 presents a superficial water source polluted by the effluents of SWWP and is near the station S1.

Leachates discharge's sampling

- L1 presents the juice obtained from the heap of waste just after the collection or before the storing.
- L2 presents a leachate got from an one-year-old heap.

Methods of analysis

Underground water quality is characterized by a number of physical and chemical parameters. The methods of analysis are:

The physico-chemical parameters (temperature, pH, electric conductivity, turbidity and dissolved oxygen) were measured in situ: The temperature with a thermometer, the pH and the conductivity with a field pH-meter and conductimeter. The total hardness TH and the alkalinities (P alk.: Phenophthalein alkalinity, M alk.: Methyl orange alkalinity) are respectively, determined by complexometry to the EDTA and by dosage using the sulphuric acid (Rodier, 1984).

The macro-elements (HCO_3^-, Cl^-, $S0_4^{2-}$, NO_3^-, Ca_2^+, Mg_2^+, Na^+ and K^+) and the micro-elements (Fe, Mn, Po_4^{3-}) were measured in the laboratory fifteen day maximum after the sampling. Until this time, the samples were conserved in cold room at 4°C, shielded from the light. Depending to the ion to be analyzed, various techniques, described in the general works of chemistry, have been used (Oga et al. 2009):

· The volumetry for the ions HCO_3^-
· The complexometry for the ions Ca_2^+ and Mg_2^+
· The Mohr's method for the ions Cl^-
· The turbidimetry for SO_4^{2-}
· The colorimetry for NO_3^-
· The flame spectrophotometry for Na^+ and K^+
. The total hardness by compleximetry
. The analyses of heavy metals were made by atomic absorption

3. Results and Discussions

Table 1 and figure 1 present the data obtained on the spatial evolution of the physico-chemical properties of the waters sampled from wells located at different distances from the discharge and SWWP.

The pH of the waters of all the wells is close to neutrality or slightly basic, it is in the range of 6.8 to 7.5. According to the standard of WHO "world health organization" (2004), the pH of a drinking water must be included between 6.5 and 8.5.

In these underground water samples, the spatial variation of the pH shows a decrease well marked between S1 and S2. Then, the pH increases to reach its initial value (S0) in the station S3 (downstream). This decrease of pH at the S2 can be probably generated by an increase of the acidity due to organic acids leached or resulting from the leachates of the discharge and the effluents of SWWP in the station S1 which infiltrate and contaminate the subterranean waters (Vengosh and Keren, 1996). The change of surrounding chemistry land by leachates has been reported also by some searchers (Statom et al. 2004; Tränkler et al. 2005).

The spatial evolution of dissolved oxygen in waters shows a slightly decreasing degree from upstream S0 to downstream S3 (table1). This reduction could be explained by the water pollution caused by the infiltration of the contaminant organic elements and the implication of dissolved O_2 in the processes of oxidation of organic matters "assimilative capacity" (Matsumoto and Tou 2006, Clague et al. 2013). The assimilative capacity refers to the ability of water to cleanse itself from organic or toxic materials (Hosono et al. 2013).

However, the slight evolution of dissolved oxygen values shows the slow power of assimilative capacity, which seems normal because they are subterranean waters with low-speed of flow debit (CCME, 1999).

However, the values of the DCO and the DBO are null, given the very low organic load in subterranean waters. This could be also related to the geological nature of the overlying soil. The same suggestions have been reported by Djermakoye (2005).

The turbidity analysis is also important because suspended compounds and caused the inconveniences in the aspect of the water and its flavor (taste of earth). The suspended compounds are undetected in all our water samples, because they are the subterranean waters and the samples are taken during summer and also this result may be related to the geological nature of superficial layers which are less eroded.

The analysis of heavy metals shows that the values of elements (Cu, Zn, Pb, Ni, Cd, Cr) are under the limit of detection of atomic absorption appliance. As reported in literature, in the subterranean waters, the content of elements heavy metals are generally weak due to their complexations to the organic matters and clays of overlying soil (Elliot, 1986; Amir et al. 2005; INERIS 2006). Burg and Gavrieli (2013) report that the removal of the trace elements is attributed to adsorption that was enabled by a rise in the pH of the contaminated water as it comes in contact with the carbonate host rock.

The spatial evolution of the electric conductivity of waters shows an increasing gradient from upstream S0 to downstream S3 and the highest value is recorded in S1 which is of the order of 1290 $\mu mScm^{-1}$. The evolution of the conductivity is related to the rate of mineralization. A very strong conductivity exceeding 1000 $\mu mScm^{-1}$ testifies an increase in the rate of the salinity of waters and a strong mineralization. We notice well since the station S1, an increase of the rate of salt. The values towards the downstream decreased but they remain important of the order of 976 µmScm^{-1} compared with the value upstream which is 452 µmScm^{-1} (little mineralization of water). In fact, the rate of salt increased (291 mg l^{-1}) in S1 with regard to S0 (193 mgl^{-1}) and remain important to downstream (285 mgl^{-1} in S3). The water has been loaded with mineral elements as result probably of leaching or chemical infiltration of the calcareous overlying layers that must be permeable (Samihi, 2009, El Assel et al. 2013). However, this variation could be also the effect of a punctual pollution because the increase of mineralization from S1, which is near of household waste discharge and SWWP, becomes important. This supposes the acheminement in undesirable mineral elements resulting from an exogenous pollution. In fact, the closest stations to downstream of these pollution resources show higher conductivity and salt rate S1 > S2 > S3. Other authors have also reported that a rise of the conductivity and the rates of salt could be originating from mineral pollution (Vengosh and Keren, 1996; WaterAid, 2006; Chen et al. 2010; Burg and Gavrieli, 2013). Table 2 and 3, show well the high conductivity and the rate of salt in waters polluted by the effluent of waste water S'1 and also in the leachates of household discharge. This confirms the effect of pollution on the rate increase of mineralization or salt (Statom et al. 2004; Tränkler et al. 2005; Chen et al. 2010; Burg and Gavrieli, 2013).

The measured concentrations of chlorides show an important increase from the upstream towards the downstream particularly from the station S1 which presents 384 mg l^{-1}, thus 2 to 3 times the initial value at upstream 157 mg l^{-1}. The chlorides ions may react with the water producing hydrochloric acid which leads locally to a decrease of pH of waters towards the downstream from the station S2. This acidity presents the inconvenience of corrosion in case of contact with copper pipe when the content in chlorides is upper to 150 mg l^{-1} (limit value must not to be exceeded). In our samples, the values exceed this threshold value and present also another risk, which in a high content can lead to the formation of organohalogene compounds that can lead to mutagenic and carcinogenic effects (Guergazi and Achour, 2005).

The values of sulfates increase considerably and reach approximately 10 times the initial value of the upstream station S0 since the station S1. The concentrations ranged from 4.6 mgl^{-1} in S0 station and 44 mg l^{-1} in S1. This important increase may be related to the effect of the surrounding pollution, as suggested by some authors that variation induced by the compositions of the sewage effluents, as well as water-rock interactions (Vengosh and Keren, 1996). In fact, the values of sulfate are very important in waters polluted by sewage waste water S'1 and the leachates of discharge L1 and L2 (Table 2 and 3). The values decrease in the S2 station but they become important at downstream station S3 with 40 mgl^{-1}. This can be explained also by the phenomenon of dissolution of gypsum. In the literature, El Assel et al. (2012) have noticed dissolutions affecting layers of senonien gypsums situated immediately under the phosphated series in Ouled Abdoun. The gypsum is a sulfate of hydrated calcium weakly dissolved in the normal conditions (7 gl^{-1}). However, the contents in our samples remain very low and acceptable between 5 and 44 mg l^{-1} and do not exceed 250 mg l^{-1} (acceptable limit value).

The values of the total hardness of the water (TH) is ranges between 34 F ° (340 mg l^{-1} of $CaCo_3$) and 72 F ° (720 mg l^{-1} of $CaCo_3$), they are superior to the standard of drinking water of about 50°F especially from the station S1. The total hardness expresses essentially the global concentration in ions calcium and magnesium in the water. The water in station upstream S0 is hard to very hard (TH = 340 mg l^{-1} > 300 mg l^{-1}) and is considered of poor quality but can be tolerated. Since S1, the TH is becoming superior to 672 mg l^{-1} and attains 720 mg l^{-1} at S3. The water with the hardness superior to 500 mg l^{-1} is normally considered to be unsafe for domestic use.

The data also show an increase of the M alk. 'Methyl orange alkanity" after the station S1. The

M alk. measures the rate of hydroxides, carbonates and bicarbonates of water. The P alk. 'Phenolphtalein alkanity" represent the hydroxide content and the half of the carbonate content.

When the difference (TH-M alk) is positive in natural water (table 1 and 2), the difference said to represent the permanent hardness (related to strong acid salts), The M alk itself is called temporary hardness:

Total Hardness TH = Permanent hardness (TH-M alk)+ temporary hardness (M alk)

When TH < M alk, as like in leachates (table 3), the M alk no longer represents temporary hardness, but only the alkaline bicarbonates that may be bonded to sodium, potassium, ammonium.

The Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium sulfate and/or magnesium sulfates in the water, which do not precipitate out as the temperature increases. Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). However, unlike the permanent hardness caused by sulfate and chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime. So, M alk. measures the alkalinity of the water and determines its buffering power, that is the capacity of influence of acidic or basic products on pH of the water. So, the more the M alk. is high, the more it is difficult to make variation in the pH of the water. While, a water with low M alk. presents a poor resistance capacity when acid substances are added lead generally to the degradation of the installations (Rodier, 1996). In natural waters, the alkalinity expressed in HCO_3^- varies generally from 10 to 350 mg l^{-1}. It could be increased by contributions of urban origins (phosphates, ammonia water, organic matters) or industrial origins (basic or acidic products). So, knowing these values in water is essential for the study of the aggressiveness of water because they depend on the calco-carbonic balance. The underground water in general tends to be harder than surface water. When the underground water becomes rich in carbonic acid, it will have a big dissolving power during its contact to soils or rocks containing significant quantities of minerals such as calcite, gypsum and dolomite. Thus, following this later described process due to acidity of water which is forced further by the pollution, it acquires a big a high hardness.

In fact, calcium is very predominant in the underground waters of this region. Their contents oscillate between 68 mg l^{-1} and 153 mg l^{-1} from S0 to S3. The station of upstream S0 presents a value within the norms (68≈60 mg l^{-1}), but after the station S1, the waters of the downstream stations presents concentrations superior to the accepted standards > 60 mg l^{-1}) (Oga et al. 2009). The magnesium contents increase significantly since the station S1 and vary from 18 mg l^{-1} to 31 mg l^{-1}.

In fact, the dissolution of Ca^{2+} and of Mg^{2+} results mainly from the infiltration of surface waters through the rocky layers limestones and dolomitiques. This dissolution can be increased by the presence in the water of carbon dioxide resulting from the atmosphere and the superficial layers of the ground more or less polluted or others sources of surrounding pollution (Tardat and Beaudry, 1984, INERIS, 2004; Oga et al. 2009; Blum et al. 2002).

In fact, taking account of data obtained from the analysis of the sample of water polluted by the effluent of waste water S'1 passing near the station S1. We notice that Ca^{2+} is the only element which presents a value more important in the sample of waters of wells than that of superficial water source polluted by the waste water effluent S'1 (table 2).

We can deduce that the rise of the content of Ca^{2+} is due to both phenomenons described previously, the surrounding pollution and dissolution of overlying layers of calcareous nature (Vengosh and Keren, 1996; Neal et al. 2002). In fact, the region is formed by the sedimentary layers of phosphate, and of intercalated marls and limestones (El Assel et al. 2012).

As well as, the values of orthophosphate showed a slight tendency to increase from upstream to downstream, however, this value has doubled in station S1 0.03 mg l^{-1}, and presented two times the value in water of well at upstream 0.017 mg l^{-1}. This is probably related to the both phenomenons described previously (pollution and erosion) (Neal et al. 2002). The contributions of pollution from wastewater effluents from SWWP and leachates of household waste discharge have been shown in the data in Table 2 and 3. The value of PO_4^{3-} in the effluent S'1 achieves to 4.07 mg l^{-1} and also in leachate it is upper to 4.5. The origin of this large load of PO_4^{3-} in the effluent wastewater could be various, either of household and / or industrial and / or agricultural origins (Neal et al. 2002). Also, this great value could be related to the dissolution of phosphate caused by the acidity generated by surrounding pollution since the land in the region has a phosphate nature.

El Assel et al. (2012) report that in the sedimentary basin of Ouled Abdoun (Region of Khouribga), the phosphate series is formed by a regular intercalation of phosphate and marno-calcareous layers of about 50 m. However, we notice that the values in well water remain very low compared to drinking water standards of 5 mg l^{-1} described in some studies (JORA, 2005).

The contents of ion potassium are weak of about 1.5 mg l^{-1}. Whereas sodium is the most abundant cation and the recorded contents lie between 101 mgl^{-1} and 276 mg l^{-1}. In fact, the content of sodium chlorides shows a very strong increase starting from the station S1. This would be probably related to an increase in dissolution by going deep saline layers halite that overlie wells since the S1. However, these contents in sodium are moderate and they are in the standards of drinkability.

Concerning the nitrogenous compounds, we begin with the nitric nitrogen NO_3^- of which the contents in the water, especially subterranean water, is of a major importance to determine also the quality of the water and the related sanitary risks. Its excessive presence can provoke an important problem of public health such as the methemoglobinemia and a risk of cancer. The highest value of NO_3^- is registered at the upstream station S0 about of 2.48 mg l^{-1}, in fact this station is surrounding the agricultural fields (Figure 1). In fact, the main reason of the presence of nitrates in subterranean waters could be due to the agricultural practices, which consists of abundant use of industrial fertilizers strongly charged in nitrate. The latter reaches subterranean waters by the land- infiltration. However, this concentration registered in station S0 remains widely lower than the WHO standard (50 mg l^{-1}).

In the downstream, the contents in nitrates are relatively weaker due to accelerated assimilative capacity of the nitrate element by bacterial entities (Rivett et al. 2008, Hosono et al. 2013). Although, in this station S1, we note the presence of other sources of pollution which are sewage effluents at the source S1' and leachates of discharge. In the leachates, the values are of the order of 2.2 mg l^{-1} (for L2) and in the source S '1 are of the order of 1.45 mg l^{-1} compared a value of the order of 0.52 mg l^{-1} in S1 (Table 2 and 3). We can say in this case that pollution did not affect the change in nitrate concentrations in groundwater.

The spatial evolution of the ions ammonium NH_4^+ shows a growing gradient from upstream to downstream (Figure 1), conversely in the content of dissolved oxygen and also those of nitrates testifying the reduction in the rate of oxidation of the NH_4^+ to nitrate element. However, the values remain low with regard to the WHO standards fixed at 0.5 mg l^{-1}. Ammonia in water is an indicator of possible bacterial, sewage and animal waste pollution (WHO, 2008, Amir et al. 2010; Chen et al. 2010; Lockhart et al. 2013). However, the elimination of the ammonia in water is possible through the chlorination practice (Guergazi and Achour, 2005).

On the other hand, maximal values of the order of 15.8; 25 and 62 mg l^{-1} are recorded in the source S'1 where waters are polluted by waste water and also in the leachates L1 and L2, respectively (table 2 and 3). We can say that the pollution had no effect on the variations of contents in ions ammonium NH_4^+ in the subterranean sources, which is due to accelerate denitrification process as mentioned in some works (Hosono et al. 2013).

The Nitrites NO_2^- presents the intermediate and unstable element between the both of the forms of nitrogen NH_4^+ and NO_3^-. The contents in nitrites, have probably, no risk as far as they are very lower than the standard of the WHO fixed to 0.1 mg l^{-1} in all stations except in the station S2 (Figure 1). In this station S2, this element presents a high value of about 1.05 mg l^{-1}. The level of this element in the polluted source does not exceed 0.06 mg l^{-1} in S'1, 0.46 mg l^{-1} in the leachates L1 and 0.8 mg l^{-1} in the leachates L2.

While, the value of the element NO_3^- decreased from 2.48 mg l^{-1} in S0 to 0.19 mg l^{-1} in station S2. Thus, the high value in S2 is probably related to a big reduction of the nitrite NO_3^- and a lack of oxygen (Figure 1).

Thus, the value 1.05 mg l^{-1} of nitrite NO_2^- in the station S2 presents a risk in case of human consumption of water from this well. Its presence in important quantity degrades the quality of the water. The nitrite is powerful oxidizers which have the capacity to transform the hemoglobin to the methemoglobin, making the blood incapable to transport the oxygen up to the tissue. The nitrite can also cause a cancer (El Kory Ould-Cheik et al. 2011). The WHO suggests a threshold value that it must not be exceeded of about 3 mg l^{-1} for an exposure with short term and only 0.2 mg l^{-1} for a long-term exposure (WHO, 2008).

Usually, natural water does not contain nitrogenous compounds. Those, resulting from the decomposition of the living matter by micro-organisms, are mineralized completely to gaseous nitrogen or remain in small quantity at the soil in stable organic form or other available mineral forms (Matsumoto and Tou 2006; Hajhamad and Almasri. 2009, Hosno et al. 2013). It is the increase of the quantity of available nitrogen in the ground that creates an imbalance between the contribution and the consumption which produces an excess of nitrogen that is finally passes towards the superficial water and underground water (Kass et al. 2005; Lockhart et al. 2013). This nitrogen is mainly in the form of nitrates and ammonium and could be bringing through human activities. Indeed, the polluted source by waste-water and the leachates from household waste discharge are very loaded with these nitrogenous forms (Table 2 and 3).

Accordingly, from the above mentioned data, we notice that water in zones since station S1 exhibit contents superior to the WHO standards for almost all the measured mineral elements (WHO, 2008).

In fact, according to the literature, the region is characterized by two phreatic surfaces (water table), one of the Eocene and other one of the turonien. The Eocene covers 7000 Km^2 and circulates in the Eocene fields in the region of Beni Oukil, El Bourouj until the border of Tadla (Figure 2). Then, it sinks to southward under the region of Tadla region where it becomes confined. It is unconfined at the level of the outcrops and is in the loading under the plain of Tadla. The chemical quality of the water of this phreatic surface was shown to be variable of lesser quality than that of the turonien one (Hammani et al. 2004).

Effectively, vulnerability depends on the type of phreatic water, unconfined versus confined, and on the mode of water circulation in the aquifer. The confined water table is better protected by the waterproof layers which overcome them. Their superficial water supply is more limited, and, so easier to be protected. Whereas, the unconfined water table is the most vulnerable, the pollutants of superficial origin can spread freely in the soil and in the unsaturated zone until piezometric level. On the other hand, the seasonal vertical fluctuation of the piezometric level help to “rince” the particules of the unsatured zone and to carry the absorbed substances.

In fact, numerous studies have reported the change of the quality of subterranean waters under the influence of the hydrological, Geo- and hydro-chemical processes, but also strongly by climatic, geo-morphological condition, the kind of ground and the anthropogenic activities such as the contribution of the chemical compounds and the bacterial entities via the various sources of pollution (Krysanova and Becker, 2000).

In fact, a slightly acid rain due to its content in dissolved CO_2, during its infiltration in the soil and the subsoil, it becomes laden with ions, and acquires physical and chemical properties that characterize the water of the whole water table. Thus, underground water is more or less mineralized depending on the following parameters: a) the nature of the crossed rocks and the minerals met during the infiltration; b) the contact time of water with the minerals, so the percolation speed of the water in the subsoil; c) water renewing speed of the water table by the infiltrated water. The salinity also increases with depth. But the mineralization acquired by the water remains more or less stable and it is used to characterize a hydro-chemical facies. Each major change in this facies is indicative of a surrounding anthropogenic pollution.

In this study area, some research works have reported that according to its properties, the water in the first water table has a lower quality compared to water in a deep water table, which is actively exploited by farmers and the population of the region (Hazan and Ferré, 1968, Hammani et al. 2004)

This is in accordance with the data we obtained on the changes in the physico-chemical properties of water as a result of environmental pollution starting from S1, in addition to the impact of erosion, dissolution and infiltration of chemicals dissolved.

We observe also, a good correlation between the spatial variation of physical-chemical parameters of water of wells since station S1 and those obtained from a surface water source polluted by the discharge of wastewater effluent S '1 (Table 2) and also with the parameters of the leachates of different ages from the household waste discharge (table 3).

Thus, the deterioration of the natural quality of groundwater in this area could be largely related to these human activities.

The sewage treatment station SWWP is of activated sludge type and located on the edge of town on the way to El Borouj (Jouraiphy et al. 2005). Geotechnical surveys at the site of the SWWP showed that the basement consists of clayey silt formations, whitish tuffs and limestone marl. In this area the topographic and geological conditions favor low infiltration of water trickling into the groundwater due to the low permeability of the facies of the unsaturated zone (2.5×10^{-5} to 1.2×10^{-4}) (Bleuchot, 1969). Thus, we can conclude that the extent of pollution in this area could be greater in cases where the underlying land STEP do not have a low permeability.

Besides, the discharge of the town is hazardous or uncontrolled and constitutes a real threat on the quality of waters of this ecosystem. The site of the discharge belongs to the plateau of phosphates, it is endowed with an average permeability as shown by soundings and the topography of the site. The leachates which are produced from household waste could infiltrate towards the in-depth substrates, besides the elements which can be leached in rainy time and transported by winds towards the downstream, this has been also reported by some authors as Tränkler et al. (2005).

Numerous authors have demonstrated that the leachates produced by household waste discharges convey an important organic and mineral pollution, which sometimes is toxic (Kerbachi and Belkacemi, 1994, Al-Yaqout et al. 2003; Alkassasbeh et al. 2009). Yasuhara et al. (1997) have demonstrated about 190 organic compounds in the leachates of the household waste discharge in Japan.

However, it is difficult to establish an average composition of the leachates (Statom et al. 2004, Tränkler et al. 2005). The study of leachates shows a huge complexity because of the big variation of their composition from one time to another (Yasuhara et al. 1997; Statom et al. 2004, Tränkler et al. 2005; Sadani, 2005). Each leachate is a particular case depending on the nature of the stored waste, of the management of the site and its evolution state and even the climate, the phase and the period of data sampling (Kerbachi and Belkacemi, 1994; Yamada and al. 1999; Al-Yaqout et al. 2003; Statom et al. 2004; Tränkler et al. 2005; Kulikowska and Klimiuk, 2008).

So, we can conclude that the household waste discharge and the effluents of waste water present the sources of pollution of the waters of these wells. The pollution of groundwater by waste water effluents has been also announced in numerous studies (Vengosh and Keren, 1996; Seiler et al. 1999; Kass et al. 2005; Badri et al. 2012; McArthur et al. 2012). It is pollution that we can classify it as historic because it backs to a time when the environmental concerns were few. However, since the underground water is, once are contaminated by a pollutant, pollution contamination is of long duration.

Captions

Table 1. Physical and chemical properties of water taken from wells: at S0 upstream (on the outskirts of the city of Khouribga) and at different distances in downstream of the SWWP and the discharge as S1 at 5.5 Km, S2 at 7.5 Km, S3 at 11 Km.

	S0 Up stream	S1	S2	S3 Down stream
pH	7.51	7.5	6.81	7.48
EC µmScm-1	452	1290	950	976
O2 dissolved mg l-1	2.46	2.39	2.35	2.17
SC mg l-1	0	0	0	0
Salt mg l-1	193	291	291	285
TH mg l-1	340	672	664	720
Ca2+ mg l-1	68	146	141	153
Cl- mg l-1	157	369	426	384
NaCl mg l-1	258	609	702	632
M alk. mg l-1	220	280	340	432
SO4- mg l-1	4.6	44	24	40
PO4- mg l-1	0.017	0.03	0.018	0.02
K+ mg l-1	1.5	1.5	1.5	1.5
Mg+ mg l-1	18	31	31	25
Na+ mg l-1	101	240	276	248

EC: Electric Conductivity, SC: Suspended Compounds, TH: Total Hardness

Table 2. Physico-chemical properties of water taken from a well at S1 station occurring away in the downstream of the SWWP and the discharge by 5.5 km, and samples taken from a surface water source (S'1) polluted by the effluent coming from the SWWP.

	S1	S1'
pH	7.5	7.89
EC µmScm-1	1290	1650
O2 dissolved mg l-1	2.39	2.21
SC mg l-1	0	105
salt mg l-1	291	426
TH mg l-1	672	540
Ca2+ mg l-1	146	84
Cl- mg l-1	369	497
NaCl mg l-1	609	819
P alk. mg l-1	0	8
M alk. mg l-1	280	640
NO2- mg l-1	0.03	0.06
SO4- mg l-1	44	88
PO4- mg l-1	0.03	4.07
NH4+ mg l-1	0.017	15.8
NO3- mg l-1	0.52	1.45
K+ mg l-1	1.5	2.95
Mg+ mg l-1	31	34
Na+ mg l-1	240	322

EC: Electric Conductivity, SC: Suspended Compounds, TH: Total Hardness

Table 3. Physical and chemical properties of leachates: L1 recovered directly of the collection truck and L2 taken after one year of household waste deposit.

	L1	L2
pH	3.76	6.74
EC µmScm-1	3530	9280
O2 dissolved mg l-1	0	0
SC mg l-1	309	213
Salt mg l-1	1.62	3.52
TH mg l-1	480	135
Ca2+ mg l-1	69	26
Cl- mg l-1	370	780
NaCl mg l-1	609	834
P alk.mg l-1	16	24
M alk. mg l-1	600	853
NO2- mg l-1	0.46	0.8
SO4- mg l-1	80	91
PO4- mg l-1	4.49	7.1
NH4+ mg l-1	24.9	62
NO3- mg l-1	0.81	2.2
K+ mg l-1	4	11
Mg+ mg l-1	39	82
Na+ mg l-1	239	871

EC: Electric Conductivity, SC: Suspended Compounds, TH: Total Hardness

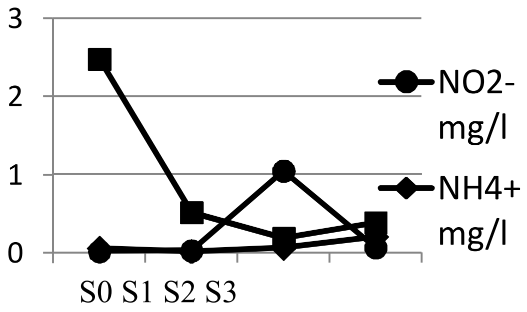

Figure 1. Changes in contents of nitrogen compounds from the station S0 in upstream to downstream until station S3.

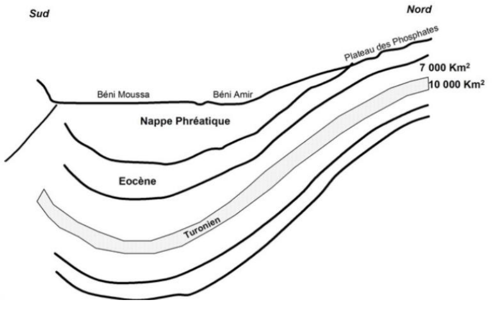

Figure 2. Tadla (Khouribga province) aquifer complex (Hammani et al. 2004)

4. Conclusion

The present study reports the results of analyses of the physico-chemical properties of the samples of waters taken from wells at various distances of the water-treatment plant of activated sludges SWWP and of the hazardous household waste discharge in the outskirts of the city of Khouribga. The obtained data demonstrate that from the station S1 in 2 Km of the discharge and SWWP, the contents of almost all the measured mineral elements are superior or at the limit of the WHO standards for the drinkability of water designed for a human consumption. The investigations realized in the region demonstrate that several factors can contribute to this evolution of the quality of the water indicated by the variation of its physico-chemical properties. Citing the most importants in the first one, we suspect the pollution due to the infiltration of the leachate of the discharge and also from the chemical elements brought by the effluents of the city waste water. It should not be also neglected the erosion phenomenon and the chemical leaching of the crossed grounds depend on the geological nature of the grounds of sedimentary deposit of phosphate alternating marls and limestone overlaid the evaporitic deposits, in particular gypseous. So, the water table is not thus shielded from the pollution and the natural assimilative capacity is not complete for certain substances. On the other hand, the multitude and the diversity of the pollution sources and their spatiotemporal variations make it very difficult to give an exact estimation. Furthermore, the risk engendered by this pollution will be more important when weather conditions in the region are favorable for their mobilization towards the hydric environment (Strong wind, erosion, stormy rains).

The danger of this pollution is very serious on the human health, especially that these wells are considered as one of the first sources of drinking water supply for the population of the region. Whom if we want to protect the health of the population, it is necessary and compulsory to check the quality of water and to proceed to their treatment and also to close and to forbid the access to the wells when the pollution is not remediable.

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