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Spatial and temporal variations of nitrates in traditional urban shallow well water of Sub-Saharan Africa: the case study of Agboville, Ivory Coast

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Abstract

High concentrations of nitrate in groundwater represent human and environmental health risks. This study aimed to determine spatial and seasonal variation of nitrate in Agboville well water and to identify their potential sources in the aquifer. Fifty (50) well water samples were collected and analyzed for selected physical and chemical parameters during four different seasons. *In-situ* and laboratory analyses were carried out using standard procedures. Fifty (50) soils samples were also collected around each well for porosity analysis. No parametric tests of Kruskal-Wallis and Mann-Whitney were used to compare nitrate values for all the different sampling sites and seasons. The results showed that average values of nitrate are consistent with the WHO guidelines (50 $mg.L^{-1}$). However, 54 % of nitrate concentrations were above 13.5 $mg.L^{-1}$ (the threshold value for anthropogenic influence) and spatial variation revealed that higher values of nitrate are observed in the high density areas. This anthropogenic pollution is mainly attributed to domestic activities, lack of sanitation, poorly installed toilets, population density and porosity of soil (55 %). Results, based on temporal variation indicate that highest contamination levels of nitrate were recorded during the long rainy season. The precipitation was other important factors that affects nitrate in well water. These results confirm the deterioration of water quality in this urban poor settlement. The population is therefore exposed to a health risk by consuming water from these wells.

1. Introduction

Groundwater is an important source of fresh water supply for every country in Africa where aquifers provide a safe and reliable source of drinking water [1]. The provision of groundwater can be associated with improvements in public health, food security and many other socio-economic benefits. Nonetheless, in recent years, this precious resource is under intense threats from both natural and anthropogenic sources in most countries of the world [2]. Nitrate (NO_3^-) constitutes a widespread contamination source in shallow underground water because it is soluble in water, easily leaches through soil and accumulates in groundwater. In nature, the nitrate ions exist as part of the nitrogen cycle. However, its rising trend in natural water has made it a contaminant of concern [3]. Nitrate concentrations in groundwater water exceeding an arbitrary threshold of 3 $mg.L^{-1}$ may be indicative of contamination of natural groundwater as a result of human activities. However, most countries as well as the World Health Organization [4] have set the maximum admissible concentration (MAC) at 50 $mg.L^{-1}$. High concentrations of nitrate are mainly attributed to agricultural activities beginning in the mid-twentieth century [5, 6, 7]. However, atmospheric deposition, discharge from septic tanks and leaking sewers, the spreading of sewage sludge to land and seepage from landfills can all contribute to the pollutant load [8,9]. Moreover, when the water infiltrates into the subsurface, biogeochemical processes (e.g., nitrification) can modify nitrogen species balance such that different forms of nitrogen (NO_2, NH_4 and NH_3) can be transformed into nitrate [2, 3, 10]. Elevated concentrations of nitrate in underground water represent human and environmental health risks [11]: (i) excessive consumption of nitrate in drinking water has been associated with the risk of methemoglobinemia or 'blue baby syndrome' in humans [12], stomach cancer and nitrate poisoning in animals [13]; (ii) nitrate export into adjacent surface water bodies may induce an increased level of nutrients (eutrophication) affecting adversely biodiversity, mammals, birds, and fish population by producing toxins and reducing oxygen levels. Besides, denitrification processes contribute to the emission of greenhouse gases due to production of N_2O [14]. In most of sub-Saharan Africa cities, high concentrations of nitrates have been found in shallow well water. Thus Ivory Coast, which is located in West Africa, high nitrates concentrations were found in shallow groundwater in many cities of which Agboville [15]. Focused study on nitrate in groundwater in Agboville dates back to 2002. These previous studies and findings provide information on the extent of groundwater contamination within an aquifer in certain districts of Agboville. However, the temporal trends in solute concentration and the source of nitrate are not clearly identified. Whereas, well water constitutes the principal drinking water supply for population (60 %) especially for the poorer ones because of the high cost for tap water standing charge and of its deteriorating quality [16]. Identification of the sources and variability of nitrate is, therefore, an important step in the improvement and management practices associated with maintaining the groundwater quality. This study was undertaken in all neighborhoods of Agboville to evaluate spatiotemporal evolution of nitrates in the shallow aquifer. The aims were: (1) to determine seasonal and spatial variation of nitrates in the different wells' water, (2) to identify and distinguish the most likely sources of nitrate.

2. Material and Methods

2.1. Study area

Agboville is located in south-eastern of Ivory Coast between 364 000 m and 368 000 m west longitude and 654 000 m and 658 000 m north latitude (Figure 1). It covers an area of 1602,1 km^2 and the total population in 2014 was 95 093 [17]. The climate is of the equatorial type with two rainy seasons (April-July and September-October) and two dry seasons (August-September and December-March) annually. Mean annual rainfall exceeds 1500 mm per year. According to [15], the basement crystalline rocks dominate the geology of Agboville. The rocks types are mainly made up of schist and granite. The occurrence of groundwater in this formation is characterized by the development of secondary porosity which is as a result of weathering and fracturing. Well and borehole in these weathered formations are the source of water for inhabitants of this district.

2.2. Choice and location of sampling wells

A preliminary study based on questionnaires and observational studies of the wells were conducted in April 2013 in two hundred (200) households. Structured observation guides and charts were used. Observations made included the nature of wells, protection of mouth of well, water usage and closeness of wells to any major pollution sources such as public latrines, refuse dump, sanitary conditions etc. based on the spatial distribution and their relative importance to the population, 50 wells were chosen and they were set out again in 4 zones according to their proximity (Figure 1). Characteristics of sampling sites are described in Table 1 [17]. Zone 1 and zone 2 are residential area and they are a low-lying area (mostly a reclaimed wetland). The most common methods of human excreta disposal are flushing toilets to septic tanks. However, unimproved type open dumping is a major form of solid waste disposal in the area. Zone 3 and zone 4 are popular area and they have a high altitude. These communities are generally low-income. However, zone 3 is more populated (46 % of population) than other zone and records highest household using well water for drinking (41 %). Poor sanitation is a common practice in zone 3 since its does not have an approved dumping site and 92, 85 % of households depend on pit latrines for excreta disposal. In zone 4, 31 % of household have used well water for drinking. Solid waste management practices in the area are grossly inadequate and services are misused resulting in environmental degradation form of solid waste disposal in the area. Wells points are named w1. w2 …. w50 and there are 13 wells in zone 1, 12 in zone 2, and 14 and 11 respectively in zone 3 and zone 4. The exact position of each well was obtained by means of GPS (MLR SP 12X).

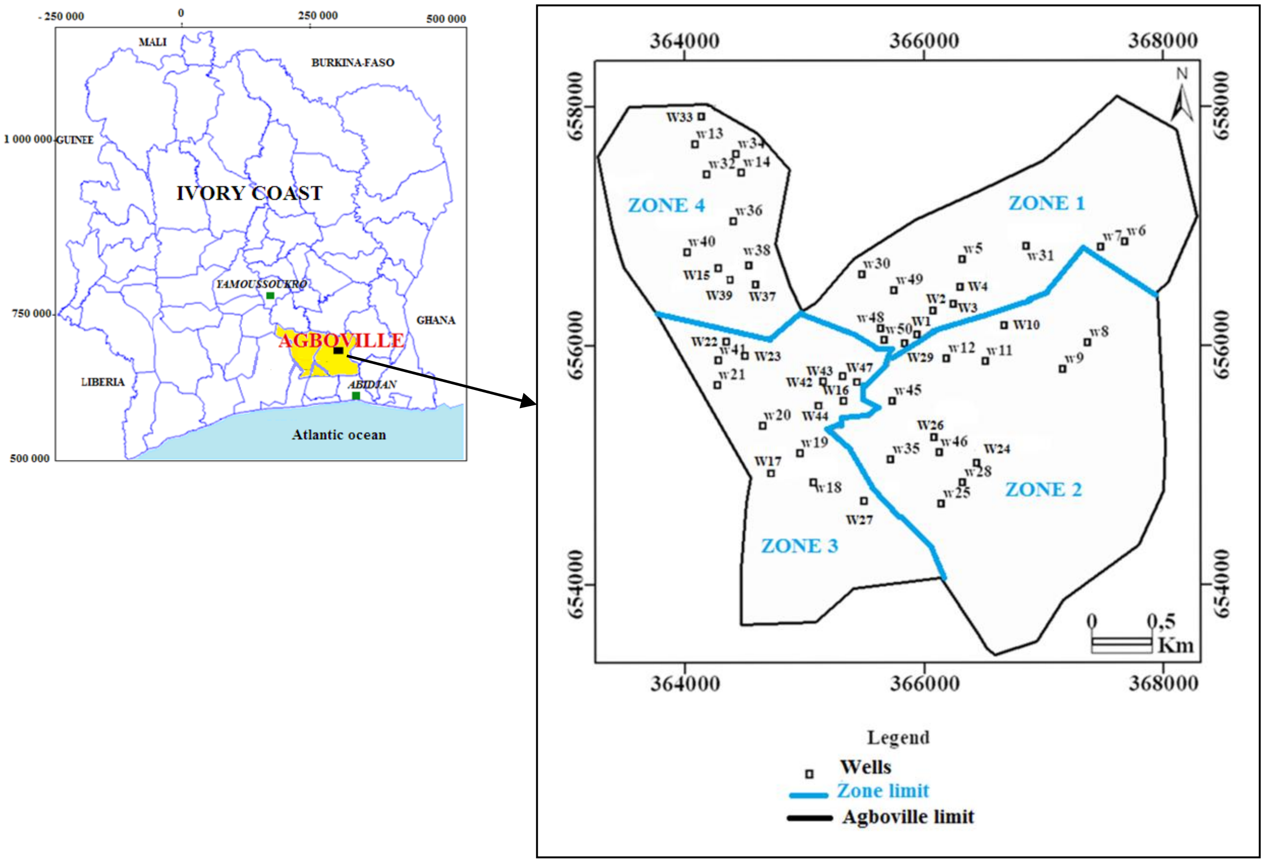

Figure 1: Map of Agboville: localization of the selected 50 sampling wells in differents zones

Table 1: Characteristics of sampling sites

Zone	Household using well water (%)	Population (%)	Sanitation facilities in use for excreta disposal		Sanitation facilities in use for households waste disposed			
			Pit latrines (%)	Flush toilets to septic tanks (%)	Nature (%)	Discharges (%)	Fires (%)	Hidings (%)
Zone 1	13	14	30.76	69.24	64	30	5	1
Zone 2	15	22	50	50	51	38	10	1
Zone 3	41	46	92.85	7.15	60	35	4	1
Zone 4	31	18	90	10	74	23	2	1

2.3. Well water sampling and analysis

From different wells (50) were collected during four (4) sampling campaigns on seasonal basis. Water sampling was carried out from January (peak of dry season), May (peak of rainy season) August (mild dry) and October (mild rainy). At each well point, one sample was taken and poured in a 500 mL clean polyethylene bottle. Samples were then transported to the laboratory in refrigerated conditions (6 ± 2°C) for hydrochemistry analyses. Electrical conductivity (EC), total dissolved solids (TDS), temperature (T) and pH were measured *in-situ* using a multipameter (HACH 44600) and *in-situ* measurements of water - levels were performed by means of graduated lead sounding cable. Ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), sulfates (SO_4^{2-}), orthophosphates (PO_4^{3-}), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined by HACH method using UV/ Vis spectrophotometer (DR6000). Total alkalinity (Alk as HCO_3^-) was determined by volumetric titration (0.02 N H_2SO_4) to pH = 4.3 and total hardness (TH) was analyzed titrimetrically using EDTA as described by [18].

2.4. Soil sampling and analysis

A total of 50 undisturbed soil samples were collected around each well using a steel tape. The samples were kept in black polyethylene bags and transferred to laboratory for porosity analysis. The samples were analyzed for selected physical parameters known to influence groundwater flow and transport of microbial and chemical contaminants. Porosity was determined using the water displacement method. A volume of 250 ml of boiled water were poured in the bucket and the sample (300 g of dry soil) immersed gently and allowed to stay for a period of at least 48 h until there were no more air bubbles emanating. Samples were removed and the remaining water measured using a calibrated measuring cylinder. The porosity was calculated as:

$$Porosity\ (\%) = \frac{Volume\ of\ water\ adsorbed\ (mL)}{Volume\ of\ soil\ (mL)} * 100 \quad \textbf{(E1)}$$

2.5. Statistical analyses

Statistical data processing Non-parametric tests of Kruskal-Wallis and Mann-Whitney and the analysis of variance were used to study the spatial and temporal variability of physicochemical parameters. These tests were used at a 95 % significance level ($p < 0.05$). This test is coupled with the boxes mustaches or "boxplot" for nitrate distribution. STATISTICA 7.1 software was used for the realization of those analyses. The self-organizing maps using MATLAB 6.2 software was applied to identify the relationships between the nitrate concentrations and other water quality variables. It was used to detect origin of pollution.

3. Results

3.1. Characteristics and environmental condition of wells

The key characteristics of the wells from which the samples were obtained is presented in Table 2. Wells with curbstone, casing and cover are most frequent in the visited concessions. This is a good system for wells protection. But most wells are generally open or semi-closed and scoops usually on the ground are reused without being cleaned. Moreover**,** the average height of curbstone in zone 3 is lower and then, well never dries up in this zone. However, well dries up sometime in February in other zone. The conditions of the wells and the surrounding area have also been described. In the study areas, some wells are down the slopes and near lowland near.

They are surrounded by trees (e.g. neem, acacia and mangoes), vegetable plantation (e.g. rice, zone 4), septic tanks or pit latrine, wastewater gutters and dumping sites for solid waste. However, in zone 3, about 57, 14 % and 25 % wells are located respectively in proximity (< 15 m, the minimum distance recommended by WHO) to pit latrine and dumping sites for solid waste. The effective porosity of the soil is higher than 50 %. These informations indicate that the majority of the wells and their surroundings are in poor conditions.

3.2. Physicochemical characteristics of the well water

The suitability of water for consumption depends on the levels of the contaminants present in it. The mean levels of physicochemical parameters used in this study can be seen in Table 3 together with their respective spatial and temporal mean p-values taken from the Kruskal Wallis and ANOVA tests.

Table 2: Summary of the characteristics / condition of wells in Agboville

Zone	Porosity of soil (%)	Sanitation facilities for wells protection						Condition of well and surrounding area				
		Height of curbstone (m)	Presence of Curbstone + Casing + Cover (%)	Presence of Curbstone + Casing (%)	Presence of casing +cover (%)	Absence of curbstone + casing + Cover (%)	Well dries up sometime in February (%)	Distance wells-pit latrine or septic tanks < 15 m (%)	Distance wells-pit latrine or septic tanks > 15 m (%)	well is surrounded by trees (%)	Well is near dumps junk (%)	Well is down slope and near lowland (%)
Zone 1	60 ± 0.05	0.53 ± 0.2	69.23	30.77	0	0	33	38.46	61.56	22	38	50
Zone 2	55 ± 0.1	0.56 ± 0.4	50	33.33	8. 33	8.34	34	33. 33	66.67	10	12	26
Zone 3	55 ± 0.1	0.47 ± 0.2	92.85	7.15	0	0	0	57.14	42.86	12	25	12
Zone 4	54 ± 0.1	0.5 ± 0.1	45.45	18.18	36.37	0	33	36.36	63.64	56	25	12

Table 3: Statistical summary of the physicochemical parameters

Parameter	WHO	Min	Max	Mean ± SD	Statistical test: Kruskal-Wallis /ANOVA p-value	
					Spatial variation	Temporal variation
pH	6 .5-8.5	3.68	8.34	5.61 ± 0.73	0.023*	0.011*
T (°C)	25	26.3	33	29.02 ± 1.12	0.018*	0.072
EC ($\mu S.cm^{-1}$)	-	62	1878	472.24 ± 342.04	0.001*	0.000*
TDS ($mg.L^{-1}$)	1000	29	937	230.62 ± 162.89	0.000*	0.955
Water-level (m)	-	0	21.45	3.93 ± 4.14	0.000*	0.000*
TH ($mg.L^{-1}CaCO_3$)	500	0.73	794	129.15 ± 131.48	0.000*	0.000*
Ca^{2+} ($mg.L^{-1}$)	150	1.72	130.6	27.83 ± 28.92	0.000*	0.000*
Mg^{2+} ($mg.L^{-1}$)	50	0	161.4	15.99 ± 23.43	0.000*	0 .093
Alk ($mg.L^{-1}CaCO_3$)	-	0	248.88	24.42 ± 37.9	0.773	0.000*
PO_4^{3-}($mg.L^{-1}$)	-	0	170	1.91 ± 12.37	0.122	0.000*
SO_4^{2-}($mg.L^{-1}$)	250	0	1200	49.5 ± 136.23	0. 366	0.000*
NH_4^+($mg.L^{-1}$)	1.5	0.01	51	1.74 ± 4.3	0.000*	0.876
NO_2^-($mg.L^{-1}$)	3	0	4.86	0.13 ± 0.41	0.008*	0.020*
NO_3^- ($mg.L^{-1}$)	50	0	224	19.59 ± 37.28	0.019*	0.000*
				Mean < 13.5	46 %	
				Mean > 13.5	54 %	

- : not available; SD: standard deviation, *: significant difference

The physicochemical parameters were compared to the maximum values recommended by WHO. Well waters are generally acidic (pH = 5.61± 0.73) and hot (29.02 ± 1.12). The EC and TDS ranged from 62 $\mu S.cm^{-1}$ - 1878 $\mu S.cm^{-1}$ and 0- 937 $mg.L^{-1}$ respectively. Waters are slightly mineralized with mean EC value of 472.24 ± 342.04 $\mu S.cm^{-1}$ and are fresh and desirable for drinking (TDS mean value = 230.62 ± 162.89 $mg.L^{-1}$ < 1000 $mg.L^{-1}$). The depth of the wells is low with mean water-level value of 3.93 ± 4.14 m. Generally, the mean of total hardness, Ca^{2+}, Mg^{2+}, SO_4^{2}, NH_4^+, NO_2^- and NO_3^- were within the permissible values (129.15 ± 131.48 $mg.L^{-1}CaCO_3$, 27.83 ± 28.92 $mg.L^{-1}$, 15.99 ± 23.43 $mg.L^{-1}$, 49.5 ± 136.23 $mg.L^{-1}$, 1.74 ± 4.3 $mg.L^{-1}$, 0.13 ± 0.41 $mg.L^{-1}$ and 19.59 ± 37.28 $mg.L^{-1}$ respectively).
According to water hardness classification, wells water registered soft water. The results suggesting that the water was suitable for human consumption in terms of the tested parameters. However, the NO_3^- content was above the threshold value for anthropogenic influence (13. 5 $mg.L^{-1}$) in 54 % of the wells and the maximum value was 224 $mg.L^{-1}$. According to Kruskall-Wallis test and analysis of variance, there were no statistical differences ($p > 0.05$) in alkalinity, PO_4^{3-} and SO_4^{2-} from all wells for spatial variation. In contrary, pH, T, EC, TDS, water-level, TH, Ca^{2+}, Mg^{2+}, NH_4^+, NO_2^- and NO_3^- presented significant difference ($p < 0.05$). For temporal variation, there were no statistical difference detected ($p > 0.05$) for T, TDS, Mg^{2+}, NH_4^+. But, a significant difference for pH, water-level, EC, TH, Ca^{2+}, Mg^{2+}, alkalinity, PO_4^{3-}, SO_4^{2-}, NO_2^- and NO_3^- has been revealed.

3.3. Spatial distribution of nitrate in the aquifer

The results of Kruskal Wallis and Mann-Whitney test combined with box plots describe the spatial variations of nitrates in Agboville (Figure 2). The median value of nitrate in well water in zone 3 (11. 5 $mg.L^{-1}$) was significantly higher ($p < 0.05$) than the values recorded in wells in zones 1 (5. 8 $mg.L^{-1}$), zone 2 (7.35 $mg.L^{-1}$) and zone 4 (4 $mg.L^{-1}$). Then, the concentration of NO_3^- in zone 2 was much higher than those in zone 1 and zone 4. But, the nitrate values did not vary significantly between the samples in zone 1 and zone 4.

3.4. Temporal variations of nitrate

As shown in Figure 3, nitrate ranged between 0.5 $mg.L^{-1}$ (January) and 224 $mg.L^{-1}$(May). There are statistically significant differences ($P < 0.05$) between nitrates values in May and other sampling months. Median values of nitrate concentrations in Agboville's wells are higher during May (17.15 $mg.L^{-1}$) than in any other months (October = 6.86 $mg.L^{-1}$, August = 5.2 $mg.L^{-1}$ and January = 5.05 $mg.L^{-1}$). A significant seasonal variation in nitrate composition well water was observed.

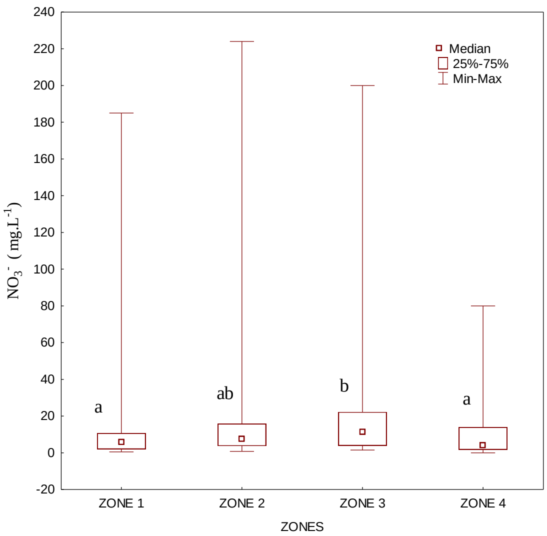

Figure 2: Box and Whisker plots of nitrate separated by spatial discriminate analysis. There were no significant differences between two boxes bearing the same letter of the alphabet. Two different letters indicate a significant variability between sampling points

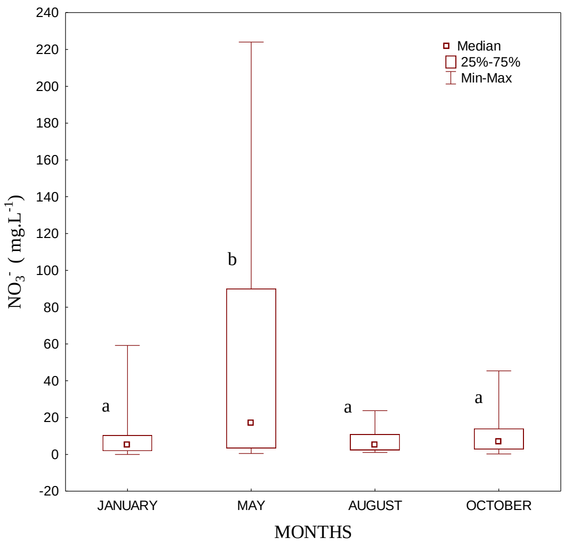

Figure 3: Box and Whisker plots of nitrate separated by temporal discriminate analysis. There were no significant differences between two boxes bearing the same letter of the alphabet. Two different letters indicate a significant variability between sampling points

3.6. Nitrate source apportionment

The distribution of samples on Kohonen map is shown in Figure 4. According to physicochemical discriminate variables, the wells distribution on the map (Figure 4a) present 20 cells (5 rows x 4 columns) and then, a hierarchical cluster analysis allowed us to group the 20 cells of the card into 3 subsets (group I, II and III). Thus, group I (GI) brings together the majority of wells in zone 3. Group II (GII) contains the majority of wells in zone 1 and 4 and group III (GIII) consists of the majority wells of zone 2. Figure 4b helps to visualize the relationships between nitrate and other variables in each zone. Thus, in the wells of the group I, high NO^{3-} concentrations are linked to high NO_2^- , EC , TDS , pH , Ca^{2+} , Mg^{2+}, alk , TH, SO_4^{2-} and relatively low to Water level. The Group II is distinguished by high ammonium concentrations (41.6 $mg.L^{-1}$). This group is characterized by high T, pH and EC. For Group III, high nitrate concentrations are linked to high ammonium, nitrite, sulfate, orthophosphate, water level and low pH.

4. Discussion

Nitrate concentration levels observed in Agboville's wells water were generally high exceeding 13.5 $mg.L^{-1}$. These values indicate anthropogenic pollution by nitrates [19]. The diversity of their origin has led to a significant difference between the levels of nitrate in different areas. In fact, the spatial variability of nitrate showed that nitrate concentrations levels in high population densities area (zone 3) are higher than those in low population densities (zone 2, zone 1 and zone 4). The majority of wells in zone 3 belong to group I and are characterized in part by high values of nitrite, sulfate, conductivity, total dissolved solids, alkalinity, calcium, magnesium and pH and secondly, by relatively low values of ammonium. This pollution may be linked to environmental conditions of these wells [14]. Indeed, this popular area (zone 3) records the highest number of households and population (41 % and 46 %), and 92.85 % of toilets in this area are traditional and 57.14 % of them are located within 15 m from the wells. Moreover, the mean porosity of the soil in this area is 55 %. The

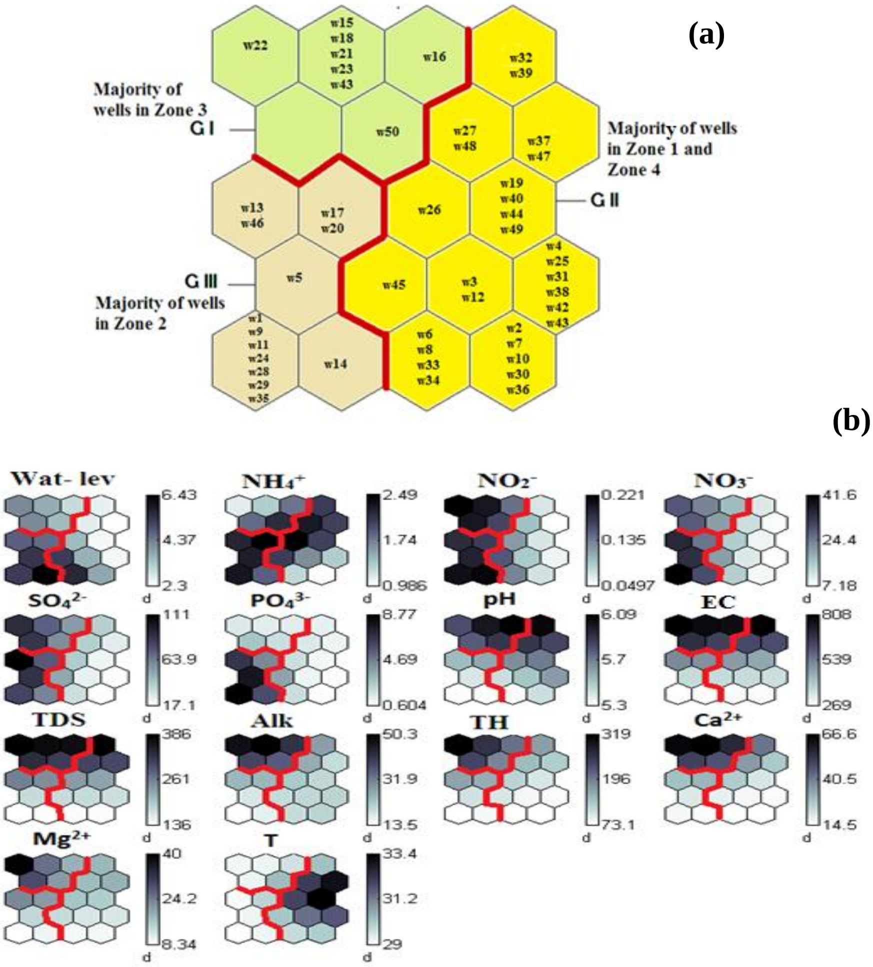

Figure 4: (a) Distribution of wells (Figure 1) on the self organising map (SMO) according to 14 physicochemical variables and clustering of the trained SMO. Clusters w1-w50 were derived from the U-matrix clustering. (b) Visualization of each variable trained with all wells on the trained SMO, with visualization in shading scale (dark = high values. light = low values): (Wat-lev = Water level, EC = Electrical conductivity, Alk = Alkalinity, TH= Total hardness, T= Temperature)

poor conditions on the wells and soil caracteristic could facilitate infiltration of water from septic tanks into groundwater without benefit of effective filtration [20,21]. Furthermore, Nitrates may come from the oxidation of ammonium to nitrite :

$$(2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 4H^+ + 2H_2O) \quad \textbf{(E2)}$$

and nitrite to nitrate [22, 23]. This is in agreement with group III waters, which records the majority wells in zone 2. These water are more acidic and richer in nitrogen compounds (NH_4^+, NO_2^- and NO_3^-), in SO_4^{2-} and PO_4^{3-}. This acidity may be related to the release of the protons H^+ in the oxidation reactions. The large amounts of ammonium, nitrite and nitrate comfort the assumption of pollution of those waters by urban waste. Indeed, ammonium is a nitrogen compound whose presence in groundwater is due to surface contamination mainly related to discharges of domestic and industrial effluents. Some wells are located near dumps (w17 and w29). The decomposition of such wastes produces ammonium and during rainy period's runoff water transport ammonium into the wells [22]. According to [24], high concentrations of orthophosphate in wells water of this group can be caused by infiltration of water from septic tanks.

In contrast, group II, which contains the majority of wells in zones 4 and 1, is characterized by low levels of nitrates. This could be related to the fact that many wells in zone 1 are located in modern concessions and benefit from a cleaner environment. However, the wells of zone 4, located in neighborhoods with high density of population or percentage of households which is estimated at 31 %, are rich in ammonium. This is also in line with the original domestic pollution due to lack of sanitation, lack of proper sanitation facilities and poor handling scoops by population [24].

At the temporal level, two major changes are observed in the well water [25]. During the wet season (May), the highest level of NO_3^- was observed at all sampling sites. Similar results were observed by [26] in Cameroon. This increase indicates that wells received either directly laden runoff pollutants or seepage water containing nitrates from the mineralization of organic waste. Indeed, nitrates are highly mobile chemical pollutants, easily leachable and easily reach groundwater [22]. Unlike the long rainy season, other seasons of the year (long dry season, short dry and rainy season) are marked by low variable values of nitrates which show no significant difference. This could be explained by the low rainy intake. These results are in agreement with those of [26].

Conclusion

This study showed that mean nitrate values for different areas and seasons were within WHO acceptable limits. However, higher values of nitrate were recorded in the high density areas and during the long rainy season. Elevated concentration of nitrate is mainly due to anthropogenic activities such as inappropriate household waste management and pit latrine and rainfall regimes. Soil porosity was also an important factor that affects nitrate in well water. The results demonstrate that the water quality obtained from shallow wells in poor area is worse. The population is therefore exposed to a health risk by consuming water from these wells. A need for civic education of the communities on the general hygienic practices is necessary. Sitting of latrine should also be at a recommended distance from a borehole to avoid leaching of wastewater.

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