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Chemical speciation of iron in urban shallow groundwater, southeastern Brazzaville, Congo

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ABSTRACT: This study assessed the groundwater quality in southeastern Brazzaville, Congo, in order to calculate iron chemical speciation. A total of twenty two groundwater samples were collected in rainy and dry seasons. Physico-chemical parameters namely pH, TDS, EC, T, D.O, TH, Alk, ORP, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, NO_3^{-}, PO_4^{3-}, F^{-}, Fe_{tot}, Fe^{2+} and Fe^{3+} were analyzed. The results indicate acidic nature and oxidizing conditions in groundwater, contamination of groundwater by domestic sewage, water septic tanks at the sight of EC values and iron content higher than permissible limit of 0.3 mg/L in the majority of groundwater samples. Modeling of iron chemical speciation in the groundwater samples using Visual Minteq computer program revealed that the predominant species were free ionic form Fe^{2+} in both season followed by $FeSO_4$(aq) for Fe(II) species. The majority of Fe(III) species were fluoro complexes FeF^{2+} and $(FeF_2)^{+}$, sulphato complex ion $FeSO_4^{+}$ and free ionic form Fe^{3+} in rainy season. The hydroxo complexes of Fe(III) are predominant in dry season.

KEYWORDS: Groundwater, Iron, Chemical speciation, Modelling, Visual Minteq.

1 INTRODUCTION

Groundwater is one of natural water resource that human being use for domestic needs, industrial and agricultural activities. In developing countries many people use shallow groundwater sources for drinking and domestic purposes. The study of groundwater chemistry reveals much information on different purposes [1, 2]. Problems which affect the quality of groundwater are waste disposal on land surface, septic tanks, use of fertilizers and other agricultural chemicals, contamination by geogenic sources [3, 4].The lithology of the area is one of the factors that control groundwater chemistry.

The impact of human activities has repercussions on the physical and chemical properties of the groundwater. Thus in the case of unsafe drinking water some diseases such as cholera, typhoid, dysentery and diarrhea can arise [5]. In developing country like Congo-Brazzaville, Soil waste dumps are frequently present and can affect the quality of groundwater through metal pollution. Iron is one of the metals found in groundwater at level high the permissible limit of 0.3 mg/L for drinking water in the country [6]. Iron is a micronutrient and the body requires it in small amounts for metabolic activities. When iron content in water is higher than 0.5 mg/L, severe toxicity in human physiological systems can occur [7]. Therefore it is primordial to determine groundwater quality in order to assess its suitability for a particular purpose [8].

Chemical speciation of metals in groundwater has been investigated in many studies using geochemical softwares such as Phreecq, Vminteq, Wham [9-14]. In water systems metals can be coordinated with some anions. The chemical speciation of metals determines their toxicity and bioavailability which are a prediction of metal behavior and possible impact in the environment [15, 16].

In the area La Poudrière, southeastern Brazzaville (Congo), many people are denied access to potable drinking water supply. In this case groundwater becomes the single water resource to maintain basic hygiene. The concentration of total iron in groundwater of this area is sometimes higher than 0.3 mg/L, the permissible limit for drinking water according WHO [17]. The aim of the study is to assess the hydrochemistry of groundwater in the study area in relation to the presence of iron and to determine chemical speciation of iron from the measured ion concentrations using the Visual Minteq computer program.

2 MATERIAL AND METHODS

2.1 PRESENTATION OF THE STUDY AREA

The study area is located in southeastern Brazzaville between 15°13’53” to 15°14’10” East Longitude and 4°15’7.2” to 4°15’28.8” South Latitude (Figure 1). The area is in the equatorial climate zone, with two seasons, rainy (October to May) and dry (June to September). Temperature varies from 25°C to 36°C in rainy season, while it is between 18°C and 24°C in dry season. The mean annual rainfall is 1470 mm. The vegetation is of savanna type (*Loutetia demeusi)* and presents a formation to sparse gramineous carpet, with a shrubby layer of *hymenocardia acida*. Aquifer is shallow and generally the wells do not exceed 2m depth. Therefore the lowering of the ground water table increases the risk of contamination.

The most well water present iron sheet as well casings in the study area. The main natural recharge to groundwater is from precipitation (rainfall). Farming activities are present around some well water sites and also agricultural activities near the River Mfilou. Belonging to the continental sedimentary basin of tertiary age, the southeastern Brazzaville is made of sedimentary deposits with recent alluvium formations covering the bed rock. These formations are also made with ochre sands or Batéké sands (silicate sandstones), which constitute the formation of Inkisi classically joined to the schisto-sandy group.

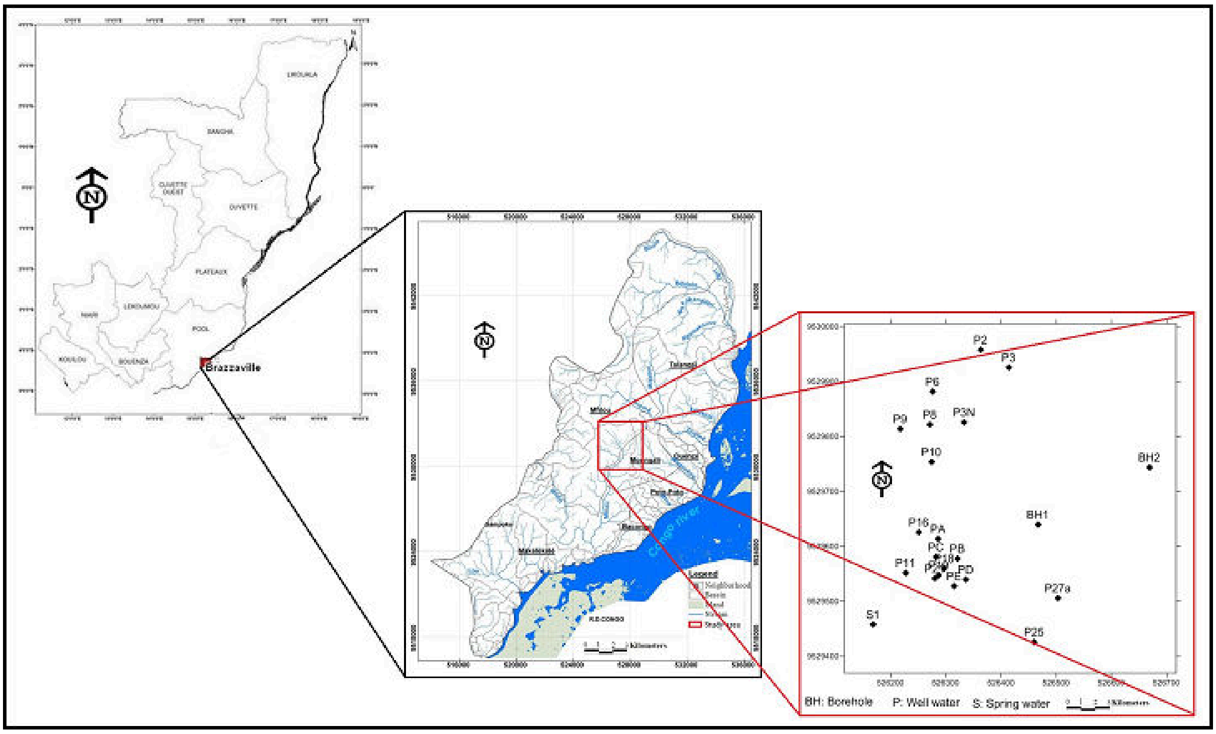

Fig. 1. Location of the study area and groundwater sites

2.2 SAMPLING AND ANALYSIS

The sampling was done in rainy (October 2012) and dry (August 2013) seasons. Twenty two samples of groundwater of which 19 wells water (P), 2 bore wells (BH) and 1 water spring (S) were collected in three times after running them for 10 minutes. Location of the monitoring groundwater sites was determined using the global positioning system (GPS) as shown in Figure 1. The analysis covers the physicochemical parameters as shown in the results. Before water sampling, all the polyethylene bottles were cleaned and rinsed thoroughly with water to be analyzed. The groundwater samples collected were labeled, transported to the laboratory and preserved in a refrigerator at a temperature of about 4 °C until analysis. All reagents used were of analytical grade. Samples were unfiltered and the concentration of iron could correspond to the total concentration if the groundwater was used by the consumers for drinking. The physico chemical parameters were determined using standard methods [18].

The measurements of pH, oxidation reduction potential (ORP), electrical conductivity (E.C), total dissolved solids (TDS), temperature (T) and dissolved oxygen (DO) were carried out in the field using Consort C933 multi-parameters portable. Total hardness (TH), Ca^{2+} was determined by EDTA complexometric titration and Mg^{2+} by calculation from total hardness and calcium. Na^+ and K^+ were determined by photometric method. Chloride (Cl^-) in groundwater was determined by argentometric titration method using potassium chromate indicator solution and standard silver nitrate titrant, SO_4^{2-} by turbidimetric method. Bicarbonate (HCO_3^-) was obtained by titration method after measured value of total alkalinity, methyl orange use as an indicator. Nitrate (NO_3^-) and orthophosphates (PO_4^{3-}) were determined by spectrophotometric method. Iron contents were determined by phenanthroline spectrophotometry method. The method involves the complexation of Fe^{2+} with 1, 10-phenanthroline to produce an intensely red-orange colored complex. Iron present in the water exists as Fe^{3+} and Fe^{2+}. Before to measure total iron contents in groundwater samples, first Fe^{3+} was reduced to Fe^{2+} by the addition in excess of a reducing agent hydroxylamine to maintain iron in the +2 state. After that, ferric ions contents were calculated by subtraction. All the water quality parameters were expressed in mg/L, except EC (µS/cm) and pH (unit).

2.3 STATISTICAL ANALYSIS

Hierarchical clustering analysis (HCA) was used to get a better separation among groundwater samples. HCA is an exploratory technique with graphic output as a dendrogram and the method is used frequently in environmental sciences [19-23]. It helps to classify group samples or group variables of a data set. In this study, HCA was performed on the data set by means of the Ward's method, using Euclidean distances as a measure of similarity. The statistical software used is Statistica 7.1.

2.4 MODELING CALCULATIONS

The geochemical computer program Visual Minteq ver. 3.0 [12] was used to determinate the chemical speciation of iron that may exist in the groundwater. This computer program has an extensive database of aqueous species for interpretation purposes. The anion concentrations determined in the study influence the

3 RESULTS AND DISCUSSION

3.1 PHYSICO-CHEMICAL CHARACTERISTICS

Groundwater data of the samples in rainy and dry seasons were statistically described as minimum, maximum, mean, median, variance and standard deviation (SD) in Table 1 and Table 2, respectively. The results indicate that pH values varied from 2.87 to 5.83 with a mean of 4.11±0.91 in rainy season and from 4 to 6.73 with a mean of 5.08±0.86 in dry season. Groundwater is acidic in nature in both seasons with a more pronounced acidity in the rainy season. This could be explained by the decomposition of the soil organic matter (high vegetation in the study area) and a pyrite oxidation [25] as describe in the following reaction:

$$FeS_2 + 15/4\, O_2 + 7/2\, H_2O \longrightarrow Fe(OH)_3 + 4\, H^+ + 2\, SO_4^{2-} \quad (\text{Eq.1})$$

This equation describes pyrite oxidation in the presence of water leading to the formation of acid (H^+) and sulfates (SO_4^{2-}). ORP values of the groundwater samples ranged from 181.10 to 404.70 mV in rainy season and from 130.27 to 395 mV in dry season. These values characterize an oxidizing environment. The variable ORP contributed to the interaction between water and redox sensitive minerals such as sulphides. In rainy season 59.09% of groundwater samples have E.C value range from 305.5 to 544.6 µS/cm and in dry season 68.18% of the samples have E.C range from 302.67 to 704 µS/cm. Overall the high values of electrical conductivity (E.C > 300 µS/cm) suggests to contamination of groundwater by domestic sewage and water septic tanks. This could explain the high concentrations of sodium observed in the corresponding groundwater samples. TDS are mainly compounds of inorganic salts, the amount ranges from 34.57 to 289.67 mg/L and from 27.33 to 374.67 mg/L in rainy and dry seasons, respectively. With reference to quality, all the groundwater samples (100%) are freshwater with TDS values <1,000 mg/L [26]. Dissolved oxygen (DO) values in groundwater samples were small in rainy season as 0.03 to 0.32 mg/L and 3.2 to 8 mg/L in dry season, which denotes an intense bacterial activity in rainy season.

Total hardness (TH) ranged from 61.67 to 100.84 mg/L $CaCO_3$ in rainy season and from74.92 to 330.52 mg/L in dry season. Water with hardness value above 300 mg/L may cause kidney and heart diseases [27]. According the classification of water depending upon hardness [28] as shown in Table 3, groundwater samples belong to soft (31.81% of samples) and medium hard (68.39 % of samples) in rainy season. In dry season, the classification was medium hard (40.90% of samples) and hard (59.10% of samples).

Alkalinity (Alk) is a measure of the ability of water to neutralize acids. The total alkalinity varied from 12.20 to 67.10 mg/L in rainy season and from 9.76 to 58.56 mg/L in dry season. These values denote a decreasing of the alkalinity from rainy season to dry season. In both seasons, the predominant cation trend in groundwater samples was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$. Sodium ($Na^+$) was the dominant cation with the concentration ranged between 48.56 to 88.44 mg/L with an average of 62.39 mg/L in rainy season and from 11.65 to 119.25 mg/L with an average of 50.98 mg/L in dry season. In all the groundwater samples, sodium concentration was lower than the maximum permissible limit of 200 mg/L in both seasons, according the WHO guideline. Source of Na^+ and Cl^- in the groundwater of the study area may be domestic wastewater, which is usually enriched in Na^+ relatively to Cl^-. Calcium (Ca^{2+}) was the second most dominant cation with concentration ranged from 7 to 18 mg/L with a mean of 12.59 mg/L in rainy season and from 10 to 54 mg/L with a mean of 26 mg/L in dry season. The other cations, magnesium (Mg^{2+}) its concentration ranged from 7 to 17 mg/L with an average of 12.4 mg/L in rainy season and from 10 to 47 mg/L with an average of 22.64 mg/L in dry season. Potassium (K^+) presents the lowest concentrations which ranged from 3.1 to 8.8 mg/L with an average of 5.6 mg/L in rainy season and from 1.9 to 8 mg/L with an average of 3.76 mg/L in dry season. Potassium has the tendency to be fixed by clay minerals which could explain the low concentrations [29]. All the concentrations of major cations are below the WHO limits [17].

Assessment of anion concentrations shows that bicarbonate (HCO_3^-) was the dominant anion with concentration ranged from 10 to 55 mg/L with a mean of 23.59 mg/L in rainy season and from 8 to 48 mg/L with a mean of 27.50 in dry season. Chloride concentrations ranged from 3 to 21 mg/L with an average of 9.36 mg/L in rainy season and from 3 to 17 mg/L with an average of 9.82 mg/L in dry season. Sulphate concentration ranged from 4 to 13 mg/L with a mean of 9.09 mg/L in rainy season and from 0.32 to 16 mg/L with a mean of 5.72 mg/L in dry season. Sulphate concentrations in the studied area are attributed mainly to oxidation of pyrite (FeS) in the aquifer [25].

Table 1. Descriptives statistics of groundwater parameters in rainy season

Parameter	Min	Max	Mean	Median	Variance	SD
pH	2.87	5.83	4.11	3.98	0.82	0.91
TDS	34.57	289.67	157.95	164.5	5347.23	73.12
EC	67.25	544.67	298.55	310.67	19108.88	138.23
T	24.30	27.30	25.94	25.80	0.72	0.85
D.O	0.03	0.32	0.16	0.17	0.00	0.07
TH	61.67	100.84	82.05	82.09	128.77	11.35
Alk	12.20	67.10	28.78	25.62	192.03	13.86
ORP	181.10	404.70	321.20	343.90	3955.59	62.89
Ca^{2+}	7.00	18.00	12.59	12.00	9.59	3.10
Mg^{2+}	7.00	17.00	12.14	12.00	6.41	2.53
Na^+	48.56	88.44	62.39	61.15	85.26	9.23
K^+	3.10	8.80	5.60	5.50	2.75	1.66
Cl^-	3.00	21.00	9.36	7.50	31.19	5.59
SO_4^{2-}	4.00	13.00	9.09	10.00	6.66	2.58
$HC0_3^-$	10.00	55.00	23.59	21.00	129.02	11.36
NO_3^-	0.30	2.55	1.17	1.05	0.37	0.61
PO_4^{3-}	0.12	0.28	0.19	0.19	0.00	0.05
F^-	0.13	0.34	0.21	0.20	0.002	0.05
Fe_{tot}	0.03	0.32	0.16	0.17	0.005	0.07
Fe^{2+}	0.02	0.17	0.07	0.075	0.003	0.05
Fe^{3+}	0.01	0.15	0.09	0.095	0.002	0.02

Table 2. Descriptives statistics of groundwater parameters in dry season

Parameter	Min	Max	Mean	Median	Variance	SD
pH	4.00	6.73	5.08	4.81	0.75	0.86
TDS	27.33	374.67	173.05	169.83	7793.25	88.28
C.E	53.73	704.00	340.61	352.50	25647.62	160.15
T	22.90	25.30	24.00	24 .05	0.42	0.654
D.O	3.20	8.00	6.00	6.35	1.75	1.32
TH	74.92	330.52	159.17	144.45	5590.78	74.77
Alk	9.76	58.56	33.55	35.38	178.01	13.34
ORP	130.27	395.00	286.61	305.35	5456.84	73.87
Ca^{2+}	10.00	54.00	26.00	23.00	203.33	14.26
Mg^{2+}	10.00	47.00	22.64	20.00	122.34	11.06
Na^{+}	11.65	119.25	50.98	53.22	933.69	30.56
K^{+}	1.90	8.00	3.76	3.25	2.04	1.43
Cl^{-}	3.00	17.00	9.82	10.00	14.63	3.83
SO_4^{2-}	0.32	16.00	5.72	5.00	25.38	5.04
HCO_3^{-}	8.00	48.00	27.50	29.00	119.60	10.94
NO_3^{-}	0.25	6.30	1.61	1.15	2.16	1.47
PO_4^{3-}	0.18	2.10	0.75	0.67	0.31	0.56
F^{-}	0.10	0.90	0.29	0.21	0.06	0.23
Fe_{tot}	0.15	0.90	0.31	0.20	0.06	0.25
Fe^{2+}	0.02	0.75	0.18	0.08	0.06	0.24
Fe^{3+}	0.13	0.15	0.13	0.12	0.00	0.01

Table 3. Classification ofwater according the hardness

Classification	Hardness range (mg/L $CaCO_3$)
Soft	0 - 75
Medium hard	75 - 150
Hard	150 - 300
Very hard	> 300

In both seasons all the anion concentrations were below the WHO limits for drinking. In aerobic conditions, nitrates are the end product of the stabilization of organic nitrogen, NO_3^- concentration of groundwater samples varied from 0.3 to 2.55 mg/L and from 0.25 to 6.30 mg/L with a mean of 1.17 mg/L and 1.61 mg/L in rainy and dry seasons, respectively. In the studied area, nitrate concentration is below the WHO permissible limit of 50 mg/L. The orthophosphate (PO_4^{3-}) concentration ranged from 0.12 to 0.28 mg/L and from 0.18 to 2.10 mg/L with a mean of 0.19 mg/L and 0.75 mg/L in rainy and dry seasons, respectively. Fluoride (F^-) exhibited low concentration in groundwater samples with a range of 0.13 - 0.34 mg/L and an average of 0.2 mg/L in rainy season. In dry season the range of F^- concentration was 0.10 - 0.90 mg/L with an average of 0.29 mg/L.

The concentration of observed total iron (Fe_{tot}) in groundwater samples varied from 0.03 to 0.32 mg/L with a mean of 0.16 mg/L in rainy season while the range in dry season was 0.15 to 0.90 mg/L with a mean of 0.29 mg/L. Ionic iron (III) concentration as Fe^{3+} ranged from 0.01 to 0.15 mg/L with a mean of 0.09 mg/L in rainy season. In dry season, the range was 0.13 to 0.15 mg/L with a mean of 0.13 mg/L. In both seasons, the concentrations of major anions exhibited the following order: $HCO_3^- > Cl^- > SO_4^2$.

3.2 HIERARCHICAL CLUSTER ANALYSIS (HCA)

The spatial classes of groundwater samples are illustrated using a dendrogram. In rainy season, the dendrogram consists of three groups of very distinct groundwater samples **(fig. 2)**. Group 1 is very characteristic of the other two because it contains the samples with the lowest alkalinity **(fig. 3)**, lowest concentration of ammonium and fluoride ions **(figs. 4** and **5)** and the highest mineralization (EC, TDS) **(fig. 6)**. The trend of mineralization was in the following decreasing order: group 1 > group 2 > group3. These three clusters are also differentiated by the concentration of ammonium ion as: group 1 < group 2 < group 3. This suggests that degradation of organic matter is greater in water points of group 3 during the rainy season. The parameter Fe_{tot} discriminates also the three clusters.

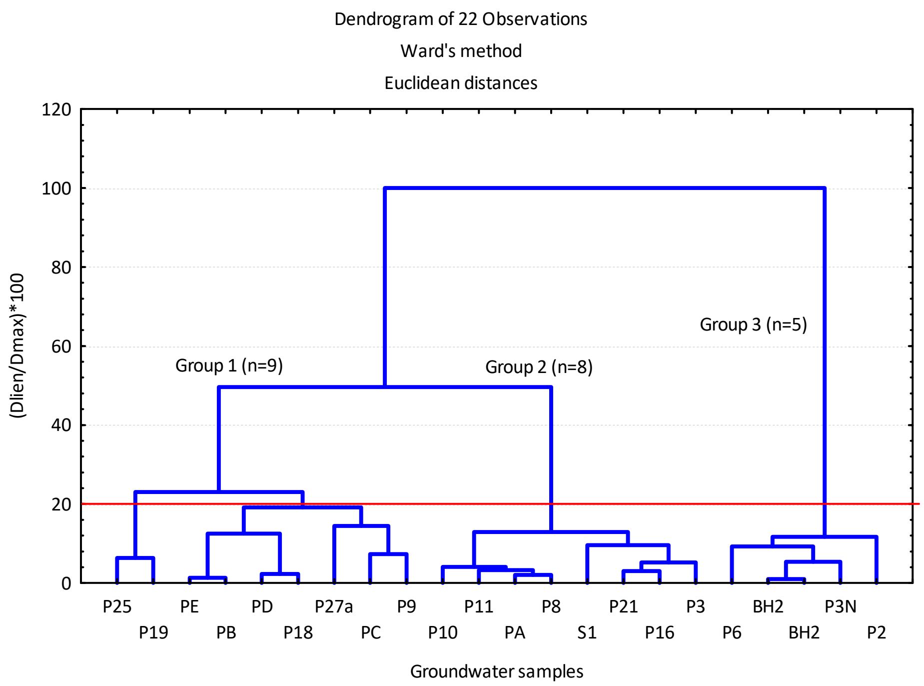

Fig. 2. Dendrogram of groundwater samples in rainy season

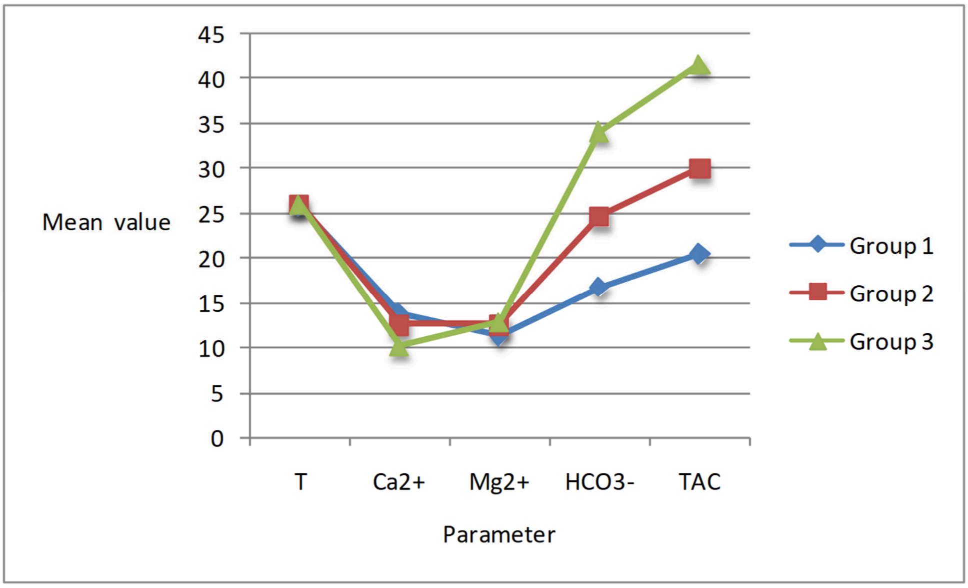

Fig. 3. Distribution of mean value of T, Ca 2+ , Mg 2+ , HCO3 and TAC in the three clusters (rainy season)

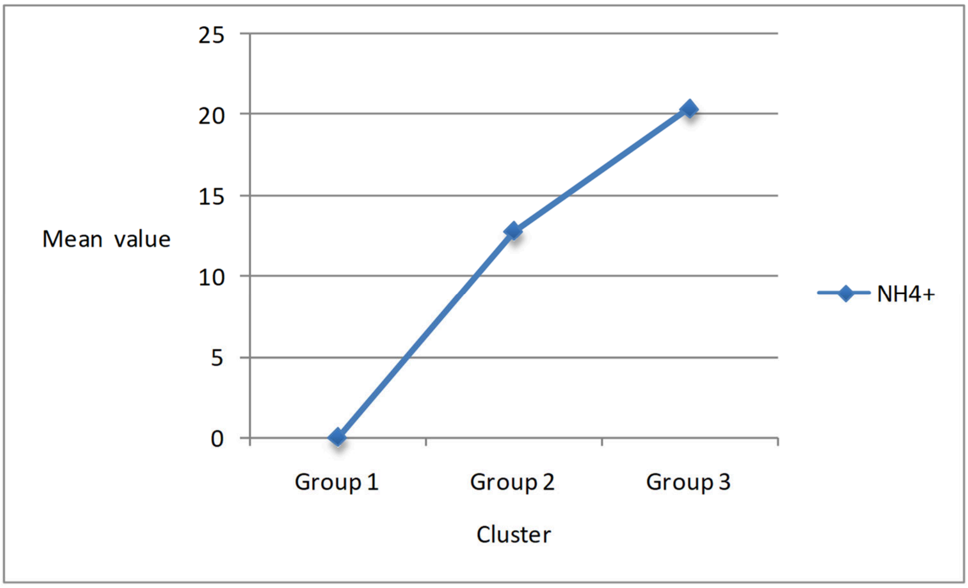

Fig. 4. Distribution of mean value of NH_4^+ concentration in the three clusters (rainy season)

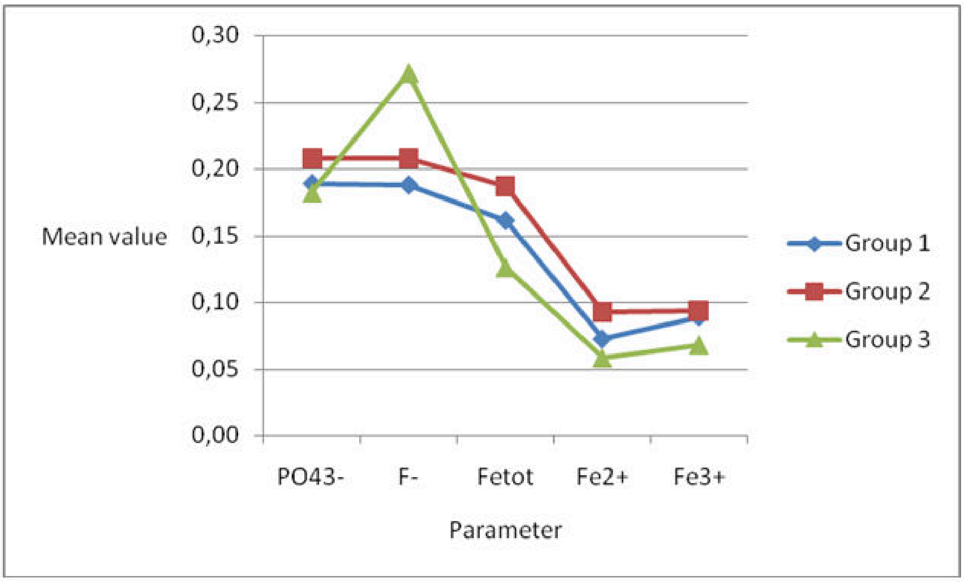

Fig. 5. Distribution of mean value of PO_4^{3-} , F^- , Fe_{tot} , Fe^{2+} and Fe^{3+} concentration in the three clusters (rainy season)

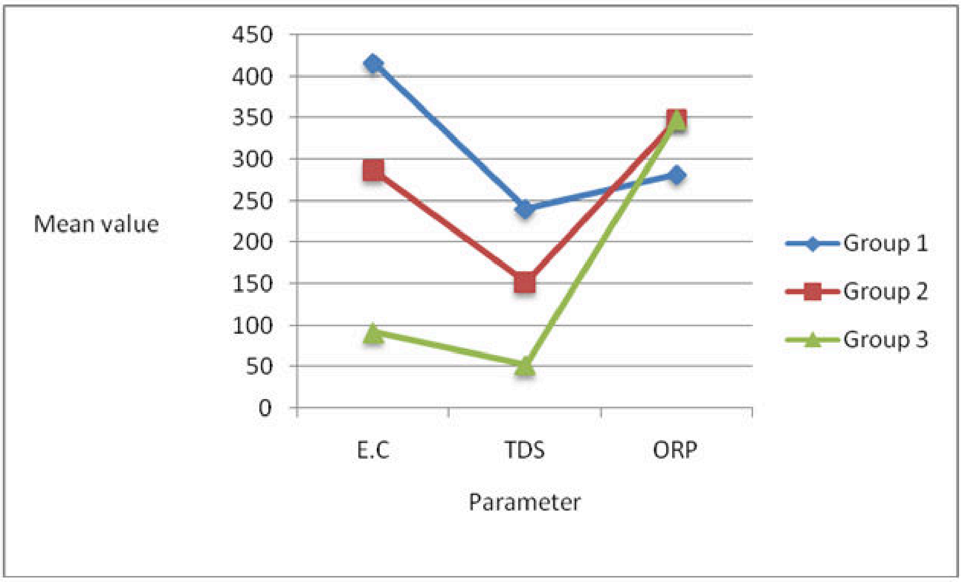

Fig. 6. Distribution of mean value of E.C, TDS and ORP in the three clusters (rainy season)

In dry season, the dendrogram presents four groups of groundwater samples **(fig. 7)**. The parameters that discriminate the four groups of groundwater samples are major ions Ca^{2+}, Na^{+}, Mg^{2+} **(fig. 8)** which translate the mineralization of water by the EC and TDS parameters and the hardness (TH) **(fig. 9)**. This mineralization is in the order: group 1 > group 2 > group 3 > group 4. Water hardness also discriminates the four groups of groundwater samples whose the predominance is in the order: group 1 > group 2 > group 4 > group 3 **(fig. 9)**. The classification of these groups of groundwater according to the hardness makes it possible to observe that the water samples in group 1 have an average hardness greater than 200 mg/L of $CaCO_3$, which classifies them as hard water.

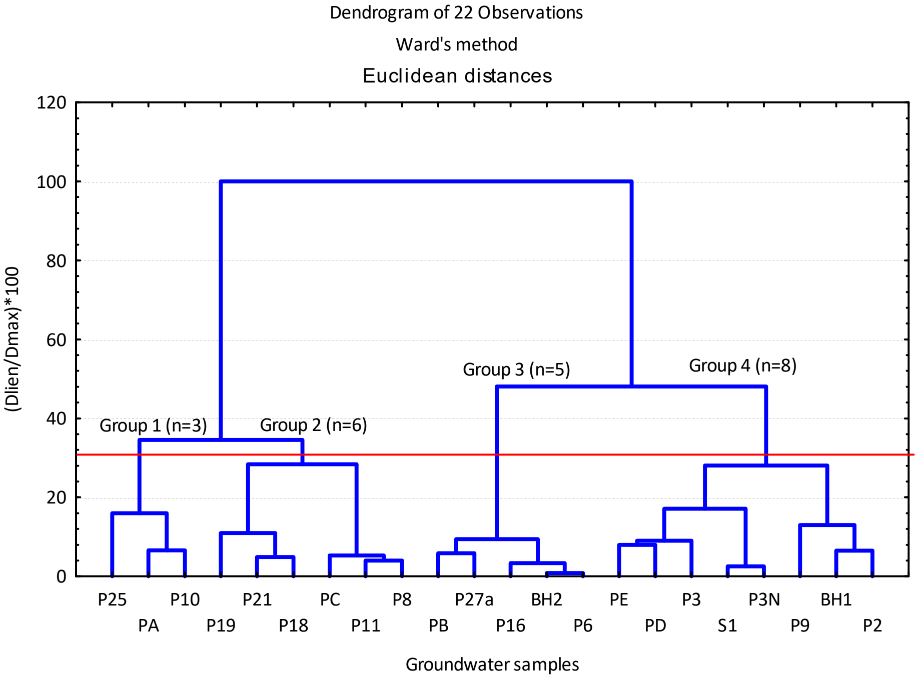

Fig. 7. Dendrogram of groundwater samples in dry season

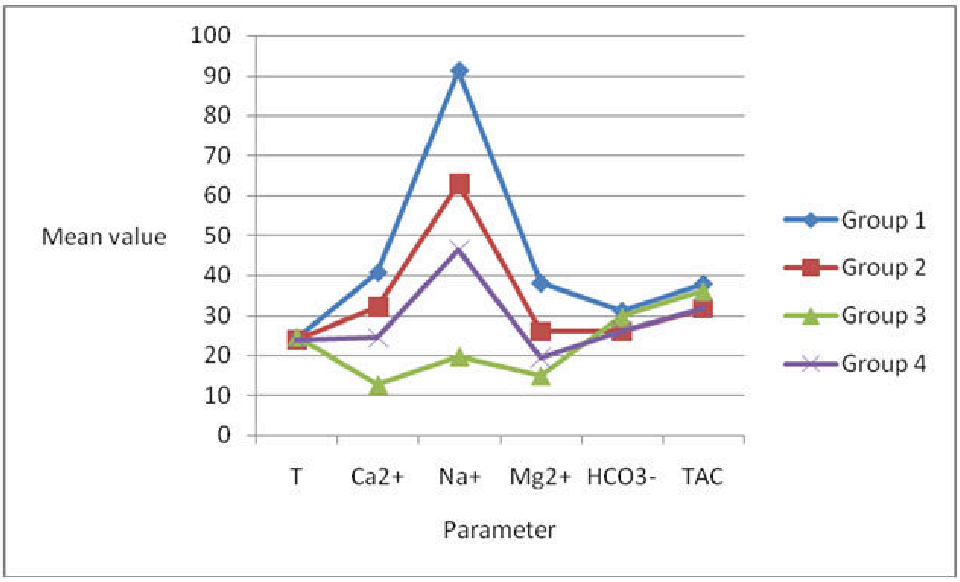

Fig. 8. Distribution of the mean value of T, Ca^{2+}, Na^{+}, Mg^{2+}, HCO_3^{-} and TAC in the four clusters (dry season)

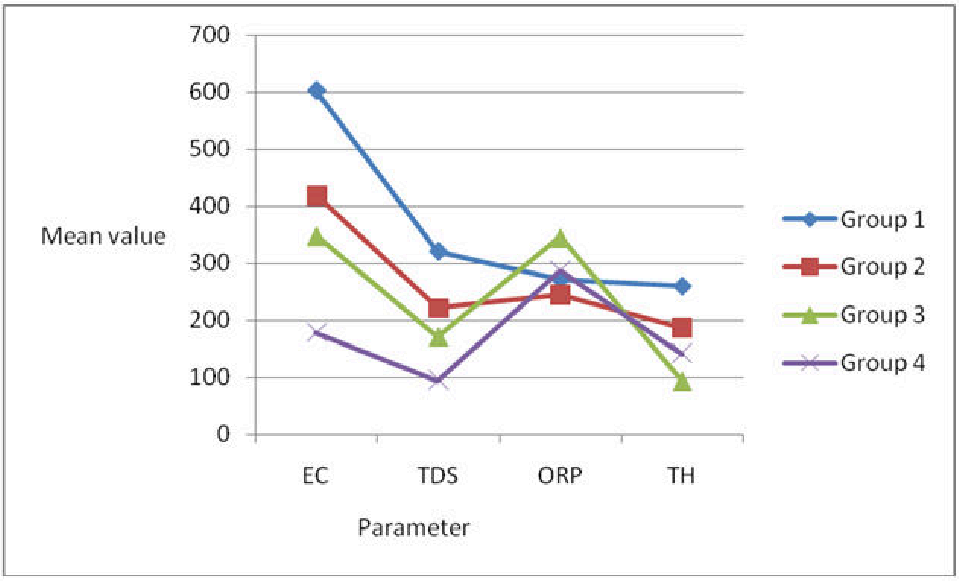

Fig. 9. Distribution of the mean value of EC, TDS, ORP and TH in the four clusters (dry season)

3.3 WATER TYPE

In the Schoeller diagram, taking into account the average composition of major ions, the facies of the groundwater samples in the different clusters are Na-HCO3 and Na-Mg-HCO3 in rainy season and dry season, respectively **(figs. 10** and **11)**

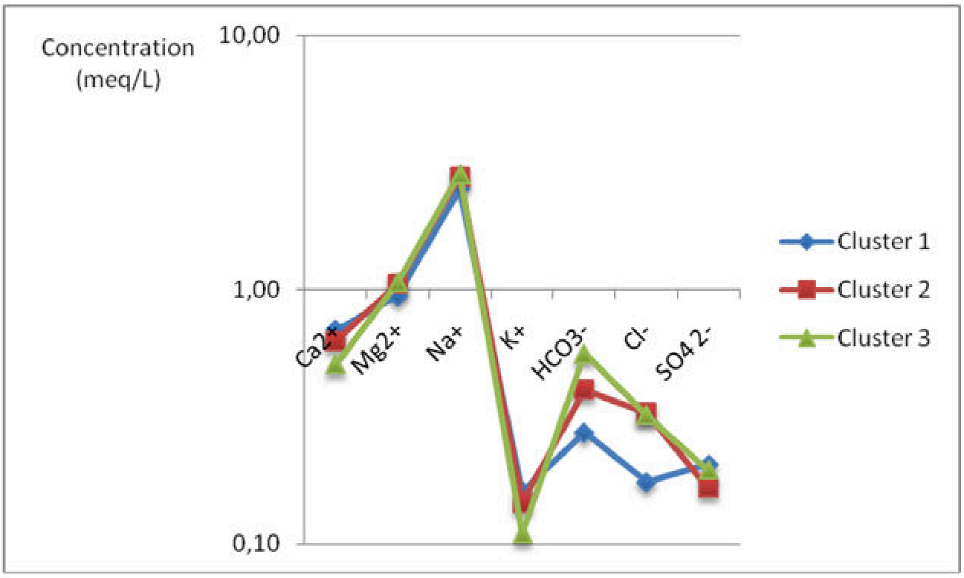

Fig. 10. Distribution of the average composition in major ions in the three clusters (rainy season)

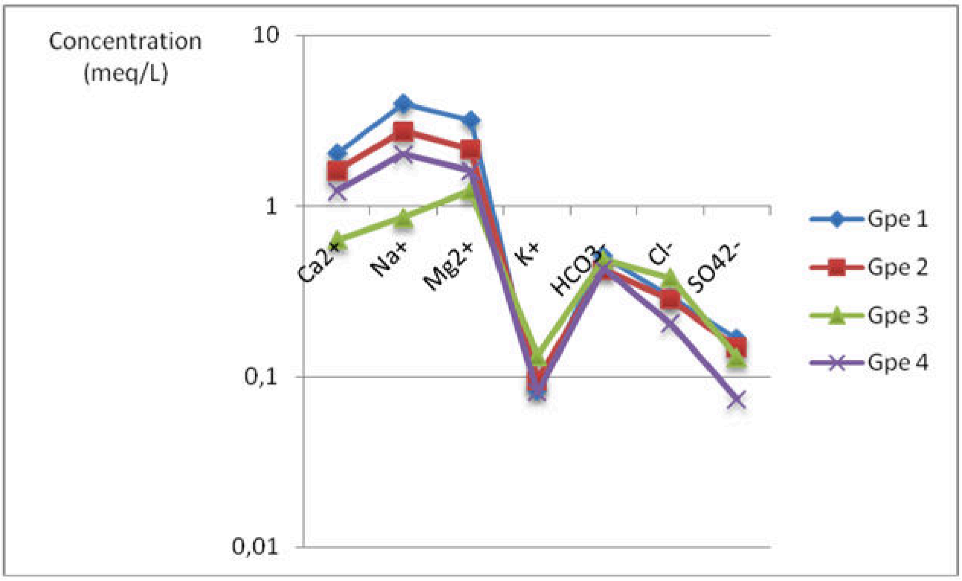

Fig. 11. Distribution of the average composition in major ions in the four clusters (dry season)

3.4 MODELING CHEMICAL SPECIATION OF IRON

The geochemical computer program Visual MINTEQ ver. 3.0 [12] was used to determinate the iron chemical species that may exist in the groundwater. This computer program has an extensive database of aqueous species for interpretation purposes. The input data take in account the parameters temperature, pH, and concentrations of Fe^{3+}, Fe^{2+}, Cl^-, SO_4^{2-}, F^- and PO_4^{3-}.

In rainy season according the computations, Fe (II) was mainly present as: Fe^{2+} and $FeSO_4$ (aq) constituting 96.04% and 3.94%, respectively of the species. $FeCl^+$ and FeF^- were present as traces **(fig. 12)**. Under the pH range of 5 to 8, the predominant dissolved form of iron Fe(II) was observed in other studies as Fe^{2+} [30]. The predominant forms of Fe (III) with their percentage distribution were FeF^{2+} (40.89%), $FeSO_4^+$ (36.49%), Fe^{3+} (15.21%) and FeF_2^+ (7.15%). The forms FeF_3 (aq), $FeCl^+$ and $Fe(SO_4)_2^-$ were present with a percentage distribution less than 1% **(fig. 13)**. Minor amounts of fluoride complexes were observed with trace constituents as iron in natural waters [31]. In water, fluoride acts as a strong anion and forms some soluble complexes with ferric ion (Fe^{3+}) and pH is a dependant parameter in the formation of these soluble complexes [32].

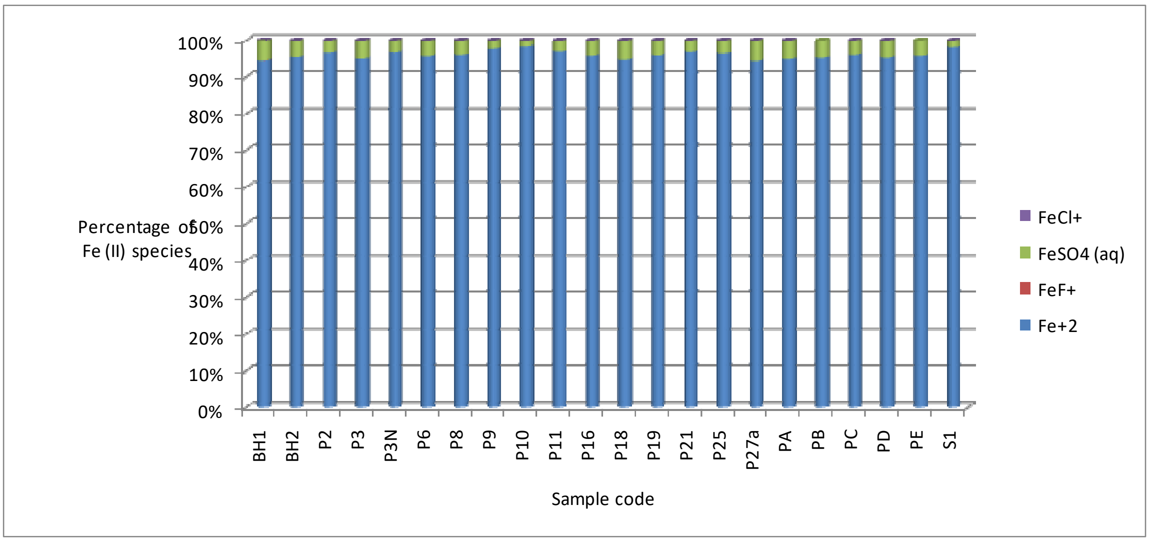

Fig. 12. Distribution of major Fe(II) species (rainy season)

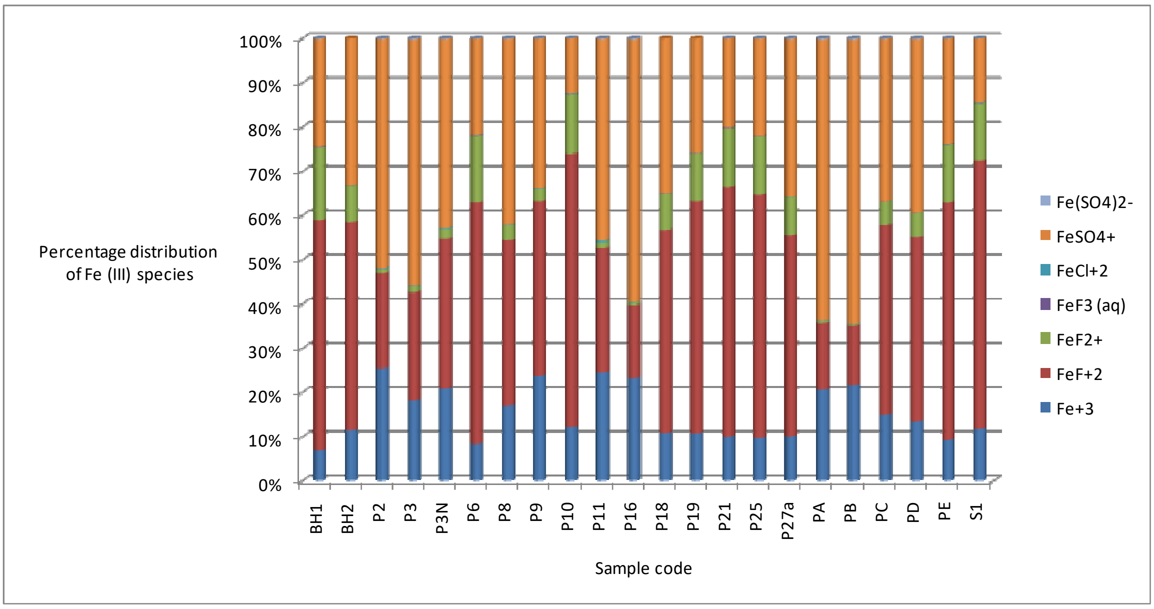

Fig. 13. Distribution of major Fe(III) species (rainy season)

In dry season, the majority of Fe(II) occurs as Fe^{2+} (98.47%), followed by melanterite FeSO4 (aq) or $FeSO_4$, $7H_2O$ (1.21%). The following forms: $FeCl^+$, FeF^+, $FeOH^+$, $FeHPO_4$ (aq) and $FeH_2PO_4^+$ were present at trace levels in all the groundwater samples **(fig. 14)**. The predominant species of Fe(III) were $Fe(OH)_2^+$ (83.35%), $FeOH^{2+}$ (11.86%) and $FeHPO_4^+$ (3.58%). Other forms such as $Fe(OH)_3$(aq), FeF^{2+}, $(FeF_2)^+$, FeF_3(aq), $FeCl^{2+}$, $FeSO_4^+$, $FeH_2PO_4^{2+}$, $FeCrO_4^+$ et $Fe(OH)_4^-$ occur at trace concentration **(fig. 15)**. Thus Fe^{2+} is the most soluble and bioavailable form of Fe(II) in the pH range observed during both seasons. Majority of the Fe(III) species (95.21%) was found as hydroxo complexes.

Some studies have shown the predominance of ferrous ion and melanterite ($FeSO_4$, $7H_2O$) in the calculation of chemical speciation of iron in groundwater [33], [34], [35], 36].

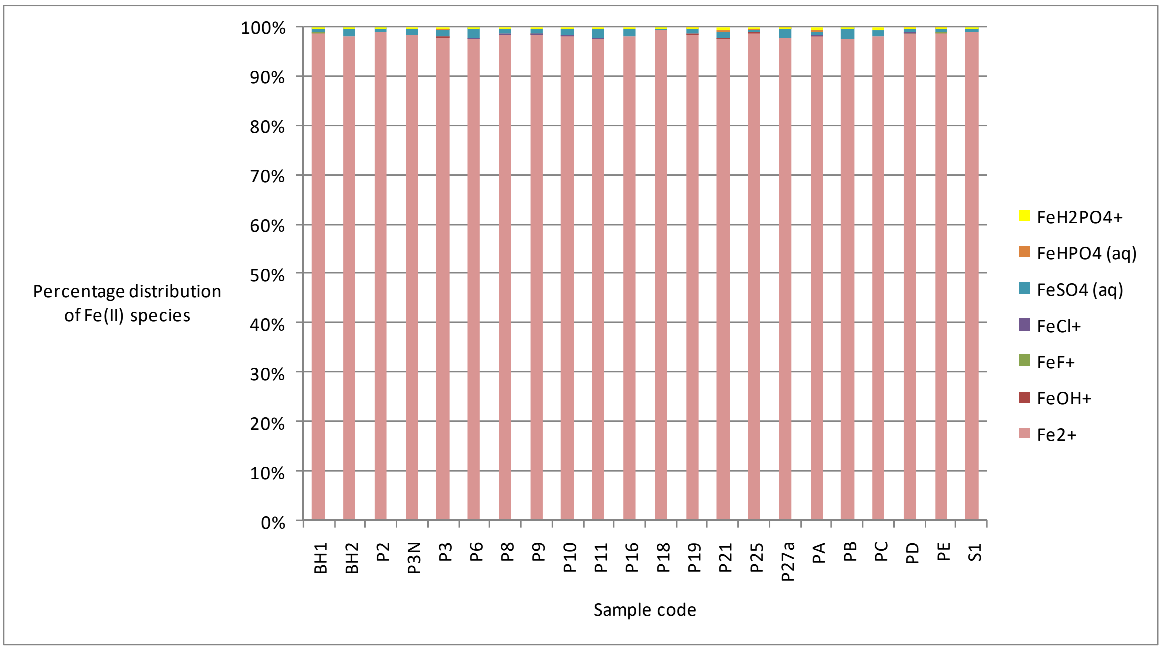

Fig. 14. Distribution of major Fe(II) species (dry season)

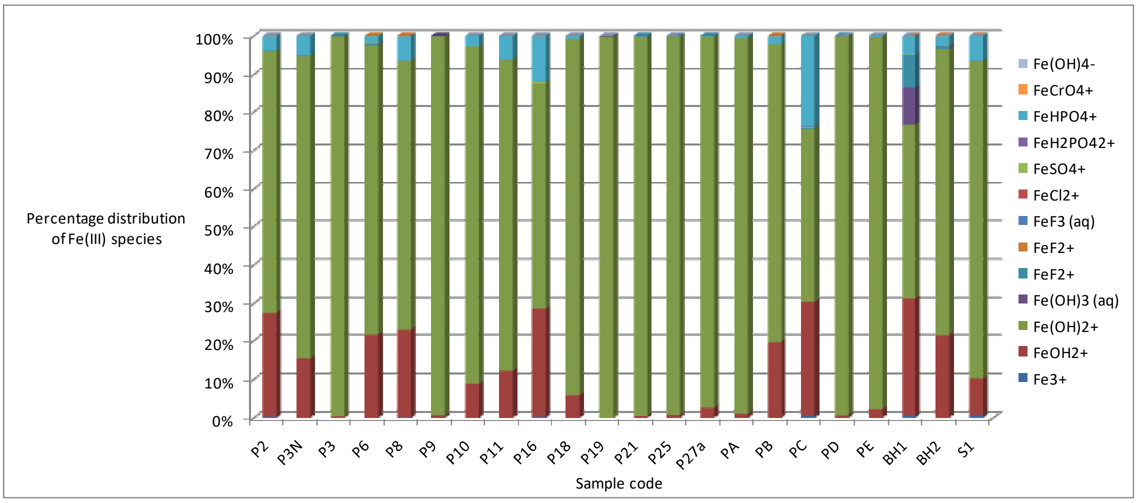

Fig. 15. Distribution of major Fe(III) species (dry season)

4 CONCLUSION

The hydrochemical analysis of the groundwater in the study area reveals that the groundwater is soft, more or less acidic tending towards neutrality in certain water points. The oxidizing conditions prevail in the groundwater during both seasons. Cluster analysis has highlighted the discriminant parameters among the groundwater sample groups, namely alkalinity, NH_4^+ that reflect a decomposition of organic matter, fluoride and total iron in the rainy season. In dry season, the discriminant parameters between groups of groundwater samples were EC and TDS, which reflect mineralization, ORP and total hardness. Calculating the chemical speciation of iron in the groundwater samples using the Vminteq program indicate that the forms Fe^{2+} following by $FeSO_4$(aq) are predominant for Fe(II) in both seasons. The majority of Fe $^{3+}$ ions in the groundwater samples is in complexed form. Fluoride complexes and the hydroxo complexes of Fe(III) occur mostly in the rainy season and are predominant in the dry season for Fe(III).

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