



Chemical Speciation of Some metal ions in Groundwaters of Yola Area Using Geochemical Model

^{1*}GABRIEL IKE OBIEFUNA; ²DONATUS MADUKA ORAZULIKE

¹Department of Geology, Federal University of Technology, Yola, Nigeria

²Geology Programme, Abubakar Tafawa Balewa University, Bauchi, Nigeria

Corresponding Author: *E-mail: gobiefuna2000@yahoo.com Mobile Phone: +2348034964345

ABSTRACT: Chemical speciation of some metal ions in groundwaters of Yola area using geochemical model were carried out to determine the water quality of the area using the PHREEQC speciation model. The study findings based on model calculations indicated that free Na^+ , Ca^{2+} , Mg^{2+} and K^+ ions are present and the consequent bioavailability are 95.83% to 99.84% at the pH ranges of 6.1 to 7.8 of the tested wells. Iron as free Fe^{2+} was bioavailable at 46.53% to 79.37% of the total iron. The lower values of free Fe^{2+} ions are related to the organic complexation of the ions. The model findings suggest that Fe^{2+} levels present a health risks in some water samples. The result also indicate that the concentration of Na^+ , Ca^{2+} , Mg^{2+} and K^+ at such level would be available for uptake by plants, animals and humans. @ JASEM

Groundwater contains a wide variety of dissolved inorganic species in various concentrations, as a result of chemical and biochemical interactions between groundwater and the geological materials through which it flows, and to a lesser extent because of contributions from the atmosphere and surface water bodies (Freeze and Cherry, 1979). The presence of various inorganic constituents in groundwater is controlled by the reaction mechanisms such as dissolution/precipitation reactions and adsorption including the rates (kinetics) of the geochemical process (Appelo and Postma, 1993). Analytical techniques such as spectrometry and chromatography provide important information about the metals concentration in water, ions in groundwater can form unlimited number of species due to the hydrolysis, complexation and redox reactions (Baes and Mesmer., 1979). The selected five metals are of importance to water chemistry. Calcium is an essential alkaline-earth element for plant and animal life forms, and the solubility of its carbonate in water results in stalactites and stalagmites and hardness in water. Sodium is widely used in the manufacture of sodamide, sodium cyanide, sodium peroxide and sodium hydride as well as in the preparation of tetraethyl lead PbEt_4 an important anti-knock agent in gasoline. Such applications tend to increase its level in the environment. Magnesium is produced from various activities especially in making organomagnesium compounds, useful in organic synthesis and is also an essential alkaline-earth element for plant and animal nutrition. Potassium is used in the manufacture of fertilizers usually as chlorides, sulphate, nitrate and carbonate and is extensively deposited in the environment. Iron is the cheapest and most abundant, useful (especially as an alloy in the production of steel) and important of all metals. Such qualities tend to increase its level in the environment. The PHREEQC speciation model was used to calculate ion activities. The PHREEQC model is a geochemical speciation model that is capable of computing specific equilibrium ion activities among the dissolved and adsorbed species and their equilibrium

solid phase. The model is able to consider the interaction of major cations with anions (Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-}) as a function of temperature, ionic strength and pH. The aim of this study is to estimate the activities of various ionic species of sodium, calcium, magnesium, potassium and iron in groundwater using geochemical models from the measured ion concentrations.

The Study Area: The study area fall within longitudes $12^\circ 20' \text{E}$ and $12^\circ 34' \text{E}$ and latitudes $9^\circ 11' \text{N}$ and $9^\circ 24' \text{N}$ and lies about 50 km south of the Hawal Massifs. It is bounded to the east by the Republic of Cameroun and to the west by Ngurore town. The northern boundary is demarcated by Gokra town and the southern boundary by the Mandarare town and occupies approximately 431 km^2 of the land surface.

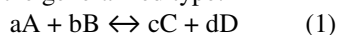
MATERIALS AND METHODS

The investigation of groundwater chemistry in the study area started with the chemical analyses of ninety-six water samples collected from shallow hand-dug wells (80), deep wells (11), surface waters (11) and precipitation (5) in Yola Area; Figure 1. Samples collection was aimed at covering and representing the lateral and vertical extent of the hydrostratigraphic units within the study area along with surface water and rainfall.

The samples from the deep wells in which pumps are already installed, were collected after a few hours of pumping and the screen interval of the well represents the average sample depth. Samples from the shallow hand-dug wells were bailed, using a stainless steel bailer, from a depth of a few meters below the water table, which more or less indicates the sample depth (Abdalla, 2009). The samples were collected in 1000-ml plastic bottles and field filtration was carried out through filter papers ($0.45 \mu\text{m}$) to remove suspended solids. They were then carefully sealed, labeled and taken for analyses. Chemical analyses were performed in the laboratory of the Adamawa State Water Board Yola, Nigeria employing standard methods, Atomic Absorption Spectrophotometry for cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Fe) and conventional

titration for anions (HCO_3^- , SO_4^{2-} , Cl^- , NO_3^-). Ions were converted from milligram per litre to milliequivalent per litre and anions balanced against cations as a control check of the reliability of the analyses results.

Geochemical Modeling: The hydrogeochemical computer model PHREEQC (Parkhurst and Appelo 1999) performs speciation calculations based on the law of mass action which states that for a reaction of the generalized type:



the distribution at equilibrium of the species at the left and right side of the reaction is given by:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2)$$

where; K = equilibrium constant and the bracketed quantities denote activities or effective concentrations. In the present investigations we equate activities with molal concentrations.

PHREEQC (Parkhurst and Appelo 1999) is a computer model for performing hydrogeochemical calculations such as exchange and surface complexations, mineral reactions and equilibrations and mixing of water. PHREEQC operates with input files in which the calculation instructions are arranged according to key-words. These keywords are largely self-instructive as is illustrated by the example input file below where the keywords have been capitalized. Several databases are available with constants for the various reactions. The aqueous concentrations in a solution are defined with SOLUTION. The symbols for the elements are listed in the first column of SOLUTION_MASTER_SPECIES in the database.

SOLUTION 1

Speciate and analyses, calculate saturation indices

Temp 25 # temperature in degrees celcius, default = 25 °C

pH 7.0 # default pH = 7

pe 4.0 # pe = -log (electron activity), default = 4

-units mmol/kgw # default units mmol/kg water

Ca 3.0 # total dissolved Ca

Na 1.0

K 2.0

Mg 4.0

Alkalinity 3.8 as HCO_3^- # mmol charge / kgw

S 1.0 # total sulphur, mainly sulphate, S (6), at pe = 4

N (5) # nitrogen in the form of nitrate, N (5) Cl 1.0

Water 1 # kg water default = 1 kg

Density 1 # density, default = 1 kg/L

END

PHREEQC has been enhanced with several new features to increase applicability, such as one-dimensional transport with dispersion and diffusive exchange with stagnant zones, exchangers and surfaces that can be coupled to varying amounts of minerals or reactants, and generalized kinetics (Parkhurst and Appelo 1999). This version has been used to calculate the data shown in Tables 2, 3 and 4.

RESULTS AND DISCUSSION

Analytical data are provided in Table 1. The pH values for tested samples varied from 6.1 to 7.8 for shallow groundwater, 6.8 to 7.8 for deep groundwater and 7.20 to 8.00 in surface water samples. Sodium concentrations range was between 0 and 157 mg/l in shallow groundwater 0.001 91.00 mg/l in deep groundwater and 2.23 to 211 mg/l for the surface waters respectively. In shallow groundwater potassium concentration ranges from 0 to 37 mg/l, 0 to 12.10 mg/l in deep groundwater and 1.20 to 9.00 mg/l for the surface waters respectively. The concentration of calcium in shallow groundwater samples are less than 25 mg/l, less than 39 mg/l in deep groundwater samples and between 1.20 to 9 mg/l in the surface water samples respectively. Magnesium concentration in shallow groundwater is less than 51mg/l, less than 55 mg/l in deep groundwater and between 12 and 84 mg/l in the surface water samples respectively. Iron concentrations range was between 0.001 and 1.80 mg/l in shallow groundwater, 0 and 0.32 mg/l in deep groundwater and 0 to 0.73 in the surface water samples respectively.

Table 1: Physicochemical parameters of Surfacewater and groundwater Samples (values in mg/l unless otherwise stated)

Parameter	Shallow Groundwater	Deep Groundwater	Surfacewater
Temp (°C)	(30-31) 30 ± 0.06	(30-32) 30.20 ± 0.60	(26-34) 29.56 ± 3.02
pH	(6.10-7.08) 7.09 ± 0.39	(6.60-7.80) 7.22 ± 0.41	(7.20-8.00) 7.57 ± 0.23
EC (ds/m)	(0.05-0.21) 0.09 ± 0.03	(0.04-0.18) 0.09 ± 0.04	(0.07 – 0.45) 0.22 ± 0.11
TDS	(33-137)60 ± 18.83	(27-121) 63 ± 26	(41 - 298) 155 ± 72.60
Na ⁺	(0-157)34 ± 33.74	(0-91) 34 ± 34.30	(2.23 – 211) 73 ± 89.04
K ⁺	(0-37)4 ± 6.89	(0-12) 4.32 ± 4.16	(1.20 – 9.00) 5 ± 2.40
Mg ²⁺	(0.50-51)21 ± 9.00	(8-55) 31 ± 13.46	(12 -84) 35 ± 19. 09
Ca ²⁺	(0.48-25) 12 ± 6.19	(0.50-38)11.30 ± 11.70	(8 – 37) 26 ± 9.25
Fe	(0-1.80) 0.35 ± 0.41	(0-0.32)0.09 ± 0.10	(0.0.73) 0.30 ± 0.26
Fe ²⁺	(0-0.70) 0.12 ± 0.16	(0-0.11)0.03 ± 0.04	(0 – 0.40) 0.17 ± 0.15
Fe ³⁺	(0-1.14) 0.22 ± 0.27	(0.21)0.06 ± 0.05	(0 – 0.44) 0.14 ± 0.13
NO ₃ ⁻	(0-23) 4.36 ± 4.63	(0.66-31) 6 ± 8.63	(9 – 59) 35 ± 17.97
Cl ⁻	(0-239) 68 ± 56	(0-172)76 ± 61.82	(28 – 455)146 ± 138.28
HCO ₃ ⁻	(19.90-251) 93.4 ± 41	(50-207)103 ± 44.4	(49 – 273) 137 ± 63.27
SO ₄ ²⁻	(0-61) 11 ± 12.28	(0-65)14.80 ± 19.66	(2 - 29) 18 ± 7.52

Table 2: Result of PHREEQC output file containing activities and concentrations of some ionic species in Shallow Groundwater samples (After Obiefuna in Preparation)

Species	Concentration mg/l	Activity mg/l	Species	Concentration mg/l	Activity
Ca ²⁺	2.923E-004	2.145E-004	Na ⁺	1.492E-003	1.380E-003
CaHCO ₃ ⁺	6.089E-006	5.636E-006	NaHCO ₃ (aq)	1.490E-006	1.492E-006
CaSO ₄	3.161E-006	3.165E-006	NaHPO ₄	4.535E-008	4.189E-008
CaHPO ₄	2.005E-006	2.008E-006	NaSO ₄ ⁻	5.455E-007	5.039E-007
CaCO ₃ (aq)	4.892E-007	4.898E-07	NaCO ₃ ⁻ (aq)	4.346E-008	4.014E-008
CaH ₂ PO ₄ ⁺	1.295E-007	1.197E-07	NaF	1.472E-009	1.474E-009
CaPO ₄ ⁻	6.941E-008	6.411E-008	NaOH	1.120E-010	1.121E-010
CaF ⁺	4.212E-009	3.890E-009	Fe+2	2.292E-006	1.690E-006
CaOH ⁺	4.741E-010	4.379E-010	FeHCO ₃ ⁺	3.518E-007	3.250E-007
CaHSO ₄ ⁺	1.742E-012	1.609E-012	FeHPO ₄	1.046E-007	1.048E-007
K ⁺	1.010E-004	9.320E-005	FeCO ₃	4.937E-008	4.943E-008
KSO ₄ ⁻	5.456E-008	5.040E-008	Fe(HS) ₂	3.371E-008	3.375E-008
KHPO ₄ ⁻	3.064E-009	2.830E-009	FeSO ₄	2.319E-008	2.322E-008
KOH (aq)	3.970E-012	3.975E-012	FeH ₂ PO ₄ ⁺	1.818E-008	1.608E-008
Mg ²⁺	8.201E-004	6.041E-004	FeOH ⁺	1.028E-008	9.492E-009
MgHCO ₃ ⁺	1.509E-005	1.394E-005	FeCl ⁺	4.483E-009	4.141E-009
MgSO ₄	1.134E-005	1.135E-005	FeF ⁺	3.397E-011	3.137E-011
MgHPO ₄	7.636E-006	7.645E-006	Fe(HS) ₃	1.884E-011	1.704E-011
MgCO ₃	7.581E-007	7.591E-007	FeHSO ₄ ⁺	1.372E-014	1.268E-014
MgH ₂ PO ₄ ⁺	4.646E-007	4.292E-007	Fe(OH) ₃ ⁺	2.158E-006	2.160E-006
MgPO ₄ ⁻ (aq)	2.637E-007	2.436E-007	Fe(OH) ₂ ⁺	1.191E-006	1.100E-006
MgF ⁺	8.771E-008	8.102E-008	Fe(OH) ₄ ⁻	3.197E-008	2.953E-008
MgOH ⁺	4.554E-008	4.207E-008	FeOH +2	3.079E-010	2.241E-010

Tabulated analytical values of major cations, anions, and pH were used to create the input data file (Obiefuna in Preparation). Generated output by the model included the calculated ionic strength in the analyzed samples and activities of various metal ionic species whether free or complexed ions. A variety of reactions may occur which influences the speciation and mobility of metal contaminants including acid/base, precipitation/dissolution, sorption and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions will depend on factors such as pH, Eh, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials and organic matter content. Groundwater flow characteristics also influence the transport of metal contaminants. **Chemical Speciation of Sodium:** In natural water system dissolved sodium occurs in +1 oxidation state. The results indicate that Na⁺ is the most soluble chemical species of sodium in shallow groundwater and represent about 99% of the sodium. Complexed species indicate that 0.09% occurs as bicarbonate, 0.03% as sulphates and less than 0.002% as other anions. In deep groundwater Na⁺ represent 99.84% of the sodium whereas complexed species revealed that 0.10% occur as bicarbonates, 0.05% as sulphate and 0.004% as carbonate respectively. In surface water Na⁺ represent 99.82% of the sodium while complexed species disclosed that 0.12% occur

as bicarbonate, 0.04% as sulphate, 0.02% as NaHPO₄ and 0.01% as NaCO₃. Sodium can be removed from natural water by ion exchange and sorption to mineral surfaces. Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals and organic matter present in soils and sediments. Ion exchange and sorption of Na⁺ controls the mobility of sodium. In surface water and groundwater systems, a significant fraction of sodium is undissolved and occurs as precipitates (NaHCO₃, Na₂SO₄), sorbed ions or surface coatings on minerals, or as suspended organic matter.

Chemical Speciation of Potassium: Potassium like sodium has only one significant oxidation state K⁺ and it tends to be soluble in most types of natural water as sodium. Chemical speciation of Potassium in shallow groundwater with different anions is shown in Figure 5. It indicate that 99.94% of potassium exists as free (K⁺), about 0.05% as sulphate, 0.003% as KHPO₄ and about 0.0005% as KOH. In deep groundwater the chemical speciation of potassium with different anions indicate that 99.93% of potassium exists as free ions (K⁺), 0.07% as sulphate, 0.003% as KHPO₄ and 0% as KOH respectively. In surface water samples an estimated 99.93% of potassium occurs in free ionic form (K⁺), 0.06% occurs as KSO₄, 0.02% as KHPO₄ and 0% as KOH respectively.

¹GABRIEL IKE OBIEFUNA;²DONATUS MADUKA ORAZULIKE

Table 3 Summary of PHREEQC output file containing activities and concentrations of some ionic species in Deep Groundwater Samples (After Obiefuna in Preparation)

Species	Concentration mg/l	Activity mg/l	Species	Concentration mg/l	Activity
Ca ²⁺	2.700E-004	1.934E-004	NaHCO ₃ (aq)	1.528E-006	1.530E-006
CaHCO ₃ ⁺	5.823E-006	s.358E-006	NaSO ₄ ⁻	6.953E-007	6.381E-007
CaSO ₄	3.704E-006	3.709E-006	NaCO ₃ ⁻ (aq)	6.124E-008	5.620E-008
CaHPO ₄	1.720E-006	1.722E-006	NaHPO ₄ ⁻	4.220E-008	3.873E-008
CaCO ₃ (aq)	6.304E-007	6.313E-007	NaF	1.050E-009	1.051E-009
CaH ₂ PO ₄ ⁺	8.284E-008	7.602E-008	NaOH	1.472E-010	1.474E-010
CaPO ₄ ⁻	8.110E-008	7.443E-008	Fe+2	2.939E-007	2.116E-007
CaF ⁺	2.807E-009	2.576E-009	Fe(HS)2	2.609E-007	2.613E-007
CaOH ⁺	5.802E-010	5.325E-010	FeHCO ₃ ⁺	4.666E-008	4.282E-008
CaHSO ₄ ⁺	1.527E-012	1.401E-012	FeHPO ₄	1.243E-008	1.244E-008
K ⁺	1.104E-004	1.012E-004	FeCO ₃	8.800E-009	8.813E-009
KSO ₄ ⁻	7.766E-008	7.127E-008	FeSO ₄	3.781E009	3.786E-009
KHPO ₄ ⁻	3.177E-009	2.916E-009	FeOH ⁺	1.770E-009	1.624E-009
KOH (aq)	5.816E-012	5.825E-012	FeH ₂ PO ₄ ⁺	1.610E-009	1.478E-009
Mg ²⁺	1.212E-003	8.719E-004	Fe(HS) ₃ ⁻	1.154E-009	1.059E-009
MgHCO ₃ ⁺	2.308E-005	2.118E-005	FeCl ⁺	6.222E-010	1.5710E-010
MgSO ₄	2.133E-005	2.136E-005	FeF ⁺	3.132E-012	2.874E-012
MgHPO ₄	1.049E-005	1.050E-005	FeHSO ₄ ⁺	1.671E-015	1.533E-015
MgCO ₃	1.562E-006	1.564E-006	Fe(OH)3	6.859E-007	6.870E-007
MgPO ₄ ⁻ (aq)	4.934E-007	4.528E-007	Fe(OH)2 ⁺	2.805E-007	2.574E-007
MgH ₂ PO ₄ ⁺	4.757E-007	4.366E-007	Fe(OH)4 ⁻	1.390E-008	1.276E-008
MgF ⁺	9.350E-008	8.581E-008	FeOH+2	5.444E-010	3.862E-011
MgOH ⁺	9.065E-008	8.319E-008	FeH ₂ PO ₄ +2	1.412E-015	1.002E-015
Na ⁺	1.464E-003	1.345E-003	Fe+3	5.336E-16	2.671E-016

Chemical Speciation of Magnesium: In natural water system dissolved magnesium occurs in +2 oxidation state. Chemical speciation of magnesium in shallow groundwater samples indicate that 95.83% of magnesium is in the free ionic form (Mg²⁺), 1.76% occurs as bicarbonate, 1.33% as sulphate, 0.89% as MgHPO₄ and 0.09% as carbonate (Figure 8). The deep groundwater disclosed that 96.27% of magnesium exists as free ions (Mg²⁺), 1.83% as bicarbonate, 1.69% as sulphate, 0.12% as carbonate and 0.04% as phosphates. The surface water samples revealed similar trends as 92.45% of magnesium occur in free ionic state, 3.94% as phosphates, 1.83% as bicarbonates, 1.21% as sulphate and 0.19% as carbonates. Under most conditions Mg²⁺ and magnesium-hydroxide complexes are the most stable forms of lead. Low solubility compounds are formed by complexation with inorganic Cl⁻, CO₃, SO₄, PO₄. In surface water and groundwater systems, a significant fraction of magnesium is undissolved and occurs as precipitates (MgPO₄, MgCO₃, MgSO₄), sorbed ions or surface coatings on minerals, or suspended organic matter.

Chemical Speciation of Calcium: Calcium like magnesium has only one oxidation state Ca²⁺ and is largely soluble in most types of natural waters. Chemical speciation of calcium with different anions in shallow groundwater show that 96.07% exists as free ions (Ca²⁺), 2% as bicarbonates, 1.04% as sulphates and 0.66% as phosphates. In deep groundwater samples 95.79% of calcium occurs as

free ion (Ca²⁺), 2.07% as bicarbonates, 1.31% as sulphates and less than 0.90% as phosphates and carbonates respectively. The surface water samples revealed values of 93.48% of calcium occurring in free ionic form (Ca²⁺), and less than 7% occurring as phosphates, bicarbonates and sulphates respectively. Calcium can also be removed from natural water by ion exchange and sorption to mineral surfaces. Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals and organic matter present in soils and sediments. Ion exchange and sorption of Ca²⁺ controls the mobility of calcium. In surface water and groundwater systems, a significant fraction of sodium is undissolved and occurs as precipitates (CaCO₃, CaSO₄), sorbed ions or surface coatings on minerals, or as suspended organic matter.

Chemical Speciation of Iron: Iron may occur in solution as Fe⁺² or Fe⁺³ oxidation state. The redox conditions in oxygenated waters favour the more oxidized form (Fe³⁺). Ferrous ions (Fe²⁺) form complexes with a number of ligands, a strong FeHCO₃ and FeCO₃ appears likely to be the major form in natural water containing dissolved CO₂. Chemical speciation of iron in shallow groundwater samples indicated that 79.37% of iron is in the free ionic form (Fe²⁺), 12.18% as bicarbonate and less than 8% as phosphates, carbonates, sulphides and sulphates respectively. In deep groundwater 46.53% exists as free Fe²⁺ ions, 41.31% as sulphides, 7.39%

¹GABRIEL IKE OBIEFUNA;²DONATUS MADUKA ORAZULIKE

as bicarbonates and less than 4% as phosphates, carbonates and sulphates. In surface water samples an estimated 22.58% of iron occurs in free ionic form (Fe^{2+}), a predominant 67% occur as sulphides while the remaining 10.42% occur as phosphates, bicarbonates and carbonates respectively. Iron is an extremely mobile ion and its removal from groundwater is in most cases an extremely difficult tasks. Under mild oxidizing conditions iron is in a +3

valence state and forms an insoluble precipitates, Fe_2O_3 while under reducing conditions is converted to +2 valence states and is present as soluble Fe^{2+} cation. Increased iron concentrations in water samples are due to re-dissolution of previously formed unstable precipitates or due to leaching of iron from the adjacent rocks that bounds the aquifers of the study area.

Table 4: Summary of PHREEQC output file containing activities and concentrations of some ionic species in surface water (After Obiefuna in Preparation)

Species	Concentration mg/l	Activity mg/l	Species	Concentration mg/l	Activity
Ca^{2+}	5.995E-004	3.909E-04	MgF^+	1.806E-007	1.619E-007
CaHPO_4	2.648E-005	2.655E-005	Na^+	3.247E-003	2.916E-003
CaHCO_3^+	1.747E-005	1.573E-006	NaHCO_3 (aq)	4.844E-006	4.856E-006
CaSO_4	8.112E-006	8.132E-006	NaSO_4^-	1.677E-006	1.504E-006
CaCO_3 (aq)	4.067E-006	4.077E-006	NaHPO_4	7.221E-007	6.476E-007
$\text{CaH}_2\text{PO}_4^+$	5.854E-007	5.250E-007	NaCO_3^- (aq)	4.273E-007	3.832E-007
CaPO_4	2.832E-006	2.540E-007	NaOH	7.138E-010	7.156E-010
CaOH^+	2.687E-009	2.409E-010	NaF	4.438E-009	4.449E-009
CaF^+	1.118E-008	1.002E-010	$\text{Fe}(\text{HS})_2$	1.562E-010	1.567E-010
CaHSO_4^+	1.517E-012	1.361E-012	Fe^{+2}	1.912E-007	1.265E-007
K^+	1.332E-004	1.192E-005	FeHPO_4	5.723E-008	5.738E-008
KSO_4^-	1.010E-007	9.058E-008	FeHCO_3^+	4.179E-008	3.748E-008
KHPO_4^-	2.952E-008	2.647E-008	FeCO_3	1.704E-008	1.708E-008
KOH (aq)	1.531E-011	1.535E-012	$\text{FeH}_2\text{PO}_4^+$	3.405E-009	3.054E-009
Mg^{+2}	1.289E-003	8.522E-004	$\text{Fe}(\text{HS})_3^-$	2.242E-014	2.010E-014
MgHPO_4	7.805E-005	7.825E-005	FeSO_4	2.436E-009	2.443E-009
MgHCO_3^+	3.367E-005	3.020E-005	FeCl^+	7.177E-010	6.436E-010
MgSO_4	2.237E-005	2.242E-005	FeOH^+	2.318E-009	2.079E-009
$\text{MgH}_2\text{PO}_4^+$	1.625E-006	1.458E-006	FeF^+	3.741E-012	3.355E-012
MgPO_4^- (aq)	8.328E-006	7.469E-006	FeHSO_4^+	4.912E-016	4.405E-016
MgCO_3	4.895E-006	4.907E-006	$\text{Fe}(\text{OH})_3$	4.088E-006	4.098E-006
MgOH^+	1.922E-007	1.724E-007	$\text{Fe}(\text{OH})_2^+$	7.852E-007	7.042E-007
			$\text{Fe}(\text{OH})_4^-$	1.854E-007	1.663E-007

Main iron precipitates are hematite (αFeO_3) goethite ($\alpha\text{-FeOOH}$) and to a lesser amounts ferrihydrite ($\text{Fe}_5\text{HO}_8.4\text{H}_2\text{O}$) or iron hydroxide [$\text{Fe}(\text{OH})_3$]. Geochemical speciation calculations suggest that at pH values between 5 and 6 copper precipitates as cupric and cuprous ferrite.

Iron precipitates can be quite massive and often cause serious clogging problems of drinking water wells.

Conclusions: The study findings based on model calculations indicated that Na^+ , Ca^{2+} , Mg^{2+} and K^+ are highly soluble and consequently will be bioavailable at the pH ranges of the tested wells. Iron is also expected to be bioavailable as 46.53% to 79.37% of the total iron is presented as Fe^{2+} . The lower values of Fe^{2+} are related to the organic complexation of the ions. Identifying ionic distributions is of particular importance as pollutants affect the groundwater environment by the chemical behavior of the ionic species and transformation of species than by total

concentrations. The adverse effects of highly soluble free Fe^{2+} are important to groundwater chemistry because their inherent toxicity is related to their bioavailability. The result suggests that Na^+ , Ca^{2+} , Mg^{2+} and K^+ at such level would be available for uptake by plants, animals and humans. It is also highly possible that such conditions may constitute a negative health impact. The model findings also suggest that Fe^{2+} levels represent a health risks in some water samples.

Acknowledgements : The Authors are grateful to the Authorities of the Federal University of Technology Yola for granting the first author study fellowship to carry out his doctorate degree research work at Abubakar Tafawa Balewa University, Bauchi, Nigeria. The authors are also grateful to the anonymous reviewers for their constructive criticisms that contributed to the success of this paper. Ibrahim

¹GABRIEL IKE OBIEFUNA; ²DONATUS MADUKA ORAZULIKE

Ahmed drafted the figures and his tireless effort is gratefully acknowledged.

REFERENCES

- Abdalla, O.A.E (2009) Groundwater recharge/discharge in semi-arid regions interpreted from Isotope and chloride concentrations. *Hydrogeology Journal* vol (3):679-690
- Appelo, C.A and Postma, D (1993) *Geochemistry, groundwater and pollution*. A.A. Balkema.
- Baes, C.F and Mesmer, R.E (1979) *The hydrolysis of cations*. John Wiley and Sons, New York
- Felmy, A.R, Garvin, D.C and Jenne, E.A (1984) MINTEQA A computer program for Calculating aqueous geochemical equilibrium. NTIS PB 84-157148(EPA-600/3- 84032) Nat. Tech. Inf. Ser. Springfield
- Freeze, R.A and Cherry, J.A (1979) *Groundwater* Prentice-Hall, Englewood Cliffs, New Jersey
- Jenne, E.A (1979) Chemical modeling-goals, problems, approaches and priorities. *American Chemical Society*. 3-12
- Millero, J (2001) Speciation of metals in natural waters *geochemical transactions*, 8.
- Obiefuna, G.I (in Preparation) *Hydrogeochemistry and groundwater quality of Yola Area, Northeast, Nigeria* Unpublished PhD Thesis Abubakar Tafawa Balewa University, Bauchi, Nigeria.
- Parkhurst, D.L and Appelo, C. A .J (1999) User's guide to PHREEQC (version 2) - A Computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water Resources Investigation Report 99-4259*, Denver, USA
- Tawfic, T.A; Blaylock, M.J and Vance, G.F (1997) Selenite adsorption and solution Complexes in reclaimed mine soils: A comparative study using geochemical models *International conference on: Water management, salinity and pollution control Towards sustainable irrigation in the Mediterranean region, Bari Italy*.