

Contamination risk assessment of fresh groundwater using the distribution and chemical speciation of some potentially toxic elements in Calabar (southern Nigeria)

A. E. Edet · B. J. Merkel · O. E. Offiong

Abstract The computer program PHREEQC was used to determine the distribution, chemical speciation and mineral saturation indices in a fresh groundwater environment with limited mining activities in the adjoining areas. The aim was mainly to determine the potential risk of a coastal plain aquifer contamination by some potentially toxic elements. The results show that the elements Ba, Cd, Cu, Fe, Mn, Ni, Rb, Sr, and Zn are distributed as free metal ions. Arsenic is in the neutral form of H_3AsO_3^0 , while three species of aluminium [Al^{3+} , AlOH_2 , $\text{Al}(\text{OH})_2^+$] dominate. The major species of uranium include UO_2CO_3 , UO_2^{2+} , UO_2^+ , and UO_2OH^+ , respectively, in order of abundance. The groundwater is saturated with respect to alunite [$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$], basaluminite [$\text{Al}_4(\text{OH})_{10}\text{SO}_4$], boehmite [$\text{Al}(\text{OH})$], Cu metal (Cu), cuprous ferrite (CuFeO_2), diaspore [$\text{AlO}(\text{OH})$], gibbsite [$\text{Al}(\text{OH})_3$], goethite (FeOOH), hematite (Fe_2O_3), magnetite (Fe_3O_4) and uraninite (UO_2). Most of the species are not mobile under the prevailing pH (3.3 to 5.9) and Eh (7 to 158 mV) conditions. The mobile ones are very low in concentration and will be immobilized

by precipitation of mineral phases. The study concludes that presently these species do not pose any risk to the aquifer.

Keywords Contamination · Groundwater · Speciation · Toxic elements · Nigeria

Introduction

The chemical species of an element is important regarding its environmental chemistry. The species also give information on the mobility and therefore availability of the metal to living things and their potential toxicity (Fergusson 1990). Thus, the monitoring and modelling of the distribution of metals, especially in mining areas, is a subject of primary importance in studies aimed at the evaluation of environmental pollution (Salomons 1995; Dinelli and Tateo 2001).

In the present study area, major industries are nonexistent, and there are no mining activities except on a small scale in the neighbouring areas. The source of elements in the area has been attributed to weathering of the adjoining Precambrian and Cretaceous rocks, where quarrying for aggregate and barite mining has been going on a relatively small scale (Edet and others 2002). However, with the present directives by the Federal Government of Nigeria to the oil companies to use local raw material, the mining of barite in the area has increased by more than 20-fold in the last 5 years. The weathered materials and waste products from these mining activities, which are processed mechanically without any chemical treatment, are carried into the rivers as runoff, which eventually get into the aquiferous layers of the study area through recharge.

This article aims at determining the distribution and chemical species of some toxic elements in the groundwater of the Calabar coastal plain sand aquifer that may be at risk from mining activities from the nearby Oban massif. In addition, the possible environmental effects of these metals and metalloids are evaluated.

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The study area

The study area is between less than 5 m in the south to more than 90 m in the north above sea level in the southeastern sector of Nigeria, an area where rainfall (mean 242 cm/a) is concentrated in the wet season (June to September), with a minimum in the dry season (October to May).

The geology of the area is coastal plain sand of Tertiary to Quaternary age, which is underlain by rocks of the Cretaceous Calabar flank and Precambrian Oban massif (Fig. 1). The sediments of the coastal plain sands consist of an alternating sequence of loose gravel, sand, silt, and clay. The Cretaceous rocks include conglomerate, sandstone, shale, limestone, marlstone, etc, while gneiss, schist, granodiorite, granite, pegmatite, etc constitute rocks of the Precambrian Oban massif.

The identified economic minerals in the Cretaceous and Precambrian areas include barite, brine, feldspar, galena, gemstone, graphite, gold, ilmenite, kaolin, limestone, manganese, marble, mica, quartz, rutile, tin and uranium (CRSG 1989). Presently, quarrying of aggregate and limestone for construction and cement production is going on. The only mining activity in the area is for barite used by the oil companies, while mining for tin, gold, gemstone and uranium by a British company (Nigeria Proprietary Company) ceased in 1939 (CRSG 1989).

Hydrogeologically, the major aquifer in the area is the coastal plain sand aquifer. This aquifer is made up of two

sub-water-bearing units, the upper gravelly aquifer with depth to water level in the range 4.6 to 48.0 m with a mean of 30.0 m to the south of the study area. The second is the underlying unit known as the sandy aquifer that is exploited in the northern part of Calabar. The depth to water level is in the range of 56.7 to 70.2 m with a mean of 62.2 m (Edet and Okereke 2002).

Methods

Sampling and measurements

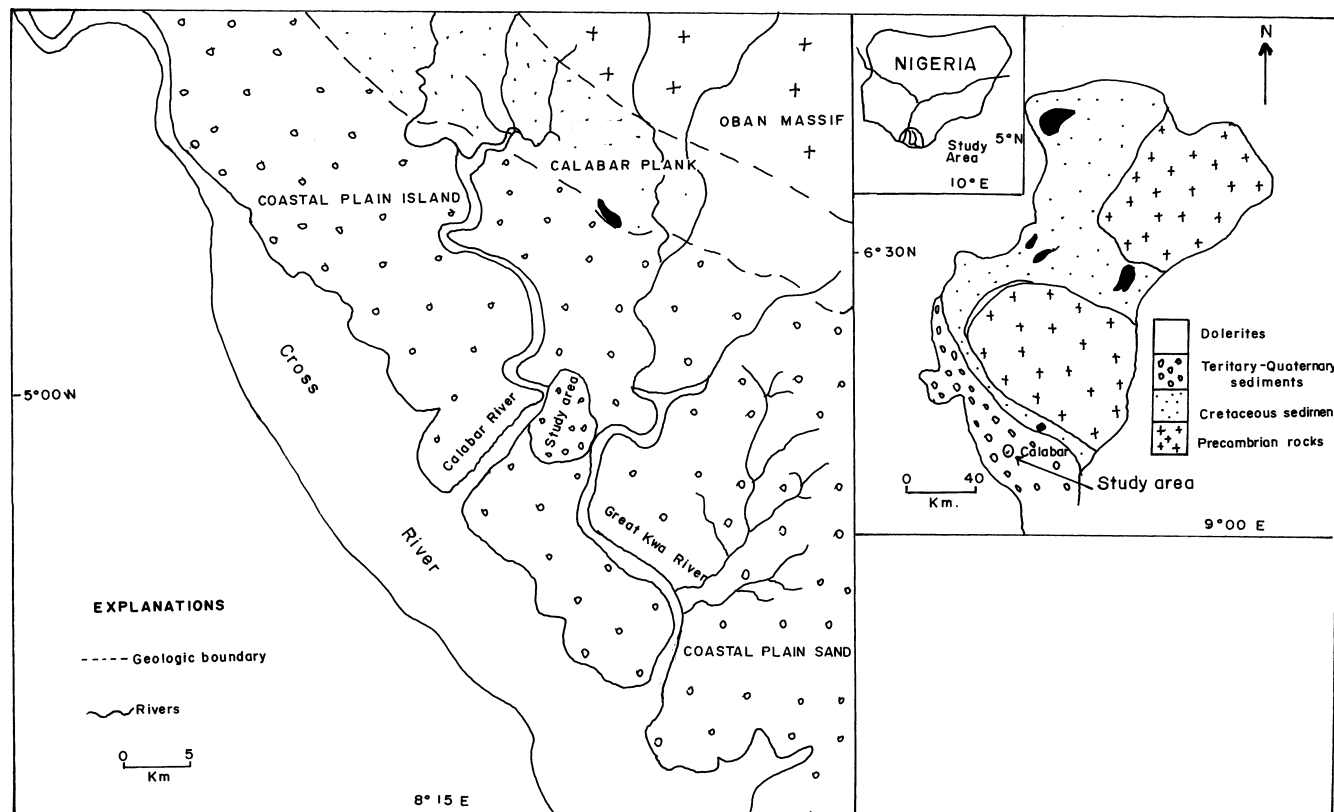
Groundwater samples were collected from 33 locations (Fig. 2). Of this number, 15, (representing 46%) are located within the upper gravelly water-bearing layer. Temperature, pH, Eh and electrical conductivity were measured in the field using standard field equipment. The details of sample collection, preservation and analysis for elements by ICP-MS are contained in Edet and others (2002). Also determined were the major cations and anions (Edet and others 2002).

Modelling

The computer program PHREEQC using the database wateq4f was used to calculate the distribution of the aqueous species. The database includes the following elements: aluminium, arsenic, barium, boron, bromine, cadmium, calcium, carbon, cerium, chlorine, copper, fluorine, hydrogen, iodine, iron, lead, lithium, magnesium, manganese, nickel, nitrogen, oxygen, phosphorus, potassium, silicon, sodium, strontium, sulphur, rubidium,

Fig. 1

Geological map of part of southern Nigeria including study area



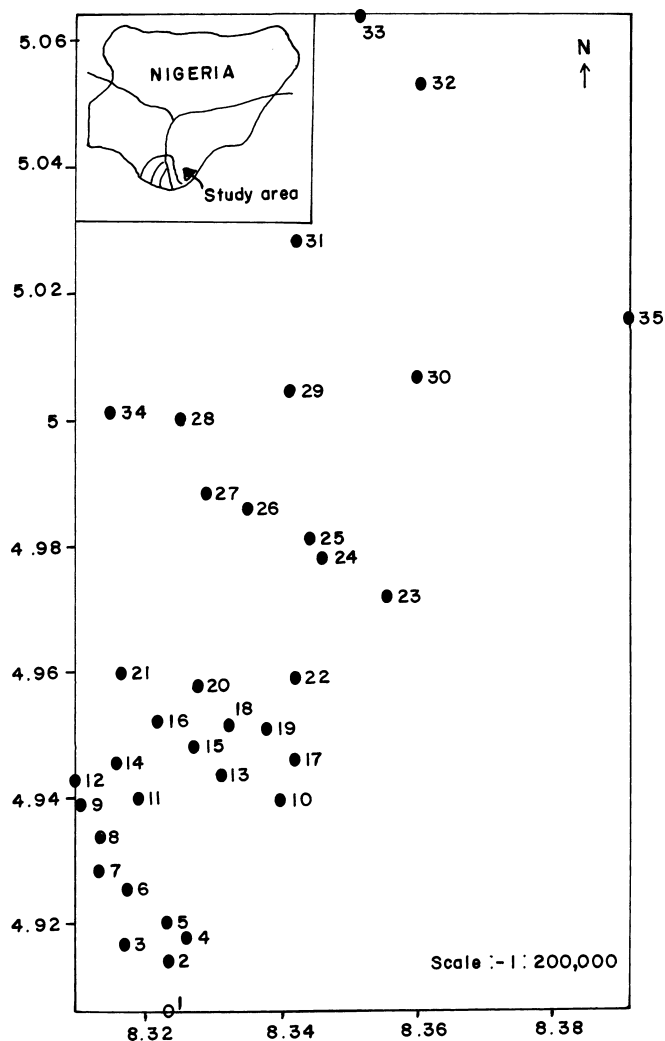


Fig. 2

Groundwater sample locations for the present study (locations 1 to 19, upper aquifer and locations 20 to 33 lower aquifer)

selenium, silver and zinc (Parkhurst 1995). The program is designed to perform a wide variety of aqueous geochemical calculations, based on an ion-association aqueous model. In addition, PHREEQC has the capability to handle environmental related pollution problems.

PHREEQC has also been used to evaluate which solid might be precipitating by means of saturation index. The saturation index (SI) is defined as the logarithm of the ratio of the ion activity product (IAP) of the component ions of the solid in solution to the solubility product (K) for the solid [SI=log IAP/K]. If the SI is zero, the water composition reflects the solubility equilibrium with respect to the mineral phase. A negative value indicates undersaturation and a positive value indicates supersaturation.

The ionic strength (I) has also been calculated with the software, PHREEQC. The ionic strength of a solution is a measure of the ion shielding that occurs around charged dissolved species (Deutsch 1997). The ionic strength is calculated as follows:

$$I = 0.5 \sum (C_i Z_i^2)$$

where C_i is the concentration in mol/L (M) of ion I and Z_i is the charge on ion.

Results

Groundwater pH and Eh

The pH of the groundwater varies from 3.3 to 5.9 (mean 4.7) considering the entire coastal plain aquifer (Table 1). With respect to the different aquifers, pH varies from 3.29 to 5.9 (mean 4.8) in the upper gravelly aquifer and 3.58 to 5.7 (mean 4.5) in the lower sandy aquifer. The Eh of the groundwater samples ranged from 7 to 158 mV for the entire area (Table 1). The range of Eh for the upper and lower aquifers is 7 to 158 mV (mean 102.7 mV) and 19 to 147 mV (mean 57.6 mV), respectively. This shows no marked difference between the two aquifers in terms of pH and Eh. The environment can be described as acidic and transitional.

Heavy metal content

Table 1 contains the summary of the chemical data for the groundwater for the entire study area and the mean values for the different aquifers. The data show that the concentrations are lower for the lower sandy layer in comparison to the upper gravelly layer. Generally, the concentrations are below the maximum admissible concentration.

The method of Ficklin and others (1992) as modified by Caboi and others (1999) based on the relationship between metal load and pH was used to classify the water in the area (Table 2). The heavy metal content (metal load) was defined as As+Bi+Cd+Co+Cr+Cu+Mo+Ni+Pb+Zn in mg/L. However, in this study, the metal load was computed as As+Cd+Co+Cr+Cu+Ni+Pb+Se+Sr+Tl+U+V+Zn. As indicated in Table 3 all the groundwater samples can be classified as acid-low metal with the exception of three locations within the upper layer (CA 1, CA 1a, CA 7) which are classified as near neutral-low metal. This indicates that leaching by acidic rainwater of the altered rocks is responsible for the acidic nature of the groundwater. The process of weathering of the Precambrian and Cretaceous rocks, tidal fluctuation in the south may be the major source of these elements (Edet and others 2003).

In addition, studies have indicated that metal concentrations in groundwater are diminished by the influx of unpolluted waters and by the removal of metals by adsorption and precipitation processes (Rosner 1998; Paulson 1999; Berger and others 2000; Dinelli and others 2001; Milu and others 2002). Hence, some metal inputs in the groundwater arising from the small-scale mining activities and weathering from the surrounding areas may have been removed due to the process described above.

Table 1Summary of chemical data ^a for the entire area (including mean values for the different aquifers)

Parameter	Units	Max	Min	Mean	Upper aquifer	Lower aquifer	MAC ^b (mg/L)
Temp	°C	29.7	26.0	27.8	27.88	27.63	
EC	µS/cm	352.0	35.0	130.6	185.33	64.50	
pH		5.9	3.3	4.7	4.81	4.43	
Eh	mV	158.00	7.00	93.76	82.11	108.71	
pe		2.69	0.12	1.59	1.40	1.85	
Si	mg/L	5.36	2.66	3.99	3.97	3.92	
Al	mg/L	3.36	0.03	0.36	0.57	0.11	
Fe	mg/L	8.71	0.02	0.59	0.82	0.33	0.20
Mn	mg/L	0.12	0.009	0.04	0.06	0.02	0.05
Mg	mg/L	3.15	0.11	0.78	1.09	0.41	
Ca	mg/L	22.50	0.40	5.44	8.26	2.12	
Na	mg/L	66.60	0.85	15.48	24.23	4.81	
K	mg/L	13.80	0.23	3.35	5.35	0.87	
Ti	mg/L	0.02	0.002	0.003	2.82	3.54	
NH ₄ ⁺	mg/L	2.52	0.00	0.24	0.37	0.10	
Cl ⁻	mg/L	68.60	0.98	13.28	21.85	2.88	
NO ₃ ⁻	mg/L	183.00	1.35	35.60	54.19	12.85	
SO ₄ ²⁻	mg/L	18.70	2.00	4.49	5.44	3.45	
HCO ₃	mg/L	24.40	6.10	11.46	13.89	8.71	
As	µg/L	0.21	0.03	0.07	0.09	0.04	0.05
Ba	µg/L	149.00	0.00	44.13	63.14	18.91	
Cd	µg/L	2.08	0.52	1.25	1.33	1.17	0.003
Co	µg/L	1.18	0.09	0.38	0.49	0.25	1.00
Cr	µg/L	3.80	0.70	1.42	1.79	0.98	
Cs	µg/L	1.08	0.04	0.25	0.39	0.08	
Cu	µg/L	64.60	0.00	16.08	15.28	16.06	
Li	µg/L	5.00	0.00	2.21	2.94	1.29	
Ni	µg/L	9.60	0.00	1.90	2.68	0.97	0.02
Pb	µg/L	20.90	1.90	5.84	5.56	6.15	0.0015
Rb	µg/L	24.30	1.04	7.60	11.57	2.66	
Se	µg/L	2.40	0.00	0.53	0.66	0.38	0.01
Tl	µg/L	0.19	0.01	0.05	0.08	0.02	0.002
U	µg/L	0.62	0.03	0.15	0.20	0.08	
V	µg/L	1.59	0.11	0.37	0.53	0.16	
Zn	µg/L	1.60	0.02	0.20	0.22	0.17	5.00
Zr	µg/L	0.56	0.00	0.03	0.32	0.02	

EC Electrical conductivity

^aAdapted from Edet and others (2002)^bMAC Maximum admissible concentration (Siegel 2002)**Table 2**

Relation between pH and metal load

Class	Metal load (mg/L)	pH	Description
1	>100	<3.0	High acid-extreme metal
2	1–100	<3.0	High acid-high metal
3	<1	<3.0	High acid-low metal
4	>100	3.0–5.5	Acid-extreme metal
5	1–100	3.0–5.5	Acid-high metal
6	<1	3.0–5.5	Acid-low metal
7	>100	>5.5	Near neutral-extreme metal
8	1–100	>5.5	Near neutral-high metal
9	<1	>5.5	Near neutral-low metal

Chemical speciation

The distribution of the different species is presented in Tables 4 and 5 while the mineral saturation indices are presented in Table 6.

Aluminium

The major species of aluminium in the groundwater include Al³⁺, AlOH₂, and Al(OH)₂⁺. The mean abundance is in the order Al³⁺ > Al(OH)₂⁺ > AlOH₂ in the upper aquifer and Al³⁺ > AlOH₂ > Al(OH)₂⁺ in the lower aquifer.

According to Bi (2000), the toxicity of Al depends on the form present in water rather than its total concentration. Free Al³⁺, aluminium hydroxide Al-OH including Al(OH)₂⁺ and AlOH₂ are thought to be the most toxic species whereas Al-fluoride complexes (Al-F) may mitigate toxicity and organically complexing aluminium (Al-org) are non-toxic (Bi 2000).

The water is saturated with respect to alunite [KAl₃(-SO₄)₂(OH)₆], basaluminite [Al₄(OH)₁₀SO₄], boehmite [Al(OH)₃], diaspore [AlO(OH)], and gibbsite [Al(OH)₃].

Table 3

Classification of the groundwater samples from the Calabar coastal plain sand aquifer

Aquifer	Location ^a	pH	Loading (mg/l)	Class
Upper	1	5.65	0.09	Near neutral-low metal
	2	5.78	0.03	Near neutral-low metal
	3	5.41	0.06	Acid-low metal
	4	5.16	0.10	Acid-low metal
	5	5.07	0.03	Acid-low metal
	6	5.92	0.07	Near neutral-low metal
	7	3.95	0.05	Acid-low metal
	8	5.57	0.08	Acid-low metal
	9	4.83	0.05	Acid-low metal
	10	5.13	0.09	Acid-low metal
	11	3.54	0.05	Acid-low metal
	12	4.9	0.05	Acid-low metal
	13	3.29	0.06	Acid-low metal
	14	4.7	0.09	Acid-low metal
	15	4.3	0.03	Acid-low metal
	16	5.03	0.07	Acid-low metal
	17	4.52	0.04	Acid-low metal
	18	3.75	0.09	Acid-low metal
	19	5.22	0.06	Acid-low metal
	20	4.77	0.06	Acid-low metal
	21	5.08	0.03	Acid-low metal
	22	3.58	0.04	Acid-low metal
	23	5.7	0.02	Acid-low metal
	24	4.04	0.02	Acid-low metal
Lower	25	4.29	0.03	Acid-low metal
	26	4.29	0.03	Acid-low metal
	27	5.15	0.03	Acid-low metal
	28	4.13	0.03	Acid-low metal
	29	4.2	0.05	Acid-low metal
	30	3.95	0.02	Acid-low metal
	31	4.6	0.04	Acid-low metal
	32	4.33	0.07	Acid-low metal
	33	3.92	0.04	Acid-low metal

^aSee Fig. 2

Under the prevailing pH-Eh conditions, the species Al^{3+} , $AlOH_2^+$ and $Al(OH)_2^+$ are mobile. The limiting phases include alunite, basaluminite, boehmite, diaspore, and gibbsite in the upper aquifer and diaspore in the lower. The high number of Al related mineral phases in the upper gravelly zone may be partly due to acid rain as precipitation is a source of recharge in the area. The low concentration of Al (mean 0.36 Al mg/L) and the saturated mineral phases that can immobilize the species causing Al to pose no threat to the groundwater.

Arsenic

Arsenic in the groundwater of the area, which is dominated by the more toxic form As^{3+} , is very low in concentration in both water-bearing units (mean 0.07 As μ g/L).

According to Smedley and Kinniburgh (2002), redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (pH <6.9); while at higher pH (pH >6.9), $HAsO_4^{2-}$ becomes dominant. Under reducing conditions at pH less than about 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate (Brookins 1988; Yan and others 2000). $H_3AsO_3^0$ is the dominant species in the groundwater of the area consti-

tuting 100% of the As and under the present pH-Eh condition, this species is immobile and thus does not constitute a problem in the area. In addition, one major barrier to the mobility of As is that it is removed relatively fast from water and bound to sediments (Reimann and Caritat 1998). Also, As can be adsorbed to clay that is present in the area. All these factors in addition to the low concentration of As, makes the groundwater safe from As pollution.

Barium

More than 95% of Ba is in the ionic form of Ba^{2+} with $BaSO_4$ generally less than 7%. The toxic form of Ba-carbonate is about 1% in the form of $BaHCO_3^+$. $BaHCO_3^+$ is present only in one location (CA 1) within the upper aquiferous layer (Table 4). The relatively high concentration of Ba (mean 44.13 Ba μ g/L) in the groundwater with respect to the other elements is attributed to the high barite in the rocks of the Oban massif (Ekwere and Ekwueme 1991; Rahman and others 1988). Ba^{2+} is immobile under the present conditions. In addition, the presence of clay will restrict its mobility.

Cadmium

The major ionic species of Cd in the groundwater is Cd^{2+} representing more than 85% of all the species of Cd. The others are $CdSO_4$ (<7%), $CdCl$ (<12%) and $CdHCO_3$ (<2%). $CdCl$ is present only in the upper aquifer and $CdHCO_3$ only in the lower aquifer. Under the present pH-Eh condition, Cd^{2+} which is toxic and carcinogenic is immobile and if present in high concentration may be adsorbed by clay; thus reducing its danger in the area.

Copper

Cu^+ is the main ionic species constituting 78% of the total Cu in the area. The $CuCl_2^-$ species represent about 22%. In the prevailing condition, Cu^+ is immobile. The groundwater is saturated with the mineral phase Cu metal (Cu) and cuprous ferrite ($CuFeO_2$) and this will restrict the mobility of Cu^+ , which is toxic if present in high doses (Reimann and Caritat 1998).

Iron

The oversaturation and near saturation of the mineral phases containing iron includes cuprous ferrite ($CuFeO_2$), goethite (FeOH), hematite (Fe_2O_3), and magnetite (Fe_3O_4). This is consistent with the high Fe content in the groundwater (mean 590 Fe μ g/L), with Fe^{2+} >95% in the upper and lower aquifers. The other species of Fe in the groundwater include $FeHCO_3$ (<6%) and $FeSO_4$ (<2%).

According to Reimann and Caritat (1998) Fe is toxic to humans in drinking water at levels >200 mg/L. In all the Eh-pH systems [(Fe-O-H), (Fe-C-O-H), (Fe-Si-O-H), (Fe-O-H-Si), (Fe-C-Si-O-H); Brookins 1988], under the present pH-Eh condition, Fe^{2+} is immobile. Mobility will also be restricted in the area by precipitation as Fe oxides (hematite, magnetite), oxyhydroxides (goethite) and co-precipitating with other metals (cuprous ferrite).

Table 4

Distribution of species in the groundwater samples from Calabar

Aquifer	Location ^a	Al		As	Ba			Cd				Cu		Mn		
		Al ³⁺	Al OH ₂	Al (OH) ₂ ⁺	H ₃ AsO ₃ ⁰	Ba ²⁺	BaHCO ₃ ⁺	BaSO ₄	Cd ²⁺	Cd SO ₄	Cd Cl	Cd HCO ₃	Cu ⁺	CuCl ₂ ⁻	Mn ²⁺	Mn HCO ₃
Upper	1	4	17	65	100	95	1	4	90	7	3	0	97	3	100	0
	2	2	12	69	100	98	0	2	97	0	3	0	99	1	100	0
	3	2	12	68	100	99	0	1	97	2	1	0	99	1	100	0
	4	26	32	43	100	99	0	1	97	3	0	0	99	1	100	0
	5	28	33	35	100	99	0	1	96	0	4	0	100	0	100	0
	6	0	16	65	100	100	0	0	96	0	4	0	98	2	100	0
	7	88	8	0	100	99	0	1	96	0	4	0	95	5	100	0
	8	6	20	66	100	98	0	2	86	0	12	0	100	0	100	0
	9	45	29	18	100	97	0	3	91	0	8	0	78	22	100	0
	10	23	33	42	100	99	0	1	98	0	2	0	90	10	100	0
	11	86	2	1	100	97	0	3	92	0	8	0	87	13	95	5
	12	40	32	23	100	98	0	2	94	0	6	0	91	9	98	2
	13	88	1	1	100	97	0	3	86	2	12	0	100	0	94	6
	14	54	28	4	100	99	0	1	93	0	7	0	91	9	100	0
	15	80	14	2	100	99	0	1	95	0	5	0	90	10	98	2
	16	35	32	26	100	97	0	3	93	7	0	0	88	12	96	4
	17	72	20	8	100	98	0	2	94	0	0	0	97	3	99	1
	18	91	6	3	100	99	0	1	92	8	0	0	80	20	97	3
	19	16	30	15	100	99	0	1	98	2	0	0	99	1	99	1
	20	47	31	20	100	99	0	1	98	2	0	0	99	1	99	1
	21	24	33	40	100	99	0	1	98	0	0	0	99	1	99	1
	22	91	3	1	100	99	0	1	98	0	0	2	99	1	97	3
	23	3	16	69	100	99	0	1	98	2	0	0	99	1	98	2
	24	84	10	6	100	99	0	1	99	0	0	1	92	8	98	2
Lower	25	78	16	6	100	99	0	1	98	0	0	0	93	7	98	2
	26	79	6	15	100	99	0	1	98	2	0	0	93	7	100	0
	27	21	32	43	100	98	0	2	98	2	0	0	99	1	98	2
	28	82	12	12	100	99	0	1	98	0	0	2	89	9	98	2
	29	81	13	12	100	99	0	1	98	2	0	0	99	1	98	2
	30	87	8	5	100	98	0	2	99	0	0	1	100	0	98	2
	31	61	25	9	100	99	0	1	99	1	0	0	100	0	98	2
	32	62	12	2	100	93	0	7	99	1	0	0	100	0	95	5
	33	88	7	5	100	98	0	2	97	3	0	0	87	13	97	3

^aSee Fig. 2

Manganese

Mn is non-toxic and more than 90% is in the ionic form as Mn²⁺ in the groundwater with about 10% in the form MnHCO₃. In the present pH-Eh of the groundwater, Mn²⁺ is not mobile; and as it is not toxic, it does not pose a problem in the area.

Nickel

The Ni species in the groundwater are Ni²⁺ (~ 94%) and NiCO₃ (~ 6%). As Ni²⁺ compounds are non-toxic (Reimann and Caritat 1998) and with its immobility under the present pH-Eh condition, Ni does not pose any threat to the groundwater.

Lead

The dominant dissolved Pb species in the area is the Pb²⁺ comprising between 70 and 99% of all the species. The species PbHCO₃ and PbCO₃ are in the range 1 to 29% and 0 to 17%, respectively. There is no marked difference in the distribution of Pb²⁺ in the different aquifers units but the distribution of PbHCO₃ and PbCO₃ are slightly higher in the upper aquifer. This is due to the relatively high pH and HCO₃ in the upper unit compared to the lower unit. Under the present condition, Pb²⁺ is mobile. However, the contamination risks of the aquifers are from Pb contamination does not pose a problem, as the concentration of Pb is low (mean 5.84 Pb µg/L) and PbCO₃ will restrict its mobility.

Strontium

The major ionic species of Sr is in the form Sr⁺ (>97%), SrSO₄ (3%) and SrHCO₃ (1%). In the present pH-Eh condition, Sr⁺ is very mobile but with SrSO₄ as the limiting phase and the low concentration (mean 23.40 Sr µg/L), the groundwater does not face any potential contamination risk with respect to Sr in the area.

Uranium

Uranium is considered chemotoxic, radiotoxic and carcinogenic (Reimann and Caritat 1998). The dominant species of U include UO₂CO₃ (19 to 71%), UO₂²⁺ (2 to 73%), UO₂⁺ (2 to 39%) and UO₂OH⁺ (1 to 20%). There is no marked difference in both the upper and lower aquifers except with UO₂²⁺, which is higher in the lower aquifer. Under various Eh-pH systems [(U-C-O-H), (U-O-H), (U-Si-C-OH), (U-Si-O-H)], (Brookins 1988) and considering the prevailing pH-Eh, U is not mobile. The groundwater is saturated with uraninite (UO₂), which is the main limiting phase. The immobility of U under the present condition, presence of limiting phase and low concentration (mean 0.15 U µg/L) caused U not to be a potential contamination risk to the groundwater.

Zinc

In all the groundwater samples, Zn²⁺ constitutes the major ionic species ranging between 94 and 98%. The minor species include ZnHCO₃ (2 to 8%) and ZnSO₄ (0 to 3%). In the present condition Zn²⁺ is not mobile and with the low

Fe ²⁺	Fe		Ni		Pb			U				Sr			Zn	
	Fe HCO ₃	Fe SO ₄	Ni ²⁺	Ni CO ₃	Pb ²⁺	Pb HCO ₃	Pb CO ₃	UO ₂ ⁺	UO ₂ ²⁺	UO ₂ O- H ⁺	UO ₂ CO ₃	Sr ⁺	Sr SO ₄	Sr HCO ₃	Zn ²⁺	Zn HCO ₃
95	3	2	100	0	70	17	8	20	2	5	57	98	2	0	94	4
98	2	0	100	0	73	15	9	22	2	7	54	99	1	0	96	3
97	2	1	100	0	73	15	8	22	2	7	56	99	1	0	98	2
96	3	1	100	0	78	16	3	20	8	7	62	97	3	0	98	2
96	3	1	100	0	92	5	3	39	17	13	30	99	1	0	98	2
96	3	1	100	0	67	16	17	19	2	5	51	99	1	0	95	5
98	2	0	100	0	86	12	2	10	64	4	22	99	0	1	97	3
97	3	0	100	0	75	13	22	13	4	9	63	99	1	0	96	4
97	3	0	100	0	84	10	6	20	23	10	47	99	1	0	97	3
98	2	0	96	4	85	12	3	6	13	12	67	99	1	0	97	3
95	5	0	94	6	73	23	4	7	69	5	19	98	2	0	94	6
98	2	0	97	3	84	11	5	15	20	11	53	99	1	0	97	3
94	6	0	100	0	66	29	5	4	71	1	14	98	0	2	92	8
98	2	0	96	4	84	12	4	14	25	10	47	99	1	0	97	3
98	2	0	97	3	83	14	3	13	42	5	41	99	0	1	97	3
96	4	0	94	6	76	18	0	28	9	6	54	99	1	0	95	5
98	2	0	98	2	90	8	2	17	43	8	31	99	1	0	98	2
97	3	0	96	4	78	20	2	7	64	2	22	99	0	1	96	4
98	2	0	98	2	91	6	1	11	13	20	53	99	1	0	98	2
99	1	0	99	1	99	1	0	21	26	13	37	99	1	0	98	2
99	1	0	98	2	91	1	0	24	20	14	43	99	1	0	98	2
96	4	0	95	5	78	21	0	5	73	2	19	99	0	1	96	4
97	3	0	94	6	80	11	9	34	9	3	48	99	1	0	98	2
98	2	0	97	3	87	12	1	16	55	4	22	99	1	0	97	3
98	2	0	98	2	89	10	1	30	40	5	22	99	1	0	98	2
98	2	0	99	1	89	10	1	22	45	6	25	99	1	0	98	2
98	2	0	96	4	84	12	4	2	13	13	71	99	1	0	97	3
97	3	0	96	4	83	16	1	4	52	5	37	99	0	1	97	3
98	2	0	97	3	88	10	2	22	48	5	24	99	1	0	98	2
98	2	0	97	3	86	13	1	11	62	4	23	99	1	0	97	3
98	2	0	97	3	84	14	2	22	25	7	44	99	1	0	97	3
95	2	3	95	5	80	14	6	5	43	6	38	97	3	0	95	2
97	3	0	96	4	80	18	2	11	57	3	28	99	0	1	96	4

concentration (0.20 Zn mg/L) will not pose any contamination risk to the groundwater.

Mineral saturation

The groundwater in the area is oversaturated with respect to diaspore [AlO(OH)] in both aquiferous layers. Most of the samples are oversaturated with alunite [KAl₃(SO₄)₂(OH)₆], basaluminite [Al₄(OH)₁₀ SO₄], boehmite [Al(OH)], and gibbsite [Al(OH)₃] in the upper aquifer in comparison to the lower aquifer. In both aquifers, the water is slightly undersaturated with respect to barite (BaSO₄) while 55% of all the samples are oversaturated with Cu metal and more than 90% saturated with respect to cuprous ferrite (CuFeO₂). The groundwater samples are almost in equilibrium with goethite (FeOOH), hematite (Fe₂O₃), magnetite (Fe₃O₄) and jurbanite (AlOHSO₄). Twelve (12) (total of 18) and 7 (total of 15) samples, respectively, for the upper and lower aquifers, showed oversaturation with respect to uraninite (UO₂).

The high content of oxides of aluminium and iron is attributed to the weathering of silicate minerals, which is accelerated, by the acidic precipitation and groundwater temperature of the area. The occurrences of the saturated or near saturated phases of Cu, Ba and U in the groundwater are attributed mainly to the minerals barite, copper, and uranium.

Ionic strength

The ionic strength (I) of the groundwater ranges between 7.73×10^{-4} and 5.18×10^{-3} (mean 2.89×10^{-4}). According to Appelo and Postma (1999), the ionic strength for freshwater is normally less than 0.02 while seawater has ionic strength of about 0.7. Also Deutsch (1997) reported that the ionic strength of most dilute groundwater is in the range of 10^{-2} to 10^{-3} . The values of the ionic strength show that the groundwater samples from the area are fresh. The mean values for the upper and lower aquifers are 5.24×10^{-4} and 1.68×10^{-3} , respectively, indicating water of relatively better quality in the lower aquifer.

It has been noted that ion shielding lowers the activity of dissolved species; therefore the higher the ionic strength, the greater the shielding and the greater the solubility of the mineral in contact (Deutsch 1997). Hence, the result of the ionic strength indicates greater solubility and hence mobility of the dissolved species in the upper aquifer in comparison to the lower aquifer.

Discussion

The speciation calculation indicates that the elements Ba, Fe, Mn, Rb, Sr, and Zn are distributed more than 90% as free ion species in all the analysed groundwater samples. The elements Cd, Cu, and Pb are distributed with more

Table 5

Summary of distribution of species in the different aquifers in Calabar (including entire area)

Area	Species	Upper aquifer			Lower aquifer			Study area		
		Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
Al	Al ³⁺	91.00	0.00	42.78	91.00	3.00	62.76	91.00	0.00	50.73
	AlOH ₂	33.00	1.00	19.28	33.00	3.00	16.47	33.00	1.00	18.21
	Al(OH) ₂ ⁺	69.00	0.00	29.94	69.00	1.00	15.94	69.00	0.00	24.21
As	H ₃ AsO ₃ ⁰	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ba	Ba ²⁺	100.00	95.00	98.17	99.00	93.00	98.41	100.00	93.00	98.27
	BaHCO ₃ ⁺	1.00	0.00	0.06	0.00	0.00	0.00	1.00	0.00	0.03
Cd	BaSO ₄	4.00	0.00	1.78	7.00	1.00	1.59	7.00	0.00	1.70
	Cd ²⁺	98.00	86.00	93.50	99.00	92.00	97.59	99.00	86.00	95.64
	CdSO ₄	8.00	0.00	1.61	8.00	0.00	1.47	8.00	0.00	1.39
	CdCl	12.00	0.00	4.39	0.00	0.00	0.00	12.00	0.00	2.39
	CdHCO ₃	0.00	0.00	0.00	2.00	0.00	0.35	2.00	0.00	0.18
Cu	Cu ⁺	100.00	78.00	93.28	100.00	80.00	95.53	100.00	78.00	94.73
	CuCl ₂ ⁻	22.00	0.00	6.72	20.00	0.00	4.35	22.00	0.00	5.21
Fe	Fe ²⁺	98.00	94.00	96.78	99.00	95.00	97.59	99.00	94.00	97.15
	FeHCO ₃	6.00	2.00	2.89	4.00	1.00	2.24	6.00	1.00	2.58
	FeSO ₄	2.00	0.00	0.33	3.00	0.00	0.18	3.00	0.00	0.27
Mn	Mn ²⁺	100.00	94.00	98.72	100.00	95.00	98.00	100.00	94.00	98.39
	MnHCO ₃	6.00	0.00	1.28	5.00	0.00	2.00	6.00	0.00	1.61
Ni	Ni ²⁺	100.00	94.00	98.22	99.00	94.00	96.82	100.00	94.00	97.58
	NiCO ₃	6.00	0.00	1.78	6.00	1.00	3.18	6.00	0.00	2.42

Table 6

Saturation indices for mineral phases and ionic strength for the groundwater in Calabar

Aquifer	Location ^a	Al(OH) ₃	Alunite	Barite	Basaluminate	Boehmite	Cu metal
Upper	1	-0.55	3.34	-1.11	2.36	1.68	1.11
	2	-0.73	1.52	-1.39	0.92	1.50	1.14
	3	-1.33	-0.38	-1.35	-1.23	0.90	1.76
	4	-1.74	-0.38	0.85	-1.96	0.48	1.50
	5	-0.75	3.09	-0.91	2.26	1.47	0.50
	6	0.00	2.89	-1.42	3.68	2.23	1.16
	7	-3.85	-3.60	-4.04	-8.47	-1.62	-0.40
	8	-0.20	3.86	-0.51	3.25	2.03	-0.42
	9	-0.98	4.31	-0.68	1.76	1.25	-0.47
	10	-1.60	-0.70	-2.15	-1.67	0.63	0.81
	11	-4.78	-3.28	-0.34	-10.17	-2.55	-1.29
	12	-1.41	2.85	-0.37	0.91	1.10	-0.48
	13	-5.10	-3.42	-0.47	-11.11	-2.88	-0.46
	14	-1.78	1.16	-0.77	-1.67	0.46	0.30
	15	-3.34	-3.07	-1.77	-6.53	-1.12	-0.65
	16	-1.03	3.62	-0.56	1.77	1.19	0.89
	17	-2.48	-0.88	-1.13	-3.17	-0.27	0.09
	18	-4.13	-3.89	-1.39	-9.00	-1.90	-0.34
	19	-1.28	0.22	-1.26	-0.83	0.95	0.63
	20	-2.23	-1.93	-1.73	-3.73	0.00	0.81
	21	-1.58	-0.80	-1.77	-1.67	0.65	0.56
	22	-5.64	-7.72	-1.30	-14.38	-3.41	-0.74
	23	-0.63	0.73	-1.91	1.57	1.60	1.12
	24	-4.58	-6.59	-1.67	-11.60	-2.34	-0.48
Lower	25	-3.57	-4.21	-1.55	-7.71	-1.34	0.27
	26	-3.70	-5.03	-1.90	-8.17	-1.48	0.26
	27	-1.39	0.40	-1.66	-0.66	0.84	-0.51
	28	-3.55	-3.03	-1.76	-7.55	-1.32	-0.77
	29	-3.55	-2.58	-1.65	-6.01	-0.97	0.50
	30	-4.38	-5.49	-1.73	-10.12	-2.16	-0.45
	31	-2.71	-2.77	-1.79	-4.85	-0.48	0.45
	32	-3.10	-1.20	-0.95	-4.75	-0.87	-0.41
	33	-4.58	-5.87	-1.61	-11.02	-2.36	-0.26

^aSee Fig. 2

Table 5
(Contd.)

Area Element	Species	Upper aquifer			Lower aquifer			Study area		
		Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
Pb	Pb ²⁺	92.00	66.00	78.72	99.00	78.00	85.71	99.00	66.00	82.00
	PbHCO ₃	29.00	5.00	14.78	21.00	1.00	11.59	29.00	1.00	13.18
	PbCO ₃	22.00	0.00	5.89	9.00	0.00	2.06	22.00	0.00	4.15
U	UO ₂ ⁺	39.00	4.00	16.44	34.00	2.00	15.53	39.00	2.00	16.24
	UO ₂ ²⁺	71.00	2.00	26.67	73.00	9.00	40.47	73.00	2.00	32.15
	UO ₂ OH ⁺	13.00	1.00	7.06	20.00	2.00	7.06	20.00	1.00	7.18
	UO ₂ CO ₃	67.00	14.00	43.89	71.00	19.00	35.60	71.00	14.00	40.12
Sr	Sr ⁺	99.00	97.00	98.72	99.00	97.00	98.88	99.00	97.00	98.79
	SrSO ₄	3.00	0.00	1.00	3.00	0.00	0.88	3.00	0.00	0.97
	SrHCO ₃	2.00	0.00	0.28	1.00	0.00	0.24	2.00	0.00	0.24
Zn	Zn ²⁺	98.00	92.00	96.22	98.00	95.00	97.18	98.00	92.00	96.67
	ZnHCO ₃	8.00	2.00	3.61	4.00	2.00	2.65	8.00	2.00	3.15
	ZnSO ₄	2.00	0.00	0.17	3.00	0.00	0.18	3.00	0.00	0.18

than 70% as free cation species. With respect to arsenic speciation, H₃AsO₃⁰ is the main component (100%) in all the samples. For aluminium, Al³⁺ dominates in 20 locations (9 and 11 locations in the upper and lower units, respectively). The species Al(OH)₂⁺ predominates in 11 locations (8 locations in the upper aquifer). The AlOH₂ dominates only in one location. In respect of uranium,

UO₂CO₃ dominates in 17 locations (11 locations in the upper aquifer), while UO₂²⁺ and UO₂⁺ dominates in 15 (6 locations in the upper aquifer) and 1 location (only in the upper aquifer), respectively. Generally, the trend of abundance for aluminium and uranium dissolved species is Al³⁺ > Al(OH)₂⁺ > AlOH₂ and UO₂CO₃ > UO₂²⁺ > UO₂⁺ > UO₂OH⁺.

Cuprite	Cuprous Ferrite	Diaspore	Gibbsite	Goethite	Hematite	Jubanite	Magnetite	Uraninite	Ionic strength
-1.53	6.31	3.36	2.12	-0.11	1.99	-1.94	0.19	1.93	1.92×10 ⁻³
-1.34	6.27	3.18	1.93	-0.26	1.73	-2.76	-0.25	1.70	1.09×10 ⁻³
-0.05	7.24	2.58	1.33	0.06	2.39	-3.06	0.72	1.60	2.87×10 ⁻⁴
-0.48	7.68	2.16	0.92	0.62	3.60	-2.58	2.45	1.92	8.41×10 ⁻⁴
-2.57	4.42	3.16	1.92	-1.49	-0.78	-1.46	-4.05	1.79	7.34×10 ⁻⁴
-1.42	6.83	3.92	2.67	0.36	2.90	-2.36	2.55	2.26	1.88×10 ⁻³
-4.21	2.80	0.05	-1.19	-2.30	-2.33	-2.72	-6.42	-0.04	1.34×10 ⁻³
-4.32	3.21	3.70	2.46	-0.66	0.97	-1.87	-1.72	1.08	3.38×10 ⁻³
-4.08	3.06	2.92	1.68	-2.10	-1.91	-1.01	-5.92	-1.12	2.58×10 ⁻³
-0.35	7.60	2.31	1.06	0.58	3.40	-2.76	1.43	-0.43	4.93×10 ⁻⁴
-6.55	-2.26	-0.86	-2.10	-6.15	-10.21	-2.12	-18.03	-0.49	2.41×10 ⁻³
-3.89	3.86	2.77	1.52	-1.40	-0.52	-1.48	-3.96	0.97	1.61×10 ⁻³
-3.67	3.47	-1.18	-2.43	-5.73	-9.34	-1.97	-16.73	-0.71	5.18×10 ⁻³
-2.36	3.58	2.13	0.87	-2.46	-2.57	-1.93	-6.99	0.49	1.89×10 ⁻³
-4.71	1.49	0.58	-0.66	-3.32	-4.54	-2.75	-9.80	0.47	1.07×10 ⁻³
-2.18	4.35	2.88	1.65	-1.74	-1.35	-1.30	-4.72	1.49	2.24×10 ⁻⁴
-3.07	2.91	1.44	0.21	-2.70	-3.39	-2.19	-8.17	0.60	8.50×10 ⁻⁴
-4.22	0.72	-0.22	-1.46	-4.36	-6.52	-2.59	-12.67	-0.27	2.45×10 ⁻³
-0.80	5.99	2.26	1.37	-0.82	0.67	-2.68	-2.59	0.52	4.43×10 ⁻⁴
-1.45	4.79	1.67	0.42	-1.70	-1.10	-2.74	-4.75	0.57	5.49×10 ⁻⁴
-1.86	4.64	2.33	1.08	-1.64	-0.98	-2.68	-4.62	0.63	4.21×10 ⁻⁴
-4.96	-0.18	-1.73	-2.97	-4.88	-7.60	-3.54	-14.33	-0.67	5.91×10 ⁻⁴
-1.58	5.93	3.29	2.05	-0.46	1.22	-2.66	-0.94	1.60	4.92×10 ⁻⁴
-4.64	2.84	-0.67	-1.92	-2.04	-1.79	-3.61	-5.48	-0.32	4.59×10 ⁻⁴
-3.56	1.51	0.34	-0.90	-3.90	-5.61	-3.00	-11.02	0.51	4.25×10 ⁻⁴
-3.28	1.86	0.21	-1.03	-3.70	-5.23	-3.12	-10.65	0.03	4.54×10 ⁻⁴
-1.85	5.80	2.52	1.27	-0.47	1.31	-2.34	-2.26	-1.52	5.03×10 ⁻⁴
-4.02	1.80	0.36	-0.89	-3.39	-4.52	-2.71	-10.19	-0.96	5.23×10 ⁻⁴
-2.88	2.50	0.71	-0.53	-3.24	-4.31	-2.46	-9.19	0.59	6.14×10 ⁻⁴
-4.38	0.58	-0.47	-1.71	-4.41	-6.68	-3.09	-12.95	-0.35	2.99×10 ⁻⁴
-2.27	2.82	1.20	-0.04	-3.01	-3.84	-2.75	-8.62	0.45	2.71×10 ⁻⁴
-3.26	3.06	0.82	-0.42	-2.48	-2.84	-1.62	-7.72	-0.62	1.05×10 ⁻³
-4.40	0.72	-0.67	-1.91	-4.36	-6.53	-3.27	-12.62	-0.43	7.73×10 ⁻⁴

The distribution of the species with respect to the different water-bearing layers are more or less the same except that Al^{3+} and UO_2^{2+} are higher in the upper aquifer compared to the lower aquifer by one fold (Table 5).

The groundwater is oversaturated with respect to alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, in 12 locations (75% in the upper unit), basaluminite $[\text{Al}_4(\text{OH})_{10}\text{SO}_4]$ in nine locations with only one location in the lower unit. Sixty percent of the groundwater samples oversaturated with respect to Cu metal were obtained from the upper unit while all the samples (with the exception of location CA 32) are oversaturated with cuprous ferrite (CuFeO_2). Diaspore $[\text{AlO}(\text{OH})]$ and gibbsite $[\text{Al}(\text{OH})_3]$ are oversaturated in groundwater in 26 (60% in the upper unit) and 18 (70% in the upper unit) locations, respectively. Groundwater samples in only four locations (all in the upper unit) are oversaturated with respect to goethite (FeOOH). Hematite (Fe_2O_3) is oversaturated in the samples from 10 locations out of which seven locations are from the upper unit. The samples are only oversaturated in five locations with respect to magnetite (Fe_3O_4). All these locations are within the upper unit. In respect of uraninite (UO_2), the samples are oversaturated in 20 locations (12 locations in the upper unit).

It is known that free metal species are the most bio-available and toxic form of trace elements that exist in natural water (Apte and others 1995). In the study area aluminium that is in its toxic form $[\text{Al}^{3+}, \text{Al}(\text{OH})_2^+, \text{AlOH}_2]$ is highly mobile but the low concentration and mineral phases will limit its mobility. Arsenic is present in neutral form (H_3AsO_3^0) and under the present Eh-pH condition is not mobile and with the low concentration, the contamination risk is very low. The mobility of Cu in the form Cu^+ will be restricted by the mineral phase cuprous ferrite (CuFeO_2). Pb^{2+} under the existing Eh-pH conditions is mobile. However, the low concentration and the limiting mineral phase PbCO_3 will greatly reduce the risk of contamination by Pb. The species Sr^{2+} is mobile under the present Eh-pH conditions; however, the low concentration and the phase SrSO_4 will limit its mobility. The different species of uranium (UO_2CO_3 , UO_2^{2+} , UO_2^+ , UO_2OH^+) are immobile. In addition, the low concentration and the presence of the limiting phase, uraninite reduces the potential risk of contamination by U. The free ion species of Ba, Cd, Cu, Fe, Mn, Ni and Zn are immobile under the prevailing Eh-pH conditions and hence does not pose any contamination risk to the groundwater.

Conclusions

The groundwater environment is acidic, transitional and low in metal load. The concentration of pollutants from the surrounding areas with the small-scale mining of barite and quarrying for aggregates is low and, if any, are diminished by the influx of unpolluted water and the

removal of metals by adsorption and precipitation processes.

Speciation calculations show that Ba, Cd, Cu, Fe, Mn, Ni, Pb, Sr, and Zn are present as free ion species in all the analysed groundwater samples. As is in the neutral form (H_3AsO_3^0). Al and U are dominated by Al^{3+} , $\text{Al}(\text{OH})_2^+$, AlOH_2 , UO_2CO_3 , UO_2^{2+} , UO_2^+ , and UO_2O . The mineral phases include alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$, basaluminite $[\text{Al}_4(\text{OH})_{10}\text{SO}_4]$, boehmite $[\text{Al}(\text{OH})]$, Cu metal, cuprous ferrite (CuFeO_2), diaspore $[\text{AlO}(\text{OH})]$, gibbsite $[\text{Al}(\text{OH})_3]$, goethite (FeOOH), hematite (Fe_2O_3), and magnetite (Fe_3O_4).

The small-scale mining activities, low concentration of elements, immobility of mineral species under the prevailing Eh-pH conditions, dilution, and precipitation of mineral phases makes the contamination risk of the coastal plain aquifer very low.

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