

Acidification of Groundwater and its Implication on Rural Water Supply in the Ankobra Basin, Ghana

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Abstract

Hydro-geochemical survey was undertaken to determine the quality of groundwater in the Ankobra Basin. Part of the data generated was used to assess the level of groundwater acidification and its implication for rural water supply in the Ankobra Basin. The results of the assessment indicate that groundwater pH range is 3.74-6.9. However, 80% of the boreholes show moderate acidic character with pH in the range 4.6-6.9. The moderate acidity probably results from carbonic acid derived from the solution of CO₂ from both the atmosphere and the soil zone. A few wells show strong acid waters (pH < 4.5) suggesting acidity resulting from sulphides oxidation. Acidification capacity of the groundwaters is very low, in fact negative, varying from -15.1 meq l⁻¹ to -10.7 meq l⁻¹. Similarly, the acid neutralizing capacity of the groundwaters is low (-1.7- 4.3 meq l⁻¹). Nonetheless, the net acid neutralizing capacity remains positive signifying the potential of the groundwater to neutralize acids in spite of the low acid neutralizing capacity. The alkalinity for acid neutralization is provided by the alumino-silicates and some mafic rocks since the groundwaters are largely undersaturated with respect to the common carbonates (calcite, dolomite and ankerite) which, therefore, provided insufficient alkalinity in the groundwaters. In the cases of the few wells that show strong acidic character, additional acid neutralization capacity is provided by dissolution of sulphate and clay minerals such as alunite and kaolinite that result in the release of aluminium ions into the groundwater. The acidity of groundwaters has given slightly sour taste to drinking water and has also led to the mobilization of trace metals particularly iron, manganese, aluminium and arsenic into the groundwater system. Since borehole supply is rarely treated, these trace metals end up in domestic supplies resulting in health implications, complaints and, in certain cases, rejection of the boreholes.

Introduction

Acidified groundwaters have been reported from many parts of the world particularly in North America and Europe (Hultberg & Wenblad, 1980; Appelo *et al.*, 1982; Grimvall *et al.*, 1986). Groundwaters in most hard-rock aquifers are also known to be vulnerable to quality problems that may have serious impact on human health (Smedley *et al.*, 1995). The rocks are often carbonate-deficient and give rise to poorly buffered groundwaters (acidic groundwaters) that encourage dissolution of elements such as Al, Mn, Be and Fe from most minerals if they are present in the rock matrix into the groundwater and make the groundwater unsafe for drinking.

In gold and base metal mining areas, acid mine drainage (AMD) resulting from inorganic and microbially-induced sulphide oxidation is a common phenomenon. This acidic runoff can infiltrate into the groundwater systems and, where acid neutralization capacity of the aquifer is low, perhaps, due to insufficiency of carbonates, may cause groundwater acidification. Ankobra Basin is endowed with mineral resources that also include some of the richest gold and only manganese mines in the country. The most abundant ore minerals in the Prestea-Bogoso area within the Ankobra Basin are pyrite and arsenopyrites, each making up about 20-30% of all the ore minerals (Barko, 1972; Adadey, 1989). Thus,

mine waste rocks within the Basin are likely to generate AMD, which could eventually lead to groundwater acidification. Acidity of groundwaters can cause corrosion problems leading to high maintenance costs and shortened life of hand pumps and accessories. It can also lead to high metal concentrations in the borehole that may cause aesthetic problems and, in extreme cases, physiological problems. Rural water supply of the Ankobra Basin (one of the most important economical river basins in Ghana) is based principally on groundwater. The need for a study on groundwater acidification and its effects on groundwater

supply cannot thus be over emphasized. The objective of this paper, therefore, is to draw attention to the groundwater acidification problems and discuss some of the causes and its probable effect on rural water supply in the Ankobra Basin. places reach the height of 200 m separated by steep sided flat-bottomed valleys varying in altitude from 46 m in the south to 76 m in the north that are parallel to one another and to the strike of the rocks. Due to the heavy rainfall and forest vegetation that prevents sheet erosion, the whole area is highly dissected and reduced to uniformly moderate relief with a gentle slope to the south (Service, 1938). Erosion is mainly restricted to river channels that cut up the plateau surfaces and the hills are usually capped with iron-pan (laterite) and bauxite (Dickson & Benneh, 1980).

The climate of the Ankobra Basin falls

supply cannot thus be over emphasized. The objective of this paper, therefore, is to draw attention to the groundwater acidification problems and discuss some of the causes and its probable effect on rural water supply in the Ankobra Basin.

Materials and methods

Description of the study area

Ankobra Basin lies approximately between latitudes 4.8°N and 6.5° N, and longitudes 1.6° W and 2.3° W, respectively, and occupies approximately 8,400 km² (Fig. 1). The physiography of the Ankobra Basin consists of a series of ridges that in some

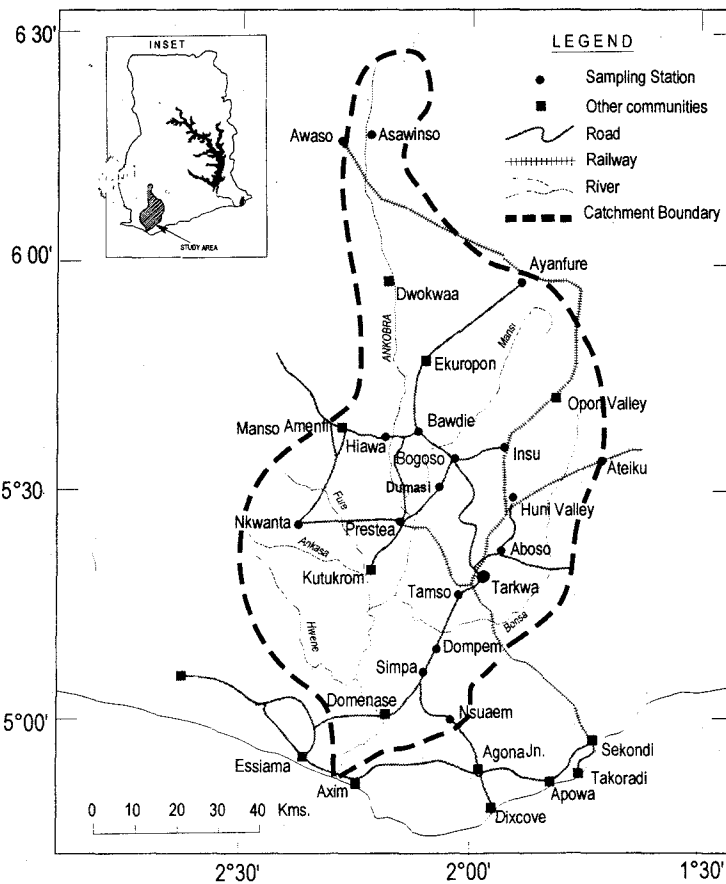


Fig. 1. Location map of the Ankobra Basin showing the sampling stations



partly under the wet semi-equatorial and partly under south-western equatorial climatic zones of Ghana (Dickson & Benneh, 1980). It is, thus, characterized by double rainfall maxima. The first peak occurs in June whilst the second peak occurs in October. The mean annual rainfall value in the northern part of the Basin (wet semi-equatorial climatic zone) is approximately 1600 mm and the southern part (equatorial climatic zone) is 2000 mm. The highest mean monthly temperature for the two climatic zones is 30 °C and occurs between March and April, and the lowest temperature is approximately 26 °C and occurs in August (Dickson & Benneh, 1980). The Basin lies deeply in the forest ecological zone of Ghana. Semi-deciduous forest occurs in the northern half of the Basin while the southern half is covered by tropical evergreen forest.

Sampling and analysis

Water samples were collected from boreholes, hand-dug wells and the major rivers in the Ankobra Basin between 15th and 20th November 1999. In all, about 60 water samples consisting of 32 ground water samples and 28 surface water samples were collected. Two samples were collected at every sampling site, each in 100 ml acid-washed high-density linear polyethylene (HPDE) bottles with strict adherence to the sampling protocol described by Claasen, (1982), Barcelona *et al.* (1985) and Gale & Robins (1989). One of the samples was meant for metals analysis and the other for anions analysis. To remove particulate matter from samples, filtering was carried out using a hand-operated vacuum pump and conventional vacuum tubing with a 0.45 µm cellulose acetate filter membrane. Sample acidification to $pH < 2$ for

preservation for metal analysis was carried out immediately after filtration using Merck™ ultra pure nitric acid while those for anion analyses were without preservation.

Temperature, redox potential (Eh), pH and electrical conductivity measurement were conducted on-site using WTW-Multiline P4 Universal Meter in an anaerobic flow-through cell attached in line to borehole pump outlet. Prior to these analyses, pumping was carried out until stable meter readings of the parameters (pH, Eh, etc.) were obtained. This was to avoid the sampling of annulus water that would be in the pump and pump systems. Since the boreholes were consistently in use, mean time for clear pumping before sample taking was 5 min. Alkalinity titration was done at the wellhead using HACH Digital Titrator Model 16900. All major ions (sodium, Na⁺; potassium, K⁺; calcium, Ca⁺⁺; magnesium, Mg⁺⁺; bicarbonate, HCO₃⁻; chloride, Cl⁻; and sulphate, SO₄⁻) as well as some trace elements such as nitrate (NO₃⁻) fluoride F⁻ were analysed using Dionex DX-120 ion chromatograph at the Ecological Laboratory, University of Ghana. The analyses of all trace metals were also carried out using ICP-MS analyses at the Geological Institute of the University of Copenhagen, Denmark. The ionic balances for the analyses varied from -3.0% to 10.8%. However, more than 85% of the analyses had ionic balance within ±5%. Ionic balance outside ±5% is largely associated with samples with very low conductivity values (total dissolved solids).

Results and discussion

Chemical data on groundwater samples is presented in Tables 1 and 2. The pH values for the groundwaters vary from 3.74 to 6.79

TABLE I

Chemical data of representative groundwater samples

No.	Temp. °C	pH	Cond μS/cm	Alk mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO ₃ mg/l	SO ₄ mg/l	Cl mg/l	NO ₃ mg/l	SiO ₂ mg/l
1	27.0	5.58	210	104	9.9	7.4	21.6	0.6	126.9	0.0	23.8	3.2	40.4
2	26.3	5.97	299	148	20.7	12.2	18.3	0.5	180.6	0.0	10.9	0.1	54.4
3	27.4	5.37	257	52	3.6	13.8	23.3	2.0	63.4	5.5	28.8	15.6	27.2
4	26.8	5.74	180	76	8.5	6.5	14.2	0.4	92.7	0.0	7.0	1.0	46.6
5	29.2	5.66	187	116	2.7	8.0	10.0	0.8	141.5	5.3	8.0	0.2	42.4
6	27.3	5.85	339	116	23.4	7.0	21.9	0.5	141.5	17.3	30.8	0.8	46.9
7	26.8	5.70	169	100	4.4	5.7	12.9	0.4	122.0	0.0	8.9	0.1	38.6
8	27.7	3.74	536	0	7.6	11.4	45.4	23.8	0.0	30.2	77.4	24.1	24.2
9	26.2	5.27	101	40	0.9	4.4	8.6	0.4	48.8	0.0	5.0	0.7	23.6
10	26.9	5.54	204	68	11.4	3.1	18.8	0.5	83.0	0.0	14.9	0.2	37.6
11	27.6	5.72	309	92	7.4	8.5	27.7	0.7	112.2	7.5	30.8	0.0	42.0
12	27.3	6.11	336	168	21.7	7.1	25.0	1.1	205.0	0.0	16.9	0.0	41.6
13	26.8	5.67	151	80	1.6	7.2	17.6	0.5	97.6	0.0	6.0	0.2	44.6
14	27.9	5.13	234	44	1.3	9.3	22.8	1.5	53.7	5.8	42.7	0.2	27.5
15	26.7	5.50	105	80	10.0	4.5	12.4	0.5	97.6	0.0	2.0	0.9	28.4
16	27.3	5.75	188	92	9.9	8.9	7.7	0.2	112.2	0.0	6.0	0.8	27.0
17	27.4	5.04	130	36	8.7	2.3	15.0	0.7	43.9	0.0	10.9	7.8	36.7
18	27.4	5.58	330	48	15.3	8.2	22.5	2.7	58.6	5.0	39.7	8.7	30.1
19	27.6	6.04	365	120	15.3	11.0	20.8	1.0	146.4	0.0	43.7	5.2	39.2
20	26.1	6.00	251	132	15.2	7.5	22.8	1.0	161.0	0.0	23.8	0.1	49.6
21	28.1	6.23	248	124	19.4	4.9	15.4	1.2	151.3	0.0	4.0	0.2	32.3
22	27.5	6.64	780	320	115.0	17.6	22.2	7.8	390.4	19.2	53.6	11.0	32.8
23	26.5	6.01	483	148	44.9	21.3	18.5	6.5	180.6	29.2	50.6	3.0	48.8
24	26.4	5.94	213	80	11.1	6.6	11.6	3.0	97.6	12.5	8.9	0.0	56.9
25	26.5	5.57	92	72	3.6	2.0	10.8	0.4	87.8	0.0	4.0	16.2	34.1
26	26.4	6.34	572	276	51.5	15.1	15.7	1.2	336.7	5.0	11.9	1.0	34.6
27	25.8	4.38	101	12	1.2	1.3	9.7	0.4	14.6	0.0	12.9	1.1	18.9
28	26.3	3.77	230	0	1.8	1.8	23.7	2.3	0.0	0.0	32.8	8.0	17.6
29	26.7	4.57	66	36	4.8	3.9	7.3.0	1.4	43.9	0.0	6.0	3.5	30.0
30	26.6	5.15	130	32	3.2	7.7	14.7	2.1	39.0	0.0	11.9	8.7	34.8
31	26.5	5.35	355	100	41.7	9.7	18.5	0.4	122.0	14.9	46.7	7.9	24.0
32	27.0	6.05	409	144	28.8	11.3	18.0	2.5	175.7	2.7	31.8	0.6	36.4
Max.	29.2	6.60	780	320	115.0	21.3	45.4	23.8	390.4	30.2	77.4	24.1	56.9
Min.	25.8	3.70	66	0	0.9	1.3	7.3	0.2	0.0	0.0	2.0	0.0	17.6
Mean	27.0	5.50	277	99	18.9	8.2	18.5	2.7	121.1	5.6	23.3	4.6	36.0
Median	26.9	5.70	234	92	9.9	7.5	18.3	1.0	112.2	0.0	14.9	1.0	36.0

with mean and median values of 5.68 and 5.70, respectively, indicating moderate to strong acidic groundwaters. Only approximately 7% of the boreholes and

hand-dug wells in the Ankobra Basin fall within the potable range (the WHO recommended pH range for potable water is 6.5-8.5) (Kortatsi, 2002).

TABLE 2

Trace metals analyses of representative groundwater samples from Ankobra Basin

No	Al mg/l	Mn mg/l	Fe mg/l	Cr µg/l	Co µg/l	Ni µg/l	Cu µg/l	Zn µg/l	As µg/l	Se µg/l	Cd µg/l	Sb µg/l	Hg µg/l
1	0.1	0.3	0.4	3.9	7.0	14.9	31.6	120.0	1.7	11.6	0.2	0.1	3.0
2	0.0	0.2	2.5	1.7	1.9	27.5	24.3	79.9	2.1	4.0	0.0	0.0	12.0
3	0.0	0.3	0.0	1.9	9.6	11.5	23.5	34.0	2.0	11.0	0.1	0.1	4.0
4	0.0	0.3	3.8	1.8	4.0	8.7	1.8	30.0	9.4	17.2	0.0	0.2	3.0
5	0.0	0.4	18.3	2.2	18.4	25.7	1.3	79.6	4.0	0.0	0.0	0.3	8.0
6	0.1	1.1	0.2	2.5	11.7	20.5	25.8	36.4	1.5	0.0	0.4	3.9	7.0
7	0.0	0.2	7.8	1.3	0.7	0.0	2.1	15.8	0.5	0.9	0.0	0.0	0.0
8	2.0	0.3	1.0	1.8	42.8	88.2	108.0	189.0	3.7	24.9	1.3	0.1	0.0
9	0.0	0.1	7.1	2.0	5.9	13.3	1.4	40.5	38.8	20.9	0.0	0.2	3.0
10	0.2	0.9	10.9	2.1	11.7	3.1	3.0	32.5	4.2	0.0	0.0	0.0	4.0
11	0.7	0.5	3.4	2.7	1.5	3.6	7.9	25.2	3.0	0.0	0.0	0.0	8.0
12	0.1	0.4	2.8	1.8	25.2	34.3	2.8	77.2	6.3	0.0	0.0	0.0	5.0
13	0.1	0.3	3.1	1.6	40.2	38.2	3.7	107.0	15.4	31.6	0.0	0.0	0.0
14	0.2	0.1	0.1	1.4	4.9	7.4	11.9	25.7	7.7	0.0	0.0	0.0	5.0
15	0.0	0.5	2.5	1.0	6.1	27.8	3.6	32.5	4.3	10.0	0.1	1.2	19.0
16	0.0	0.1	0.0	1.3	0.4	7.8	19.0	14.4	0.1	0.0	0.0	0.0	38.0
17	0.3	0.4	0.1	2.1	0.6	3.4	26.5	27.1	1.8	0.0	0.0	0.1	24.0
18	0.0	0.5	0.3	1.8	0.4	1.7	11.6	22.6	1.5	0.0	0.0	0.0	5.0
19	0.3	0.4	0.2	0.0	0.5	3.1	7.4	57.6	0.2	0.0	0.0	0.0	6.0
20	0.0	1.1	0.0	1.5	1.3	12.5	3.9	25.4	0.3	0.6	0.0	2.2	0.0
21	0.0	0.5	1.0	0.5	4.8	13.7	1.3	32.3	0.4	10.5	0.0	0.1	8.0
22	0.0	0.4	1.8	1.5	0.6	0.9	1.0	19.5	0.3	0.0	0.0	0.0	0.0
23	0.1	2.4	0.0	2.2	1.5	4.7	1.4	12.0	0.8	9.0	0.0	0.0	11.0
24	0.7	0.4	0.1	3.1	9.7	12.1	6.2	55.0	0.8	0.0	0.0	0.0	5.0
25	1.1	0.6	0.0	1.6	12.2	11.9	15.4	43.5	0.2	0.7	0.0	0.0	29.0
26	0.1	0.1	0.2	2.2	0.8	4.0	267.0	212.0	0.5	0.0	0.0	0.0	12.0
27	0.0	0.4	0.0	1.2	3.5	5.5	34.6	27.8	0.2	0.0	0.5	0.0	8.0
28	0.4	0.0	0.1	3.0	0.4	5.8	22.9	48.9	0.5	12.3	0.0	0.1	6.0
29	0.0	0.0	0.0	3.0	0.3	5.0	27.6	42.8	0.3	1.8	0.0	0.0	15.0
30	0.2	0.6	0.3	2.1	2.0	4.0	2.1	18.6	0.1	0.0	0.0	0.0	4.0
31	0.1	0.0	0.1	3.8	0.2	6.4	15.9	30.7	0.3	0.0	0.0	0.0	10.0
32	0.1	1.3	9.8	1.6	8.8	10.0	2.2	1040.0	4.5	15.4	0.0	0.1	12.0
Max.	2.0	2.4	18.3	3.9	42.8	88.2	267.0	1040.0	38.8	31.6	1.3	3.9	38.0
Min.	0.0	0.0	0.0	0.0	0.2	0.0	1.0	12.0	0.1	0.0	0.0	0.0	0.0
Mean	0.3	0.5	2.8	1.9	8.3	15.5	29.0	109.0	4.6	6.3	0.1	0.4	9.2
Median	0.1	0.4	0.3	1.8	4.0	8.7	7.9	34.0	1.5	0.6	0.0	0.0	6.0

Edmunds & Kinniburgh (1986) in a regional survey of groundwater in the United Kingdom observed that low alkalinity groundwaters were most susceptible to

acidification. Similarly, Hultberg & Wenblad (1980) indicated that alkalinity decreases overtime are indeed a good warning against groundwater acidification in future.

Acidification (Ac) is thus often defined as loss of alkalinity (Henriksen, 1979). This implies that

$$Ac = Alk_0 - Alk_t \quad (1)$$

where Alk_0 = the original or the pre-acidification alkalinity Alk_t = the present-day alkalinity.

An attempt has been made to apply equation (1) to compute the acidification capacity of the groundwaters in the Ankobra

and, consequently, has not been used in acidification status assessment. Nonetheless, according to Henriksen (1980) and Henriksen & Kirkhusmo (1982), the original alkalinity could be estimated from the sum of non-marine calcium and magnesium concentrations of the groundwater. Thus the present day data can be used to estimate acidification according to equation (1). Consequently, a modified empirical formula

TABLE 3

Alkalinity data for the few boreholes for which the original data exist

Location	Borehole number	1983 alkalinity (Alk ₀) (as mg l ⁻¹ CaCO ₃)	2001 alkalinity (Alk _t) (as mg l ⁻¹ CaCO ₃)	Alk ₁₉₈₃ - Alk ₂₀₀₁
Benso	21/E/13-3	40.0	32.0	8.0
Benso	21/E/13-4	40.0	36.0	4.0
Essamang	05/B/10-1	80.0	52.0	28.0
Essamang	05/B/10-2	80.0	68.0	12.0
Essamang	05/B/10-3	105.0	69.0	36.0
Hemang	20-B-65-4	45.0	43.0	2.0
Nsuem	18/I/98-3	85.0	80.0	5.0

Basin. The present alkalinity and an original alkalinity data (DC International, 1984) for a few of the boreholes are presented in Table 3.

The data in Table 3 shows that the average acidification capacity in seven boreholes over a period of 18 years is approximately 13.6 mg l⁻¹ of CaCO₃. Nonetheless, the 1983 data, that is the original data at the time of borehole (pre-acidification alkalinity) is very limited and its accuracy could not be guaranteed. This is because nothing was stated on how the measurements were carried out; whether in the field or in the laboratory and after what time intervals were they carried out. Thus, the computed acidity values may be overestimated or underestimated. In other words, computed acidity values are not accurate and, therefore, cannot provide a reliable result

for acidification computation based on the same definition of acidification but depending only on the present data is given as follows: $Ac = 0.93 (Ca^* + Mg^*) - 14 - Alk + Al$ (2) where Ca^* and Mg^* are non-marine calcium and magnesium, respectively, and all concentrations are expressed in meq l⁻¹ (Henriksen, 1980; Henriksen & Kirkhusmo, 1986; Caritat *et al.*, 1998).

Though the southern half of the Ankobra Basin is along the coast, petrographic evidence does not indicate the existence of marine-derived carbonates (Service, 1938). The calcium and magnesium concentrations of the groundwater in the Ankobra Basin are, therefore, essentially non-marine. Consequently, the formula in equation (2) is applicable to the groundwaters from the Ankobra Basin. The result of the computation for representative groundwater

TABLE 4

Computed net acidification potential of groundwater in the Ankobra Basin

No.	Ca	Mg	K	Na	NO ₃	Cl	SO ₄	Cl	Al	Ca ⁺⁺ Mg [*]	Alk	ANC	Ac	ANC- Ac
1	0.49	0.61	0.02	0.94	0.05	0.16	0.00	0.67	0.01	1.10	1.70	1.33	-14.60	15.93
2	1.03	1.00	0.01	0.80	0.00	0.00	0.00	0.31	0.00	2.04	2.43	2.54	-14.50	17.03
3	0.18	1.14	0.05	1.01	0.25	0.15	0.12	0.81	0.00	1.32	0.85	1.20	-13.59	14.79
4	0.43	0.53	0.01	0.62	0.02	0.49	0.00	0.20	0.00	0.96	1.25	1.38	-14.31	15.69
5	0.14	0.66	0.02	0.44	0.00	0.00	0.11	0.23	0.00	0.79	1.90	0.91	-15.13	16.04
6	1.17	0.58	0.01	0.95	0.01	0.85	0.36	0.87	0.01	1.74	1.90	1.47	-14.23	15.70
7	0.22	0.47	0.01	0.56	0.00	0.00	0.00	0.25	0.00	0.69	1.64	1.01	-14.97	15.98
8	0.38	0.94	0.61	1.97	0.39	0.00	0.63	2.18	0.23	1.32	0.00	0.70	-10.74	11.43
9	0.04	0.36	0.01	0.37	0.01	0.21	0.00	0.14	0.00	0.41	0.66	0.64	-14.24	14.88
10	0.57	0.25	0.01	0.82	0.00	0.00	0.00	0.42	0.00	0.82	1.11	1.23	-14.32	15.55
11	0.37	0.70	0.02	1.20	0.00	0.00	0.16	0.87	0.03	1.07	1.51	1.26	-14.28	15.54
12	1.08	0.59	0.03	1.09	0.00	0.16	0.00	0.48	0.08	1.67	2.88	2.31	-14.63	16.94
13	0.15	0.37	0.01	0.54	0.01	0.00	0.00	0.06	0.02	0.52	1.31	1.00	-14.67	15.67
14	0.08	0.59	0.01	0.77	0.00	0.00	0.00	0.17	0.01	0.67	0.72	1.27	-14.00	15.27
15	0.07	0.77	0.04	0.99	0.00	0.00	0.12	1.20	0.01	0.83	0.72	0.53	-13.89	14.42
16	0.49	0.73	0.01	0.34	0.01	0.14	0.00	0.17	0.00	1.22	1.51	1.38	-14.33	15.72
17	0.27	0.17	0.02	0.56	1.23	0.00	0.00	0.31	0.00	0.44	0.92	-0.53	-14.47	13.95
18	0.76	0.67	0.07	0.98	0.33	0.00	0.10	1.12	0.00	1.44	0.79	0.93	-13.41	14.34
19	1.01	0.90	0.03	1.11	0.08	0.00	0.00	1.23	0.03	1.92	1.51	1.74	-13.45	15.19
20	0.76	0.61	0.02	0.99	0.00	0.54	0.00	0.67	0.00	1.37	1.31	1.72	-14.00	15.71
21	0.97	0.40	0.03	0.67	0.00	0.82	0.00	0.11	0.03	1.37	2.03	1.95	-14.51	16.46
22	3.73	1.45	0.20	0.97	0.18	0.35	0.40	1.51	0.00	5.18	5.24	4.26	-14.39	18.65
23	1.38	1.47	0.13	0.80	0.05	0.00	0.61	1.43	0.00	2.85	2.43	1.71	-13.74	15.45
24	0.55	0.54	0.08	0.50	0.00	0.14	0.26	0.25	0.00	1.10	1.31	1.17	-14.25	15.42
25	0.18	0.16	0.01	0.47	0.26	0.00	0.00	0.11	0.00	0.34	1.18	0.45	-14.83	15.27
26	2.57	1.24	0.03	0.68	0.02	0.00	0.10	0.34	0.01	3.81	4.52	4.07	-14.87	18.94

** All concentrations in meq l⁻¹

samples are presented in Table 4. A commonly used assessment technique based on equation (2) of the acidification status of ground or surface waters is hardness-alkalinity plot (Jacks *et al.*, 1984; Caritat, 1995).

Fig. 2 is a plot of total hardness against alkalinity for representative groundwater

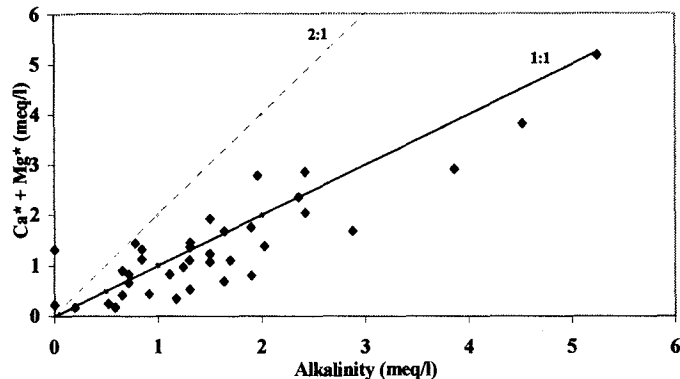


Fig. 2. Scatter plot of total hardness versus alkalinity of representative groundwater samples from the Ankobra Basin area

samples taken from the Ankobra Basin. According to Caritat *et al.* (1998) a slope of 1:1 on this kind of diagram epitomizes waters which are in equilibrium with atmospheric CO₂ and minerals such as carbonates in the soil, regolith and bedrock. On the other hand, a slope of 2:1 or greater (alkalinity to hardness ratio of 0.5 or less) signifies the influence of strong acids, usually interpreted to be of anthropogenic origin. In Fig. 2, most of the groundwater samples fall along or close to the line with the slope 1:1 suggesting equilibrium with CO₂ and rock minerals or natural acidification and buffering. In this case anthropogenic acidification is very little. The two samples that plot close to or to the left side of the 2:1 line, point to the fact that though acidification of the groundwater samples within the Ankobra Basin is predominantly due to natural weathering processes, isolated cases of acidification

due to anthropogenic factors (mainly mining activities) do occur.

The acid neutralizing capacity (ANC) of water can be calculated from the formula:

$$\text{ANC} = (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) - (\text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-) \quad (3)$$

where all concentrations are expressed in meq l⁻¹ (Stumm, 1992). ANC values are also included in Table 4. The acid neutralizing capacity of the ground waters are low with ANC varying from -1.7 meq l⁻¹ to 4.26 meq l⁻¹ with a mean value of 1.15 meq l⁻¹ suggesting buffering agents other than carbonates. This is consistent with the under saturation of the groundwaters with respect to the

common carbonates (calcite, dolomite and ankerite). These carbonates have saturation indices universally less than 0. The Ac of the ground waters is also very low varying between -15.1 meq l⁻¹ to -10.7 meq l⁻¹ with a mean value of -14.1 meq l⁻¹. The relationships between ANC, NANC (net acid neutralizing capacity) and Ac are presented in Fig. 3. It is obvious from Fig. 3 that though the ANC is low it remains positive for most samples while Ac remains negative. This gives a positive net acid neutralizing capacity. The connotation of this is that in spite of the low acid neutralizing capacity due to insufficiency of carbonate, the groundwaters still have the potential to neutralize acids probably due to the presence of alumino-silicates and some mafic rocks. A typical weathering reaction equation of albite (a common alumino-silicates mineral in the rocks within the Ankobra Basin) to

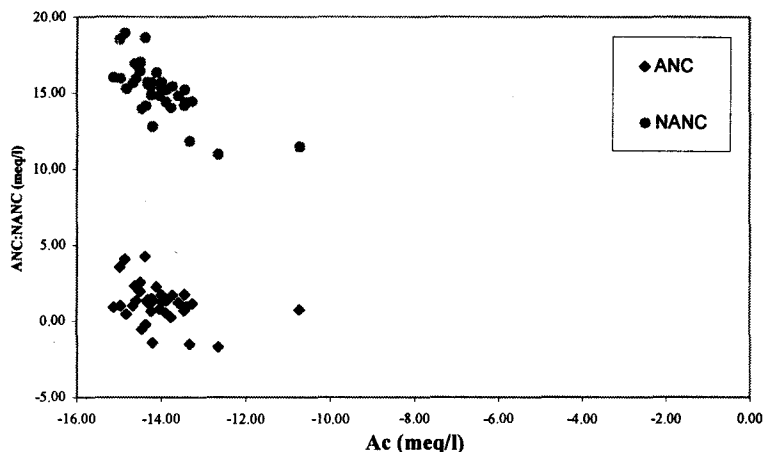
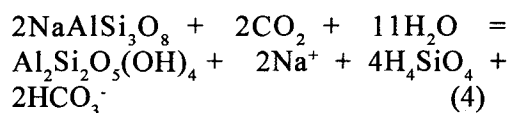


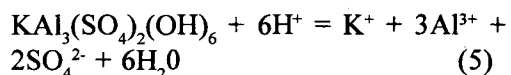
Fig. 3. Scatter plot of acid neutralizing capacity; net acid neutralizing capacity versus acidification capacity for the groundwaters in the Ankobra Basin.

produce the alkalinity for neutralization of acids is given in equation (4)



Additional acid neutralization potential

A few groundwater sources (boreholes) as at Dumasi (44-I-45-4: pH=3.87; Al = 2.3 mg l⁻¹), Tamso (20-I89-1: pH=3.94; Al = 1.28 mg l⁻¹), all within the Ankobra Basin, show strong acidic character and, at the same time, have high concentration of aluminium. This observed phenomenon suggests that due to the extreme acid condition, additional acid neutralization capacity is derived from the dissolution of either sulphate minerals particularly alunite or clay minerals such as kaolinite or gibbsite (Langmuir, 1997). Typical alunite dissolution to produce Al³⁺ is as follows:



Speciation using Phreeqc for Windows (Parkhurst & Appelo, 1999) has confirmed the production of Al³⁺ in some boreholes in

the Ankobra Basin through alunite or kaolinite dissolution. For instance, in the borehole (44-I-45-4) at Dumasi the saturation indices for alunite and kaolinite were 0.29 and 0.11, respectively, suggesting alunite and kaolinite dissolution proceeded until the groundwater had reached equilibrium with both minerals and

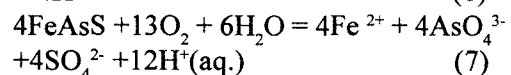
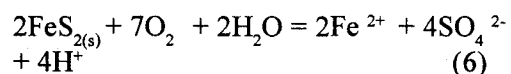
no longer able to dissolve more. Alunite and kaolinite thus probably become the major contributors of aluminium to the groundwater. Similar reactions occur in some of the surface waters.

Origin of acidity of the groundwaters

According to Berner & Berner (1987), under normal atmospheric conditions, rainwater pH is approximately 5.7 units. Furthermore, Appelo & Postma (1999) stated that natural groundwater pH unaffected by anthropogenic processes is not expected to be less than 4.6. Thus, the moderately acidic nature of the groundwaters in the Ankobra Basin accompanied by low concentrations of sulphate and TDS suggest that the acidity is apparently produced by natural processes possibly the production of carbonic acid from the atmospheric CO₂ during rainfall or the dissolution of the soil-generated CO₂ and probably small quantities of dissolved organic acids. According to Langmuir (1997), in natural waters having pH values between about 4.5 and 7 the acids are weak and usually include carbonic acid and smaller amounts of organic acids such as fulvic

acids. The CO₂ in the atmosphere is part of the atmospheric gases that occur through natural processes while the soil-zone CO₂ is produced as a result of roots respiration. Organic acids are produced mainly from the decay of organic matter. The forest vegetation and copious rainfall of the Basin provide avenues for the decay of leaves and other tree organic matter. Evidence of the abundance of organic matter in the soils of the Ankobra Basin is the brown colouration of surface waters almost throughout the year.

For those samples (e. g. borehole 44-I-45-4 at Dumasi) that show negative acid neutralizing capacity or strong acid character, oxidation of sulphides predominantly pyrite and arsenopyrite, apparently plays major roles in the groundwater acidification. Oxidation of pyrite and arsenopyrite can be described by equations (6) and (7):



Assuming a complete and congruent reaction, the stoichiometric oxidation of pyrite and arsenopyrite to generate acid gives molar Fe²⁺/SO₄²⁻ ratios of 0.5 and 1 for equations (6) and (7), respectively. The sulphate concentration in the groundwaters in the Ankobra Basin is remarkably low (0.01-0.55 mmol l⁻¹; mean = 0.14 mmol l⁻¹; median = 0.07 mmol l⁻¹, and most of the Fe²⁺/SO₄²⁻ molar ratios (median value of 0.02) are also generally much lower than the stoichiometric values for pyrite and arsenopyrite oxidation. This may give the impression that pyrite/arsenopyrite oxidation does not occur in the Ankobra Basin.

Sulphide oxidation may have occurred except that iron may probably have co-precipitated with other trace metals as ferric oxyhydroxide complex. Furthermore, the concentrations required for reactions in equations (5) and (6) to occur may not be high. For instance, if a complete and congruent reaction (equation 6) is assumed, the highest measured arsenic concentration of 0.049 mg l⁻¹ for the groundwater that occurs in a borehole at Dumasi would require the oxidation of 0.107 mg of arsenopyrite. This would also produce corresponding concentrations of only 0.036 mg l⁻¹ and 0.063 mg l⁻¹ of Fe²⁺ and SO₄²⁻, respectively. Therefore, despite the low concentration of Fe²⁺ and SO₄²⁻, sulphide oxidation may still have taken place.

Implication of groundwater acidity for rural water supply

The greatest consequence of groundwater acidity in the Ankobra Basin is the mobilization of trace metals into the groundwater system. The concentration of trace metals of representative samples for the Ankobra Basin (Table 2) indicates that the trace metal load of the groundwater is generally low perhaps due to the fact that the trace metal load of the host rocks is low. However, the mobilization of Fe, Mn, Al and As into the groundwater is significant and borehole-water within certain localities, particularly in the middle part of the Basin around the towns of Hiawia, Bawdie, Bogoso, Dumasi and Prestea, are relatively poor in quality and the taste sour.

The concentration of iron in boreholes within the Basin varies from 0 mg l⁻¹ to 18.3 mg l⁻¹ with mean and median values of 2.8 mg l⁻¹ and 0.3 mg l⁻¹, respectively. Iron, like all other cations in the groundwater, is

derived from solid phase rock minerals. That is, the attack of the acidic groundwaters on iron species in the rock such as goethite, hematite and, possibly magnetite, in the presence of organic matter. These iron species are common in the rock types that occur in the Ankobra Basin. Iron could also be leached from amphiboles and pyroxenes.

Speciation with Phreeqc for Windows (Parkhurst & Appelo, 1999) indicates that under the existing *pE-pH* conditions the common form of iron in the groundwater is the soluble ferrous ion (Fe^{2+}). When exposed to air, the ferrous ion (Fe^{2+}) is oxidized to the ferric state (Fe^{3+}) that is insoluble and precipitates as ferric hydroxide. This causes brown colouration of the water and stains sinks and laundered textiles, imparting aesthetic or sensory problems to the water. The sensory effect that it causes commonly leads to the rejection of the boreholes. For the aesthetic effect that it produces, World Health Organisation (WHO, 1993) decided to limit its concentration in potable water to 0.3 mg l^{-1} . However, an upper limit of 1.0 mg l^{-1} should suffice for most purposes (WHO, 1993). With reference to the upper limit of 1.0 mg l^{-1} , approximately 40% of boreholes have iron problems in the Ankobra Basin.

Manganese concentration in the groundwaters in the Ankobra Basin is in the range $0.0\text{-}2.4 \text{ mg l}^{-1}$ with a mean and median of 0.5 mg l^{-1} and 0.4 mg l^{-1} , respectively. Manganese is mainly derived from the attack of the moderately acidic groundwaters on hornblendes in the igneous rocks and manganiferous oxides in the Birimian rocks. Manganese dissolves under mildly reducing conditions to produce the mobile divalent manganous ion (Mn^{2+}). When exposed to air, the manganous ion is oxidized to the

hydrated oxides that form black colouration and stain plumbing fixtures and laundered textiles. The growth of certain problematic bacteria that concentrate manganese and give rise to taste, odour and turbidity problems in the distributed water is also supported by manganese (Griffin, 1960; Wolfe, 1960).

The WHO (1993) recommended guideline limit for water potability with respect to manganese is 0.5 mg l^{-1} . Approximately 25% of the boreholes have potential manganese problem. Similarly, 20% and 5% of the boreholes have concentrations of aluminium and arsenic exceeding the WHO (1993) recommended guideline limit for water potability of 0.2 mg l^{-1} and 0.01 mg l^{-1} , respectively. Other trace metal concentrations are low in the groundwater simply because they exist in only minor concentrations in the rock matrix.

Conclusion

Most of the groundwaters are moderately acidic suggesting acidity resulting from carbonic acid derived from the solution of CO_2 from both the atmosphere and the soil zone. A few wells show strong acid waters ($\text{pH} < 4.5$) suggesting acidity resulting from sulphide oxidation.

The acidification capacity of the groundwaters is also very low (in fact negative). Similarly, the acid neutralizing capacity of the groundwaters is also low but remains positive. The net acid neutralizing capacity is positive indicating that, in spite of the low acid neutralizing capacity, the groundwater still has the potential to neutralize acids. The groundwaters are generally undersaturated with respect to the common carbonates (calcite and dolomite) which, therefore, provided

insufficient alkalinity for acid neutralization. Weathering of alumino-silicate and mafic rocks thus provides alkalinity for acid neutralization. In the cases of the few wells that show strong acidic character, additional acid neutralization capacity is provided by the dissolution of sulphate and clay minerals such as alunite and kaolinite.

The greatest connotations of the acidity of groundwaters in the Ankobra Basin for rural water supply are the mobilization of trace metals particularly iron, manganese, aluminium and arsenic into the groundwater system and the slight sour taste of drinking water. Since borehole supplies are rarely treated, these trace metals end up in domestic supplies resulting in health implications, community complaints and, in certain cases, rejection of the boreholes.

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