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# HYDROCHEMICAL ANALYSIS OF GROUNDWATER FROM THE KETA BASIN, GHANA

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*Multivariate statistical tools and mineral speciation were used to determine the main controls on the hydrochemistry of groundwater from the Keta Basin, Ghana. Groundwater was also assessed to determine its suitability for irrigation purposes. The study indicates that the hydrochemistry is controlled largely by the intrusion of seawater into the basin. Two hydrochemical facies, the $SO_4$ - Ca - K - Mg - $NO_3$ and Cl - Na - $HCO_3$ facies, have been defined in this study. Saturation indices calculated from mineral speciation indicate that groundwater in the area is generally saturated with respect to gypsum and anhydrite, supersaturated with respect to calcite, aragonite and dolomite, and undersaturated with respect to halite. The extremely high salinity in groundwater from some wells and boreholes in the area is attributed to the role seawater plays in groundwater hydrochemistry in the basin. Chemicals from agricultural activities play a minor role in the hydrochemistry. The sodium adsorption ratio, electrical conductivity, permeability index, residual sodium carbonate and sodium percent were the parameters used to assess the suitability of groundwater for irrigation. Groundwater is generally of acceptable quality for irrigation. Over 50% of the samples tested fall within the low sodicity, medium salinity range, which is an acceptable range for irrigation under well drained conditions. Moreover, more than 80% of the samples have permeability indices higher than 70%, which indicates that groundwater in the area will not adversely affect the hydraulic properties of the soils in the Keta Basin area.*

## INTRODUCTION

Aquifers of the Keta Basin constitute some of the most prolific shallow aquifer systems in Ghana. The Keta Basin is a fault controlled sedimentary basin along the southeastern coast of Ghana, dominated by the Volta River estuary. Groundwater plays a pivotal role in the domestic water and irrigation needs of the people in the area. Many dug wells (< 10 m deep) in Quaternary to Neogene clastic sediments are used for domestic water supply, watering of livestock and for dry season irrigation (Jørgensen and Banoeng-Yakubo, 2001). In addition, extensive drilling in the 1950s confirmed the existence of deeper aquifers in Cretaceous – Eocene limestone which have since been exploited for urban water supply.

One of the major problems in the drinking water quality and management of domestic water supply in the Keta Basin is salinization of groundwater in dug wells and in deep wells and boreholes (Gill, 1969; Bannerman, 1994). Many prospected well sites have been abandoned due to salinity problems in the aquifers. Moreover, some existing water supply wells in the area have been abandoned due to increasing salinity over time. However, water of suitable taste and quality is required to sustain primary health care in the area. The irrigation industry will need water of acceptable salinity and sodicity to thrive whilst maintaining soil quality for future agricultural use. High salinity waters can reduce soil hydraulic properties and affect its effectiveness as a good agricultural soil for future use. In particular, when the sodium content of irrigation water is high compared to the sum of the magnesium and calcium content, it has the potential to lead to the clogging of soil particles, leading to a reduction in the permeability of soils (Appelo and Postma, 1993). This can have long term effects on water infiltration capacity of soils, thereby affecting aquifer recharge from precipitation.

The objective of this study is to analyze hydrochemical data from aquifers of the Keta Basin to determine the main controls on the hydrochemistry and determine the suitability of groundwater from the Keta Basin for irrigation purposes. Groundwater in this area is already being used for dry season irrigation. This paper intends to determine the long term effects of this activity on agricultural soils in the area.

## GEOLOGY AND HYDROGEOLOGY OF THE KETA BASIN

The Keta Basin is a fault-controlled Mesozoic/Tertiary sedimentary basin along the coast of the Gulf of Guinea (Jørgensen and Banoeng-Yakubo, 2001). The sedimentary sequence in this basin is known from borehole and well logs to comprise Lower to Middle Devonian marine shale, sandstone, and siltstone, overlain by Jurassic dolerites and sills (Akpati, 1978). A series of Cretaceous – Eocene marine sediments, composed of limestone, shale, and glauconitic sandstone crops out on the eastern edge of the basin close to the Togo – Ghana boundary (Jørgensen and Banoeng-Yakubo, 2001). Two limestone horizons exist in the subsurface in the Keta basin. The upper horizon is exposed by boreholes in the Anyako and surrounding areas (Figure 1), northwest of Keta. The lower limestone horizon is exposed in the Keta area and probably represents a single hydrogeologic unit that is recharged from areas at higher altitudes farther inland.

Four major aquifers are distinguished on the basis of geography and geology. These are (Nerquaye-Tetteh, 1993; Jørgensen and Banoeng-Yakubo, 2001):

- The weathered Dahomeyan gneisses along the northeastern rim of the basin. These outcrop at Akatsi and surrounding areas overlain by Neogene to Recent continental sedimentary deposits of sands and gravels.

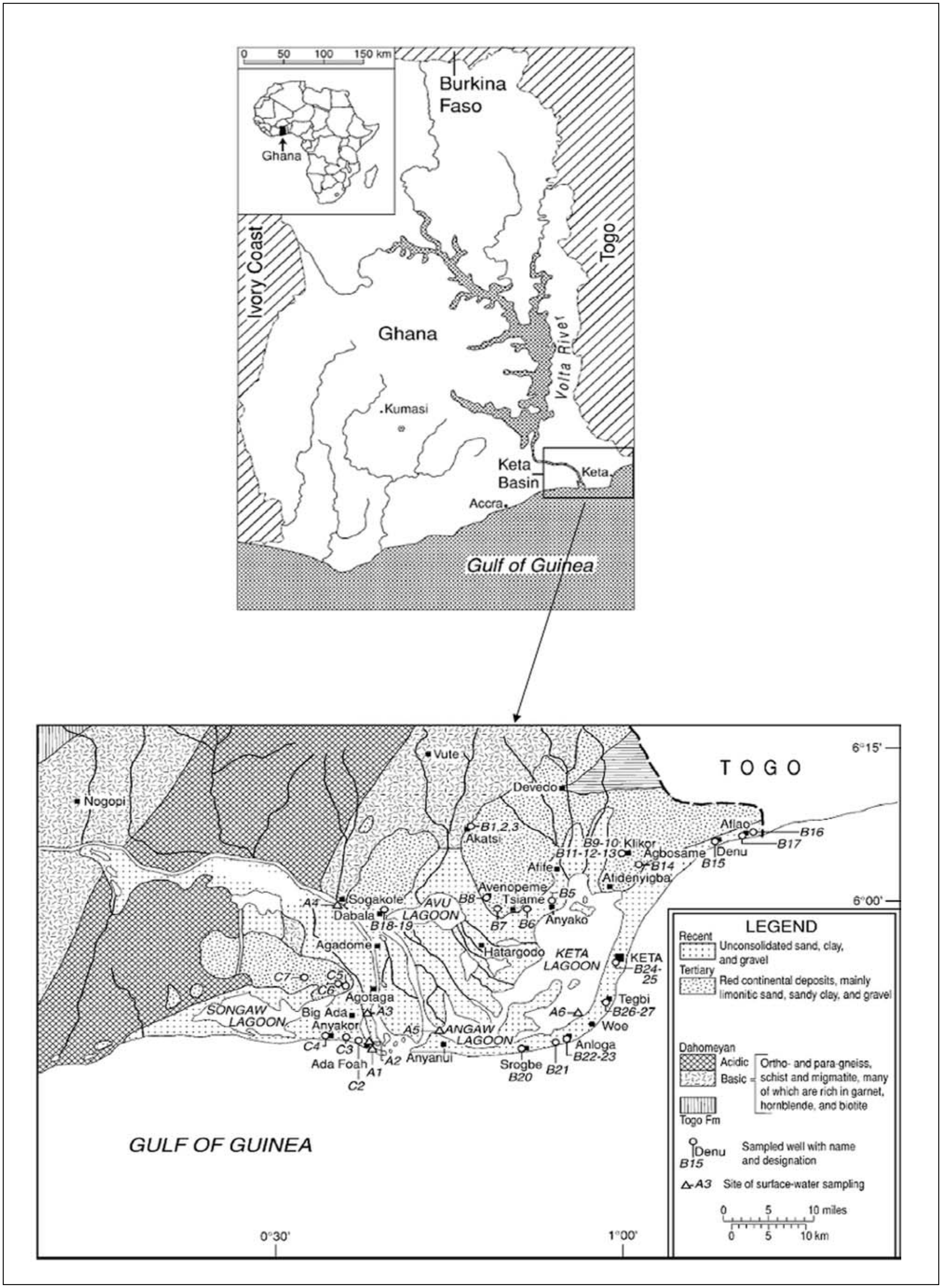


Figure 1. The location and geological map of the Keta Basin.

· The surficial Noegene continental deposits of unconsolidated to semi-consolidated limonitic argillaceous sands in the northeastern and central parts of the basin.

· The Cretaceous – Eocene marine limestones and sandstone beds that are exploited for drinking in the central and southeastern parts of the basin. These units constitute the major and most important deeper aquifer in the Keta Basin (Jørgensen and Banoeng-Yakubo, 2001).

· The Quaternary coastal marine sands and gravels in the Volta River estuary and Keta Lagoon area. These deposits of unconsolidated sand and gravel are generally associated with high groundwater recharge. However, areas below sea level may periodically undergo salinization due to seawater intrusion (Gill, 1969; Nerquaye-Tetteh, 1993).

Mean annual rainfall in the Keta basin is 810 – 870 mm (Akiti, 1987; Dickson and Benneh, 1995). There are two rainy seasons and two dry seasons in the area. Over 70% of the annual rainfall in the basin occurs during the major rainy season (April – July). The second rainy season occurs in September – November. Average monthly humidity in the Keta Basin is 65 – 75% and the annual mean temperature is 27.2 °C.

## METHODOLOGY

Groundwater hydrochemical data from the Keta Basin were analyzed using multivariate statistical methods and mineral speciation methods to determine the sources of variation of the hydrochemistry. The hydrochemical data comprised the concentration of sodium ($Na^+$) ion, potassium ($K^+$), magnesium ($Mg^{2+}$), calcium ($Ca^{2+}$), chloride ($Cl^-$), sulfate ($SO_4^{2-}$), nitrate ($NO_3^-$), electrical conductivity (EC), and pH. Hierarchical cluster and factor analysis were then applied to the data to determine the direction of variation of the hydrochemistry of groundwater in the basin. SYSTAT 12 (Systat Inc., 2007) was used for the multivariate analysis. Mineral speciation was performed using the raw hydrochemical data to determine the main minerals responsible for the variation in the hydrochemistry.

Multivariate statistical methods have gained wide acceptance as data classifying tools in basin wide hydrochemical analysis. In particular, the combined use of factor analysis with principal components and cluster analysis has enabled the determination of the main sources of variation in a set of hydrochemical data. These methods have been successfully used to classify different sediment types (e.g. Huisman and Kiden, 1998; Tebens et al. 2001), and hydrogeochemical processes (e.g. Cameron, 1996; Duffy and Brandes, 2001; Gupta and Subramanian, 1998). Momen et al. (1996) used cluster analysis and PCA to identify the temporal and spatial variation of water chemistry in Lake George in New York. Multivariate statistical tools have also been used to study contaminant sources in environmental systems. For instance Tariq et al. (2005) used factor and cluster analysis to trace metal levels in tannery effluents in Peshawar in Pakistan.

When combined with mineral speciation and inverse geochemical modeling, multivariate statistical tools are robust at determining facies associations at the basin scale. Yidana et al. (2007) for instance used multivariate tools in combination with PHREEQC (Parkhurst and Appelo, 1999) modeling to characterize the hydrochemistry of groundwater from the southern Voltaian sedimentary rocks in the Afram Plains area. They were able to determine the sources of variation of the hydrochemical parameters of groundwater from the Afram Plains section of the southern Voltaian sedimentary sequence. PHREEQC (Parkhurst and Appelo, 1999) is a robust mineral speciation software package that calculates the saturation index (SI) of a mineral defined in accordance with Equation 1 (Appelo and Postma, 1993).

$$SI = \log\left(\frac{IAP}{K_t}\right) \tag{1}$$

where IAP is the ion activity product and $K_t$ is the equilibrium constant for the mineral. When SI is 0, the water is said to be in equilibrium with the mineral and the solution is saturated with the ions that form the mineral. Above 0, the water is supersaturated with respect to the mineral. This means that precipitation of this mineral might begin to take place in the system. Most minerals do not readily precipitate even when the SI is above 0 since several other factors, including the presence of nuclei to begin precipitation of minerals, may come into play. An SI value below 0 means the water is undersaturated with respect to the mineral. It implies that the product of the concentrations of the ionic constituents of the mineral is less than the equilibrium constant, $K_t$.

The assessment of the irrigation quality of the groundwater was performed using the USSL (1954) categorization scheme for irrigation water types. This categorization scheme uses the Sodium Adsorption Ratio, SAR, (Equation 2) (Appelo and Postma, 1993) and electrical conductivity (EC) of water to determine its effects on plants and soils when it is used as irrigation water.

$$SAR = \frac{m_{Na^+}}{\sqrt{(m_{Mg^{2+}} + m_{Ca^{2+}})}} \tag{2}$$

where $m_i$ stands for the concentration of each ion in mmol/l.

The Wilcox (1955) diagrams and Permeability Indices, *PI*, of groundwater samples from the basin were also used to assess the quality of groundwater in this area for irrigation purposes. The Wilcox diagram plots the sodium percent (Equation 3) of the water against the salinity and then categorizes the water as being of excellent, very good, acceptable or unacceptable irrigation quality.

$$Na\% = \frac{(Na^+)}{(Na^+ + Mg^{2+} + Ca^{2+} + K^+)} x100 \tag{3}$$

where the quantities of $Na^+$, $Mg^{2+}$, $K^+$, $Ca^{2+}$ are in meq/l.

PI (Equation 4) is an index which measures the perceived effect of the water on the infiltration properties of irrigation soil.

$$PI = \frac{(Na^+ + \sqrt{HCO_3^-})}{(Na^+ + Mg^{2+} + Ca^{2+})} \tag{4}$$

where the quantities are measured in meq/l.

Furthermore, the Residual Sodium Carbonate (RSC) was calculated to determine the effect of carbonate and bicarbonate ions in water on the quality of the water for irrigation purposes. *RSC* is calculated from Equation 5, where the quantities are measured in meq/l.

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \tag{5}$$

## RESULTS

The result of the hierarchical cluster analysis (HCA) is illustrated in the dendrogram shown in Figure 2a. There are two main clusters. The first cluster contains $SO_4^{2-}$, $Ca^{2+}$, $K^+$, $Mg^{2+}$, pH and $NO_3^-$, and probably represents groundwater affected by fertilizer and agricultural chemicals in the area. Apparently, the pH of groundwater in the area is affected predominantly by these agricultural processes. The second cluster has $Cl^-$, $Na^+$ and $HCO_3^-$, and probably represents the effects of seawater intrusion, precipitation and evaporative enrichment. The result of K-means clustering performed using two k values, appears to be in agreement with the HCA results. Figure 2b illustrates the results of the k-means clustering. Factor analysis performed on the data with varimax rotation revealed two factors which represent over 76% of the total variance. Usually in a groundwater system the bicarbonate ion can be derived from three main sources: precipitation, the incongruent weathering of silicate minerals, or the weathering of carbonate minerals. One of the most prolific aquifers in the Keta basin is a limestone aquifer. Seawater also contains appreciable quantities of the bicarbonate ion and can significantly alter the concentration of this ion when seawater is in contact with the aquifer in question. Sodium, calcium, magnesium and potassium in

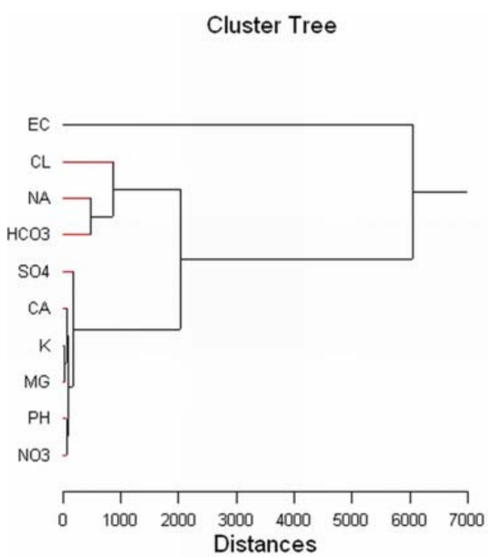


Figure 2a. A dendrogram showing two main hydrochemical groups in the Keta Basin.

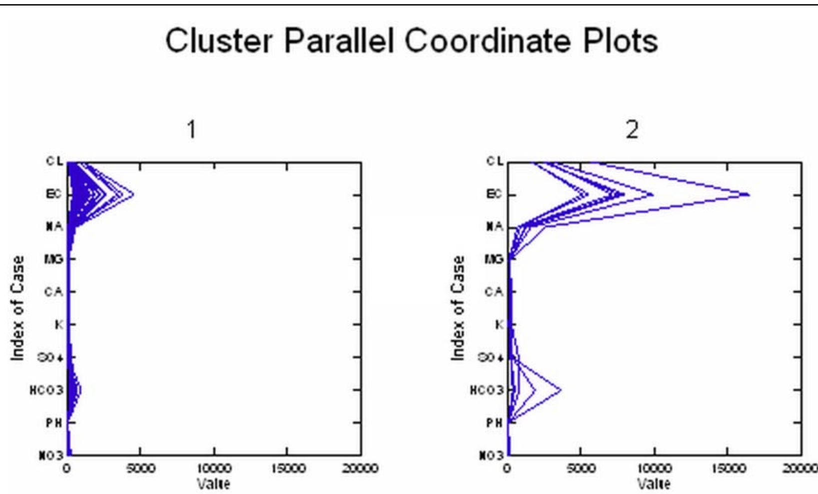


Figure 2b. K-means clustering showing two main water groups in the Keta Basin.

Table 1. Results of the Factor Analysis with principal components and varimax rotation.

| Factor<br>Parameter | 1 | 2 |
|---|---|---|
| pH | 0.215 | **0.638** |
| EC | **0.991** | -0.021 |
| NA | **0.986** | 0.038 |
| K | **0.884** | -0.267 |
| CA | **0.705** | **-0.521** |
| MG | **0.945** | 0.096 |
| SO4 | **0.923** | 0.050 |
| CL | **0.977** | -0.035 |
| NO3 | 0.115 | **-0.641** |
| HCO3 | **0.633** | 0.270 |

groundwater are usually derived from the weathering of silicate minerals or carbonates and precipitation. Seawater can also introduce modest quantities of these ions in groundwater when the groundwater table falls below sea level and conditions are created for seawater intrusion. In the case of the Keta Basin, the main controlling factor in the hydrochemistry appears to be a marine influence. This is largely due to the very close proximity of the basin to the Gulf of Guinea. Agricultural chemicals (fertilizers and herbicides) from the area play a role in the groundwater hydrochemistry, albeit a minor one.

The results of the factor analysis are summarized in Table 1. The first factor correlates highly with all the parameters measured except pH and $NO_3^-$, which are correlated with the second factor. Results of the factor analysis appear to compare with that of the cluster analysis. The first factor probably represents effects of seawater intrusion on groundwater quality in the Keta Basin. Factor 2 illustrates the effects of agricultural chemicals on the groundwater quality in the area. The most significant effect on groundwater quality, however, appears to be the intrusion of seawater.

The mineral speciation analysis performed on the raw chemical data revealed that groundwater in the Keta Basin is generally saturated with respect to anhydrite and gypsum, supersaturated with respect to aragonite, calcite and dolomite, and undersaturated with respect to halite. The supersaturation of calcite, aragonite and dolomite results from the concentration of bicarbonate, calcium and magnesium in groundwater from seawater and also from the dissolution of some minerals in the aquifer matrix. Supersaturation of calcite and aragonite as well as dolomite does not necessarily imply immediate precipitation of these minerals. This is because a number of factors affect precipitation. These include, but are not limited to the presence of nuclei for the formation of precipitates and other competing agents for the same anion (carbonate anion). Undersaturation of halite in groundwater implies the continuous dissolution of this mineral in the groundwater system. The rock matrix is not known to contain appreciable quantities of halite. However, the adjacent sea appears to contribute significant quantities of $Na^+$ and $Cl^-$ ions to groundwater chemistry, thus rendering it unsuitable for most household uses on the basis of taste.

EC values of groundwater from the Keta and surrounding areas are quite high. They range from 1200 μS/cm to over 10000 μS/cm in wells dug in the Keta area. In this area, the lithology comprises limonitic sands, sandy clay and gravel. EC values taken from 18 wells in neighboring Tegbi area ranges between 400 μS/cm and 16400 μS/cm. Figure 3 shows the classification of groundwater in the Keta basin based on the USSL (1954) scheme. In this classification scheme, there are four different categories arising from various combinations of the *SAR* and EC. The role of sodium in the classification of irrigation waters is usually emphasized because it reacts with soils and thereby leads to the clogging of particles, thus reducing the permeability of the soil (Kelly, 1951; Todd, 1980; Domenico and Schwartz, 1990). When the SAR of irrigation water is extremely high, it indicates the preponderance of sodium over the combined weight of magnesium and calcium in the system. Irrigation water of this quality can lead to the clogging of soil particles, ultimately reducing the infiltration properties of the soil. This situation is not favorable for healthy plant root development. In Figure 3, about 50% of the data falls in the S1 – C2 and S1 – C3 category, representing low sodicity, medium salinity and low sodicity, high salinity waters. Medium salinity waters may be used for irrigation on well drained, coarse soils where the ions can easily be flushed away from the root zone of plants. In the Keta Basin, the soil type is sand of variable texture depending on the location. The rest of the data fall in the S2 – C4, S3 - C4 and S4 – C4 categories. These waters may not be used under any circumstance for irrigation of any soil without prior treatment.

Figure 4 presents a similar classification: about 50% of the data fall within the 'good to permissible' range in the diagram. To a large extent, these waters can be used without any threats to soil infiltration capacity of the soil. This is because even though the salinity is quite high, the effect is taken care of by the SAR factor. About 2 – 5% of the samples fall within the 'excellent to good' range.

Fifteen percent of the samples are classified under the 'permissible to doubtful' range, 25% fall within the 'doubtful to unsuitable' and the remaining 3% is in the 'unsuitable' range. It must be emphasized, however, that these classifications are contingent upon the soil type and the kind of drainage conditions prevailing in the area. In the Keta Basin, the climate and soil type will probably permit moderate drainage conditions for the ions down to the root zones of plants. Irrigation activities should nevertheless be practiced with some amount of care to avoid imminent danger to the soil.

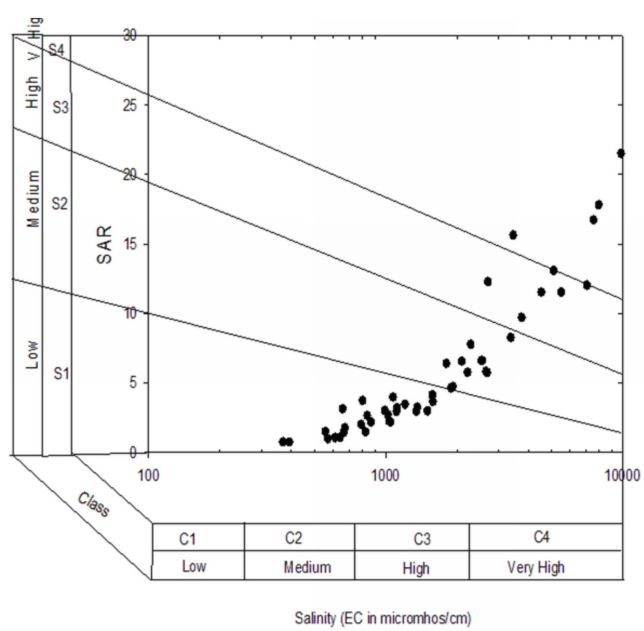


Figure 3. Categorization of groundwater from the Keta Basin on the basis of irrigation quality.

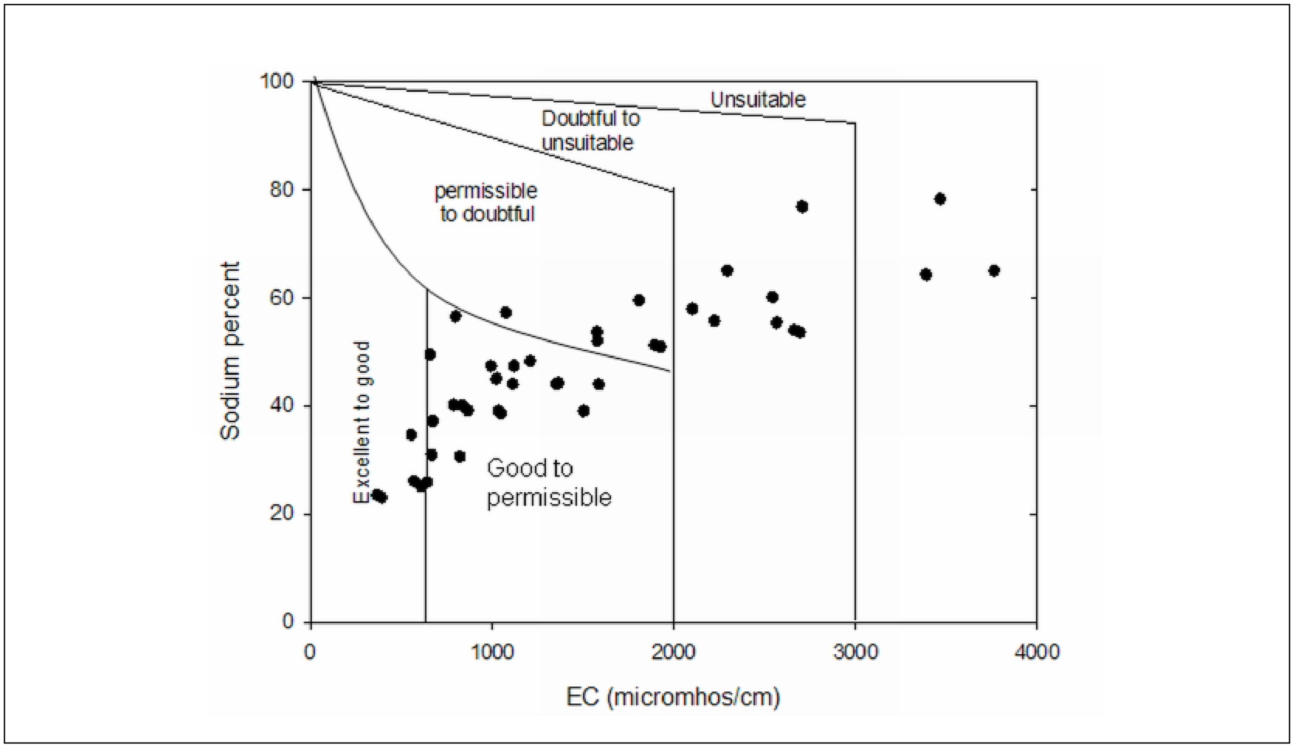


Figure 4. A Wilcox diagram for classifying the irrigation quality of groundwater in the Keta Basin.

Irrigation waters are classified into three categories on the basis of PI. Class I and Class II waters are those with PI of 75% or more (Kelly 1951). Class I waters have PI greater than 75%; Class II waters are characterized by PI between 25% and 75%. Class I and II waters are characterized as good irrigation waters and will have no imminent harm on soils when used. Class III waters have PI values of 25% or less and are undesirable for irrigation. These waters may not be used under any circumstance for irrigation. More than 80% of the samples have PIs higher than 70% (0.70). Two samples taken from Denu and Tegbi had *PI*s of 65% and 69%.

According to the USSL (1954), water with an RSC value less than 1.25 meq/l is safe for irrigation, a value between 1.25 and 2.5 meq/l is of marginal quality and a value greater than 2.5 meq/l cannot be used for irrigation. In the study of groundwater from the Keta Basin, more than 80 % of the data have RSC values lower than 1.25 meq/l. This is in keeping with the results of the other assessment methods and indicates that groundwater in the area is largely usable for irrigation purposes. Different crops, however, have different salt tolerance levels. It is therefore prudent to consider the crop type's salt tolerance level against the salinity level of the groundwater before considering it for irrigation.

## CONCLUSION

Groundwater is the main source of water for most uses in the Keta Basin. In this study, it has been determined that the primary source of variation in the hydrochemistry of groundwater in the basin is seawater intrusion. The extremely high chloride concentrations in some wells which have been abandoned in the area is traceable to this main factor. Two distinct hydrochemical facies, the $SO_4^{2-}$ - $Ca^{2+}$- $K^+$ - $Mg^{2+}$ - $NO_3^-$ and $Cl^-$ -$Na^+$ - $HCO_3^-$ facies, have been defined from multivariate analysis of groundwater chemistry from this basin. Chemicals from irrigation and other agricultural practices in the area appear to be the second most important factor controlling the hydrochemistry. Though salinity is quite high in groundwater from this basin, this study finds that groundwater is generally of acceptable quality for use in irrigation of most crops. The assessment was based on a combination of SAR and EC of the water as well as a measure of the waters' PI, RSC and sodium percent. Under the USSL classification system, over 50% of the samples fall within the low sodicity – medium salinity range. This category is generally acceptable for irrigation under well drained conditions. PIs of the samples indicate that over 80% would not have any severe effects on the permeability of soils when used for irrigation. The RSC and sodium percent of the water similarly indicate that groundwater from wells and boreholes in the basin is of acceptable irrigation quality.

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