Contributory geochemical factors for variation in groundwater quality along confluence of Mula-Mutha and Bhima River, Dist. Ahmednagar, Maharashtra

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Abstract
Sixty groundwater samples were collected in different seasons from the study area. The water soluble products of congruent weathering reactions such as Na, K, Ca, Mg, HCO₃, and SiO₂ have been probed. Apart from these, anthropogenic parameters such as Cl, NO₃, PO₄, and SO₄ have also been analyzed. The mathematical and graphical tools are used to assess the groundwater quality for drinking and irrigation purpose. The study reveals that the concentration of major ions is controlled by the water-rock interactions. The water is not at all suitable for drinking purpose. As per pH, TDS, SAR, chloride and sulphate concentration water is suitable for irrigation purpose. Critical verification of hardness, EC, RSC, salinity hazard compels to assign water quality doubtful for irrigation purpose. Such doubtful zones need special care and suggested to adopt alternative salt tolerance cropping pattern. Also it is advised to avoid excessive use of artificial fertilizer and excessive irrigation.

INTRODUCTION
In India, groundwater constitutes about 53% of the total irrigation potential of the country (FAO 2003) and about 50% of the total irrigated area is dependent on groundwater irrigation (Central Water Commission 2006). Sixty percent of irrigated food production is from groundwater wells (Shah et al. 2000). Modern land use applications (agricultural and industrial), and demands for water supply has limited the globally essential groundwater resources in terms of both its quality and quantity. Groundwater quality depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water-rock interaction (Domenico 1972; Schuh et al. 1997). Once contamination of groundwater in aquifers occurs by means of agricultural and industrial activities and urban development, it persists for hundreds of years because of very slow movement of water in them (Jerry 1986) and prompts investigations on their quality (Aksoyan et al. 2007). Since physico-chemical composition of groundwater is a measure of its suitability as a source of water for drinking, agriculture (irrigation) (Babiker et al. 2007), an attempt has been made in the current study to assess the effects of natural and anthropogenic activities and increased human population on groundwater quality and their variation by defining the principal hydrochemical nature of the groundwater.
The study Area
The Deccan basalts, one of the largest volcanic provinces, is located in the western part of India, covering an area of approx. $5 \times 10^5$ km$^2$ with an estimated volume of approx. $10^6$ km$^3$ (Courtillot et al. 1986). The present study area is a part of the semi-arid zone on the eastern flanks of Sahyadri is of Maharashtra (Fig. 1). The basic lithologic unit of the area is basalt of Deccan Volcanic Province of Cretaceous-Eocene age. These Traps have an average elevation of 750 meters and the thickness of lava pile varies from 200 to 2000 m. The study area experiences a sub-tropical climate, with an average rainfall of 700 mm y$^{-1}$ and is located about 50 km from Pune. The major land use of the study area is for agricultural purpose. The sugarcane is the chief crop of the area. The water from dug wells is used for drinking and agriculture purpose. The decreased water level in these water bodies is common feature. In summer, the water table is fairly shallow. Inconsistent rainfall in the area entails the drought conditions in many regions and reoccurred many a times. This region is drained by the River Bhima and its tributaries. The regional, slope is from NW to SE and it decreases along the flow. Small water divides occur in the region due to relict hills, especially near the confluence.

![Figure 1: Map of the study area](image)

The lithology of region between the two rivers is mainly composed of weathered basalt. To the north of the confluence, dug wells are mainly in the highly weathered basalt with large density of fractures and fissures. The sampling stations (dug wells) are located in and around the confluence, where the groundwater occurs in water bodies within weathered basalt and in altered vesicular horizons. The presence of joints, fracture, vesicles, cavities, inter-granular pore space and boundary surfaces between different flows and flow units in the weathered basalt and alluvium provide space for the occurrence of ground water (N.J. Pawar 1993). The presence of clays and red bole horizons act as barriers to the downward movement of ground water which favors in formation of aquifers in overlying permeable flows.

METHODOLOGY
The groundwater samples were collected from nearby area of confluence of Bhima and Mula-Mutha rivers. In the present study, the groundwater is probed to understand the lithogenic and anthropogenic contribution. The samples of dug wells were collected and 30 sampling sites in the area were established (Fig.1). To magnify the spatio-temporal trend in the quality of groundwater, sampling was carried out before and after the monsoon seasons. In all 60 samples were chemically analyzed. The pH, EC, well depth, bicarbonate, carbonate and CO$_2$ were recorded in the field. Water samples were collected in prewashed (1 lit) polythene bottles and packed air-tight. In the laboratory Na, K Ca, Mg, SiO$_2$, Nitrate, Phosphate, Sulphate, Chloride amounts were determined adopting guidelines of APHA.

RESULT AND DISCUSSION
Temporal variations of pH, TDS or EC endorse the dominance of water rock interactions in establishing groundwater quality. Gibbs diagram uncover the fact that weathering reactions of rock minerals is chief controlling factor.

Among anions, majority of bicarbonate implies the dissolution of rock minerals (e.g. Calcite). In premonsoon season pH varies from 8.26 to 8.99 and in post monsoon season 7.34 to 8.13. As per WHO (1993) and ISI (1983) limits most of the water samples are suitable for irrigation and drinking purpose with exception (sample number 2) of few for drinking. TDS is a measure of amount of dissolved minerals and salts. Considering all major constituents found in natural water the TDS values are less than 1500 ppm which is maximum permissible limit of WHO and ISI, except sample number 23 and 24. Caroll (1962) proposed four classes of water based on TDS values, of which water samples with TDS<1,000 mg/l belong to the fresh water class. The TDS of water samples are less than 1,000 mg/l. Only five samples in premonsoon and eight in postmonsoon belong to brackish water category.
Table 1: Water quality classification based on (carrol 1962)

<table>
<thead>
<tr>
<th>TDS in mg/l</th>
<th>Water Quality</th>
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</thead>
<tbody>
<tr>
<td>0-1,000</td>
<td>Fresh water</td>
</tr>
<tr>
<td>1,000-10,000</td>
<td>Brakish water</td>
</tr>
<tr>
<td>10,000-100,000</td>
<td>Salty water</td>
</tr>
<tr>
<td>&gt;100,000</td>
<td>Brine</td>
</tr>
</tbody>
</table>

Table 2: Classification of water based on hardness by Sawyer and Mc Cartly (1967)

<table>
<thead>
<tr>
<th>Hardness as CaCO$_3$ (ppm)</th>
<th>Water Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-75</td>
<td>Soft</td>
</tr>
<tr>
<td>75-150</td>
<td>Moderately hard</td>
</tr>
<tr>
<td>150-3,000</td>
<td>Hard</td>
</tr>
<tr>
<td>&gt;3,000</td>
<td>Very hard</td>
</tr>
</tbody>
</table>

Table 3: Drinking water specification given by ISI (1983) and WHO (1993) and minimum, maximum and average ion concentration

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>0-500</td>
<td>1,500</td>
<td>Maximum permmissible limit (mg/l)</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-8.5</td>
<td>6.5-8.5</td>
<td>0</td>
</tr>
<tr>
<td>Calcium</td>
<td>75</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Magnesium</td>
<td>50-150</td>
<td>50-30</td>
<td>100</td>
</tr>
<tr>
<td>Potassium</td>
<td>0-12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sodium</td>
<td>0-0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>0-600</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Chloride</td>
<td>0-250</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0-400</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Maximum water samples are in category $C_3S_1$ followed by $C_2S_1$. Few samples are in $C_1S_2$ category. Seasonally sodium hazard values decreased in postmonsoon compare to premonsoon which may be because of higher

The presence of major ions, such as calcium, magnesium, bicarbonate, chloride and sulphate in water causes hardness and makes it unsuitable for drinking. Sawyer and McCarty (1967) classified water on the basis of hardness. Hardness values of all water samples are found to fall within hard category. Therefore it is difficult to advice for drinking as it can cause kidney stone and heart diseases (Schroeder 1960). Generally Ca$^{2+}$ and Mg$^{2+}$ maintain a state of equilibrium in most groundwater (Hem 1985). During equilibrium more Mg$^{2+}$ in groundwater will adversely affect the soil quality rendering it alkaline resulting in decrease of crop yield (Kumar et al. 2007). Paliwal (1972) developed an index for calculating the magnesium hazard (magnesium ratio (MR)). MR values for the present study exceeds the limit in post monsoon seaso and remains at the borderline in pre monsoon season. This change can be attributed to dissolution in post monsoon while precipitation in pre monsoon of the calcite mineral. The water is not suitable for irrigation purpose. This implies the dissolution and ion exchange reactions of magnesium bearing minerals may interfere. The land from study area is under agricultural practices. Therefore it is necessary to observe the amount of salts of sodium, magnesium and calcium present in the ground water. To understand this RSC, SAR, Salinity hazard are useful. RSC is calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water used for agricultural activities (Raju NJ 2007). RSC ranges from 0.45-10.30 in post monsoon and -0.68 - 11.80 in pre monsoon which indicates the unsuitability of water for irrigation purpose. SAR and salinity hazard values are useful for USSL based classification of water.
dissolution of calcium and magnesium bearing minerals. One may infer the ion-exchange reactions can be contributing factor. High salinity and low sodium hazard signifies water is suitable for irrigation purpose almost in all types of soil with little danger of exchangeable sodium (Kumar et al. 2007). Representations are also noted in C_3S_1 category indicating water suitable for plants having good salt tolerance but unsuitable for irrigation in soils with restricted drainage (Mohan et al. 2000). In premonsoon season 10% of the samples fall in C_3S_2 category, indicating water having high salinity and medium sodicity. High salinity, medium sodicity water cannot be used on fine-grained soils with restricted drainage (Srinivasamoorthy et al. 2010). This is because restricted flow is likely to result in the accumulation of salts in the root zones of crops, leading to salinity and soil clogging crisis. Water samples in C_3S_2 category are not suitable for irrigation purposes due to very high salinity and sodium hazards which affect the plant growth.

Kelly’s index
Kelly’s index is used for the classification of water for irrigation purposes. Sodium measured against calcium and magnesium is considered for calculate this parameter. A KI (>1) indicates an excess level of sodium in waters (Kelly 1940). Therefore, waters with a KI (<1) is suitable for irrigation, while those with greater ratio are unsuitable (Sundaray et al. 2009). 25% water samples are found to be less than one in both the seasons while rest are more than one which implies that the water is not suitable for irrigation purpose. Rise in sodium percentage may be because of weathering of feldspar minerals.

Chloride and Sulphate
In the study area halite minerals are not present, therefore chloride source is anthropogenic but source of sulphate can be gypsum and anthropogenic both. Average values of chloride in premonsoon 212 and in postmonsoon 120 which is less than maximum desirable limits set by WHO and ISI. Sulphate concentration in premonsoon is ranging from 5 to 170 and in postmonsoon from 3,5 to 565 which allows the use of groundwater for drinking as well as irrigation purpose.

CONCLUSION
1. Physico-chemical properties of groundwater are controlled preferably by lithogenic factors followed by anthropogenic factors in the present study area.
2. As per pH, TDS, SAR, Chloride and sulphate data, values are found to be closer to maximum permissible limit. Therefore though it is in the limits of WHO and ISI, it is not advisable for drinking purpose.
3. RSC values are totally against the use of groundwater for drinking and agriculture purpose but at the same time SAR values are found to be in the specified limits. USSL classification show water is
4. KI is one more parameter which does not allow the use of water for irrigation purpose.

REFERENCES
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